Nanostructured and Advanced Materials

Edited by

A. Vaseashta, D. Dimova-Malinovska
and J.M. Marshall

NATO Science Series

II. Mathematics, Physics and Chemistry – Vol. 204
Nanostructured and Advanced Materials
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Series II: Mathematics, Physics and Chemistry – Vol. 204
Nanostructured and Advanced Materials for Applications in Sensor, Optoelectronic and Photovoltaic Technology

edited by

A. Vaseashta
Nanomaterials Processing & Characterization Laboratories,
Marshall University,
Huntington, WV, U.S.A.

D. Dimova-Malinovska
Central Laboratory for Solar Energy & New Energy Materials,
Bulgarian Academy of Sciences,
Sofia, Bulgaria

and

J.M. Marshall
University of Wales,
Swansea, U.K.

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PREFACE

The principal aim of this NATO Advanced Study Institute (ASI) "Nanostructured and Advanced Materials for Applications in Sensor, Optoelectronic and Photovoltaic Technology" was to present a contemporary overview of the field of nanostructured and advanced electronic materials. Nanotechnology is an emerging scientific field receiving significant worldwide attention. On a nanometer scale, materials or structures may possess new and unique physical properties. Some of these are now known to the scientific community, but there may well be many properties not yet known to us, rendering it as a fascinating area of research and a suitable subject for a NATO ASI. Yet another aspect of the field is the possibility for creating meta-stable phases with unconventional properties and the ultra-miniaturization of current devices, sensors, and machines. Such nanotechnological and related advanced materials have an extremely wide range of potential applications, viz. nanoscale electronics, sensors, optoelectronics, photonics, nano-biological systems, nanomedicine, energy storage systems, etc. This is a wide-ranging subject area and therefore requires the formation of multi-disciplinary teams of physicists, chemists, materials scientists, engineers, molecular biologists, pharmacologists, and others to work together on the synthesis and processing of materials and structures, the understanding of their physical properties, the design and fabrication of devices, etc. Hence, in formulating our ASI, we adopted an interdisciplinary approach, bringing together recognised experts in the various fields while retaining a level of treatment accessible to those active in specific individual areas of research and development. In addition to materials and devices formally falling within the field of nanotechnology, the remit of the ASI covered other advanced materials having various closely related underlying concepts and applications. These included amorphous, porous, and polycrystalline silicon, metal oxide semiconductors, wide bandgap materials, and conducting polymers.

To maximize global participation, the Organizing Committee focused on a promotional strategy that garnered a tremendous response not only from NATO and partner countries but also from the Asia-Pacific rim. Such a substantial response presented a welcome but arduous task for the Organizing Committee charged with selecting the most deserving participants. Realizing that a productive ASI would result from the involvement of a large number of participants from multiple scientific disciplines, the organizers accepted a wide range of promising candidates who could be funded through NATO. In addition, several participants from Japan and Thailand, not eligible for NATO support, attended on a fee-paying basis.

The lectures progressed in a logical manner from basic principles to state-of-the-art applications of nano-structured and advanced materials for sensor,
optoelectronic, and photovoltaic devices. They were delivered by twelve experts who were highly experienced and internationally-recognised authorities in their various fields. Additionally, focused seminar, poster and interactive feedback sessions allowed for extended interactions between subject matter experts and the other participants. As a venue for such collaborative learning, this program received an enthusiastic response from the participants.

The ASI was held at the “Izgrev” Guest House Complex in Sozopol, an ancient, historic and picturesque coastal town on Bulgaria’s Black Sea coast, which offered a tranquil, congenial setting for the event. The scientific programme lasted for ten days, with some time free to visit nearby towns, shop, or simply relax. The shops, restaurants and bars in the rustic downtown and nearby beach areas provided a much-needed break after lectures and in-depth discussions at the ASI. In addition, a very interesting cultural festival took place in Sozopol during the period of ASI. The participants also shared a sightseeing excursion to Nessebar, followed by a traditional Bulgarian dinner complete with folk dancing. The balance of technical and social events stimulated interactions between participants, including many discussions of the possibilities for future collaborations.

The Co-Directors interpret the ongoing interactions and positive feedback from participants as an affirmation of a successful ASI. This relied not only upon the efforts of the Co-Directors, the other members of the International Organizing Committee (Herbert Hofmeister, Joe Marshall and Stanislav Pietruszko), the lecturers, seminar speakers and other participants, but also upon the various individuals who supported our efforts so effectively. Much appreciation is extended to Georgy Davtchev, the Manager of the “Izgrev” Guest House Complex, and to his staff. Our local ASI organizers, Avgustina (Gusti) Rachkova, Suzi Kavlakova, Mimi Kamenova, Christosko Dikov, and Christo Angelov handled the everyday logistics with the utmost consideration and efficiency. On a self-funded basis, Vesselin Hubanov undertook the valuable additional role of amassing an impressive collection of photographs of both the ASI program and the related social events. A limited selection of these is included at the end of this volume.

Our gratitude also goes to the NATO Science Committee for approval of our application, and in particular to Dr. Fausto Pedrazzini, the Programme Director of the NATO Public Diplomacy Division, for his encouragement, expertise and financial support. Ms. Annelies Kersbergen, of the NATO Publishing Unit (Springer) has provided us with much appreciated expert advice in the preparation of these Proceedings.

Several funding agencies, namely UNESCO (contribution to the costs of preparation of the abstract book), and INVOTAN, NSF and TUBITAK (travel support for some participants) are acknowledged for their generous help. The Co-Directors also acknowledge financial support from the University of Kansas
(funding for the best poster award presentation in each session), and from Seki Technotron Corporation (funding for refreshments during these sessions).

A debt of gratitude is owed to Joe Marshall for his "surgical" (sometimes "amputative") editing precision, and for his patience in re-formatting various manuscripts and coping with those which trickled in well after the deadlines. We understand that relaxation after such activities caused an unexpected surge in revenues at his local pub.

We also particularly remember:

- the clarinet playing of Richard Hurley, with the band at the Farewell Dinner (see photographs),
- the poem delivered during the Closing Ceremony by Herbert Hofmeister (reproduced at the end of this volume), and
- last, but not least, the many expressions of support and thanks, collected together in a book by participants and presented to us at the closing Ceremony.

The Co-Directors hope and anticipate that this ASI will provide continued success for all participants as they pursue their research and collaboration in the fields of nanotechnology and advanced electronic materials.

Ashok Vaseashta (Huntington)
Doriana Dimova-Malinova (Sofia)

Co-Directors
February 2005

Organising Committee
D. Dimova-Malinova
H. Hofmeister
J. M. Marshall
S. Pietruszko
A. Vaseashta
1. Introduction

At each new level of complexity, entirely new properties appear, and the understanding of these behaviours requires research which, I think is as fundamental in its nature as any other." quoted P. W. Anderson [1]. The physical and chemical properties of materials in reduced dimensions show a size dependence and may exhibit properties different from the bulk. There are several examples of rather remarkable properties attributed to the reduced dimensions. Materials at the nanometer scale have a lower melting point [2] and reduced lattice constant [3]. Certain materials, normally stable at elevated temperatures, show stability at much lower temperatures in reduced dimensions; and hence ferroelectric and ferromagnetic materials may loose their characteristics at a nanometer scale [4]. Nanostructured materials may show different elasto-plasticity from that of large-grained bulk material [5]. With recent technologically advanced systems, it is possible to reproducibly fabricate and study nanostructured systems such as nanotubes, nanowires, nanoparticles, and nano-porous materials. In these the electrons may be confined strongly in one or more dimensions, resulting in a significant improvement in their characteristics as compared to the bulk. From a fundamental standpoint, the dimension of the systems under investigation corresponds to many fundamental physical quantities, viz: the wavelength of the electromagnetic field, the cyclotron radius in a magnetic field, the relaxation length of quasi-particles, the radius of the electron correlation length, the radius of Abrikosov or Josephson fluxon, the de-Broglie electron wavelength, and the effective path length of electrons, phonons, etc. From an electrical characteristics standpoint, the "phase coherence length", as the distance over which a particular electron in a conductor can exhibit quantum interference, has interesting characteristics due to comparable dimensions producing effects such as universal conductance fluctuations and localization. Hence, with a precise bottom-up and/or top-down fabrication approach, it is feasible to fabricate a fundamentally and entirely new class of materials. A list of properties of systems with different dimensionalities is given in Table 1, providing a basic phenomenological
understanding of the basic physics of electrons in a given dimension. In one-dimensional systems such as nanotubes, nanowires, and nano-pores, the role of electron-to-electron (e-e) interactions is difficult to address. However, the current technological innovations in producing relatively perfect zero and one-dimensional structures have led to the achievement of interesting physical properties.

### TABLE I. Properties of systems with different dimensionalities.

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<th>Non-interacting Physics</th>
<th>Coulomb Interaction</th>
<th>Lattice Coupling Disorder</th>
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<td>Nanotubes, polymers, lithographically patterned wires (1D)</td>
<td>1D Sub bands</td>
<td>Luttinger liquid (perturbations)</td>
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<td>Quantumization</td>
<td></td>
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<tr>
<td>Quantum Wells, Layered materials, etc. (2D)</td>
<td>2D Sub bands</td>
<td>Fermi liquid</td>
</tr>
<tr>
<td>Quantum Hall</td>
<td></td>
<td>Anyons, Skyrmions</td>
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<td>Bulk Crystalline Solids (3D)</td>
<td>Band structure</td>
<td>Fermi liquid</td>
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<tr>
<td>Metals</td>
<td>Mott insulator (strong interactions)</td>
<td>Superconductivity (strong disorder)</td>
</tr>
<tr>
<td>Insulators</td>
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Since the discovery of carbon nanostructures in 1985 and the observation of carbon nanotubes (CNTs) in 1991, the study of nanostructured materials has become one of the most promising disciplines in science and technology. Revolutionary progress in synthesis and continuously emerging technologies has led to the development of various nanostructured and advanced electronic materials with remarkable electrical, optical and mechanical properties, with unique applications. These materials show a tremendous potential for the development of new devices and sensor designs with unique capabilities [6]. Carbon-based nanostructures exhibit unique properties and morphological flexibility, rendering them inherently multifunctional and compatible with organic and inorganic systems. The applications of carbon nanotubes (CNTs) include quantum wire interconnects [7], diodes and transistors for computing [8], high power electrochemical capacitors [9], data storage devices [10], field emitters for flat panel displays [11-13] and terahertz oscillators [14]. Successfully contacted CNTs have exhibited a large number of useful quantum electronic and low dimensional transport phenomena [15], such as true quantum wire behaviour [16], chemical and biological sensors for the single-molecule limit [17], room temperature single electron transistors [18], Luttinger-liquid behaviour [19], the Aharonov-Bohm effect [20] and Fabry-Perot interference effects [21]. Typical CNTs have aspect ratios ~ 1000. The high conductivity and the small radius of curvature at the tips
makes them ideal candidates for low voltage field emitters, as cold-cathodes for x-ray generation [22]. Other applications of nanostructures include DNA-templated FETs [23], chemFETs [24], carbon nanofibre reinforced composites [25], nanoporous silicon photonic devices [26,27] and biosensors [28,29].

On a different yet related note, the current trend in clinical medicine is to decentralize laboratory facilities and conduct clinical trials employing direct reading, portable, lab-on-chip systems. Recent threats of chemical and biological warfare demand successful bio-defense systems requiring the development of a novel and complex set of materials and devices. A heightened awareness of the potential for inadvertent or deliberate contamination of the environment, food, and agricultural products has made decentralized sensing an important issue for several federal agencies. Recent progress in nanostructured materials and their possible applications in chemical and biological sensors could have a significant impact on data collection, processing and recognition [30]. The versatility of the carbon-carbon bond presents the opportunity for attaching different functional groups to the end of a CNT. Similarly, surfaces of several nanoporous materials and nanoparticles can be modified to attach a variety of molecules. Functionalization of the nanostructured materials is a key step in the formation of biosensors, as modified nanotube tips and nanoporous and nanoparticle surfaces offer the possibility of probing systems at the nanometer scale. Recent advances in nanotechnology and processing have resulted in solid-state biosensors offering unprecedented compatibility of inorganic materials with the chemical/biological agents, thus enabling stable, direct, and reproducible screening and detection. Compared to earlier catalyst systems based biosensors, the next generation affinity biosensors deliver real-time information about the antibodies to antigens, cell receptors to their glands, and DNA and RNA to nucleic acid with a complimentary sequence. Nanowires modified with specific receptors can be assembled into integrated nano-biosensors for parallel detection and diagnosis of trace amounts of dangerous viruses and bacteria. The basic concept involves linking the antigen to the nanotube while retaining its conformation, which will in turn induce an antibody response without triggering the immune system. Furthermore, CNTs are being investigated for use in vaccine delivery. Hence, a nanotechnology-based sensor platform will not only enable the direct detection of biological and chemical agents in a label-free, highly multiplexed format over a broad dynamic range, but also demonstrates viability for timed release of vaccine in therapeutic devices. The platform utilizes functionalized nanotubes, nanowires, and therapeutic templates to detect molecular binding with high sensitivity and selectivity. It is capable of detecting a broad range of molecules, viz., DNA, RNA, proteins, ions, small molecules, cells and even the pH values. Detection is possible in both the liquid and gas phase, and is highly multiplexable, allowing for the parallel and label-free detection of multiple agents.

A brief overview of the nanostructured materials is presented here. An extensive review of nanostructured material properties has encouraged us to suggest
their use in electrical, photonic, and potential nanotechnology based device designs and chem-bio sensor platforms. For exploring novel physical properties and phenomena and realizing potential applications of nanostructured materials, the ability to reproducibly and precisely control the dimension and orientation of the desired structure is of paramount importance. In addition to sensor and devices designs, certain fundamental issues and challenges for the successful realization of nanotechnology-based platform are presented.

2. Nanostructured Materials

2.1 ZERO-DIMENSIONAL NANOSTRUCTURES: NANOPARTICLES

Nanoparticles include single crystals, polycrystalline, and amorphous materials with all possible morphologies, such as spheres, cubes, and platelets. In general, the characteristic dimension of the particles is in the range 20 to 200 nm. Quantum effects are observed for sufficiently small characteristic dimensions and the particles are referred to as quantum dots (QDs). However, crystalline nanoparticles are referred to as nanocrystals. Many techniques, such as top-down and bottom-up approaches, have been developed and applied for the synthesis of nanoparticles. A plethora of applications using nanoparticles already exists, and with the advancement in fabrication technologies of both spherical and isometric (prismatic and rod-like) metals, oxides and semiconductors, many possible applications are suggested in literature. One of the most interesting aspects of metal nanoparticles is that their optical properties depend upon their size and shape, due to surface plasmon resonance (SPR) - the frequency at which conduction electrons oscillate in response to the alternating electric field of incident electro-magnetic radiation. However, it should be noted that only metals with free electrons create SPR. Elongated nanoparticles display two bands corresponding to the longitudinal and transverse mode electron oscillations. The wavelength of the maximum absorption intensity of the longitudinal plasmon absorption increases linearly with increasing nanorod aspect ratio [31], and if such gold nanorods are encapsulated in micelles in aqueous solution fluoresces with a very high quantum yield in comparison to that of bulk gold films. In addition to their own properties, the environment in which the particles are dispersed is also of critical relevance to the optical properties, viz.: the refractive index of the surrounding medium and the average distance between neighbouring metal nanoparticles, which leads to a variety of applications in sensors. Magnetic nanoparticles, which are functionalized and subsequently immobilized with a suitable molecule have applications which include targeted drug delivery, ultra-sensitive disease detection, gene-therapy, high throughput genetic screening, biochemical sensing, and rapid toxicity cleansing. This makes magnetic nanoparticles highly attractive as in-vivo probes or in-vitro tools to extract information on biochemical systems. Recently, the development of multi-functional nanoparticle probe based semiconducting QDs for in-vivo cancer targeting and
imaging in living animals was reported [32]. However, laboratory studies of pulmonary toxicity in rats demonstrate that lung exposure to nanoparticles produces a greater adverse inflammatory response compared to larger particles of identical composition. The evidence suggests that nanoparticles in the lungs largely escape alveolar microphage surveillance and gain access to the pulmonary interstitium, a potentially vulnerable anatomical region [33]. Hence, the advantages and potential risks regarding health and environmental effects of engineered nanoparticles have led to rather interesting research directions.

2.2. ONE-DIMENSIONAL NANOSTRUCTURES: CARBON NANOTUBES AND NANOWIRES

Carbon nanotubes are tube-like structures that result from a special arrangement of carbon atoms. They are fullerene-related structures consisting of graphene cylinders closed at either end with caps containing pentagonal rings, of the order of half a fullerene molecule [34,35]. In order to understand the structure of a nanotube, we start from graphite, which consists of layers of carbon atoms arranged in a honeycomb structure, stacked on top of each other. Carbon nanotubes are nanometer-wide tubular arrangements of $sp^2$ hybridised carbon atoms where three hybrid $sp^2$ orbitals are formed at 120° to each other within a plane. The in-plane covalent $\sigma$-bond binds the atoms in the plane. The remaining $\pi$-bond is perpendicular to the plane, and is much weaker. A carbon nanotube is thereby formed when one single layer of graphite is wrapped onto itself and the resulting edges joined. Figure 1(a) shows different arrangements of nanotube formation from the graphene sheet. The structure of a nanotube can be defined using a roll-up vector $c (m,n)$ and/or a chiral angle $\Theta$, as shown in Fig. 1(b). The roll-up vector can be defined as a linear combination of base vectors $a$ and $b$ of the basic hexagon, as

$$c = n\bar{a} + m\bar{b}$$

(1)

where $m$ and $n$ are integers. The roll-up vector is perpendicular to the axis of the nanotube. Different types of nanotube are formed by choosing the values of $m$ and $n$. Three major categories of such nanotube structures can be identified, viz., $m = n$ (Armchair), $m = 0$ or $n = 0$ (Zigzag), and $m \neq n$ (Chiral). Based on the geometry, the diameter $d$ and the chiral angle $\theta$ can be calculated as

$$d(nm) = 0.0783\sqrt{n^2 + nm + m^2}$$

$$\theta = \sin^{-1}\left[\frac{\sqrt{3m}}{2(n^2 + nm + m^2)}\right]$$

(2)

CNTs can be further categorized as single wall (SWNT) and multi-wall (MWNT) nanotubes. SWNTs consist of one single graphene sheet rolled up into a cylinder and have diameters from 1 to 5 nm. A MWNT is an arrangement of coaxial tubes of graphene sheets forming a tube within a tube-like structure. Each MWNT
**Figure 1.** Different types of nanotube (a), and the chiral vector c \((m,n)\) for a graphene sheet (b).

<table>
<thead>
<tr>
<th>Property</th>
<th>SWNT</th>
<th>Benefits</th>
</tr>
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<tbody>
<tr>
<td>Typical size</td>
<td>0.6 – 1.8 nm in diameter</td>
<td>High aspect ratio</td>
</tr>
<tr>
<td></td>
<td>1.33 – 1.4 gm/cc</td>
<td>High resolution</td>
</tr>
<tr>
<td>Density</td>
<td>100 GPa, E = 1 TPa</td>
<td>Unbreakable tips</td>
</tr>
<tr>
<td>Resilience</td>
<td>Bent at large angles</td>
<td>Robust probes</td>
</tr>
<tr>
<td></td>
<td>and re-straightened</td>
<td>Unbreakable tips</td>
</tr>
<tr>
<td>Current density</td>
<td>≈ 1 B Amps/cm²</td>
<td>Stable operation</td>
</tr>
<tr>
<td>Fundamental gap</td>
<td>0 eV – 0.5 eV</td>
<td>CMOS, Nanoelectronics</td>
</tr>
<tr>
<td>Conductance quantization</td>
<td>12.9 kΩ cm⁻¹</td>
<td>Ballistic transport</td>
</tr>
<tr>
<td>Field emission</td>
<td>Low turn on voltage</td>
<td>High resolution</td>
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<tr>
<td></td>
<td>(1–3 V/µm)</td>
<td>display, X-rays</td>
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<tr>
<td>Heat transmission</td>
<td>≈ 6KW/m.K</td>
<td>Excellent heat</td>
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<td></td>
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<td>Dissipation</td>
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<td>Phonon mean free path</td>
<td>100 nm.</td>
<td>Nanoelectronics</td>
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<tr>
<td>Relaxation times</td>
<td>10⁻¹¹ sec.</td>
<td></td>
</tr>
<tr>
<td>Temperature stability</td>
<td>≈ 2800° C in vacuum</td>
<td>No probe</td>
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<tr>
<td></td>
<td>≈ 720° C in air</td>
<td>contamination</td>
</tr>
<tr>
<td>Low tip surface capacitance</td>
<td></td>
<td>Minimum capacitance coupling</td>
</tr>
<tr>
<td>Contact independent</td>
<td></td>
<td>Excellent nanoscale electrical contacts</td>
</tr>
<tr>
<td>of clamping force</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chemically inert</td>
<td></td>
<td>Biocompatibility</td>
</tr>
<tr>
<td>Hydrophobic</td>
<td></td>
<td>Used in solutions</td>
</tr>
</tbody>
</table>
has from 2 to 50 such tubes. They have inner diameters of 1.5 to 15 nm, outer diameters from 2.5 to 30 nm, and lengths of several microns. Table 2 provides a list of properties of CNTs and their possible applications.

2.3. TWO-DIMENSIONAL NANOSTRUCTURES: NANOPOROUS MATERIALS

Controlled semiconductor fabrication steps have recently produced porous silicon (PS) with a controllable surface topography at the nm resolution that allows chemical surface modification. Two aspects of porous silicon are of particular relevance for device applications, viz. it can be used as a sensitive biosensor for proteins, antigens, and DNA, and it can be modified with a wide range of biological and organic molecules. Use of Nano-PS membranes in sensors, in-vivo implants, and therapeutics application is under extensive investigation [36]. Sailor et al. [37] have demonstrated the biocompatibility of nano-PS materials for application such as biomedical implants, artificial organ, and cell-based experimentation. Although efforts in this area are still in early developmental stages, combining the biocompatibility of the material with its highly bio-sensitive nature is likely to provide applications in tissue-based bioassay, drug-delivery, and health monitoring systems. Our own studies are focussed towards the following objectives, i) develop novel protocols for the surface modification and patterning of silicon structures with varying porosity, ii) functionalize the surface with suitable chemistry to monitor binding events related to antigens and antibodies of pathogens and toxins, iii) develop theoretical and computer simulation of multi-parametric bio-transport and response of porous silicon sensors, and iv) develop a knowledge database of the surface structures and binding events using characterisation tools such as confocal Raman, atomic force, transmission and scanning electron microscopy. We have extended the investigation to include functionalised nano-porous templates for novel diffusion-controlled drug delivery devices, coupling drug-delivery for controlled discharge or suppression of immune response to a release device, and addressing each molecule by a radio frequency. An exhaustive discussion of synthesis techniques appears in the literature. However a brief discussion related to certain special cases, such as CNTs, nano-PS and templates, and self-assembly of nano-particles is presented here. Figure 2 shows a schematic of the areas under investigation in the present studies, range, and possible applications.

3. Fabrication Routes

3.1 NANOPARTICLES

A top-down approach consists of attrition, repeated thermal cycling, and lithography. Such processes yield nanoparticles of varying dimensions, relatively
broad size distributions, and impurities. Bottom-up approaches are commonly preferred in the synthesis of nanoparticles, involving methods such as homogeneous nucleation from vapour or liquid, or heterogeneous nucleation on substrates. A full review of existing methods for preparation of the nanoparticles is beyond the scope of this article, however, it should be noted that the synthesis methods can be grouped into broad categories, viz.: thermodynamic approach, which consists of generation of super-saturation, nucleation and growth; and kinetic approach, which consists of either limiting the precursors during the growth process or by confining the process in a limited volume. Metal nanoparticles are typically prepared using wet chemical synthesis routes, such as phase transfer, reduction, reverse micelles, or electrochemical methods. Semiconductor nanoparticles (QDs) are synthesized techniques, such as by using MBE, CVD, wet chemical methods, reverse micelles, electro deposition, or pyrolytic decomposition. Irrespective of the method used for nanoparticles fabrication, the processing conditions are controlled such that the nanoparticles are mono-dispersed, have uniform size distribution, and consist of identical crystal structure, chemical composition, and morphology. The nanoparticles used for sensors in this report were prepared using a two-phase reduction method and by directed self-assembly of monolayers strategies.

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3.2 NANOTUBES, NANOWIRES, NANORODS, AND NANOHORNS

Rapid advances in the use of CNTs in new and innovative designs and devices have necessitated different synthesis routes for producing nanotubes with higher yield, consistent properties, and reproducibly. One of the foremost methods has
been the arc-discharge technique [38], where two graphite electrodes (rods) are placed about 1 mm apart. The typical rod temperature is 3000-4000 K. An arc is generated across the electrodes by a dc current of 50-300 A, in a He atmosphere at pressures of 50-760 torr. After an hour's discharge, a deposited carbon rod builds up at the end of the cathode. Its cross section has three regions – a grey core, a black
ring and an outer grey shell, as in figure 3a. The black ring is where carbon nanotubes typically form, in a bundle. The grey regions are amorphous carbon. Formation of the nanotubes requires a higher temperature than for the amorphous carbon. He gas acts as a quencher in the arc-discharge process. A higher He pressure corresponds to a higher growth rate of the carbon deposit. To achieve a homogeneous deposition, the substrate is kept at a constant temperature. The growth mechanism proceeds via nucleation, extension of nucleation to SWNT and MWNT by sequential addition of C₂ dimers, and termination of the growth. Transition elements such as Co, Fe, and Cu can produce SWNTs by producing catalyst sites.

Another popular method of growing the CNTs is by a process involving deposition of hydrocarbons over catalysts [39]. Typically hydrocarbons such as acetylene and methane are allowed to flow over a surface which has thin layers of catalytic metal deposited on it, as shown in figure 3b. Catalytic decomposition of the hydrocarbon causes the carbon atoms to nucleate and grow on the metal particles. The temperature is generally maintained at 600-800°C for formation of MWNTs and at 900-1200°C for SWNTs.

Laser ablation is an attractive method for producing CNTs for use in composite materials and molecular electronic devices. A computer-controlled scanning laser (typically ArF excimer) beam is focussed on a rotating metal-graphite composite target [40], as in figure 3c. The system is evacuated to 10 mtorr and then filled with Ar gas with a flow rate of 600 sccm at 500 torr base pressure. The laser converts a small amount of the composite solid material into a plasma of atoms and molecules. This contains mainly C, C₂, C₃, Ni, Co and their ions, leaving the target with extremely high initial velocities. This material collides with the background gas, generating a series of shock waves, which provides additional heating that dissociates and ionises the gas phase. The growth of nanotubes by this method proceeds by the condensation of pure carbon vapour. Metal atoms from the electrode chemisorb on the carbon cluster and migrate to the dangling bonds at the carbon cluster edge, preventing the closure of the fullerene. Colliding carbon atoms diffuse through the metal atoms and insert themselves between the carbon edges and the metal particles, lengthening the fullerene into a nanotube. Adjustments of the duration of the laser ablation plasma, fluences, and scan rate are some of the growth parameters to optimise the nanotube quality.

Via catalytic decomposition using a hydrocarbon, CNTs can be produced over metal/silica or metal/zeolite surfaces. The diameter of the CNTs is determined by the pore size of the support structure and the size of the metallic particles, and by the flow rate of the hydrocarbon-containing gases, such as acetylene, ethylene, or methane. The length of the CNTs is proportional to the reaction time and their structure depends on the reaction temperature. CNTs deposited using arc-discharge tubes have well-graphitised and faceted tips, while the CVD grown tips are rounded or sometimes are hollow, i.e. with no end caps [41]. In addition to the catalysts described above, others such as discrete iron-oxide nanoparticles [42] can be used for deposition of the CNTs.
Microwave plasma enhanced CVD (MPECVD) is commonly used for the growth of highly aligned CNTs [43]. The apparatus is used to grow nano-crystalline diamond (NCD) thin films using bias enhanced growth (BEG), conventional, and hydrogen deficient growth processes [44-46]. In the BEG process, a negative bias is applied to the substrate and the bias current density (BCD) to the substrate is controlled. In the hydrogen-deficient process, the carbon dimer (C₂) is used as a reactive species in hydrogen-deficient (CH₄/Ar or C₆₀/Ar) MPCVD. The NCD films grown by this method consist of 3-15 nm diamond crystallites with 1-10% sp² carbon residing at the boundaries. Single-walled carbon cones with morphologies similar to those of nanotube caps have been prepared using MPECVD. Several low-cost synthesis routes for nanohorns [47] and nanocones [48] currently exist. Using a self-assembly fabrication route, SWNTs have been produced by thermolysis of nanopatterened precursors [49]. The SWNTs produced by this method consist of ordered arrays of nanotubes with identical diameter, chirality, and aspect ratio.

3.3 NANOPOROUS SURFACES AND TEMPLATES

Nanoporous silicon and variable porosity templates are widely used in sensor designs and for therapeutic applications. Most of the techniques already used for semiconductor processing can be used for the development of nanoporous materials. In general, the processing can be divided into two groups, viz. vapour phase deposition (top-down) and liquid based growth (bottom-up). Examples of vapour phase deposition include sputtering, evaporation, molecular beam epitaxy (MBE), chemical vapour deposition (CVD) and atomic layer deposition (ALD). Examples of liquid based growth include Langmuir-Blodgett (LB) films and self-assembled monolayers (SAM). Depending upon the device design, the fabrication processes produce either ordered or random mesoporous surfaces. Several review articles have covered the processes to produce substrates of desired characteristics.

For the present investigation, a bulk silicon crystal is rendered porous by partial electro-chemical dissolution in hydrofluoric acid (HF) based solutions, depending upon the etching conditions. PS has a very complex, anisotropic nanocrystalline architecture of high surface area. The PS surface is hydrophobic and these treatments lead to its modification, to become a biomaterial. The PS biocompatibility can be improved by a suitable change of the surface parameters. There are several possible methods for influencing the roughness and chemical state of the surface. Its physico-chemical properties are controlled by the process technology. Nanocrystalline silicon reacts with the compounds to create a carbon-silicon bond that produces a stabilizing coat. We developed sensors of PS with varying porosity on Si-p+ (100) and Si-p+ (111), p = 0.01-0.018 Ω cm, followed by different treatments for surface structure modification/stabilization. In addition, the biocompatibility is determined by two main properties: the normal electrochemical potential and the surface energy with respect to the living body. Studies of the electrochemical potential of a number of materials used in medicine have shown that only carbon, gold, and platinum have values close to those of
living tissue: + 0.330, + 0.332, and + 0.334 mV, respectively. The surface energies of these elements range from 20 to 30 erg/cm², which likewise corresponds to the values for living tissue. Generally, the carbon layer structure is formed by mixing sp² and sp³ bonding. A high fraction of the sp³ bonds in the structure of the mixed sp³ + sp² bonding, yields a highly hydrophobic surface which is responsible for the cell attachment. For biological applications, we have achieved 35-50% porosity on Si-p+ (100) and Si-p+ (111), ρ = 0.01-0.018 Ω-cm. Different PS surface treatments, viz. i) thermal treatment in O₂, ii) thin carbon, or silicon carbide layer deposition, iii) thin gold layers, iv) surface derivatization by an electrochemical method, are currently under investigation. Using metals such as gold, platinum, and several metal oxides, the dependence of the size of a metal or oxide particle on its catalytic reactivity is also investigation. Such investigations provide information on the confinement of the particles and its effect as an effective catalyst.

4. Applications of Nanostructured Materials

4.1 BIOLOGICAL APPLICATIONS

Biosensors are simple, inexpensive measurement systems that use biological molecules, usually enzymes, antibodies or nucleic acids, to recognize sample molecules of interest via hydrogen bonding, charge-charge interactions, and other biochemical interactions to provide molecular information. The integration of biological systems and nanostructured materials requires information to be induced across the interface in a consistent and reproducible format. Recent advances in the fields of nanotechnology and processing have resulted in solid-state biosensors offering unprecedented compatibility of inorganic materials with chemical/biological agents, thus enabling stable, direct and reproducible screening and detection. As compared to earlier catalyst system based biosensors, the next generation affinity biosensors deliver real-time information about the antibodies to antigens, cell receptors to their glands, and DNA and RNA to nucleic acid with a complimentary sequence. Food safety has become one of the most critical issues in sensing, due to the zero-tolerance mandate for the presence of micro-organisms in foods. The sensitivity of conventional biosensors is in the range 10³-10⁴ colony forming units (CFU)/ml. The dimensional compatibility of nanostructured materials renders nanotechnology as an obvious choice, derived from its ability to detect at ≈ 1 CFU/ml sensitivity. Figure 4 illustrates the dimensional compatibility of chemical and biological agents to nanostructured materials, and the range of some of the most commonly used methods of detection.

Conventional methods of pathogen detection require time-consuming steps to arrive at consequential data. Methods such as enzyme linked immuno-sorbent assay (ELISA) and polymerase chain reactions (PCR) have been employed for pathogen detection, because of their improved speed and reliability. The times required for ELISA and PCR are from 10 to 28 hours [50] and from 4 to 6 hours [51],
respectively, while the assay time for optical biosensors is of the order of 2 hours under ideal conditions. An advantage of biosensors is their improved sensitivity compared to that of ELISA and PCR methods. An appropriate protocol is being developed for biosensors, employing immuno-detection principles to significantly reduce the assay time as well as to detect smaller concentrations of bacteria with fewer false positives. Currently, tools are available to study the expression properties manifested by specific types of genetically modified plants at the molecular and nanoscale level. Studies of DNA and nucleotide based micro-array expression patterns are beginning to explore signal transduction phenomena. Signalling genes are thus ideal candidates for their expression through chemically inducible promoters, to be used in various sensors.

4.1.1. **Carbon Nanotubes and Nanowires**

CNTs are currently used as biosensors for detecting individual bio-molecules and other biological agents. The CNTs are conducting, can act as electrodes, can generate electro-chemiluminescence (ECL) in aqueous solutions, can be derivatized with a functional group that allows immobilization of biomolecules, have high surface-to-volume ratios for adsorption, and surface-to-weight ratios (~ 300 m²g⁻¹). The functionalization of the CNTs is a key step in the formation of biosensors, as modified nanotubes tips offer the possibility of probing systems at the nanometer scale. CNTs are functionalized in several configurations, viz. covalent and non-covalent, defect, sidewall, endohedral, and π-stacking. Most biosensor applications often require uniform functionalization via an electrically active pathway. Oxidation of the nanotubes with HNO₃-H₂SO₄ leads to high concentrations of carboxylic, carbonyl, and hydroxyl groups on the surface and removal of the tip to expose the tube interior. Carboxyl groups are readily derivatized by a variety of reactions allowing linking of biomolecules, such as proteins, enzymes, DNA, or even metal nanoparticles. The covalent modification of nanotubes facilitates the creation of well-defined probes that are sensitive to specific intermolecular interactions of many chemical and biological systems. Integration of transducer and
A. VASEASHTA

A probe enables the quick, accurate, and reversible measurement of target analytes without using reagents. The possibility of covalent modification of SWNTs offers mapping of functional groups at a true molecular resolution. Furthermore, chemical processes to link catalysts, such as transition-metal complexes, to the ends of CNT will be useful in creating or modifying the structures at a molecular scale, creating interconnections for electronic devices, and developing new classes of materials.

Covalent functionalization of the sidewalls for the SWNTs provides stability and best accessibility, but at the expense of damaging the sidewalls, thereby diminishing the mechanical and electronic properties of the SWNT. Due to these issues, non-covalent routes to nanotube functionalization offer ease of synthesis and minimum disruption of the tubular structure. As an example, non-covalent functionalization of a SWNT by careful selection and application of a polymer wrapping around it can be obtained [24,52]. The non-covalent association of polymers with nanotubes provides an electrically non-interactive baseline association with them; while the reactive groups of the polymers allow for interaction with specific molecules. When these interact with the polymer coating, the electrical properties of the nanotube are altered, enabling detection of the molecules. Preliminary results for CNT-based sensors have shown conductance changes of several orders of magnitude [53]. Non-covalent wrapping to barcode DNA has been suggested by us and others [54]. By using sequence-specific attachment, CNT electronic devices with specific molecular-recognition features of DNA have been reported [55]. Furthermore, a possible interfacing of CNTs with electro-active proteins, by establishing molecular links, is likely to become a convenient vehicle for studying cell organization. Recently obtained readings from oocyte cells using single CNT, albeit preliminary, strongly suggest the feasibility of probing biological systems through nanostructured materials based systems.

4.1.2. Nanoparticles

Electrochemical biosensors use gold or silver nanoparticles or magnetic particles, for detecting the oxidation signal of electroactive DNA bases in the presence of DNA hybridization. Normally, a probe sequence is immobilized within the recognition layer, where a base-pairing interaction recruits a target molecule to the sensor. It is vital to develop sensing strategies to maintain the critical dynamics of target capture, to generate a sufficient recognition signal. Standard electrochemical techniques, such as differential pulse voltammetry (DPV), potentiometric stripping analysis (PSA), square-wave voltammetry (SWV), etc. are used as genosensors. These devices can be used for monitoring sequence-specific hybridization events directly [56], based on the oxidation signal of guanine, DNA intercalators (metal coordination complexes, antibiotics etc.) [57], or using metal tags such as gold or silver nanoparticles or magnetic particles, for detecting the oxidation signal of gold or silver, or electroactive DNA bases in the presence of DNA hybridization [58], as in figure 5(a). For electrochemical sensors, the hybridization detection of samples was transduced by means of different electrochemical techniques performed using a
potentiostat such as the Autolab PGSTAT 30 electrochemical analysis system. The oxidation or reduction signal of the electro active DNA bases or metal indicators was measured and used as an analytical signal. The detection limit for the different PCR amplicons was found to be 1 - 100 femtomoles of DNA [59].

A second type of biosensor is developed by using SPR to detect *E-coli* O157:H7 bacteria, by immobilizing antibodies by a coupling matrix on the surface of a thin film of precious metal such as gold deposited on the reflecting surface of an optically transparent wave-guide. When visible or near-infrared radiation is made to totally internally reflect at the interface of the metal and the reflecting surface by a prism, SPR occurs. When the antigens interact with antibodies, the refractive index of the medium surrounding the sensor changes, which in turn causes a shift in the angle of resonance. The change in resonance angle is proportional to the change in the concentration of antigens bound to the surface. In order to investigate the capability of a self assembled monolayer (SAM) based SPR biosensors for pathogen detection, first an initial baseline was established and various experiments were conducted. Immobilization using *Escherichia coli* O157:H7 polyclonal antibodies suspended in NaOAc (pH 5.5) produced a pixel change of 12, while *Escherichia coli* O157:H7 (pH 7.4) polyclonal antibodies suspended in PBST produced a pixel change of 7. Increasing the concentration of antigen in direct assay resulted in an increased response. Upon passing the antigen sample at a concentration of $4 \times 10^8$ CFU/ml for 10 min, a change in the pixel value of 0.1 was noted, while a concentration of $7 \times 10^9$ CFU/ml produced an average change in the pixel value of 0.1667. One pixel change is equivalent to a 0.006º change in angle. For the same concentrations of antigens and different concentrations of secondary antibodies in the sandwich assay, the response obtained was almost 30 times higher than for the direct assay. Figure 5(b) shows a schematic of SPR and a typical response curve. Figure 5(c) shows an AFM image of a rod shaped *Escherichia coli*, bound to its corresponding antibody on a SAM-based gold chip.

Preliminary studies clearly showed that the SAM based LEICA SR 7000 SPR biosensor can be used to monitor biomolecular interactions, and to rapidly detect pathogens. With improvements in the detection protocol and sensor chips, the sensitivity and specificity can be enhanced considerably. As an extension to the detection, and to increase the sensitivity and specificity of the binding assays, particularly in the case of antibody binding, surface plasmon fluorescence spectroscopy (SPFS), will be applied simultaneously with SPS. As the reflectivity monitored at different incident angles reaches a minimum corresponding to the excitation of the surface plasmons, the surface field intensity is maximized, yielding a mirror image of the plasmon reflectivity curve. This intensity enhancement can be employed to increase the fluorescence emission of surface bound dye molecules excited by the amplified electromagnetic field.

### 4.1.3. Nanoporous Surfaces

In addition to nanotubes and nanoparticles, novel materials such as porous silicon (PS) [28,29] and porous carbon [60], with pore sizes compatible with the dimensions of chem-biological agents have been used for biosensor applications. A mesoporous carbon matrix is used for stable immobilization of the biological
molecule, and C$_{60}$ serves as electron mediator. Both C$_{60}$ and nanotubes have been shown to be good electron mediators when used with a mesoporous carbon matrix or modified metal electrodes. Carbon nanotube based transducers, however, show a significant advantage over such materials, due to the well defined defect free structures and also to the fact that the nanotubes promote homogenous electron transfer reactions. PS offers a controllable surface topography at a nanometer resolution in three dimensions, and allows chemical surface modification [37]. Use of PS as a biocompatible material for in-vivo diagnostics and slow or on-demand vaccine-delivery is currently under investigation, as it is used as a sensitive biosensor for proteins, antigens, and DNA. The PS biosensors are developed using bulk silicon crystal, by partial electrochemical dissolution in hydrofluoric acid solutions, as described earlier.

<table>
<thead>
<tr>
<th>Type of Sensor</th>
<th>Advantages</th>
<th>Range</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct DNA electrochemistry</td>
<td>Highly sensitive; Requires no labelling step; Amenable to a range of electrodes</td>
<td>$10^{-15}$ m of target</td>
<td>Low S/N ratio; Cannot be multiplexed; Destroys the sample</td>
</tr>
<tr>
<td>Indirect DNA electrochemistry</td>
<td>Highly sensitive; Usually requires no labelling step; Multiple-target detection at same electrode</td>
<td>$10^{-18}$ m of target</td>
<td>Probe substrate can be Difficult to prepare; Destroys the sample</td>
</tr>
<tr>
<td>DNA-specific redox indicator detection</td>
<td>Moderate to high sensitivity; Well suited to multiple-target detection; samples remain unaltered</td>
<td>$10^{-15}$ m of target</td>
<td>Chemical labelling step required unless ‘sandwich’ method used; Sequence variations can be problematic</td>
</tr>
<tr>
<td>Nanoparticle-based electrochemistry amplification</td>
<td>Extremely sensitive; Well suited to multiple-target detection; Highly multiplexable</td>
<td>$10^{-15} - 10^{-21}$ m</td>
<td>Many development steps in assay; Reliability/robustness of surface structures problematic; Sample usually destroyed Still in development stage; Robustness not yet established; No prototype deployment to date</td>
</tr>
<tr>
<td>Nanowires and nanoporous based detection</td>
<td>Extremely sensitive; Well suited to multiple-target detection; Highly multiplexable</td>
<td>$10^{-15} - 10^{-21}$ m</td>
<td></td>
</tr>
<tr>
<td>DNA-mediated charge transport</td>
<td>Highly sensitive and simple assay; Requires no labelling; Mismatch detection; Sequence independent; May be Multiplied.</td>
<td>$10^{-15}$ range</td>
<td>Biochemical preparation of target sample required</td>
</tr>
</tbody>
</table>
The PS surface is hydrophobic, and functionalization renders it as a biomaterial. The PS biocompatibility is improved by a suitable change of the surface parameters, and is determined by two main properties: the normal electrochemical potential and the surface energy with respect to the living body. Studies of the electrochemical potential of a number of materials used in medicine have shown that only carbon, gold, and platinum have values close to those of living tissue. Table 3 lists different types of sensor platform, their sensitivities, and merit analysis.

4.2 NANOELECTRONICS AND NANOPHOTONICS

Recent progress in microelectronics and VLSI-ULSI technology has resulted in exceedingly complex and faster circuits with feature sizes less than 100 nm, e.g. transistors with gate lengths of 10 nm have already been demonstrated [61]. While CMOS technology seems to be scalable for many years ahead, new technologies based on entirely new device concepts have emerged. These may eventually replace the CMOS technology either by quantum mechanical effects or by devices which feature nanostructured materials, formed either by employing top-down or self-organized processing techniques. Due to the reduced dimensions, the quantized electronic states of the nanostructures influence their electrical and optical properties.

The electronic structure of CNTs has been computed based on a 2D structure of a graphene sheet and quantization of the wave vector in the circumferential direction. It was demonstrated that CNTs with chirality \((n,m)\) will have metallic conduction if \(n-m = 3q\), where \(q\) is an integer [62]. The 1D energy dispersion relation of the CNTs shows that it has a finite bandgap in most directions in \(k\)-space, but the has zero bandgap along specific directions, or behaves like a zero-bandgap semiconductor. Hence, the momentum of the electrons moving around the circumference of the tube is quantized. Metallic tubes have a Fermi velocity \(\approx 3 \times 10^5\) m/sec, which is comparable to typical metals. Semiconductor tubes have a bandgap \(\approx 0.9\) eV/d, where \(d\) is the diameter in nm. Since a SWNT has dimensions in the nm range along the x-y direction, and since the z-direction is a continuous one, the dispersion relation consists of a series of 1D subbands. The total density of states is due to the spin degeneracy and sub-lattice degeneracy of the graphene. The density of states shows peaks at the band thresholds, called Van Hove singularities [63], affecting the electrical and optical properties of 1D systems. Using the Landauer formula [64], the conductance quantization is

\[
G = \left( \frac{4e^2}{h} \right) T, \tag{3}
\]
where e is the electron charge, h is the Planck's constant and T is the probability or transmission coefficient for electrons. For $T = 1$, the conductance of a SWNT is

$$\frac{4e^2}{h} = 155 \mu S$$  \hspace{1cm} (4)

with a corresponding resistance of about 6.5 k\(\Omega\). Additional resistance comes into play due to contact resistance and scattering centres reducing the mean free path in the tube. When a magnetic field is applied parallel to the tube axis, according to the perturbation theory the band gap would oscillate with increasing magnetic field, causing the tube to oscillate between semiconductor and metallic states. These Aharonov-Bohm (AB) oscillations [20], are associated with the weak localization, a quantum mechanical treatment of backscattering of electrons, which contains interference terms adding up constructively in zero field. The net effect is to enhance backscattering, thus leading to a resistance larger than the classical Drude value. The AB effect period of h/2e requires backscattering on the scale of the diameter of the NT, clearly indicating that the transport in CNTs in not ballistic, as reported in the literature [65,66]. Magnetic measurements on nanotubes confirm that they are diamagnetic and show a pronounced anisotropy of susceptibility. The magnetic susceptibility of tubes aligned parallel to the field was found to be much greater than that of tubes perpendicular to the field.

CNTs have non-linear optical properties, which depend on the diameter and symmetry of the tubes, indicating the discrete polarization absorption properties of CNTs. For aligned nanotube yarns, photons having their polarization direction parallel to the axis of the nanotubes are absorbed, whereas those that are perpendicularly polarized are transmitted [67], having a degree of polarization of 0.92. Recently, the development of left-hand materials consisting of arrays of closely spaced pairs of metal nanowires placed in a dielectric host was reported [68]. The structure of such closed loop pairs forms a displacement current and supports resonant modes with negative magnetic permeability above the resonance. Functionalised nanoparticles have been the subject of intense investigation for use in SPR. Left-hand photonics, along with the electrical transport characteristics of the CNTs, can revolutionize the integrated opto-electronics industry. Integration of nanotubes in a polymer matrix has recently been investigated for the formation of LEDs. Likewise, topics such as III-V nanowires on silicon, bandgap engineering, photonic crystals based on aligned CNTs [69] and the liquid-crystal mediated synthesis of low dielectric constant materials [70] have been the subject of intensive investigation for opto-electronic integrated circuits (OEIC), systems on chip (SOC), and network on chip (NOC) applications.
4.2.1 Field Emission in CNTs: Display, Imaging and X-Ray Generation

SWNTs and MWNTs are found to be excellent field emitters at relatively low operating voltages, as compared to the thermionic emission mechanism, where electrons are emitted from a heated filament (hot cathode). As compared to Spindt-type and diamond tip emitters, the electron emission from CNTs offer a robust and viable alternative due to the large aspect ratio, structural integrity, high electrical and thermal conductivity, chemical stability, and the possibility of large-scale production. Recently, there have been studies to utilize CNTs as field emitters for display panels, cold-cathodes for x-ray generation, and for photonic devices. Although, the field emission currents from either aligned or randomly oriented single carbon nanotubes have been extensively studied, a systematic and thorough investigation is indispensable, as the field emission depends strongly on the morphology, diameter, spatial distribution, alignment, and the contact between the CNT and substrate, as well as the condition of the CNT tip. The emission current from a metal surface is determined by the Fowler-Nordheim (F-N) equation:

\[ I = aE_{apl}^2 \exp\left(-b\phi^{3/2} / \beta E_{apl}\right) \]  

(5)

where \( I \), \( E_{apl} \), \( \phi \), and \( \beta \) are the emission current, applied field, work function, and field enhancement factor, respectively. For metals with a typical work function and a flat surface, the threshold field is prohibitively high, around \( 10^4 \) V/\( \mu \)m. Field emission sources rely on the field enhancement factor due to sharp tips/protrusions, so that they tend to have a smaller virtual source size because of the role of the \( \beta \) factor. The larger the \( \beta \) factor, the higher is the field concentration and the lower is the effective emission threshold voltage. A change in the electronic structure of the nanotube cap can affect the field emission current and its temperature dependence. DFT calculations indicate that the large electric field present at the tip during the electron emission condition helps stabilize the adsorbates and lower the ionization potential, furthering electron emission.

We investigated electron emission from carbon nanotubes in a vacuum, and the onset of emission occurred at an electric field of 1.45 V/\( \mu \)m, which is similar to the values reported in literature. An emission current of 0.35 mA was observed at an electric field of 3.8 V/\( \mu \)m, and the experimental data fitted well into a Fowler-Nordheim (F-N) plot. This represents a very large current density for such small dimensions, and is quite close to the theoretical limit for resistive heating. The turn-on field, \( E_{to} \), and the threshold field, \( E_{thr} \), are the electric fields required to produce current densities of 10 \( \mu \)A/cm\(^2\) and 10 mA/cm\(^2\), respectively. These figures of merit correspond to typical values employed in panel display applications. The values of \( E_{to} \approx 4.85 \) V/\( \mu \)m and \( E_{thr} \approx 14 \) V/\( \mu \)m
are consistent with those reported in the literature [71,72]. The field amplification factor $\beta$ was estimated to be around 850 from the I-V and F-N plots. The field amplification factor is calculated from the geometrical shape of the tube for a given work function. For this consideration, a simplified formula by Brodie and Spindt [73] was employed. The emission current of a single emitter is related to the applied field, $E_{\text{appl}}$, as

$$I = A \frac{1.5 \times 10^6}{\Phi} E_{\text{appl}}^2 \beta^2 \exp\left(\frac{10.4}{\sqrt{\Phi}}\right) \exp\left(-\frac{6.44 \times 10^7 \Phi^{1.5}}{E_{\text{appl}} \beta}\right). \quad (6)$$

One of the difficulties in the calculation is a-priori knowledge of the work function. It is possible to calculate both $\phi$ and $\beta$ by performing energy distribution measurements. The work function for a catalytic MWNT has been reported to be equal to 5.3 eV [74]. If we assume $\phi \approx 4.9$ eV and $A = 10^{-9}$ cm$^2$, the relation reduces to

$$I = 3.4 \times 10^{-14} E_{\text{appl}}^2 \beta^2 \exp\left(-7 \times 10^8 \frac{2}{E_{\text{appl}} \beta}\right). \quad (7)$$

Using this equation, the field enhancement factor can be estimated from the I-V characteristics. Studies leading to emission stability, tip longevity, and triple junctions to boost emission are currently under investigation. The CNTs can emit very large electron currents for extended periods of time, without any catastrophic failure. Under an applied electric field, the CNTs tend to align themselves in the field direction. SWNTs have smaller diameters and have demonstrated a stable emission current of $\sim 2$ $\mu$A, corresponding to a current density of $10^8$ A/cm$^2$. Recently, higher current densities approaching $10^{15}$ A/cm$^2$ were announced by Nano Proprietary Inc. CNT field emitting surfaces can be printed or even painted with nanotubes, or even grown in-situ. Both catalytically- and arc-produced MWCNTs function essentially identically. Recently, a low threshold field $\sim 1.6 - 2.6$ V/\(\mu\)m was reported for MWCNTs and boron doped MWCNTs embedded in a polystyrene matrix [75]. Freestanding CNTs often provide non-uniform current distributions and limited current stability due to mutual shielding, residual pressure and heating effects. To improve the field emission stability, approaches such as the synthesis of massive arrays of mono-dispersed CNTs in a porous silica template by MOCVD and growth using a single mask self-aligned process with an integrated gate electrode are used [76]. Due to the low threshold voltage of the electron emission and higher current density, several prototype devices and device configurations have been developed, such as field emission display
(FED) devices, field emission x-ray sources for medical applications, ignition switches, photonic devices, lamps, gas discharge tubes providing surge protection and microwave generators.

4.2.2 Gas sensors
CNTs can potentially be used as wires between two metal electrodes and the conductance between the electrodes measured as a function of gate bias voltage. Since the electrical characteristics are strong functions of its atomic structure, mechanical deformation and chemical doping are likely to cause changes in conductance, thus making such devices small and sensitive sensors of their chemical and mechanical environment. Chemical sensors based on an individual or ensembles of SWNTs detected 200 ppm of NO₂ and < 2% of NH₃ in a few seconds [77]. Hence, sensors made from SWNTs have a high sensitivity and fast response time even at room temperature. The first principle calculations using DFT on several molecules, such as CO, NH₃, NO₂, O₂, and H₂O, show the direction of the charge transfer and hence the doping of the semiconductor tube [78], which results in a change in conductivity. For H₂O, a simulated molecular configuration shows repulsive interaction, and no charge transfer is observed in the presence of water molecules [79]. This offers an important option of using SWNTs in water as biochemical sensors. Gas sensors operate by a variety of different fundamentally different mechanisms. Ionization sensors work by detecting the ionization characteristics of distinct gases, but they are limited by the size and high voltage operation and large power consumption. CNTs exhibit excellent field emission characteristics due to the existence of a very large field at the tips even at very low voltages, which could be utilised in the production of compact, battery powered gas ionization sensors. The field emission based ionization gas sensors are expected to show good sensitivity and selectivity, to be unaffected by the extraneous factors such as temperature, humidity, and gas flow, and to offer several advantages over nanotubes sensors mentioned above. The CNTs have demonstrated electric field induced changes in bandgap, which is interesting as it will lead to the detection of ionic species without inducing charge transfer or doping of the SWNTs.

4.3. NANOMECHANICS
Nanostructured materials exhibit many unique and desirable mechanical characteristics with regard to their flexibility, extensibility, yield strength, adhesion, cyclic fatigue, twisting distortion and control over strain energy storage. The production of mechanical work at the nanoscale and the transduction of energy from a nano to micro-scale system will result in many advances in integrated systems, which require coupling mechanical response
with electrical, optical, magnetic, and chem-bio stimuli in recognizing molecular level interactions. However, to develop tools to perform mechanical work at the nanoscale, the understanding of the mechanisms and limits of mechanical deformation, their stability, and the transfer of energy to and from nanostructured materials is critical. The exceptional mechanical properties of CNTs, and their potential use in structural components and devices, have been widely reported in the literature. Their use in atomic force microscopy (AFM) and scanning tunnelling microscopy (STM) as probe tips [80] to measure surface topography, perform direct manipulation and fabrication at an atomic scale, and to investigate biological structures and the spatial arrangement of chemical functional groups in chemical force microscopy (CFM) [81]. In fact, the electronic and mechanical degrees of freedom are tightly coupled in the CNT system. Due to an inverse dependence of the bandgap on the local bending curvature, i.e. the diameter and helicity of the CNT, the property is used to sense local mechanical deformation by a change in the conductance of the tube, resulting in an electromechanical sensor. Use of CNTs as nano-tweezers to grab, manipulate and characterize sub-micron clusters and SiC and GaAs nanowires [82] leads to the potential for creating new types of quantum dots and quantum wires and for manipulation or modification of biological systems, i.e. the structures within a cell.

Nanotubes can be deflected by applying an electrostatic potential [83]. A detailed analysis shows that the charge is located at the tip of the nanotube and the deflection is proportional to the square of the electrostatic voltage. It is also found that nanotubes can be resonantly excited at their fundamental frequency by altering the applied potential, which correspond to those determined for cantilevered elastic beams. The property can be used to determine masses in the picogram range, to measure force at a single molecule level, and in ultra-high frequency modulators and nano-relays [84], and provides the ability to measure extremely small forces. Hence, cantilever based chemical deflectors can be used as actuators which use a change in the dimensions of the nanotube caused by an applied electric potential [85]. The discovery that CNTs can be filled with metal resulted in interesting applications in information storage [86] and nano-thermometers, as it was observed that height of a continuous 1D column of liquid gallium in a CNT varies linearly and reproducibly with temperature from 50-500°C [87].

The exceptional mechanical properties of CNTs, in conjunction with the high strength to weight ratio, renders them ideal as reinforcing fibers in super-strong composites. Initial investigations report the elastic modulus of nanotube composites to much less than expected [88]. Hence, to understand the deformation mechanisms for a high interface/volume ratio, and to optimise the properties of nanotube based composites, it is necessary to study the interface mechanism and load transfer at the nm scale. Some of the necessary parameters
for optimisation for stiffness and strength are dispersion, alignment, and interfacial load transfer. One of the proposed mechanisms to enhance interfacial bonding is by functionalization or chemical attachment of the nanotubes with a polymer matrix. Molecular dynamics simulation results [89] report that the shear strength improves significantly with chemical cross-linking of the CNTs. Several other mechanisms range from molecular level entanglement [90] to reduction in buckling [91]. However the above investigations may not apply in the transition from continuum to discrete behaviour. Several means of functionalising nanotubes have been described in the literature. Initial investigations to study the effect of functionalization on the mechanical characteristics of CNTs under tension, employing simulations based on the Tersoff-Brenner bond-order potential [92], were conducted. The simulation results showed that for CNTs with helicity \( m=n \), there is a marginal increase in the local stiffness with a small number of vinyl attachments. The stiffness is dependent on the tube diameter, chirality, number and types of hydrocarbon attachment. Although a more detailed investigation is in progress, the initial simulation clearly shows a transition from a continuum to a discrete behaviour.

5. Next Generation Sensors, Detectors and Applications

As discussed in the preceding section, CNTs are ideal candidates for field emission. Field emission devices were the first reported application in which CNTs were use as cathodes. The electrons are extracted in a triode configuration with a metal mesh used as a gate electrode. A 32x32 prototype FED was first realized using CNTs as electron sources with a pixel size of \( 200 \times 200 \mu \text{m}^2 \). The diode display had 128 addressable lines and demonstrated a brightness of 1800 cd/m² at 3.7 V/\mu m. Recently, Samsung introduced a 9"x9" full colour FED with 576x240 lines. Despite recent developments, many technological challenges remain to be addressed, leaving the active matrix liquid crystal display (AMLCD) as a key technology, and low cost organic light emitting diode (OLED) technology to take an active role.

X-ray radiation is extensively used in many industrial and medical applications. The emission of x-rays takes place using a filament which is resistively heated to over 1200°C to emit electrons which are accelerated and then bombard a target. In comparison, electron emission employing field emission is more attractive, as it takes place at room temperature and is controllable using a rather small voltage. X-ray tubes which can generate a sufficient flux for diagnostic imaging applications have been reported [93]. Such devices can produce focused electron beams with a very small energy spread, plus a programmable pulse width and repetition rate, leading to the possibility of portable and miniature x-ray sources. Other futuristic applications
include lamps with lifetimes > 8000 hours, nanotube-based gas discharge tubes for the protection of telecommunication networks against power surges, and microwave generators. Figure 6 (a) shows a prototype design of a photovoltaic device based upon the field emission properties of carbon nanotubes. Although a theoretical calculation of the maximum conversion efficiency of such devices is still under investigation by the author, it is predicted that they will have a much higher conversion efficiency than conventional junction based photovoltaic devices.

Research is currently in progress to fabricate nano-materials by integrating nano-fabrication and chemical functionalization, particularly in the case of nano-electrode assemblies interfaced with biomolecules for the development of biosensors. DNA molecules are electro-active at certain potentials that can be used to identify the hybridization process. These sensors will be integrated into the next-generation 'gene-chips', especially where detection of less than an attomolecule, such as amino acids or DNA, is critical. The recent discovery of quantum confined particles or quantum dots (QDs) having unique optical and electronic properties, such as size- and composition-tunable fluorescence emission from visible to infrared wavelengths, a large absorption coefficient across a wide spectral range and a very high level of brightness and photo-stability, will lead to the development of multifunctional nanoparticle probes for cancer targeting and real-time in-vivo imaging in living cells. The broad
excitation profiles and narrow, symmetric emission spectra in high quality QDs are well suited to optical multiplexing, in which multiple colours and intensities are combined to encode genes, proteins, and small molecule libraries [94]. In-vivo studies on mice show that QDs accumulate at tumour sites. Such QDs were encapsulated with triblock copolymers and treated chemically with tumour-targeting ligands having drug-delivery functionalities [95]. These results suggest new possibilities for ultra sensitive and multiplexed imaging of molecular targets. Other nano-technology projects include a nanoscale barcode for genome-wide screening such as disease susceptibility and therapeutic responses, blood fingerprinting, and the development of a technology capable of directing nerve growth through scar tissue for spinal chord regeneration, to name but a few.

One of our recent projects concerns the study of duchene muscular dystrophy (DMD), one of nine types of muscular dystrophy, a severely degenerative, lethal genetic disease primarily affecting voluntary muscles, caused by absence of dystrophin, a protein that helps keep muscle cells intact. New experiments on mice with DMD show that gene therapy can reverse some symptoms of the disease even in very old mice. A major limitation to gene therapy thus far has been the absence of a method by which a new gene could be efficiently delivered to the dystrophic muscles. We are investigating the regenerative potential of satellite cells immobilized with a new dystrophin gene on nanostructured templates, which would be delivered to all the affected muscles of mice with muscular dystrophy. The satellite cells, normally associated with healthy muscle fibres are inactive, unless there is muscle damage caused by mutation on the gene encoding dystrophin. The repair and regeneration process of damaged muscles is mediated by fusing satellite cells to the damaged muscle fibres. Hence the use of therapeutic templates based on nanostructured materials can be developed and inserted for targeted gene delivery.

The exceptionally high Young’s modulus of individual CNTs has applications in lightweight composite materials. The applications that exploit the mechanical properties of CNTs are in the realm of electronic materials mounted on the tip of a scanning probe microscope, such as an AFM. One of the most remarkable characteristics is the possibility of bandgap engineering by controlling the microstructure. Hence, a pentagon-heptagon defect in the hexagonal network can connect a metallic to a semiconductor nanotube, providing an Angstrom-scale heterojunction with a device density approximately $10^4$ times greater than in present day microelectronics. Ferromagnetically filled CNTs usually exhibit coercivities greater than that of the bulk metal [87]. Fe-filled CNTs provide distinct magnetic properties such as an easy axis of magnetization perpendicular to the substrate plane, and enhanced coercivity. Owing to the nanoscale dimensions of the CNTs, this
development offers a significant potential for the storage of data at approximately 20-40 GB/cm$^2$ capacities. Some of the possible applications of nanostructured composites are: a superconductor with a record room T$_c$ (see figure 6 (b); a the phonon quantum generator (phaser) of hypersound of extremely high frequency; a noiseless loss-less nanoantenna operating in the super-frequency range[96]; a low-barrier emitter for flat displays; a solar cell with a record efficiency [6] and many other unique applications in photonics.

6. Challenge

Nanoscience and nanotechnology addresses some of the greatest challenges of the 21$^{st}$ century, by providing routes to synthesize materials by design and establishing the connection between structure and function of biomolecules to human physiology. Since nanomaterials are ideal building blocks for the fabrication of structures, nano-devices and functionalized surfaces, one of the key challenges for such applications is to precisely control the growth of these materials at desired sites with a desired structure and orientation. The current effort is to grow a micro-patterned multi-walled CNT array with a controlled density and purity, for application as a nano-electrode assembly. Several challenges in the preparation of the CNTs and devices are (a): control of the nanotube diameter and chirality, (b): control of doping, and (c): formation of reliable contacts. One of the primary challenges is in the synthesis of the CNTs of specified length and chirality as pure species. One of the fundamental questions remaining concerns the new insights that can be gained about electro-optical and biological systems from the capability to examine single-molecule properties. In addition to finding an economical fabrication method for the production of CNTs, effort is underway to estimate the figures of merit for the high power, high frequency and high temperature operation of future devices based on CNTs

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A. VASEASHTA

1. Introduction

The formation of high-quality polycrystalline silicon (poly-Si) on foreign substrates is one of the most challenging tasks in processing thin film solar cells, thin film transistors, image sensors, active matrices and liquid crystal displays. In order to produce cheap and efficient solar cells, stable TFT and active displays, a large number of different thin film technologies have been developed. The most successful until now involve recrystallization of deposited a-Si films. Several crystallization techniques have been applied: Solid Phase Crystallization (SPC) [1] Excimer Laser Annealing (ELA) [2] and Metal-Induced Crystallization (MIC) [3, 4]. SPC utilizes the annealing of an amorphous Si film. Crystallites nucleate and grow until the whole layer is transformed into poly-silicon. However, the crystallization temperature is too high (> 600°C) for cheap glass substrates to be used, and the time for full crystallization is too long (~ 60 hours). ELA poly-Si films obtained by this process are of good quality, but it has some disadvantages: it is expensive, needs special expensive facilities and the uniformity of the films over large areas is not satisfactory. Conventional laser annealing using pulsed excimer lasers yields grains with a size of ~ 1µm. As in figure 1, such grains are too small for material of good quality [5]. Electronic charges at the grain boundaries (GB) reduce the material quality. Pinning of the Fermi level by deep states around midgap is the reason for the high sensitivity of Si to defects. Figure 2 gives band diagrams for GBs in Si, showing the symmetric depletion regions around them. The barriers hinder current transport by majority carriers, so that the carrier mobility is lower than in crystalline Si. Interfacial charges attract minority carriers, increasing the recombination and thus lowering the open circuit voltage and efficiency in polycrystalline solar cells. Growing Si with a (110)-surface texture seems to be the key to obtaining GBs with a low density of crystallographic defects [6]. If one avoids oxygen, and uses hydrogen passivation, it is possible to suppress the remaining electronic activity due to crystallographic imperfections at the [110] type boundaries.
Although significant improvements have been made in the area of solid phase and laser crystallization, no breakthrough has been made in the formation of uniform, large grained poly-Si films with a grain size larger than several μm.

Recently, metal induced crystallization (MIC) has attracted attention as an alternative process. It is a promising technology for the low-temperature fabrication of large-area polycrystalline silicon (poly-Si) with grain sizes larger than the thickness of the Si layer, for photovoltaic, TFT and display applications [7-11]. It is an economically attractive process for producing poly-Si at a low temperature (< 550°C) in a short time, from small-grained or amorphous Si deposited on a low-cost substrate such as glass or plastic. Various different metals have been used for performing of MIC, such as Au [12], Al, [4, 7-10,13], Sb [14], In [15], Ag [16] which form eutectics with Si, or metals such as Pd [17,18] Pt, [19], Ti [20] and Ni [21-25], which form silicides. [18,19,23,24].

The preparation of poly-Si films by MIC is based on an annealing step of amorphous Si films, deposited by different methods. When a-Si is in contact with certain metals, its crystallization temperature is found to be drastically reduced.

During the process, significant reactions can take place between the semiconductor and the metal film. The study of such metal-semiconductor interactions started with the investigation of contact formation in semiconductor devices. According to reported results [26], the reaction between the metal and a-Si occurs at the interlayer by diffusion, and it lowers the crystallization temperature. The enhancement is due to a change in the Si-Si covalent bonds at the Si/metal interface, due to the free electrons from the metallic phase [27].

Figure 1. Conversion efficiency of crystalline Si thin film solar cells as a function of grain size. Open squares: tandem or triple cells combining crystalline and amorphous Si. Open circles: p-i-n junction cells; closed circles: p-n junction cells (the solid line is a guide for the eye). Triangles: monocrystalline Si transfer cells. For comparison, the efficiencies of cells fabricated from wafer based float zone Si (FZ-Si) and of thin film cells from CIGS and triple junction a-Si:H (dashed lines) are given [5].

Figure 2. Band diagram at a grain boundary in p-type (a) and n-type (b) Si. The Fermi level is pinned around midgap [5].
has been found that dissolution and transport of the semiconductor take place in the metal at temperatures well below that at which any liquid phase exists [28]. Studies of dissolution and migration of Si in Al films in the case of Aluminium Induced Crystallization (AIC) indicate an enhancement of the diffusivity by as much as 1.5 orders of magnitude [26]. During isothermal heat treatment, the semiconductor film is dissolved into the metal film, where it diffuses and precipitates. The enhancement in diffusivity is not accompanied by a measurable enhancement of solubility over values for Si in wrought Al. However, the concentration of solute Si dissolving into the metal solvent from the amorphous material will be higher than if dissolution were occurring from crystalline material. In dilute solution, the concentration of solute is proportional to exp(G/kT), where G is the free energy per solute atom. Therefore, the excess free energy, ΔG, associated with the amorphous material in contact with the solvent should enhance the solute concentration. These processes are solid-solid reactions, since this behavior is observed at temperatures lower than that of the eutectic in the system. The metal film is saturated with Si, the dissolved semiconductor becomes supersaturated and this can be relieved by crystallite growth. The nucleation and growth of precipitates out of the supersaturated solution is a familiar process that occurs upon cooling [29]. Crystallite formation is possible at constant temperature (as in MIC) due to the higher free energies of amorphous semiconductors compared to those of single crystals. Similarly, single crystals and thin films of Ge in contact with evaporated Al films are found to saturate the solid Al film with dissolved Ge at temperatures well below that of the eutectic. It is reported that the formation of metal-a-Si bonds starts at 150°C for a-Si/Al [30] and 130°C for a-Si/Au [12]. For the metals which form silicides, silicide precipitation has been observed at temperatures as follows: a-Si/Ni – T > 450°C [23-25]; a-Si/Cu - T = 175°C [31]; a-Si/Pt and a-Si/Pd - T > 200°C [23-25, 32]. In spite of the large variety of metals used, Al and Ni have found the largest applications for the MIC of a-Si films.

2. Aluminium Induced Crystallization

The main goal of the study of the processes during AIC is to produce poly-Si films by a low-cost technology, for use as seeding layers for the epitaxial deposition of thicker Si on large cheap substrates for solar cell applications.

Various different structures with a-Si and metal layers have been prepared. The metal film (Al) can be deposited on a glass substrate before a-Si deposition, or on top of an a-Si film [4,7-11]. Recently, AIC has been performed by annealing a-Si in an Ar atmosphere using AlCl₃ as the source of Al [33], or by the introduction of Al atoms and clusters by co-sputtering of Si and Al [10,11]. The a-Si film has been deposited by PE CVD [34], d.c. and r.f. magnetron sputtering [4,7-11] or electron beam evaporation [35]. Thus, the a-Si film could be hydrogenated or without H. The prepared stacks are annealed in vacuum, inert gas (Ar, N₂, N₂+H₂, H₂), or in air.
Various methods have been used to study the crystallisation and properties of the poly-Si film, mainly SEM, TEM, XRD, Auger and Raman spectroscopy. Auger spectroscopy profiles [36] of the as-deposited and annealed stack, which consists of a-Si(150nm)/Al(50nm)/SiO2(50nm)/c-Si, are shown in figure 3. The a-Si is deposited by d.c. magnetron sputtering on Al films evaporated on SiO2-covered c-Si wafers. The as-prepared Si/Al bilayer has a sharp interface between the outer a-Si and inner crystalline Al layers. After annealing, most of the Si and Al layers have exchanged: most of the Al has moved to the surface and the Si has moved to the substrate. As indicated by the oxygen signal, no compositional changes appear to occur upon annealing. XRD analyses demonstrate that the poly-Si film has a {111} texture. In situ X-ray diffraction after AIC of the stack a-Si(500nm)/Al(500nm)/SiO2/c-Si, where the a-Si:H is deposited by PECVD on an oxidized Si substrate, show that the <111> silicon peak appears when an annealing temperature of 200°C is reached, and its height increases with annealing time (figure 4) as reported in [37].
METAL-INDUCED CRYSTALIZATION

The authors found AIC to follow an Arrhenius-type dependence. The activation energy for the thermally activated phenomena controlling the crystallization was calculated to be 1.1 eV, which is close to the reported value of 1.2 eV for the diffusion of Al in a-Si:H. Lower activation energies were reported when a-Si:H:D and a-Si:F films were annealed to produce poly-Si by AIC - 0.7 and 0.4 eV respectively [38]. When the Al film is covered by aluminium hydroxide, the activation energy is reported to be 0.50-0.65 eV for the crystallisation of unhydrogenated a-Si [39]. Thus, the process of AIC will depend on the properties of the a-Si film. It has also been reported that the structure of the poly-Si depends on the structure and composition of the underlying Al film [40].

The formation of poly-Si films is controlled by the diffusion of Si atoms from the a-Si through the a-Si/Al interface into the Al layer, which regulates the supply of Si for poly-Si growth. On the other hand, the diffusion of Si atoms within the Al layer determines the speed of the grain growth. In addition to these two processes, the nucleation rate is also dependent on the annealing temperature. SEM images of two samples, prepared on identical substrates but annealed at different temperatures (375 and 525°C) are presented in figure 5. The sample annealed at the lower temperature contained significantly larger grains than that treated at 525°C, due to the lower ratio of nucleation rate to growth velocity for the former. This means that with increasing temperature, the nucleation rate increases faster then the velocity of grain growth. Therefore, to process large-grain poly-Si using AIC, lower temperatures are preferred. The trade off is the slower crystallization process.

In terms of crystallographic quality, faults in the crystallographic structure of individual grains manifest themselves as streaks with a different contrast to the surrounding grains, as in figure 5a. At higher magnification, small (~ 1 μm) black dots arising from trapped Al clusters can be detected.

The interaction of the a-Si and Al layers in an a-Si/Al/glass structure has been studied using Focused Ion Beams (FIB) of the cross sections of the samples, [41]. Figure 6 demonstrates a series of samples before and after annealing at 500°C for 5, 10, and 60 min. All samples were prepared in the
Figure 6. Cross-sectional FIB micrographs of the \( \alpha \)-Si/Al/glass structure: (a) before annealing, (b) after annealing for 5 min, (c) 10 min, and (d) 60 min at 500°C. The samples are tilted by 45° [41].

same thermal evaporation and sputtering process, to ensure identical conditions prior to annealing. The Al layers in figures 6a and b show slight gray variations within the layer. These were caused by channeling of the ion beam during imaging. The ions penetrate into the polycrystalline Al to different depths according to the crystallographic orientation of the Al grains, consequently giving rise to variations in the secondary electrons generated. This effect is particularly prevalent in polycrystalline Al. No channeling could be detected in either poly-Si material or multicrystalline Si wafers. Figure 6a shows the \( \alpha \)-Si/Al/glass structure before any heat treatment. During 5 minutes of annealing at 500°C, Si nuclei are formed within the Al layer at the Al/\( \alpha \)-Si interface, as in figure 6b. The material contrast of the FIB was confirmed by EDS investigations. After annealing for 20 min, the Si nuclei had grown further into the Al layer, until they were confined between the \( \alpha \)-Si/Al interface and the glass substrate. Sandwiched between these two boundaries, the grains continued to grow laterally, as in figure 6c. Crystal growth ceased when adjacent grains met, finally forming a continuous polycrystalline silicon film on the substrate (figure 6d). During the poly-Si growth, the Al segregated to the top of the sample. Silicon which was not incorporated into the poly-Si layer formed small crystals within the newly evolved Al layer. These are observed as dark areas in the Al layer in figure 6d. The overall process during interaction leads to an exchange of layer positions, leaving the poly-Si film on the glass with the Al layer on top.

It has been pointed out that the thickness ratio of the \( \alpha \)-Si and Al films determines the thickness of the poly-Si layer obtained after AIC [41]. It was concluded that to form continuous poly-Si films under steady temperature conditions, the \( \alpha \)-Si layer must be at least as thick as the Al one, but that thicker \( \alpha \)-Si layers will not give any advantage in the final thickness of the polycrystalline Si layer. A layered structure with \( \alpha \)-Si and Al films of equal thickness is, therefore, the most relevant one to study.

It has been found that the aluminium oxide layer, formed during the preparation of the initial stack, is still present after the annealing step. The Al\(_2\)O\(_3\) layer has a corundum structure [13]. The thickness of this layer is
Figure 7. Structural changes in the system Al/Al₂O₃/a-Si with a Si nucleus [13].

Figure 8. Optical microscopy pictures of the surfaces of samples of glass/Al/Si (a) and glass/Si/Al (b) annealed in air [11].

laterally inhomogeneous - it varies between 2 and 8 nm. The nucleation of poly-Si starts at the Al/Al₂O₃ interface. The ideas of the role of the interfacial Al₂O₃ are summarized in figure 7. The Al oxide is a stable interlayer, the thickness of which is laterally inhomogeneous. The material transport of Si and Al occurs through this interlayer by diffusion. At favored sites, seed formation of Si crystallites occurs, and these grow to large grains.

Differences have been found in the structure and surface morphology of poly-Si films when the a-Si is deposited on an Al film and when Al is deposited on top of the a-Si. [13]. Optical microscopy pictures of the surface of these samples (figure 8) demonstrate that the average poly-Si grain size is slightly larger when the Al is deposited on top (30-40 µm) than when it is below (20 µm). The distance between the grains on the film surface is larger in the first case. In this case, the a-Si/Al interface provides less seeds for crystal growth, probably due to oxidation of the a-Si surface during the 2 days storage after deposition. This is important for the use of poly-Si films as seeding layers for the deposition of thicker poly-Si films by other methods. The grain sizes of the poly-Si films estimated from SEM and optical microscopy images are up to 40 µm, for different annealing conditions. The fractal structure of the Si crystallites can be seen. Such a structure has been observed in poly-Si films obtained by MIC using Ag [16], Au [12] and Cu [31].
Raman spectra of these samples are presented in figure 9. Comparison of the two spectra shows that the TO–LO phonon peaks have the same position. However, the band for the poly-Si with Al on top of the a-Si is sharper, and its FWHM is narrower by 4 cm\(^{-1}\).

The poly-Si films were prepared by MIC of a-Si with Al clusters, prepared by co-sputtering of Si and Al. The crystallinity of the samples with different contents of Al (deposited by r.f. magnetron sputtering at room temperature and 350°C, and annealed at 500°C in vacuum) was investigated by Raman spectroscopy, and the spectra are shown in figure 10. The sample with the lowest Al content (\(\phi = 103\)) demonstrates a Raman spectrum typical of a-Si; a broad band at approximately 470 cm\(^{-1}\). Samples with higher Al contents (\(\phi = 34\)) have a Si–Si TO–LO phonon band, centered at approximately 512–516 cm\(^{-1}\), showing the presence of a crystalline phase.

A shoulder at approximately 470 cm\(^{-1}\) is observed for the sample with the highest Al content, indicating the presence of an additional amorphous phase. The sample with the lowest Al concentration, deposited at a higher substrate temperature (350°C) also shows a sharp band at approximately 514 cm\(^{-1}\) and a shoulder at approximately 470 cm\(^{-1}\). This indicates that AIC can take place with a lower Al content when the films are deposited on a heated substrate. A lower limit for the Al concentration for co-sputtered films exists, which determines whether the AIC of Si takes place.

The main particularity of AIC is that the poly-Si films obtained are p-type doped – a low resistivity of about 0.66 to 0.44 Ωcm and a carrier concentration of about 2.5x10\(^{18}\) cm\(^{-3}\) have been reported [11]. This offers the possibility for using poly-Si obtained by AIC as a p+-type layer in heterojunction structures.
Figure 11: Raman spectra of samples of glass/Al/a-Si (1, 3, 4, 5) and glass/Al/a-Si:H (2), annealed under the conditions given in Table 1. The optical images (with corresponding numbers) show the poly-Si films formed. The black spots in (2) are pores which appear after the etching of the precipitated Al.

Table 1. Parameters deduced from the Raman spectra of the samples shown in figure 11.

<table>
<thead>
<tr>
<th>Curve no.</th>
<th>Annealing conditions</th>
<th>TO-LO peak position, cm⁻¹</th>
<th>FWM, cm⁻¹</th>
<th>Stress, MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Air, 500°C, 7 hrs</td>
<td>517</td>
<td>11</td>
<td>1000</td>
</tr>
<tr>
<td>2</td>
<td>Air, 500°C, 7 hrs</td>
<td>521</td>
<td>7</td>
<td>&lt;250</td>
</tr>
<tr>
<td>3</td>
<td>N₂, 500°C, 5 hrs</td>
<td>520</td>
<td>9</td>
<td>250</td>
</tr>
<tr>
<td>4</td>
<td>N₂+H₂, 500°C, 5 hrs</td>
<td>521</td>
<td>7</td>
<td>free</td>
</tr>
<tr>
<td>5</td>
<td>H₂, 500°C, 3 hrs</td>
<td>521</td>
<td>5</td>
<td>free</td>
</tr>
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</table>

It has been reported [42] that the process of AIC is enhanced when annealing is performed in an atmosphere including H₂. Figure 11 displays the Raman spectra of samples annealed in different ambiances. The grain size is inversely proportional to the FWHM of the Si-Si TO-LA–like peak, so it can be deduced that the grain size increases when the annealing is performed in the presence of H₂. The decrease in the value of the tensile stress (Table 1) is accompanied by a significant reduction of the grain boundary volume, and of Al precipitation there.

It is suggested that the H₂ stimulates crystalline grain growth during annealing, by increasing the diffusion rates of Al and Si. It is supposed that due to the reduction properties of H₂, the Al₂O₃ film (formed during storage of the Al film in air) is reduced, and an aluminium hydroxide can be constituted. This leads to an enhancement of the material transport during AIC. Polycrystalline films of SiGe have also been prepared by AIC of a-SiGe films deposited by the co-sputtering of Si and Ge [11]. The Raman spectra of polycrystalline SiGe films annealed at two temperatures, 500 and 540°C, for 3 hrs are shown in figure 12. The spectra contain peaks typical of poly-crystalline SiGe alloys at 284, 398 and 480 cm⁻¹. These correspond to the Ge–Ge, Si–Ge and Si–Si
Figure 12. Raman spectra and an optical image of the surface of samples of glass/Al/Si+Ge annealed at $T_{an}=540$ (1) and 500°C (2), and glass/Si+Ge, annealed 500°C (3). The Ge content in the a-(Si+Ge) films is about 40 at.% [11].

Polycrystalline Si$_{1-x}$Ge$_{x}$ films with different Ge concentrations (x) have been prepared [43] by AIC at an annealing temperature of 415°C (below the eutectic temperature of Ge-Al) in vacuum or in N$_2$. The a-SiGe films were deposited by electron beam evaporation of a premixed SiGe target. It was shown that the crystallization process can be employed throughout the entire alloy range, and results in polycrystalline material without significant phase separation.

All of these results demonstrate that AIC is a solid state process - the crystallization takes place at the temperatures far below the eutectic temperature for the Al-Si system. It would involve considerable breaking and making of bonds. The strong covalent nature of the Si-Si bond would impose a high activation energy for this process. However, diffused metal atoms forming interstitials in Si are known to change the type of bonding from covalent to metallic at the Al/Si interface, and contribute to a large reduction in the activation energy [44]. The metastable silicide layer at the interface accelerates the inter-diffusion of Al and Si, leading to the formation of an intermixed Al-Si layer. The phase diagram of the Al-Si binary system indicates that the solubility of Si in Al is practically negligible. The supersaturation of Si in Al is thus relieved through the precipitation of Si by nucleation and growth along the Al/a-Si interface. The growth of these precipitates
METAL-INDUCED CRYSTALLIZATION

is controlled by the diffusion of Si from the silicide layer. The precipitates show a tendency towards lateral growth and grow to quite large sizes (~ 50μm), compared to the film thickness (150-500nm). It has been observed that the silicide layer formed at an intermediate temperature (125°C, as in [14]) decomposes completely at 300°C [45], giving rise to a mixed phase of crystalline Si and Al. The Si crystallites organize as dendrite single crystals, preferentially oriented along a <111> axis perpendicularly to the film surface. Only Edelman et al. [38] have reported obtaining a <100> axis orientation perpendicular to the film surface. However, this was for the AIC of fluorinated a-Si films. The crystallization process depends on the temperature and time of annealing, the thickness of the Al and Si films, the composition of the Al surface (the presence of pure Al, aluminium oxide or hydroxide), the presence of H and F in the amorphous Si layer and the ambience in which annealing is performed.

3. Nickel Induced Crystallization of a-Si Thin Films

A number of studies of the micro-structural variations for the NIC of a-Si have been performed. Addition of very small amounts of Ni to a-Si films, followed by heating to temperatures less than 550°C, resulted in the formation of NiSi₂ precipitates, whether the Ni was deposited on the a-Si film as a thin film [22, 23, 45-49] or by ion implantation [50]. In the case of Ni, the crystallization could be classified as vertical metal induced and laterally induced crystallization.

Nickel induced lateral crystallization (NILC) has been performed by depositing a 10nm film by e-beam evaporation on the surface of a 1μm thick a-Si film, cleaned in dilute HF. The a-Si was prepared by low pressure CVD at 550°C, on oxidized c-Si substrates. The Ni layer was patterned

Figure 13. Optical micrograph of a sample with selectively deposited Ni on a-Si after annealing for 16 h at 500°C. The 50-mm-wide Ni lines (area 1) are surrounded by the bright MILC region (area 2). Area 3 is a-Si. The thicknesses of the Ni and Si films are 10 and 70nm, respectively; The typical Raman spectra shown were obtained in: (a) the Ni covered region (area 1), (b) the MILC region (area 2), and (c) the amorphous Si region (area 3) in a sample, after heat treatment [51].
Heat treatment was performed in a conventional atmospheric pressure horizontal furnace. The a-Si under and near the Ni-covered regions was found to have crystallized after heat treatment at 500°C for 1-90 hrs. An optical micrograph of a sample is shown in figure 13. The region with the darkest contrast (area 1) was originally covered with Ni. This is surrounded by a region (area 2) with the brightest contrast, which is in turn embedded in a gray region (area 3). Typical Raman spectra are also shown. The broad structure near 480 cm$^{-1}$ in the spectrum from area 3 indicates that the film remained amorphous. Instead of a broad structure, sharp peaks near 520 cm$^{-1}$ were detected in the spectra from areas 1 and 2, indicating that the a-Si in these regions has crystallized. This provides direct evidence that MIC and Metal Induced Lateral Crystallization (MILC) have occurred in areas 1 and 2, respectively. The FWHM of the Raman peak obtained in area 2 is about 7.8 cm$^{-1}$, smaller than the 8.3 cm$^{-1}$ obtained in area 1, probably indicating that the average grain size in the MILC region is larger than that in the MIC region. Consistent with the Raman results, TEM shows that the polycrystalline film in the MIC area under the Ni coverage is composed of small grains, while the MILC area outside the Ni coverage is composed of significantly larger grains. The TED micrograph in figure 14b taken in the MIC area indicates a nearly random distribution of grain orientations, while that in figure 14c taken in the MILC area indicates that the large grains are primarily (110) oriented. The AES spectra obtained in the different areas demonstrate that no Ni signal was detectable either in the MILC or the amorphous region. The Ni signal is significant in area 1, indicating that a large amount of Ni still remains in the area of original coverage. The atomic concentrations were estimated to be 4.64, 11.63, and 83.73% for O, Ni, and Si, respectively.

It has been shown that in the presence of an electric field, the temperature of crystallization for the NIC can be lowered [52]. It was reported that a-Si can be completely crystallized at 600°C within 30 min. This annealing time is extremely short compared to that (20 hrs) for conventional Ni-induced crystallization. The growth of needle-like crystallites seems to take place from the mother crystallites. The crystallization of the a-Si occurs at the silicide/a-Si
interface, as a result of Ni migration from the Si interface to the a-Si interface. This leaves tails of c-Si and then needle-like crystallites in an a-Si matrix, as in figures 15b and c. The electron diffraction pattern indicates that the crystallites orient along the <110> direction normal to the film surface (figure 15c). This can be explained by the fact that the surface energy of the (111) plane in Si is the lowest compared to that of any other orientation. The needle-like crystallites have lengths up to a few μm and widths ~ 100 nm (figures 15 and 16) [53,54].

Crystallization of an a-Si film on a c-Si substrate, when a very thin Ni layer is deposited on the substrate, has also been achieved by annealing at 500°C. For this, the Ni and Si must be deposited at a high temperature (450°C). This can be explained by the formation of silicides during the deposition, which will be nuclei for the epitaxial growth of Si during annealing. Thus, the substrate temperature must be kept high enough to form a Ni silicide [54].

Polycrystalline Si films have been obtained by the NIC of a-Si+Ni films deposited by r.f. magnetron co-sputtering on glass substrates after annealing in air at temperatures below 560°C, with and without the application of an electric field [22]. The Raman spectra of the annealed samples show that the crystallinity of the layers depends on the Ni concentration. It has been demonstrated that a threshold value of the Ni concentration exists. Figure 17 displays the Raman spectra of two sets of samples of with different Ni contents (C_{Ni} = 15 and 21 at.%), deposited at different substrate temperatures, T_s, and annealed at 560°C for 6 hours. The spectra have a Si-Si TO-like band at about 519-520 cm⁻¹, due to the poly-Si phase, and a shoulder at about 470 cm⁻¹.
indicating the presence of an additional amorphous Si phase. The position of the Si-Si TO-like band and the FWHM (12 cm$^{-1}$) of the TO-like bands do not change with increasing $T_s$. A comparison of the spectra in Figure 17 shows that the quantity of the amorphous phase in the films decreases with increasing Ni concentration. The Raman spectra can be fitted by two Gaussian bands, corresponding to the crystalline and amorphous phases. The degree of crystallinity was calculated by the Raman intensity ratio. It increased from 0.17 to 0.56 when $T_s$ increased from 150 to 350°C for samples with $C_{Ni} = 21$ at.%. This value was lower for films with lower $C_{Ni}$ (15 at.%) , but increased from 0.05 to 0.2 with increasing $T_s$. Films with $C_{Ni} < 15$ at.% did not crystallize under the same annealing conditions. Their Raman spectra (not shown here) corresponded to those of a-Si. When the density of Ni atoms in the a-Si+Ni films was lower than a certain value, no NiSi$_2$ precipitates were formed and so there were no crystallization nuclei.

The tensile stress of the poly-Si was calculated from the wave number shift of the Si-Si TO-like peak compared to the Raman line in the measured spectrum of stress-free c-Si. This gave stresses from 250 to 500 MPa for samples with Ni concentrations of 21 and 15 at.%, respectively. In comparison with the results for AIC in the literature [11,22], the NIC results demonstrate lower tensile stresses in the poly-Si films. In AIC, the short-range order in the poly-Si is perturbed by Al-Si bonds (poly-Si, obtained by AIC is $p^+$-type doped) and so a larger shift in the Raman spectrum appears. In NIC, the a-Si crystallizes on the surface of the NiSi$_2$. NiSi$_2$ and Si have a small difference in the lattice constant - 0.4% - so less tensile stress is induced in the crystallized phase. As mentioned before, Ni atoms are not embedded in the poly-Si crystallites, as is the case for AIC. Thus, they do not induce significant disorder, giving a lower tensile stress in the poly-Si films. The main difference between AIC and NIC is due to the different reaction behaviors of Al and Ni with Si. Ni is known to create silicides. In contrast, Al forms a eutectic at 577°C and metastable Si-Al bonds starting from room temperature, which decompose at 300°C [45]. It has been shown that Ni silicides (Ni$_2$Si, NiSi, and NiSi$_2$) can be formed at temperatures below 350°C [23-25]. The phases are controlled by the annealing temperature.
and by the Ni/Si ratio. At 350°C, the NiSi transforms into the thermodynamically favored end phase, NiSi₂. It has been demonstrated [46] that the formation of NiSi₂ precipitates occurs after the heating of a-Si films containing implanted Ni ions. The precipitates act as nucleation sites and can migrate through the a-Si. They act as a template for the formation of crystalline silicon. The phenomenon of NIC is thought to be due to the migration of NiSi₂, because its crystal structure is the same as that of Si and the difference in the lattice constants between the two is only 0.4%. The needlelike Si crystallites are formed by silicide-mediated crystallization of a-Si. This facilitates the formation of crystalline silicon on the {111} face of the NiSi₂ precipitates. Crystallization appears to proceed from these nuclei in the (111) direction. The grains have a (100) preferential orientation perpendicular to the substrate. The rate of this solid phase metal-induced crystallization can be enhanced by the presence of an electric field (figure 18) [23,47].

4. Applications of Poly-Si Films Prepared by MIC

The first application of poly-Si films prepared by AIC was for thin film solar cells, in 1981 [35]. Thin films of Al and a-Si were deposited sequentially by e-beam evaporation on 1 Ωcm n-type <111> crystalline Si, or on polycrystalline Si substrates with a grain size of 0.5-3 mm. After performing AIC at 500°C in an N₂ atmosphere, the Al from the surface of the poly-Si film was etched and Au or Al was used for the front contact. Efficiencies of 10.4 and 8.5% were observed for cells on c-Si and polycrystalline wafer substrates, respectively, under simulated AM 1.1 sun illumination.

Recently, a study of the minority carrier diffusion length, Lₙ, of AIC-grown Si has been performed to determine whether these films can be used as the absorber layer (i.e. base region) in c-Si solar cells. The AIC-grown Si films were formed at 460°C on single-crystal n-Si wafers (1 Ω.cm n-type FZ Si) and glass, respectively (figure 19). The measured dark I-V characteristics of both types of cell are shown in figure 20. At 1 sun, the cell on the c-Si substrate had a open circuit voltage, Vₜₙ, of 337 mV, a short circuit current, Jₛₑ, of 10.3 mA/cm², a fill factor, FF, of 57% and an efficiency of 2.0%. The cell deposited on a glass
substrate had a $V_{oc}$ of 144 mV, a $J_{sc}$ of 1.8 mA/cm², a FF of 31% and an efficiency of 0.1%. The low values for these cells, compared to the results by Tsauer et al. [35], was explained by possible contamination of the AIC film from the equipment used for deposition and annealing.

From current-voltage and quantum efficiency measurements, the authors [55] showed that the $L_n$ of their AIC grown p⁺ films was only about 100 nm, regardless of the substrate material. This value is too low to enable the use of such an film as an absorber in a thin film c-Si solar cell. Thus, the most exciting application of these poly-Si films is their use as seeding layers on glass.

There is a recent report of the use of poly-Si films as seeding layers. Si films, about 5 μm thick, were deposited on an AIC seeding layer by Ion Assisted Deposition (IAD) [56]. A TEM image of a 5 μm thick Si film on 0.4 μm poly-Si made by AIC at 500°C is shown in figure 21. The grain size of the IAD Si film was about 5μm, and the film was continuous and smooth. The authors [56] believe that the IAD method is capable of achieving poly-Si thin film solar cells on seeded glass with conversion efficiencies of about 10%.

Figure 19. Structures of c-Si solar cells made on Si wafers and glass substrates [55].

Figure 20. Measured dark I-V, 1-sun I-V, and $J_{sc}$–$V_{oc}$ curves of a Si wafer (a) and a glass (b) substrate cell [55]. Also shown in (a) is the n=1 behavior of the cell of Tsauer et al.
Polycrystalline thin film silicon solar cells have been prepared using MIC of an amorphous Si film and a thin Ni layer [34]. MIC using a nm-scale Ni layer produced a highly activated n-type layer at a 550°C annealing temperature. A schematic diagram of a solar cell structure is shown in figure 22. The a-Si films were deposited by VHF (100 MHz) PECVD, using 100% SiH₄ and H₂-diluted PH₃ or B₂H₆ to obtain n-type or p-type layers, respectively. Three different structures were prepared. The first one featured p-, i- and n- layers all crystallized by NIC. In the second one, only the n- and i-type Si layers were prepared by NIC. In the third one, only the n-layer was polycrystalline. 1.0 nm Ti and 0.6 nm Ni layers were deposited on the surface of the n-type a-Si:H layer before NIC (see figure 22a). The Hall mobility and carrier concentration of the NIC n-layer were 15 cm²/V·sec and 5x10¹⁹ cm⁻³, respectively. Figure 22b shows the light-induced I-V characteristics for the
three types of cell with NIC Si films. The cell with only the n-type poly-Si layer demonstrated the best characteristics, due to the low Ni concentration. The lowest Ni concentration in the i-layer (less than $10^{16}$ cm$^{-3}$) was detected by SIMS depth profiles of Ni in this structure compared with the other two. Since the structure was not optimized, the cell did not demonstrate a high efficiency. However, its external quantum efficiency was relatively high in the long-wavelength region near the n-layer (figure 22c).

TFTs have also been produced using poly-Si films prepared by NIC, [24,57]. The MILC device [57] had a threshold voltage of 1.2 V, a field effect mobility of 120 cm$^2$/V/sec, and a maximum on/off current ratio of $6\times10^7$.

5. Conclusions

The crystallization temperature of an a-Si film can be considerably reduced in the presence of metal layers or clusters. The metals used for MIC can be divided in two groups: silicide forming metals such as Ni, Cr, Pd, Pt, Co and metals which do not form silicides, such as Al, Au, Ag, Cu. The main difference in the poly-Si films produced using metals from the two groups is in their structural properties. Poly-Si films produced by AIC have a columnar structure with preferential $<111>$ orientation perpendicular to the film surface. They are doped with Al and have p$^+$ type conductivity.

In contrast, when silicide-forming metals are used for lateral induced crystallization, there is needlelike crystal growth parallel to the $<111>$ direction with the $<110>$ axis perpendicular to the film surface. No metal contamination has been detected in the crystallized Si layer. The laterally-induced crystallization takes place at a rate which increases if an electric field is applied.

Using non-silicide-forming metals, the crystallization temperature of a-Si is lower than in the case of silicide-forming metals. The poly-Si films have a columnar structure and the polycrystalline grains have a fractal shape with a $\{111\}$ texture perpendicular to the film surface.

The presence of metal clusters has been detected in poly-Si after annealing. Poly-Si films obtained by AIC are characterized by a higher tensile stress (750-1500 MPa) than in the case of NIC (250 and 500 MPa), because of the small difference in the lattice constants of NiSi$_2$ and Si. They are heavy p$^+$-doped.

The deposition temperature of the a-Si films and the thicknesses of both the metal and the a-Si film, or the metal concentration, are very important parameters for the crystallization of a-Si by metal induced crystallization.

The annealing atmosphere has an important influence on the structural properties of poly-Si films, and on the process of crystallization. Annealing in H$_2$ results in a decrease in the crystallization time for AIC, and in the tensile stress.

Metal induced crystallization is a very low thermal budget process for the fabrication of polycrystalline silicon films on glass or plastic substrates. Despite
the intensive study of the properties of such Si films, much effort is still needed in order to understand the process of preparation, and to obtain homogeneous films with large grains on sufficiently large areas to be suitable for active and seeding layers for solar cells, and for other microelectronics applications.

References

ELECTRONIC CHARACTERISATION AND MODELLING OF DISORDERED SEMICONDUCTORS

J. M. MARSHALL¹ and C. MAIN*
Emeritus Professor, School of Engineering, University of Wales Swansea, and * University of Dundee, Division of Electronic Engineering and Physics, Nethergate, Dundee DD1 4HN.

1. Introduction

The suitability of a semiconductor material for various device applications is critically dependent upon such factors as the mobilities and lifetimes of its charge carriers. However, many of the materials of interest are utilised in forms (amorphous, nanocrystalline and polycrystalline films, etc.) which feature significant degrees of structural and/or compositional disorder. This can exert a profound influence on the electronic properties, and can also make the interpretation of experimental data appreciably more complex and challenging.

This paper commences with a brief review of the conventional concepts of electronic transport in the solid state. It then describes the manner in which these must be modified to incorporate the effects of disorder, how parameters such as the carrier mobilities are influenced, and how some of the techniques used to determine these properties are affected. Finally, it is shown that computer-based modelling constitutes an extremely powerful tool for both predicting and understanding the experimental behaviour.

2. Electronic Transport in Crystalline and Disordered Semiconductors

2.1. CLASSICAL APPROACH TO ELECTRONIC TRANSPORT

The first attempt at a quantitative theory of electronic conduction in the solid state was made in 1900 by Drude [1]. It addressed metallic conduction, and was

¹ Address for correspondence: 64 Ridgeway, Killay, Swansea SA2 7AP, U.K.
basically an adaptation of the kinetic theory of gases. The significant modification made in this theory was that a "free" electron would be expected to experience very frequent scattering (with a mean free path, $\lambda$, of a few interatomic spacings) due to the rapid variations in potential within the lattice (i.e. electrostatic interactions with other electrons and the positive nuclei). Under an applied electric field $F$, such an electron will accelerate at a rate $Fe/m$, where $e$ and $m$ are the electronic charge and mass respectively. If this acceleration continues for an average time $\tau$ before scattering occurs, and any field-induced velocity is lost (randomized) thereafter, then the electron will have an average drift velocity $v_{\text{drift}} = Fe/2m$. In addition to this, it will possess a thermal velocity, $v_{\text{th}}$, given by $mv_{\text{th}}^2/2 = 3kT/2$, where $T$ is the temperature and $k$ is Boltzmann's constant. This will be $\sim 10^7$ cm/sec at room temperature - many orders of magnitude larger than $v_{\text{drift}}$ for normal values of $F$. However, since $v_{\text{th}}$ is randomly directed, it will not contribute to the electric current (except via the generation of noise), but only to the lifetime between scattering events. Thus, this will be $\tau = \lambda/v_{\text{th}} \leq 10^{-14}$ sec at room temperature. The carrier mobility, $\mu$, (the average drift velocity per unit field) will then be $\mu = v_{\text{drift}}/F = e\tau/2m$, with an expected room temperature value of the order of $10^3$ cm$^2$V$^{-1}$sec$^{-1}$.

With the added assumption that each atom in a metal contributes a small integer number of electrons to the free electron pool, this model gave reasonable values of electrical conductivity. However, it was unable to explain why only a small fraction of the electrons possessed by each atom were free to participate, or (for example) why some materials (e.g. Sn in Group IV of the periodic table) were metals, whilst others (e.g. C, Si and Ge in the same group) were not. Moreover, when measurements on materials such as good single crystal silicon became possible, room temperature mobility values of $\geq 10^3$ cm$^2$V$^{-1}$sec$^{-1}$ were found. This implied that a free electron could move through the rapid variations in local potential for many inter-atomic spacings, before scattering occurred.

2.2. BAND THEORY OF SOLIDS

The above problems were resolved, at least in the case of good single crystal materials, once it was realised that moving electrons had a wavelike nature, with the (time averaged) varying quantity (\(\Psi\)) being linked (as $\Psi^2$) to the probability of an electron occupying a particular location (i.e. the Schrödinger equation).

Applying this concept to electron propagation in an infinite periodic lattice, it became easy to predict that the (classically continuous) spectrum of possible electron energies should split (due to what were basically coherent reflections of the travelling wave) into bands of allowed energies, separated by forbidden energy gaps. Moreover, it became clear that an electron would only be scattered
when it encountered some deviation from perfect periodicity (thermal vibrations, missing or impurity atoms, grain boundaries, etc.). Also, it was readily shown that within a crystal, an electron could behave as if it possessed an "effective" mass, \( m^* \neq m \).

The combination of these factors, together with the utilisation of a more sophisticated approach to the analysis of the scattering, led to a mobility \( \mu = e\tau/m^* \). This could easily be much higher than the classical Drude value, primarily because of the high value of \( \tau \) if the deviations from periodicity were small. It also became easy to understand, in terms of the occupancies of the energy bands at zero temperature, why some materials could be metals (with a partially filled conduction band) and others potentially perfect insulators (with a full valence band and an empty conduction band).

2.3. THE INFLUENCE OF DISORDER ON THE BAND STRUCTURE AND ELECTRONIC PROPERTIES

![Figure 1. A periodic lattice (left hand side) can be transformed into a highly disordered one (right hand side) via relatively small variations in bond length and angle (exaggerated here). Most atoms retain their four-fold coordination, but a few cannot do so, creating broken bonds.](image)

The above approach proved to be so powerful in analysing the properties of pure single crystal materials that for many years the existence of allowed energy bands was usually regarded as being intimately linked to presence of an almost perfectly periodic structure. However, this raised considerable problems with respect to non-crystalline solids. In a material such as vitreous SiO\(_2\), the absence of a long-range periodic structure could be expected to invalidate the emergence of energy bands, so that the material should have been a metal (no energy gap between the uppermost occupied and lowermost unoccupied states at zero temperature), and thus (e.g.) have been opaque to light. Similarly, the existence of materials such as amorphous selenium, which was well known to exhibit semiconducting properties, could not be explained.

In order to understand the above situation, it is necessary to realise that materials loosely described as "amorphous" solids do not, in fact, usually feature the total lack of order which is strictly implied by the term. Rather, as shown in figure 1, the short-range order typical of the single crystal material is mostly
retained. However, relatively slight variations in interatomic bond length and angle rapidly combine to destroy the longer-range order, which typically almost disappears at distances greater than two or three interatomic spacings. Also, although most atoms retain the bonding configuration of the single crystal, a small fraction cannot do so.

In these circumstances, it is more appropriate to consider the emergence of energy bands via a "tight binding" approach. With this (e.g. figure 2), the bands arise from the smearing out of the individual atomic (and molecular) allowed energy levels, as the interatomic (or intermolecular) separation decreases.

![Figure 2](image)

*Figure 2. Tight binding approach to the emergence of energy bands in a solid (carbon), as the inter-atomic spacing, a, is progressively reduced.*

This approach can be applied (although generally less quantitatively than that above) to a single crystal material. Its advantage in the present circumstances is that it gives at least a qualitative approach to the case of a disordered one. Most of the outer electrons will remain in the same interatomic bonds as in the crystal (i.e. in the valence band (v.b.)). However, the variations in bond length and (mainly) angle can yield modifications of the energy required to break them (i.e. in the local energy gap). There will also be additional states within the gap, associated with the "dangling bonds" occurring at atoms for which the local coordination is not satisfied (see figure 1). Dangling bonds occupied by a single electron may not be energetically favourable, in which case there is a re-ordering of the occupancy to produce doubly occupied (" D−") and unoccupied (" D+") states. Alternatively, in materials such as hydrogenated amorphous silicon, a-Si:H, the dangling bonds may largely be passivated as Si=H bonds. Of course, due to the variations in local environment, such deep states will not exist at discrete energies, but will again be smeared out in energy to some degree.
To resolve these difficulties, we must examine the process by which electrons move around within such materials. In the extended electronic states sufficiently far within the conduction and valence bands, we would expect (iso-energetic) transport to be of a conventional form, as in Section 2.2. However, as the boundary between the extended and localised states is approached, scattering will become increasingly frequent and the iso-energetic mobility will fall. The lower limit (for of the order of the inter-atomic spacing) yields a calculated room temperature mobility of about \(10 \text{ cm}^2\text{V}^{-1}\text{sec}^{-1}\), as in the Drude theory. Alternatively, re-consideration of the transport as a Brownian diffusive process \[2\] yields a limiting value of \(\mu \approx \frac{e\nu_{\text{e}}R^2}{6kT} \approx 1 \text{ cm}^2\text{V}^{-1}\text{sec}^{-1}\), where \(\nu_{\text{e}}\) is an electronic frequency (\(\sim 10^{15} \text{ Hz}\)) and \(R\) the inter-site scattering distance, again of the order of the interatomic spacing).

Within the localised states just below the extended ones, transport between iso-energetic states must become a quantum-mechanical tunnelling process. The mobility will then be of the form \[2\]

\[\mu_{\text{hop}} = (e\nu_{\text{ph}}R^2/6kT)e^{-2R'/R_o}e^{-(W/kT)}\]  

where \(\nu_{\text{ph}}\) is an "attempt to tunnel" frequency (often taken as \(\sim 10^{12} \text{ Hz}\), envisaged as being the top of the phonon frequency spectrum), \(R'\) is the inter-site

The net result of the above considerations is to generate an energy distribution of states, of the form shown schematically in figure 3. It can been seen that with sufficient degrees of disorder, the energy gap of the single crystal material becomes filled with a continuous distribution of disorder-induced localised states. The "tails" of states at the original band edges arise due to random variations in the local potential, while those closer to the centre of the original gap are mainly due to (energetically broadened) bonding defects, etc., as described above. There is then no formal energy gap separating occupied and unoccupied states, which is why theorists were initially puzzled by such experimental observations as optical transmission at sufficiently long wavelengths, or the occurrence of insulating or semiconducting electrical properties in disordered materials.

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where \(\nu_{\text{ph}}\) is an "attempt to tunnel" frequency (often taken as \(\sim 10^{12} \text{ Hz}\), envisaged as being the top of the phonon frequency spectrum), \(R'\) is the inter-site
separation, \( R_o \) the site localisation length, and \( W \) any activation energy associated with the tunnelling process. Even if we set \( R' \) to be the interatomic spacing (i.e. take all atomic sites to be localised hopping centres at the same energy!), allowing one to assume \( R_o \gg R' \) and \( W = 0 \), the maximum value of this mobility will be about \( 10^{-2} \text{ cm}^2\text{V}^{-1}\text{sec}^{-1} \) at room temperature. Further into the localised states (where the density of states is generally lower), the value will drop rapidly, primarily due to the effect of the \( \exp(-2R'/R_o) \) term. Thus, there will be an extremely rapid fall in the iso-energetic mobility as the transition energy between extended and localised states is crossed.

It should be noted that the above analysis, like almost all aspects of the theory of disordered semiconductors, contains various questionable simplifications. In particular, the localised states are often treated as point defects. A more accurate description should include the effects of longer-range variations in potential, particularly at energies close to the transition region between extended and localised states. Similarly, in (e.g.) polycrystalline materials, it is unlikely that the localised states can be taken as being isotropically distributed, as opposed to (e.g.) being concentrated mostly at grain boundaries. Even so, the general conclusion of a rapid fall in the iso-energetic mobility remains valid and is widely used.

![Figure 4](image)

**Figure 4.** Expected energy variations of the density of states, \( N(E) \), iso-energetic mobility, \( \mu(E) \), occupation probability for electrons (c.b.) and holes (v.b.), \( f(E) \), and their resulting contributions to the electrical conductivity, \( \sigma(E) = e N(E) \mu(E) f(E) \), in a disordered semiconductor.

The consequence of the above view of a disordered semiconductor is illustrated in Figure 4. Because of the rapid variation of the mobility, the contributions of carriers to the electrical conductivity can peak (at sufficiently high temperatures) close to the boundary separating the localised and extended states. For this reason, these boundaries are termed "mobility edges", and the region between them is called a "mobility gap".
These terms can, for many purposes, be regarded as convenient replacements for the terms "band edges" and "band gap" in single crystal semiconductors. Indeed, they are sometimes even replaced by the latter terms, although this is clearly technically incorrect. However, the distinction should be remembered, as should the fact that conduction must become dominated by hopping between localised states at sufficiently low temperatures (where the energy variation of N(E).f(E) overcomes that of μ(E)).

Note that the above approach also explains the observation of low levels of optical absorption at sufficiently long wavelengths. Although there are unoccupied allowed localised states at energies just above the occupied ones in the lower half of the mobility gap, the large distances between the states in mid-gap will yield very low tunnelling transition probabilities.

However, the optical gap will in general remain smaller than the mobility gap (and not well-defined). This is because a transition between an occupied localised state in the lower part of the gap and an unoccupied extended state in the conduction band (or between an occupied extended valence band state and an unoccupied localised state in the upper part of the gap) does not involve tunnelling, and therefore has a much higher probability. Analyses based upon this concept have been advanced to explain the energy dependence of the optical absorption coefficient [2], yielding the so-called Tauc gap, etc. However, we feel that these should be treated with caution since (a) they involve no consideration of the energy variations of the optical transition matrix elements, and (b) the underlying implication that variations in N(E) feature simple (e.g. linear, parabolic or even constant) energy dependences, over ranges of 1 eV or more, seems very improbable. A common alternative empirical approach is simply to take the optical gap to be the energy at which the absorption coefficient attains a value of 10^4 cm⁻¹, yielding useable absorption in devices such as solar cells.

2.4 EQUILIBRIUM CARRIER TRANSPORT IN DISORDERED SEMICONDUCTORS

2.4.1. Trap-limited Band Transport
The existence of significant concentrations of localised states in disordered semiconductors suggests that it is unlikely that carrier motion in the extended states will persist unhindered for an extended period of time. Rather (ignoring recombination), it is likely that such motion will be interrupted by repeated trapping into, and subsequent release from, localised states of varying depths.

Consider first, for simplicity, the case of a single set of shallow localised states, as shown in figure 5. An electron moving in the extended states with a "free" mobility μo can become temporarily trapped in one of these centres. It will
stay there until it finds enough energy to escape back into the extended states and continue its progress. This mechanism is termed "trap-limited band transport". The periodic trapping/release will result in a reduced "drift" mobility, \(\mu_d\). If the average time which an electron spends free between trapping events is \(\tau_f\) and the average time before subsequent re-release is \(\tau_r\), then the ratio of these two quantities is equal to the ratio of the concentrations of instantaneously free and trapped carriers, \(n_f/n_t\), and

\[
\mu_d = \mu_o \times \text{fractional time spent free} = \mu_o \times \frac{\tau_f}{(\tau_f + \tau_r)} = \mu_o \times \frac{n_f}{(n_f + n_t)}.
\]  

If \(N_t\) is the total density of trapping centres, and \(N_c\) the effective density of states at the conduction band mobility edge (i.e. the number in the bottom \(kT\) slice, where most of the free carriers are located), then, by the Maxwell-Boltzmann approximation to the Fermi-Dirac statistics:

\[
n_f = N_c \exp\left(-\frac{E_f-E_t}{kT}\right); \quad n_t = N_t \exp\left(-\frac{E_t-E_f}{kT}\right).
\]  

At sufficiently high temperatures (with \(N_t < N_c\)), the time between trapping events will dominate over that spent before subsequent release, so that \(\mu_d \rightarrow \mu_o\). However, at low temperatures the reverse will be the case, giving

\[
\mu_d \rightarrow \mu_o \times \frac{\tau_f}{\tau_r} = \mu_o \times \frac{N_c}{N_t} \exp\left(-\frac{E_c-E_t}{kT}\right) = \mu_o \times \frac{N_c}{N_t} \exp\left(-\frac{-\Delta E}{kT}\right).
\]  

If the drift mobility can be measured, e.g. via the time-of-flight technique (see below and [3] for extensive further detail) over a sufficiently wide range of temperature, as in figure 6, then (ignoring secondary factors such as the temperature dependence of \(\mu_o\)) valuable information can be obtained on the free carrier mobility, the depth, \(\Delta E\), of the traps limiting the drift mobility, and the ratio \(N_c/N_t\) (i.e. the trap density, if a reasonable value of \(N_c\) can be assumed).
In the case of a disordered semiconductor containing energetically-distributed traps, the situation will obviously be more complex. However, for suitable simplified forms of the energy variation of the bandtail states, one can employ a modified version of equation (2), in which \( n_t \) now becomes the total equilibrium concentration of trapped carriers. For example, in the case of a linear bandtail of total depth \( \Delta E \), equation (4) becomes

\[
\frac{P_d}{P_o} = \left( \frac{\Delta E}{kT} \right) \exp\left(-\frac{\Delta E}{kT}\right).
\]

Basically, for this and other rapidly-truncated energy distributions, the low-temperature drift mobility is controlled by carriers trapped within the bottom \( kT \) of the tail (or the energy at which \( N(E) \) decays to negligible proportions), and changes in the detailed form of \( N(E) \) only influence the pre-exponential factor.

Another very commonly-used (although with little theoretical justification) model envisages an exponential bandtail: \( N(E) = N_o \exp\left(-E/kT_o\right) \). Here, the high-temperature case (with \( \mu_d \to \mu_o \)) is that for which \( T > T_o \). At lower temperatures, computation of the equilibrium value of \( n_t \) in such a case would require use of the full Fermi-Dirac occupation statistics as the Fermi level is approached. We will, however, consider the non-equilibrium (transient photodecay) situation below.

2.4.2. Conduction by Hopping in Band Tails

A competing alternative process to trap-limited band transport is that of direct intersite hopping within a band tail. Whether or not a carrier is likely to make a hopping transition to a neighbouring site, before release to the extended states, obviously depends upon the inter-site separation, the value of \( R_o \) in equation (1) and the temperature. However, at sufficiently low temperatures, hopping transport must eventually dominate. For a truncated distribution such as the

![Figure 6. Temperature dependence of the trap-limited drift mobility, for the case of a single set of shallow traps.](image-url)
linear band tail discussed above, this would tend to be dominated by hopping transitions within (or close to) the bottom kT component of the tail. The expression for the resulting mobility would be similar to equation (1), with R' becoming the mean separation of sites in the bottom kT component.

More complex variants are also possible. For instance, if the density of localised states just below the mobility edge is sufficiently high, then a carrier may be more likely to make a hopping transition to a nearby deeper state, rather than to return to the extended states. In such a case, the effective transport path (peak in $\sigma(E)$) would be within the bandtail itself. Moreover, for an exponential bandtail, it has been pointed out [4] that such a peak in $\sigma(E)$ will occur progressively deeper within the tail as the temperature falls. Additionally, carriers can still be slowed down by trapping events involving deeper states, giving an overall mechanism of "trap-limited hopping". This can be described by an expression similar to equation (4), but with $\mu_c$ being replaced by the hopping mobility in the dominant shallow traps close to the peak in $\sigma(E)$, $N_c$ becoming their concentration, and $\Delta E$ being the energy separation between these states and the deeper ones limiting the drift mobility.

The above situation is obviously very complex, compared to the case of a single crystal material (and it will become even more so below!). However, we complete this Section by noting that in materials developed for various device applications, every effort is made to minimise the concentrations of localised states. Thus, it is may be possible, at normal temperatures, to assume that iso-energetic transport is dominated by states close to the mobility edge, and that hopping between deeper states can be neglected in comparison to trap-limited band transport. However, in other cases of interest, as we shall show, this may well not be the case.

2.5 TRANSIENT CARRIER TRANSPORT IN DISORDERED SEMICONDUCTORS

A further significant complication to the above, already tortuous, situation is that the properties of interest are often those applicable over a finite timescale, as opposed to occurring under thermal equilibrium conditions. This is obviously the case in a measurement of the drift mobility (see below), and also in device applications (e.g. in solar cells, where photo-induced carriers take a limited finite time to drift to the collection electrodes, or in thin-film transistors for a similar reason).

The basic significance of this is that carriers which are (assumed to be) initially generated in or injected into the extended states may not have time (whilst they transit the device in question) to interact with the deep states which
would ultimately limit their motion. In this case, the measured drift mobility (or that applicable for device purposes) will be dependent to a significant extent upon the appropriate timescale. In the limiting case in which carriers could be extracted before any trapping, the free mobility would obviously apply. At longer times, for a localised state concentration which decreases continuously with energy from the mobility edge, carrier trapping would first tend to occur into the shallowest states, by virtue of their higher concentrations. Subsequently, "thermalisation" (i.e. a transition in the energy of maximum occupation) to progressively greater depths would occur. Thus, the trapped carrier distribution might be expected to evolve with time as indicated schematically in figure 7. Obviously, the ratio of the concentrations of free and trapped carriers will decrease continuously with time, as therefore will the effective drift mobility.

\[ E_{th}(t) = kT \ln(vt), \]
where \( v \) is the attempt-to-escape frequency for the trapped carriers. This represents the energy for which the carrier release time is equal to the time since initial generation of the excess carriers. It is argued that for traps shallower than \( E_{th}(t) \), sufficient time will have elapsed to allow the establishment of a quasi-thermal equilibrium between the trapped and free carrier populations. For deeper centres, the occupation will be determined simply by trapping considerations, and will thus follow the energy variation of \( N(E) \).

Although the above concept allows a very convenient simplification of the analysis, we do not consider it to be valid in the general case. A more fundamental approach is to regard thermalisation as being primarily controlled by trapping, rather than release, considerations [5]. Even so, the thermalisation energy concept can sometimes be employed, with appropriate caution, in a variety of circumstances of practical interest, as illustrated below.
2.6. MEASUREMENT AND INTERPRETATION OF TRANSIENT CARRIER TRANSPORT

2.6.1 Measurement Techniques

The thermalisation of initially-free excess charge carriers is most readily examined via transient photoconductivity experiments [3]. Here, excess carriers are typically generated by a short flash of strongly-absorbed light from a pulsed laser.

Specimens may feature a "sandwich" structure, with strongly-absorbed illumination through one of the two (blocking) electrodes (figure 8a). In this case, the experiment constitutes a thin-film modification of the original Haynes-Shockley experiment. However, for materials of suitably high resistance, the dielectric relaxation time can be much longer than the transit times of carriers across the specimen. It then becomes possible to study either electron or hole transport, simply by selecting the polarity of the applied field (as opposed to only being able to study minority carriers in the conventional Haynes-Shockley case).

An alternative approach uses a coplanar electrode configuration, as in figure 8b. Here, both species of carrier will contribute to the photocurrent, so that it is necessary to infer which provides the dominant contribution from other experiments. Subject to this, in this (ideally "extraction free") case, it becomes possible to study the photocurrent over a much more extended time period (until recombination forms a limitation, or even thereafter, provided the photocurrent remains detectable (see below)).

2.6.2 Anomalously-Dispersive Transient Photoconductivity in Disordered Semiconductors

In disordered semiconductors, the transient photoconductivity often does not feature the conventional (see figure 9) form, but rather exhibits a continuously decaying I(t) over a much more extended timescale. Figure 9a shows the type of transit pulse obtained in a room temperature time-of-flight experiment (figure 8a).
for electrons in high-quality a-Si:H [6], or for holes in a-Se [7]. Following initial equilibration of the drifting charge packet, there is a plateau region, during which carriers drift through the specimen at an approximately constant velocity. The packet also spreads out by conventional diffusion during this period. This gives a spread of arrival times at the extraction electrode, so that the current does not fall to zero at a uniquely-defined transit time. However, it is still possible to identify the average transit time, $t_o$, as the point at which the current falls to 50% of its plateau value. From this, the average drift mobility can be calculated.

In contrast, at lower temperatures in these cases, and over the whole accessible temperature range in many other cases (e.g. hole carriers in a:Si:H [8] and a-As$_2$Se$_3$ [9]) the observed pulses are of the general form shown in figure 9b. The current in the "pre-transit" regime (see below) now falls continuously, implying a progressive reduction in the average carrier drift velocity. There is also a much greater spread of carrier arrival times in the "post-transit" regime.

In this "anomalously-dispersive" situation, it is clearly impossible to define a transit time in the manner adopted for the conventionally-dispersive case. However, in early studies [10] it was discovered (empirically) that if the data were re-plotted in log-log format (figure 9c), then two regimes featuring approximately power-law decays of the current with time could be distinguished. Thus, it was possible to identify the time, $t_o^*$, representing the transition between the two regimes, as in the figure. It is important to note that this represents the approximate time of arrival of the leading edge of the carrier packet at the extraction electrode. Thus, the drift mobility calculated from it will be that for the fastest carriers completing their transits. This mobility will also be dependent on the applied field and specimen thickness - the continuous fall in the average carrier drift velocity during the pre-transit ( $t < t_o^*$ ) regime means that in thicker specimens and/or at lower fields, there will be more time for this effect to occur.

Figure 9. Conventionally dispersive (a) and anomalously dispersive (b, c) carrier transit pulses
Obviously, from Section 2.5, this phenomenon of "anomalous dispersion" can be understood in terms of the thermalisation of initially-free carriers with localised states of progressively increasing depth, if the carrier motion occurs by trap-limited band transport. However, as will be shown below, the behaviour may also reflect thermalisation in situations in which transport occurs by hopping directly between the localised states.

2.6.3 Interpretation of Anomalously-Dispersive Transport Data

From Section 2.5, it can be seen that the thermalisation of a set of initially free excess carriers is intimately related to the detailed form of the localised states with which they interact. Thus, transient photoconductivity data should contain valuable information on the nature and energy distribution of the shallow trapping centres involved. Various techniques, featuring different levels of complexity, have been advanced for extracting such information (e.g. see [3] for detailed reviews of this topic), and there is still significant activity in seeking to refining these. Below, we will only attempt a brief overview of some of the underlying concepts.

The simplest approach [11] to the interpretation of transient photoconductivity data arises from the thermalisation energy model of the relaxation process [12-14]. Here, it is argued that for a suitable (i.e. an exponential or similarly continuous and slowly-decaying) trap distribution, most of the trapped carriers will be situated within kT of Eth(t), as in figure 7 (note the logarithmic scales for N(E) and n(E) - with linear scales, the peak close to Eth(t) is much more pronounced). Moreover, this population is assumed to be in quasi-thermal equilibrium with that of the free carriers providing the photocurrent at this time. Thus, adapting equation (4), one can write the time-dependent effective drift mobility as

\[ \mu_d(t) = \mu_\infty \cdot \frac{n(t)N_c}{n(t)N_c/kT} \cdot \exp(-Eth(t)/kT). \]  

Rearranging this, and remembering that Eth = kT ln(vt), we obtain

\[ N_t(E_{th}) = \text{const} / (I_{ph}(t) \cdot t), \]  

since the photocurrent, I_{ph}(t), is obviously directly proportional to \( \mu_d(t) \). Thus, a plot of \( 1/(I_{ph}(t) \cdot t) \) against Eth(t) should map out the N_t(E) distribution. Care is needed in this procedure, to ensure that measurements are genuinely being performed in the "pre-transit" regime (i.e. that carrier losses by extraction at the electrodes, or by recombination, are negligible).
At the opposite extreme, consider the "post-transit" (\(t > t_{o}^{*}\)) regime of the photocurrent in a sandwich cell specimen. Here, most of the carriers have already been lost by extraction, and the residual current is controlled by the emission of those carriers which chanced to become trapped in atypically deep centres. It can then be shown [15] that equation (7) should be replaced by the expression

\[
N_{t}(E_{th}) = \text{const}' \cdot (I_{ph}(t) \cdot t),
\]

(8)
i.e. (other than for a different constant term on the r.h.s.) its complete inverse!

The above "pre-transit" and "post-transit" procedures are now quite commonly used in exploring materials of interest in the present context (particularly thin film amorphous, polycrystalline and nanocrystalline semiconductors). They naturally tend to broaden out sharp features in \(N(E)\), because of the assumption that all carriers are released after a time equal to the time constant of the centre concerned, and also that \(n(E)\) always peaks at \(E_{th}\). They can thus seriously distort such distributions, making them appear much closer to a simple exponential bandtail [16]. Also, they obviously depend critically upon the assumption of a trap-limited band transport mechanism, with no contributions to thermalisation or to the photocurrent via hopping etc. However, subject to these caveats, they can prove extremely valuable and relatively easy to apply to experimental data.

Before leaving this topic, it worth mentioning some of the more recent variants of the above interpretive techniques; in particular those based upon Fourier or Laplace transformation of the photocurrent data (e.g. [17]). Such transformations firstly convert the raw \(I_{ph}(t)\) data into the complex frequency domain \(I_{ph}(\omega)\). A further manipulation yields a discrete representation of \(N(E_n)\), where \(E_n = kT \cdot \ln(n/\nu_{\omega})\). This expression is formally equivalent to that for the thermalisation energy, but does not imply some of the underlying assumptions concerning the thermalisation process. Impressively, such techniques are applicable to data from either the pre-transit or post-transit regimes (or both), or where significant recombination losses are occurring. The most recent variants are also able to yield a significant reduction in the "\(kT\) broadening" effect, producing much more accurate reproductions of even sharply structured energy distributions.

3. Modelling of Transient Carrier Transport in Disordered Solids

As noted at various points above, the understanding of the properties of non-crystalline solids is greatly hindered by the difficulty of treating the effects of
disorder in a rigorous manner. There is currently no equivalent of the Bloch theorem and associated concepts which allowed precise and elegant analyses of the properties of single crystal materials.

In the above situation, as far as the authors are aware, all techniques so far advanced for interpreting experimental data for disordered semiconductors involve important assumptions and simplifications. The idea of a thermalisation energy, as defined above, is just one common example, of particular relevance here. It is employed not just in the interpretation of the transient photoconductivity, but also in many other related time-dependent experiments, such as deep level transient spectroscopy.

It is also common to use highly simplified models for the energy distribution of the localised states. The assumption of an exponential distribution is encountered particularly frequently. This is primarily, we believe, because it can greatly simplify calculations, rather than because its presence is predicted theoretically - a Gaussian bandtail is much easier to justify. However, another factor is that the broadening effects outlined above can distort even quite highly structured energy distributions towards an apparently exponential form (see [16] and comments below).

In these circumstances, it becomes extremely valuable to assess the validity of the assumptions being made in any interpretive technique. Here, computer-based numerical modelling has proved particularly effective. Also, in addition to allowing checks to be made of the underlying assumptions, it can provide valuable new insights into the details of the transport processes etc.

The first attempts to undertake such modelling (e.g. [18]) utilised a Monte Carlo procedure. This remains an extremely useful approach, since any underlying assumptions can be clearly identified, and their consequences explored. To examine the decay of the trap-limited transient photoconductivity for any required form of localised state distribution, the following basic steps are involved:

(a) Use an appropriately-weighted random number, in conjunction with the overall free carrier trapping time constant, to determine the time (properly distributed about the time constant value) before an initially free carrier becomes trapped,

(b) Use a second random number, together with the N(E) being studied, to choose the depth of the centre into which trapping occurs,

(c) Use a third random number, together with the trap depth and attempt-to-escape frequency, to decide the time before release to the extended states,
(d) Loop back to (a), to continue following the progress of the carrier until the required conditions (e.g. arrival at an electrode or expiry of a specified time limit) have been met,

(e) Repeat the above procedures for a large number of carriers, combining the results to yield the required data (current vs. time, trapped carrier energy distribution vs. time, etc.).

This Monte Carlo approach can be extended in various ways, for example to explore transport by hopping as opposed to trap-limited band transport (see below). Its only significant drawback is that data for significant numbers (typically \( \geq 10^4 \)) of carriers must be combined, to reduce the noise level associated with the individual random events. Thus, it can require considerable amounts of computation time, and sometimes (e.g. for the modelling of hopping in a random spatial array of sites) of computer memory.

An alternative approach (e.g. [19]) for the modelling of trap-limited band transport is to divide the \( N(E) \) distribution into thin (e.g. \( \leq kT \)) slices, and generate a matrix containing the rates for trapping into and release from these. This can then be employed to obtain information similar to that extracted via the Monte Carlo approach. Such procedures allow much more rapid computation, but do have some limitations. For example, because the matrix elements are average values, it is more difficult to generate and study noise data for various trap distributions. Also, because of problems associated with the choice of slice widths (see below), it has only very recently (e.g. [20,21]) become possible to consider extending it to study properties involving transport by intersite hopping.

### 3.1 EXAMPLES OF THE NUMERICAL MODELLING OF TRAP-LIMITED BAND TRANSPORT

![Figure 9. Monte Carlo simulation of the room-temperature transient photocurrent for a sandwich-configuration specimen of a material featuring a linear band tail of depth 0.25 eV. The arrow indicates the direction of increasing free carrier transit time (i.e. decreasing applied field).](image)
Here, we provide some illustrative examples to demonstrate how the above procedures can be employed, and to indicate the insights they can provide.

Figure 9 displays the results of a Monte Carlo simulation of the (recombination-free) transient photocurrent for a specimen (sandwich configuration) having a linear band tail of depth 0.25 eV. The currents in the pre- and post-transit regions clearly do not have the simple power-law forms which occur for an exponential trap distribution. Rather, the pre-transit current tends to saturate at low applied fields, since carriers have had sufficient time to reach quasi-thermal equilibrium with states at the bottom of the tail (with a drift mobility of the form given in equation (5)).

The results of applying various analytical techniques to some of the data in figure 9 are shown in figure 10. The pre-transit technique, (using equation (7)) clearly distorts the true distribution into an approximately exponential one, with a characteristic temperature equal to the experimental one, over much of the energy range, as emphasised by the exponential plots in figure 10a. Obviously, the thermalisation energy $E_{th}(t) = kT \ln (vt)$ must increase indefinitely with time, even though the band tail has a finite depth in this case. This clearly illustrates an important fundamental limitation of the procedure. It also demonstrates that non-exponential energy distributions will tend to be distorted towards an exponential form, explaining why so many measurements tend to suggest such a distribution!
The post-transit procedure (equation (8) and figure 10b) again attempts to compute \( N(E) \) for energies beyond the tip of the linear tail. However, the distortion is rather less than in figure 10a, as can be understood by a full consideration of the approach [22].

As shown in figure 10c, the transform procedure provides a considerably improved regeneration of the true linear form, but still yields a false exponential region (with \( T_o = T \)) beyond the tip of the tail.

![Figure 11](image)

*Figure 11.* Trap distribution for a composite exponential + Gaussian \( N(E) \), as calculated by (a) pre-transit and transform analyses of low field data, and (b) a post-transit analysis of high field data. The solid lines indicate the true \( N(E) \), while the dotted line in (a) is an exponential distribution with \( T_o = T \).

Obviously, an \( N(E) \) as sharply structured and terminated as the linear one is not to be expected in reality. Thus, figure 11 shows similar data for a more realistic distribution, comprising an exponential tail plus an additional Gaussian feature. Here, the pre-transit technique again gives generally poor results, and even generates a peak in \( N(E) \) close to 0.2 eV, where the true distribution goes through a local minimum. The transform technique again gives a much better reproduction of the actual \( N(E) \), but once more is unable to regenerate the correct distribution beyond about 0.4 eV. In this case, the post-transit technique is the most effective, as shown in figure 11b. It does not completely regenerate the minimum \( N(E) \) at about 0.2 eV, but does prove more effective in reproducing the rapidly-decaying regions. The reason for this is explained elsewhere [22]. It is also worth noting here that more recent variants of the transform technique [e.g. 23, 24] are progressively reducing the "kT broadening" effect.

From the above illustrations, it can be seen that computer-simulation can provide valuable insights into the effectiveness of the various procedures which have been advanced for interpreting transient photoconductivity data in disordered semiconductors.
In particular, it can be concluded that:

(i) If any procedure yields an approximately exponential \( N(E) \), with a characteristic temperature close to that at which the measurements were made, the results must be regarded with extreme suspicion.

(ii) Measurements over a range of temperatures should then be made, to assess the reliability of the conclusions.

3.2 NUMERICAL MODELLING OF HOPPING TRANSPORT

The procedures examined in the previous Section all feature the assumption that transport occurs by trap-limited band transport. This is probably reasonable for measurements at sufficiently high temperatures, in materials which do not feature very high degrees of disorder. However, when these conditions are not met, hopping transport will obviously constitute a competing mechanism. It is therefore valuable to develop computational procedures for addressing this situation.

Obviously, one can generate a large array of sites, randomly distributed in position and appropriately distributed in energy (e.g. \([25, 26]\)), and then use a Monte Carlo approach to model carrier motion. However, this is demanding of both computer memory and computation time (especially since a carrier may tend to jump back and forth many times between two closely neighbouring sites, before eventually moving on to a more distant one). Thus, a much more common approach has been to divide a continuous energy distribution into a "ladder" of discrete sets of traps, as in figure 12.

![Figure 12. Division of a continuous energy distribution of localised states into a ladder of discrete sets of centres.](image-url)
One can then compute average separations of sites within and between these slices, and use this as the basis for an analysis. However, there is a critically serious flaw in such a procedure. This is that these average separations are obviously dependent on the slice widths, $\Delta E$, chosen. This is vitally important, in view of the dominant role of the term $\exp(-2R'/R_o)$ in equation 1. One could choose $\Delta E = kT$, but this is entirely arbitrary (and the iso-energetic hopping rates within a slice would then become significantly dependent on the temperature, which is clearly illogical).

Fortunately, procedures have now been evolved by the authors to circumvent this problem [27]. These "differential" and "fractional" approaches both give very similar results, independently of the chosen slice width (provided this is $< kT$). We will not describe them here, but figure 13 provides a brief illustration of their use [27]. Significantly, although thermalisation occurs solely by hopping, the functional form of the photodecay is very similar to that which would be obtained for trap-limited band transport with an identical exponential bandtail (i.e. a power law decay, of gradient $1-(T/T_o)$). Thus, the simulation demonstrates that it is very difficult to distinguish between the two different transport processes from transient photoconductivity data. It is also possible to use these approaches to study various other details of the thermalisation process, such as the time evolution of the trapped carrier distribution. Initially, this was done for the zero-temperature case [28], but more detailed examinations have subsequently been performed (e.g. [29]). Also, Main et al. [20] have recently
studied cases in which both hopping and thermal release to the extended states are included. An additional example of how such modelling can provide insights into the interpretation of experimental data is provided below.

The data in figure 13 were generated for the case of a featureless exponential bandtail. However, experimental data which yield a more structured \( N(E) \) are more interesting, and can provide additional information. In particular, consider the case in which a "bump" occurs in the computed \( N(E) \), at some energy defined by the thermalisation energy \( E_{th}(t) = kT \ln(vt) \). Note that this can be written in the form \( E_{th}(t) = kT \ln(t) + kT \ln(v) \). Thus, an incorrect assumption of the value of \( v \) will simply displace the whole calculated energy distribution linearly along the energy axis. Hence, from measurements taken at different temperatures, it should possible to chose a value of \( v \) which causes the peak to occur at the same energy at all temperatures. As well as establishing the correct energy for the feature, such an approach will also indicate the appropriate value of \( v \), and thereby (via detailed balance considerations) the capture cross section of the traps.

However, when this approach has been applied in practice, under the assumption of trap-limited band transport (for example in our studies of the transient photoconductivity in CVD diamond), unreasonably small values of \( v \) have been obtained (e.g. \( v < 100 \) Hz for the CVD diamond studies). This stimulated us to consider what would be expected to happen if the thermalisation occurred via hopping, rather than trap-limited band transport.

![Figure 14](image.png)

*Figure 14. Model density of localised states used to study the transient photoconductivity due to thermalisation by hopping.*

Figure 14 shows the model density of localised state distribution chosen for this study. It featured a steep initial exponential bandtail, followed by a Gaussian feature centred at 0.4 eV, and a shallower exponential tail extending further into the gap. In the computer simulation, release to the extended states was suppressed, so that thermalisation could occur only via hopping transitions.
Figure 15. Transient photocurrent due to hopping, and the computed N(E) at three different temperatures, for the localised state distribution in figure 14. The assumed value of $Q$ is $10^{12}$ Hz.

Figure 15 displays the computer-simulated transient photoresponses for hopping thermalisation in this N(E), at three different temperatures, plus the densities of states calculated by applying the Fourier transform analysis program developed by Main et. al. [17], with the assumption of trap-limited band transport mechanism, taking $Q$ as $10^{12}$ Hz. Consider first the two upper graphs. The calculated N(E) is a reasonable representation of the two exponential components, plus a feature, apparently centred at about 0.275 eV. The time corresponding to this energy, via the thermalisation energy expression, is $t_{\text{peak}} = 0.9 \mu\text{sec}$. Aside from the (probably) expected broadening of the Gaussian feature, it is immediately clear that the its calculated central energy does not correspond to the 0.4 eV value for the actual N(E). At this relatively low temperature, thermalisation by hopping is dominated by transitions to states at deeper energies, with the requirement for the supply of energy mitigating against transitions to (possibly closer) shallower states.
Now consider the two central graphs, for which the temperature has been halved. Again, there is evidence of a feature in the calculated N(E). However, the thermalisation energy equation, taking $v$ as above, now places the peak of this at 0.135 eV. The corresponding value of $t_{\text{peak}}$ is 1.2 $\mu$sec - i.e almost the same as in the case of the higher temperature data. Obviously, this is due to the fact that hopping transitions to deeper states dominate the behaviour at these temperatures, so that the actual temperature of measurement plays a very minor role.

At higher temperatures (the bottom two graphs), transitions to nearby shallower states (as intermediate steps before thermalisation to deeper ones) have an increased influence. This slightly reduces $t_{\text{peak}}$, to 0.4 $\mu$sec. However, it is clear that the temperature dependence of the $t_{\text{peak}}$ is extremely weak.

To calculate a more appropriate value of $v$ from these data and corresponding ones obtained at other temperatures, one can re-write the thermalisation energy equation in the form $\ln(t_{\text{peak}}) = (1/kT)E_{\text{peak}} - \ln(v)$. Thus, a graph of $\ln(t_{\text{peak}})$ vs. $1/kT$ should have a gradient of $E_{\text{peak}}$, and an x-axis intercept of $-\ln(v)$.

![Figure 16](image)

Figure 16. Plot of $\ln(t_{\text{peak}})$ vs. $1/kT$, for the determination of $E_{\text{peak}}$ and $v$ from simulated transient photodecay data for hopping thermalisation within the localised state distribution shown in figure 14.

Figure 16 presents such a plot, for these data. The resulting parameters are $E_{\text{peak}} = 0.02$ eV and $v = 3 \times 10^6$ Hz. Obviously, the former bears no resemblance to the actual 0.4 eV depth of the Gaussian feature. Equally obviously, the latter is also unrealistic - in the case of trap-limited band transport, such a low value would imply a capture cross section for the localised states of such a small magnitude ($\sim 10^{-20}$ cm$^2$) that they would be completely ineffective in trapping initially-free carriers over a realistic experimental timescale.
Obviously, the origin of the above discrepancies is the assumption that trap-limited band transport, as opposed to intersite hopping, is controlling the thermalisation process. The values of $v$ obtained for this particular model $N(E)$ are not as low as those obtained in our experimental studies, but are certainly unrealistically small. Moreover, the calculated peak energy of the Gaussian feature bears no resemblance to its true value.

Therefore, from this example of the value of computer modelling in gaining insights into the interpretation of experimental transient photodecay data in disordered semiconductors, it can be concluded that:

(i) Thermalisation by hopping could easily be misinterpreted as thermalisation by trap-limited band transport.

(ii) To differentiate between the two (where sufficient structure exists in the calculated $N(E)$), it is essential to perform measurements over a range of temperatures, to check whether the resulting calculated values of parameters such as $v$ are reasonable. If not, then a re-appraisal of the interpretation is essential.

4. Conclusions

The bulk of this paper has comprised an attempt to describe the present state of understanding of electronic transport in disordered semiconductors. We hope that it will be clear that this relies upon many simplifying assumptions, which may or may not be justified. To slightly mis-quote the late Professor George Porter, we have two confessions to make. The first is that 50% of the information provided in the paper is probably wrong, or at least drastically oversimplified. The second is that we do not (yet) know which 50% it is!

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1. Introduction

The rare earths are characterized by the progressive filling of the 4f shells of their electronic configurations. They occur in a group of fourteen elements, known as the lanthanides. These elements, which are associated with the filling of the 4f-shell, commence with cerium (Z = 58) and end with lutecium (Z = 71).

Since the beginning of the twentieth century, the radiative transitions of lanthanide ions have received academic and industrial attention. The study of the photophysics of the lanthanides has given rise to intriguing science. Moreover the technological applications of lanthanide luminescence encompass not only fluorescent tubes and colour televisions, but also immunoassays, optical amplifiers and in the future, perhaps, organic light-emitting diodes.

Lanthanide organic compounds have been widely reported as having the desirable properties of exhibiting intense narrow-band emissions via efficient intramolecular energy transfer from the ligand excited state to the central metal ions under UV excitation. The luminescence spectra are intensified greatly by complexation of lanthanide ions with organic ligands. These lanthanide ions form stable crystalline complexes with heterocyclic ligands, such as bipyridyl (bpy) and phenanthroline (phen), which exhibit efficient energy transfer to the chelated lanthanide ions. However, rare earth (RE) complexes with organic ligands for practical uses are limited because of poor thermal stability and mechanical properties, although they also have good phosphor characteristics. This drawback can be overcome by protecting them by a glassy surrounding.

2. Calculation of the Energy Levels

The energy levels of the triply charged ions may be obtained with the highest accuracy from the analysis of the free ion spectra. Another way of obtaining
information on the free ion states is to calculate the energy levels theoretically. Such calculations are practically a necessity for guiding the interpretation of the empirical results. Moreover, the calculations furnish the only way to obtain eigenvectors.

The methods for dealing with this problem were developed first by Slater. They were extended and described in considerable detail by Condon and Shortley [1] and later systematized by Racah [2], Judd [3], Wybourne [4] and Dieke [5]. The recent developments can be found in [6].

The object of the theory is the calculation of the energy levels and the wave functions of atoms even of such complexity as the rare earth ions. As in all quantum mechanical calculation of complex systems, the theory starts with a system which is sufficiently simplified by the omission of certain interactions for its properties to be obtained without undue complications. This is the so-called zero-order approximation, characterized by the Hamiltonian $H^0$ with the energies $E_n^0$ and wavefunctions $U_n$.

The zero order approximation considers the outer electrons in a central field produced by the nucleus and the 54 electrons in the completed xenon-like shell but disregards the electrostatic repulsion between the outer electrons, and any influence of their spins. All outer electrons are, therefore, completely independent of each other and the energy cannot depend on the relative orientations of their orbits.

In this approximation, all states of a configuration have the same energy. The state of an individual single electron is characterized by four quantum numbers, e.g. $n$, $l$, $m_l$, $m_s$. A configuration of $N$ electrons is the assembly of states in which the principal quantum number $n$ and the orbital angular momentum $l$ for each electron are given, but $m_l$ and $m_s$ can take all possible values. This can also be expressed by saying that the size and shape of each electron orbit is given but its orientation in space and the spin orientation are arbitrary. For the crystal spectra of the rare earths, the configuration where all outer electrons are in 4f orbits, the $4f^N$ configuration is of greatest importance.

The degeneracy of a configuration in the zero order approximation is given by the product of $2(2l_i+1)$ for all outer electrons when no equivalent electrons are involved. For the $4f^N$ configuration which consists entirely of equivalent electrons, the degeneracies are given by the binomial coefficients \( \binom{14}{N} \) which are 1, 14, 91, 364, 1001, 2002, 3003, 3432 or $N=0$ to 7. For the second half of the group, the degeneracies are the same as in the first half, in the opposite order in accordance with the principle that $N$ 4f electrons are equivalent to 14 - $N$ holes in the completed shell and a configuration with a certain number of holes has the same number and kind of states as a configuration with the same number of electrons.
If the interactions between the electrons and between the orbital and spin angular momenta are introduced by appropriate terms $H^1$, $H^2$, etc. in the Hamiltonian, some of the degeneracy is removed. When the ion is then placed in a crystal field, all of it may be removed so that only non-degenerate states remain. The modification of the states through the influence of the interactions can be calculated from conventional perturbation theory. There are more than 3000 different wavefunctions to deal with in one configuration near the middle of the rare earth group. This shows that the mere writing down of the wavefunctions and interaction matrices alone would be a nearly impossible task. For this reason, systematic methods have been developed, chiefly by Racah [2], which reduce the labor of computation considerably. In complicated cases, the calculations are still tedious but manageable with some patience. The computation problem is essentially the following.

The chief interactions in the free ion are the electrostatic repulsion between the outer electrons expressed by

$$H^1 = \sum_{ij} \frac{e^2}{r_{ij}}$$

(1)

summed over all electron pairs, and the spin-orbit interaction by

$$H_2 = \sum_{i=1}^{n} \zeta_i (l_i \cdot s_i)$$

(2)

where $\zeta_i$ is the spin-orbit interaction constant for the $i^{th}$ electron. For a Coulomb field with an effective nuclear charge $Z''$,

$$\zeta_i = \alpha^4 R Z'' / r_i^3$$

(3)

with $\alpha$ the fine structure constant and $R$ the Rydberg constant. The effective charge $Z''$ is, in general, different from the effective charge $Z'$ occurring in the electrostatic interactions.

If the interaction between the states within one configuration is taken into consideration and, thus interactions between states of different configurations are left out, this is the approximation usually employed. It is reasonably good for the $4f^N$ configuration of trivalent rare earth ions because this configuration is isolated from all others with which it could interact. Because of symmetry considerations (parity), the nearest configuration that can interact with $4f^N$ is $4f^{N-1}$ or $4f^{N-1}5d$, $4f^{N-1}6p$ or $4f^{N-1}6s$ which are of the order of $10^5$ cm$^{-1}$ above it. Broken-shell configurations such as $5p^54f^{N+1}$ can be of importance even though
the energy difference is much larger, since the overlap integral may be quite large (Rajnak and Wybourne [4]). According to the radial integral calculations, the contribution from $4p^5 4p^{N-1}$ is even more important.

When only the influence of the electrostatic interaction is considered, we have the following situation. From the original states in which each electron is characterized by the four quantum numbers, $n, l, m_e, m_s$ (where only $m_e$ and $m_s$ are of importance for further consideration, as $n$ and $l$ are fixed for the whole configuration), we can by standard methods obtain linear combinations expressing the wave functions of states characterized by the quantum numbers $L, S, L_z = M_L, S_z = M_S$. $L$ and $S$ correspond, as usual, to the total orbital and spin angular momenta, respectively, and $M_L$ and $M_S$ to the projection of these vectors on a fixed axis, usually the $z$-axis. The energy does not depend on $M_z$ and $M_s$. The energy actually does not depend directly on the numerical value of the total spin $S$ either. In this approximation, $S$ serves merely to identify a symmetry property of the state. Each level characterized by $L$ and $S$ is $(2L+1)(2S+1)$-fold degenerate. Electrostatic interaction (mixing of states) can take place only between two levels with the same $L$ and $S$. Such interacting levels do not exist for one- and two-electron configurations, but interacting pairs become increasingly common as $N$ increases. The maximum number of interacting levels for a particular value of $L$ and $S$ is given in the second row of Table 1.

In order to obtain energies and eigenvectors, it is necessary to solve secular determinants of order equal to the number of interacting states that is at most of the order of the number given in Table 1.

**Table 1.** Maximum number of interacting levels under electrostatic $\mathbf{H}^1$ and spin orbit $\mathbf{H}^2$ interaction

<table>
<thead>
<tr>
<th>$N$ =</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mathbf{H}^1$</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>4</td>
<td>7</td>
<td>9</td>
<td>10</td>
</tr>
<tr>
<td>$\mathbf{H}^1 + \mathbf{H}^2$</td>
<td>1</td>
<td>3</td>
<td>7</td>
<td>19</td>
<td>30</td>
<td>46</td>
<td>50</td>
</tr>
<tr>
<td>Total number of levels</td>
<td>2</td>
<td>13</td>
<td>41</td>
<td>107</td>
<td>198</td>
<td>295</td>
<td>327</td>
</tr>
<tr>
<td>Multiplets</td>
<td>1</td>
<td>7</td>
<td>17</td>
<td>47</td>
<td>73</td>
<td>119</td>
<td>119</td>
</tr>
</tbody>
</table>

3. **Matrix Elements of Operators**

Calculation of the energy levels of an atom or ion normally proceeds by first figuring the matrix elements of the electrostatic perturbation potential $V$, defined as:

$$ V = \sum_{i=1}^{N} \left[ -\frac{Ze^2}{r_i} - U(r_i) \right] + \sum_{i<j}^{N} \frac{e^2}{r_{ij}} $$

(4)
The first term is purely radial and contributes to energy shifts that are the same for all levels belonging to a given configuration without affecting the energy-level of the configuration. The repulsive Coulomb interaction of the electrons will be different for different states of the same configuration. The summations in Eq. (4) are over the coordinates of all the electrons. However, the term energies of a configuration which contains closed shells are the same, apart from a constant energy shift of all the terms, as those of the configuration in which the closed shells have been omitted. Thus in considering the energy-level structure of a configuration, we shall restrict the summation in Eq. (4) to those electrons in incomplete shells. Hence in calculating the energy-level structure of a configuration, produced by the repulsive Coulomb interaction, we must calculate matrix elements of the type

\[ \tau S L J M \sum_{i<j} \frac{e^2}{r_{ij}} \tau' S' L' J ' M ' \] (5)

Since the electrostatic Hamiltonian commutes with the angular momentum operators corresponding to \( L^2 \), \( S^2 \), \( J^2 \), and \( M \), the matrix elements will be diagonal in \( L \) and \( S \) (although not in \( \tau \)) and independent of \( J \) and \( M \). Calculation of the matrix elements of Eq. 5 commences by first expanding the interaction between each pair of electrons in Legendre polynomials of the cosine of the angle \( \omega_{ij} \) between the vectors from the nucleus to two electrons. \( r< \) indicates the distance from the nucleus (the point of origin) to the nearer electron and \( r> \) the distance from the nucleus to the further away electron.

The energies and wavefunctions can be expressed in terms of certain integrals, the so-called Slater integrals

\[ F^K = \int_0^\infty \int_0^\infty \frac{r_<^k}{r_>^{k+1}} R_i^2(r_i)R_j^2(r_j) \mu_i^2 \mu_j^2 r_i^2 r_j^2 dr_i dr_j \] (6)

where \( r< \) is the lesser and \( r> \) the greater of \( r_i \) and \( r_j \). The Slater integrals are usually expressed in terms of a subscripted quantity \( F_k \), where for \( f \) electrons the relationships are \( F_2 = F^2/225; \ F_4 = F^4/1089; \ F_6 = a F^6/7361.64 \). If the wavefunctions of the central field approximation are known, the integrals \( F_k \) can be calculated.

For the \( 4f^N \) configuration, only the integrals \( F_0, F_2, F_4, F_6 \) need be considered. Here, a further simplification can be made which for the \( 4f^N \) configuration probably introduces only small errors in comparison to those present because of neglect of the inter-configuration interaction. If the central field is a Coulomb one, it can be characterized by a single constant, the
effective nuclear charge $Z'$. In that case, the $F_k$ must all be functions of $Z'$ or of $F_2$ one can write $F_4 = 0.145F_2$; $F_6 = 0.0164F_2$ and (for the triply ionized rare earth) $F_2 = 12.4Z' = 12.4(Z – 34)$ approximately. The parameter $F_0$ is a common additive constant to all levels and for this reason, is of no importance for the structure of the configuration.

Recent investigations have shown that the wavefunctions, in fact, deviate considerably from being hydrogenic, but in spite of this, the ratios remain relatively stable. As more experimental details of the crystal and first ion levels become available, these problems will become increasingly important. The simplified theory has, nevertheless, proved very serviceable in clarifying the level assignment. Although the theoretical calculations are of limited validity they give a reasonably good account of the observed energies.

The calculated levels are, however, good enough for the identification of the empirical levels, at least the lower ones, and once identified, the latter can, of course, be determined with any desired accuracy. The energies and the assignments of the grand and exited levels can be found in [7] where the electronic levels are presented.

4. Results of Theoretical Calculations

Most detailed theoretical calculations of energy levels and wavefunctions have been carried out on the $4f^n$ configuration of the trivalent ions and are of direct interest for the crystal spectra. The results may be seen in figure 1 [7].

The general relations are to be found in the book of Wybourne [4]. In all cases, the calculations for $4f^n$ and $4f^{14-n}$ are the same but with a positive $\zeta$ for $n < 7$ and a negative numerically different $\zeta$ for $n > 7$.

Some examples for the simple cases are $4f^1$ and $4f^{13}$: This is the case of (Ce$^{3+}$, Yb$^{3+}$). There is no problem here, as there is only one electron.

For $4f^2$ and $4f^{12}$: Pr$^{3+}$, Tm$^{3+}$ here the relatively small number of levels and the fact that nothing more complicated than the solution of a cubic equation is required makes this a problem suitable even for a desk calculator.

The electrostatic interaction involves no non-diagonal matrix elements, and the positions of the various multiplets can be directly given:

- $3H$: $E_1 = 0$
- $3F$: $E_2 = 15F_2 + 18F_4 - 273F_6 = 13.133F_2$
- $1G$: $E_3 = -5F_2 + 148F_4 + 91F_6 = 17.952F_2$
- $1D$: $E_4 = 44F_2 - 48F_4 + 728F_6 = 48.979F_2$
- $3P$: $E_5 = 70F_2 + 84F_4 - 127F_6 = 61.286F_2$
- $1I$: $E_6 = 50F_2 + 60F_4 + 14F_6 = 58.923F_2$
- $1S$: $E_7 = 85F_2 + 249F_4 + 1729F_6 = 149.461F_2$

The last column gives the results in a Coulomb field.
By diagonalizing the electrostatic and spin orbit matrices, the wave function of the total levels is obtained to a good approximation and their energy calculated [1,2,6,7].

5. Optical Transitions in Trivalent Rare Earths

The optical transitions so typical of the spectra of rare earth (RE) ions in crystals and solutions usually correspond to intra- \( f^N \) transitions of predominantly electric-dipole character. For a free ion, electric-dipole transitions between states of the same configuration are strictly parity forbidden, and thus any explanation of the observed spectra of crystals or solutions must concern itself with non-centro-symmetric interactions that lead to a mixing of states of opposite parity. This mixing may result from several distinct mechanisms. One of the most obvious mechanisms is simply the coupling of states of opposite parity by way of the odd terms in the crystal field expansion.

The systematic theoretical approach explaining the contribution of the next configuration to the \( f \) configuration via odd terms in the crystal field expansion and the energy difference between the two configurations together with the radial integrals can be found in the literature [3,5-8].

Several selection rules follow in application of the triangular conditions to the 3-\( j \) and 6-\( j \) symbols contained in the theoretical equations. These are:

\[
\Delta l = \pm 1; \quad \Delta S = 0; \quad \Delta L \leq 21; \quad \Delta J \leq 21.
\]

The \( \Delta l = \pm 1 \) selection rule means that for \( f^N \) configurations the perturbing configurations may differ only by the single substitution of \( n'd \) or \( n'g \)-electrons. Spin-orbit interaction will usually lead to a breakdown of the selection rules on \( S \) and \( L \). The selection rule \( \Delta J \leq 6 \) will be valid as long as \( J \) is a “good” quantum number. This selection rule is seen in the usual absence of the transitions \( 5D_0 \rightarrow 7F_3 \) and \( 7F_5 \) in Eu\(^3+\) spectra. In general, the oscillator strength \( f \) of a transition may be expressed as

\[
f_e = \frac{8\pi^2 mc}{3he^2} \bar{\nu}(\mathcal{A}|P^{(1)}_\rho|B)^2 \frac{(n^2 + 2)^2}{9}
\]

\[
= \bar{\nu} \sum_{\lambda,q} \zeta(\lambda,q,\rho)(l^N aSJJ z U^{(\lambda)}_{q+\rho}' l^N a'S'L'J'J' z )^2
\]

where

\[
\zeta(\lambda,q,\rho) = \frac{8\eta^2 mc (n^2 + 2)^2}{3he^2} Y^2(\lambda,q,\rho).
\]
Equation (7) in a simplified form is

\[ f_m = \frac{8 \pi^2 mc}{3h^2} \left| \frac{e}{2mc} (\alpha_{SLJJ_z} L + g_s S \alpha_{SLJJ_z'}) \right|^2 n \]

\[ = 4.028 \times 10^{-11} \overline{U}(\alpha_{SLJJ_z} L + g_s S \alpha_{SLJJ_z'})^2 n \]

where \( \overline{U} \) is in units of cm\(^{-1}\) and \( n \) is the refractive index. The matrix of \( L + g_s S \) will be given by

\[ (\alpha_{SLJJ_z} L + g_s S \alpha_{SLJJ_z'}) = (-1)^{J-J_z} \left( \begin{array}{cc} J & 1 \\ -J_z & \rho \end{array} \right) \times (\alpha_{SLJJ} L + g_s S \alpha_{SLJJ'}) \]

where \( \rho = 0 \) gives the \( z \)-components of \( S \) and \( L \), which will correspond to the absorption or emission of \( \sigma \)-polarized light, and \( \rho = \pm 1 \) gives the \( x \pm iy \)-corresponding to \( \pi \)-polarized light.

The above equations hold for a perturbing configuration of the type \( n' l_{N-1} l' \). Perturbing configurations of the type \( n' l'_{N+1} n l \) will differ in the angular factors by not more than a phase factor. The summation index is limited to even values (that is, 2, 4, and 6 for \( f \)-electrons).

The following selection rules may be readily established [1]:

- \( \Delta l = 0; \Delta S = 0; \Delta L = 0; \Delta J = 0, \pm 1 \) (not \( 0 \leftrightarrow 0 \)),
- \( \Delta J_z = 0 \)
- \( \Delta \mu = 0 \) \( \sigma \)-polarization,
- \( \Delta J_z = \pm 1 \)
- \( \Delta \mu = \pm 1 \) \( \pi \)-polarization.

In the trivalent RE the transitions of interest take place between states within the \([Xe]4f^5d^06s^0\) configuration (with \( n = 1 \) for \( \text{Ce}^{3+} \) to \( n = 13 \) for \( \text{Yb}^{3+} \)). As a consequence, they are parity forbidden and consist mainly of weak magnetic dipole (MD) and induced electric dipole (ED) transitions. The intensities of the MD transitions are practically not influenced by the chemical surroundings of the ion, whereas those of the ED transitions are quite sensitive to it. Judd-Ofelt theory has been very successful in understanding and predicting the spectral intensities of the latter, especially for ions in inorganic glasses and crystals. Also, the absorption spectra of lanthanide complexes in solution and molecular crystals have been subjected to analyses on the basis of Judd-Ofelt theory [3, 8], but it has rarely been used to predict the emissive properties of lanthanide complexes. A wide variety of lanthanide complexes has been synthesized and studied over the past decades, some of which are highly
luminescent. One of the attractions of luminescent lanthanide complexes is that the organic ligand can be endowed with specific physical and chemical properties through chemical design and synthesis [9-14].

6. Radiative Transitions in Rare Earths

Radiative relaxation from an excited state $\Psi J$ of a lanthanide ion usually occurs to various lower lying state $\Psi'J'$, giving rise to several lines in the emission spectrum. For example, the red luminescence of Eu$^{3+}$ is a result of transitions from its $5D_0$ state to all of the lower lying $7F_j$ levels.

The spontaneous emission probability, $A$, of the transition $\Psi J \to \Psi'J'$ is related to its dipole strength according to

$$A(\psi J, \psi' J') = \frac{64\pi^4 N}{3h(2J+1)} \left[ \frac{n(n^2 = 2)^2}{9} D_{ED} + n^3 D_{MD} \right]$$

(11)

Here, $N$ is the average transition energy in cm$^{-1}$, $h$ is Planck's constant ($6.63 \times 10^{-27}$ erg s), and $2J + 1$ is the degeneracy of the initial state (1 for $5D_0$). $D_{ED}$ and $D_{MD}$ are the electric and magnetic dipole strengths (in esu$^2$ cm$^2$), respectively. The factors containing the medium’s refractive index, $n$, result from local field corrections that convert the external electromagnetic field into an effective field at the location of the active center in the dielectric medium.

The transitions from $5D_0$ to $7F_{0,3,5}$ ($J' = 0, 3, 5$) are forbidden both in magnetic and induced electric dipole schemes ($D_{ED}$ and $D_{MD}$ are zero). The transition to $7F_1$ ($J' = 1$) is the only magnetic dipole contribution. Magnetic dipole transitions in lanthanide ions are practically independent of the ion’s surroundings and can be well calculated by theory ($D_{MD} = 9.6 \times 10^{-12}$ esu$^2$ cm$^2 = 9.6 \times 10^{-6}$ debye$^2$).

The remaining transitions ($J' = 2, 4, 6$) are purely of induced dipole nature. According to the Judd-Ofelt theory, the strength of all induced dipole transitions (absorption and emission) of a lanthanide ion in a certain matrix can be calculated on the basis of only three parameters $\Omega_\lambda$ using the expression

$$D_{ED} = e^2 \sum_{\lambda=2,4,6} \Omega_\lambda \left| \langle J \| U^{(\lambda)} \| J' \rangle \right|^2$$

(12)

The elementary charge $e$ is $4.803 \times 10^{-10}$ esu. The $\Omega_\lambda$ parameters belong to the particular combination of the RE ion and its coordinating environment, and are usually determined experimentally. $\left| \langle J \| U^{(\lambda)} \| J' \rangle \right|^2$ are the square reduced
matrix elements whose values are independent of the chemical environment of the ion. A set of values of all matrix elements for all lanthanide ions is now available in the literature, but smaller sets can be found. The matrix elements that may be used in eq. (12) for Eu$^{3+}$ are tabulated in Table 2.

| 5D$_0$→ | $\langle \langle |\mu_{\alpha}^{(2)}| \rangle \rangle ^2$ | $\langle \langle |\mu_{\alpha}^{(4)}| \rangle \rangle ^2$ | $\langle \langle |\mu_{\alpha}^{(6)}| \rangle \rangle ^2$ |
|---------|---------------------------------|---------------------------------|---------------------------------|
| 'F$_2$  | 0.0032                          | 0                               | 0                               |
| 'F$_4$  | 0                               | 0.0023                          | 0                               |
| 'F$_6$  | 0                               | 0                               | 0.0002                          |

Table 2. Squared reduced matrix elements for calculation (using eq. (6)) of the dipole strengths of the allowed induced ED transitions in the emission spectrum of Eu$^{3+}$ [14]

Transitions arising from the 5D$_0$ level of the 4f$^6$ electronic configuration of Eu$^{3+}$ are intensities between the magnetic dipolar 5D$_0$ → 7F$_1$ (≈ 590 nm) and the electric dipolar 5D$_0$ → 7F$_2$ (≈ 610 nm) transitions. The higher this ratio, the closer the local symmetry around Eu$^{3+}$ is to an inversion center. A tabulation of most of the transitions can be found in [10] (see Appendix).

In the standard theory, the integrated coefficient of the spontaneous emission of a transition between two manifolds $J$ and $J'$ is given by

$$A_{JJ'} = \frac{4e^2 \omega^3}{3\hbar c^3} \left[ \frac{n(n^2 + 2)}{9} S_{ed} + n^3 S_{md} \right]$$

(13)

where $\omega$ is a regular frequency of the transition, $e$ is the electronic charge, $c$ is the velocity of light, $\hbar$ is Planck’s constant over $2\pi$ and $n$ is the refractive index of the medium. The electric and magnetic dipole strengths, respectively, $S_{ed}$ and $S_{md}$ (in units of $e^2$), are given by

$$S_{ed} = \frac{1}{(2J + 1)} \sum_{\ell = 2,4,6} \Omega_{\ell} \langle \alpha' J' | \mathbf{U}(\ell) | \alpha J \rangle^2$$

(14)

where the quantities $\Omega_{\ell}$ are the Judd-Ofelt intensity parameters as described before and $m$ is the electron mass.

$$S_{md} = \frac{\hbar^2}{4cm_ec^2} \langle \alpha' J' | L + 2S | \alpha J \rangle^2 \frac{1}{2J + 1}$$

(15)
The reduced matrix elements appearing in Eq. (14) are evaluated in the intermediate coupling scheme [6], and the angular momentum operators \( L \) and \( S \) are in the units of \( \hbar \). The corresponding expression for the oscillator strength may be obtained from the relation

\[
P_{JJ'} = \frac{2J+1}{2J'+1} \frac{mc^2}{2\omega^2 e^2 n^2} A_{JJ'}
\]

where \( B_{\lambda p} \) depends on the radial wave function, and the odd crystal parameters and energy difference between the \( 4f \) and next excited configuration [6, 14] of the opposite parity.

Here we are discussing only the static model and omitting the vibronic interaction.

\[
B_{\lambda p} = \frac{2}{\Delta E} \langle r^t+1 \rangle \theta(t,\lambda) \rho \left[ \frac{(\lambda+1)(2\lambda+3)}{(2\lambda+1)} \right]^{1/2} \left( \langle r^\lambda \rangle / (1 - \sigma_\lambda) C^{(\lambda)} / \| C^{(\lambda)} \| \right) \Gamma_p \delta_{t,\lambda+1} (18)
\]

where \( \Delta E \) is the energy difference between the barycenters of the excited \( 4f^{N-1} 5d \) and ground \( 4f^N \) configurations, \( \langle r^\lambda \rangle \) is a radial expectation value, \( \theta(t,\lambda) \) is a numerical factor, \( \sigma_\lambda \) is a screening factor, \( C^{(\lambda)} \) is a Racah tensor operator of rank \( \lambda \), and \( \delta_{t,\lambda+1} \) is the Kronecker delta function. The first term in the right-hand-side of Eq. (18) corresponds to the forced electric dipole mechanism, as expressed by the average energy denominator method, and the second term corresponds to the dynamic coupling mechanism within the point dipole isotropic ligand polarizability approximation.

The measured intensity of an absorption band is related to the probability (P) for absorption of radiant energy (oscillator strength) by the expression

\[
P = \frac{2303cm^2}{N\pi 2^2} \int e_i(\nu) d\nu = 4.318 \times 10^9 \int e_i(\nu) d\nu
\]
7. Relaxation Processes in Trivalent Rare Earths

The luminescence intensity of emission from a given level depends on the radiative and non-radiative probabilities. The quantum yield is expressed as

$$QY = \frac{\sum Ar}{\sum Ar + Wnr}$$

(19)

where $Ar$ are the radiative transition probabilities and $Wnr$ the non-radiative ones. Ion energy transfer can affect the quantum efficiency due to additional non-radiative relaxations. These can arise from multiphonon decay, and concentration quenching, in addition to energy transfer to neighboring ions. All these processes will lower the quantum efficiency. A multiphonon decay mechanism is responsible for the non-radiative decay in most cases. The results of multiphonon relaxation rates have been summarized for amorphous materials [12,13]. The rates as functions of the energy gaps are straight lines, as in fig. 1.

Figure 1. Multiphonon relaxation rates as a function of the energy gap between the emitting and next lower level.
Table 3 gives the maximum energies corresponding to the vibrational nodes of the various lattices.

<table>
<thead>
<tr>
<th>THE HOST</th>
<th>B SEC⁻¹</th>
<th>A CM</th>
<th>HΩ CM⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>GLS, ALS</td>
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<tr>
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<td>5.4x10¹²</td>
<td>4.7x10⁻³</td>
<td>1200</td>
</tr>
<tr>
<td>-Borate</td>
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<td>3.8x10⁻³</td>
<td>1400</td>
</tr>
<tr>
<td>BeF₂</td>
<td>9x10¹¹</td>
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<td>LaBr₃</td>
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<td>LaF₃</td>
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</tr>
<tr>
<td>Y₂O₃</td>
<td>2.7x10⁸</td>
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<td>SrF₂</td>
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<td>Y₃Al₅O₁₂</td>
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<tr>
<td>YalO₃</td>
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<td>4.6x10⁻³</td>
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<td>LiYF₄</td>
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<tr>
<td>ZrO₂</td>
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<td>470</td>
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</table>

The ab initio calculation of the transition rate between two electronic states with the emission of p phonons involves a very complicated sum over phonon modes and intermediate states. Due to this complexity, these sums are extremely difficult to compute: However, it is just this complexity which permits a very simple phenomenological theory to be used. There are an extremely large number of ways in which p phonons can be emitted and the sums over phonon modes and intermediate states are essentially a statistical average of matrix elements. In the phenomenological approach it is assumed that the ratio of the pᵗʰ and (p-1)ᵗʰ processes will be given by a coupling constant characteristic of the matrix in which the rare earth is situated and not depending
on the rare-earth electronic states. For a given lattice at low temperatures the spontaneous relaxation rate is given by

$$W(0) = Be^{a\Delta E}$$

(20)

where $B$ and $\alpha$ are characteristic of the host ($\alpha$ is negative). Thus, a graph of the spontaneous rate versus energy gap will be a straight line in a case when this approach is valid. Experimental data have shown that the approach is very good for a large variety of hosts. In this way, all multiphonon rates can be inferred from a few measured rates (see fig. 2).

The dominant emission process is the one which requires the least number of phonons to be emitted. The minimum number of phonons required for a transition between states separated by an energy gap $\Delta E$ is

$$p = \frac{\Delta E}{\hbar \omega_{\text{max}}}$$

(21)

where $\hbar \omega_{\text{max}}$ is the maximum energy of optical phonons. With increasing temperature, the stimulated emission of phonons by thermal phonons increases the relaxation rate $W$ according to

$$W(T) = W(O)(1 + \bar{n}(\hbar \omega_{\text{max}}))^p$$

(22)

where $\bar{n}$ is the average occupation number of phonons at energy $\hbar \omega_{\text{max}}$. See Table 3 for the maximum phonon energies in various lattices.

The non-radiative relaxations in the rare earth ions are related to their excited state populations and are governed by the energy difference between the emitting level and the next lower level, separated by the number of phonons of the host. In the weak-coupling case, for the rare-earth ions, the temperature dependence of the non-radiative rate is given by:

$$W(T) = \beta \exp\left[- (\Delta E - 2\hbar v_{\text{max}}) \alpha \left[ \exp(\hbar v / kT) - 1 \right]^{-1} + 1 \right]^p$$

(23)

where $p = \Delta E / \hbar v$, $\Delta E$ is the energy difference between the levels involved, $\alpha$ and $\beta$ are constants, and $v_{\text{max}}$ the highest available vibrational frequency of the surroundings of the rare-earth ion. For example, Eu$^{3+}$ may not only emit from $^5D_0$ (red), but also from $^5D_1$ (green) and $^5D_2$ (blue). The Tb$^{3+}$ ion may not only emit from $^5D_4$ (green), but also from $^5D_3$ (blue). However, this depends critically upon the host lattice.
8. Energy Transfer Between Two Rare Earth Ions

This process is observed when there are two different ions in a matrix. We may excite one ion, the donor, and observe fluorescence from another ion, the acceptor. We shall discuss here only the energy transfer between rare earth ions in a glass matrix [12,13].

Rare earth ions are especially suitable for energy transfer studies due to their well-defined and narrow electronic levels, to which absorption occurs and from which fluorescence is observed. Symbolically, energy transfer can be written as

\[ 2(\text{D}) \rightarrow 1(\text{D}) \rightarrow 1(\text{A}) \rightarrow 2(\text{A}) \text{ or } D^* + A \rightarrow D + A^* \quad (24) \]

The donor system returns from the excited state 2(D) to the ground state 1(D) and the energy released is used to bring the activator system from the ground state 1(A) to its excited state 2(A). In the case of a rare earth, the transfer is a non-radiative one, i.e. no photon will appear in the system during transfer. Förster predicted that for the organic system, the rate of energy is proportional to the overlap of the donor emission and the acceptor absorption spectra and to \( R^{-6} \), where \( R \) is the distance between the donor and the acceptor. The discussion of Förster was extended by Dexter for ions in inorganic crystals. For detailed descriptions see [7,12]. The probability of energy transfer by dipole-dipole (dd) interaction in a simple case where the Born-Oppenheimer approximation holds is given by Dexter [12] as

\[
P_{da(dd)} = \left( \frac{3h^4 c^4 Q_a}{4 \pi R^6 n^4 \tau_d} \right)^4 \left( e / k^{1/2} \varepsilon_c \right) \int f_d(E) f_a(E) / E^4 \cdot dE \quad (25)\]

where \( R \) is the separation of nuclei of donors and acceptors, \( \varepsilon_c \) is the electric field within the crystal, \( \varepsilon \) is the electric field in vacuum and \( f_d(E) \) is the observed shape of the emission band normalized to unity; \( \int f_d(E) \cdot dE = 1 \). \( E \) is the energy; the subscripts \( d \) and \( a \) refer to donors and acceptors, respectively; \( f_a(E) = \sigma(E) \) is the normalized function of the acceptor absorption \( Q_a = \int \sigma(E) \cdot dE \), the measured area under the absorption band, and \( \int F_a(E) \cdot dE = 1 \). \( \tau_d \) is the decay constant of the pure donor; and \( \sigma \) is the absorption cross section. The equation may also be written as follows:

\[
P_{da(dd)} = \frac{3hc^2 Q_a Q_d g_d}{4\pi^3 n R^6 g_d^*} \left( \frac{\varepsilon}{k^{1/2} \varepsilon_c} \right)^4 \frac{f_d(E) F_a(E)}{E^2} \cdot dE \quad (26)\]
where $g$ are the degeneracies of the initial an excited state of the donor, and $Q$ are the areas of the acceptor and donor absorption curves.

In addition to dipole dipole energy transfer we may observe energy transfer due to exchange interaction. The probability $p(\text{exc})$ of these can be written, according to Dexter, as

$$p(\text{exc}) = \frac{2\pi}{h} Z^2 f_d(E) F_a(E) dE$$

(27)

In this formula, $Z$ is not accessible to direct optical measurement and $Z^2$ varies with distance $R$ as $\exp(-R/L)$, where $L$ is an effective average Bohr radius of donor and acceptor ions in excited and unexcited states.

While the former two interactions are electrostatic in origin, the exchange interaction arises from the antisymmetry requirements of the electronic wavefunction for a system consisting of a donor and an acceptor.

9. Spectroscopy of Rare Earth Complexes

The oscillator strength of rare earth ions embedded in oxide glasses is very low, the phenomena are a result of the fact that the transitions are forbidden by the Laporte rule. The intensities of the luminescence of REs can be strongly increased by incorporating the ion into a complex. Such complexes could be seen as light conversion molecular devices (LCMDs), coining the term ‘antenna effect’ which includes the absorption, energy-transfer, emission sequence involving distant absorbing (the ligand) and emitting (the lanthanide ion) components, thus overcoming the very small absorption coefficients of the lanthanide ions. The design of efficient lanthanide complexes has become an important research goal. The transitions can be intensified by incorporating the ions in complexes. Interest in the photophysical properties of lanthanide ion complexes has grown considerably since Lehn [14,15-18] proposed the system then being pursued by several groups, working with many different classes of ligands (e.g. cryptands, podandts, calixarenes, macrocyclic ligands, b-diketones, heterobiaryl ligands, carboxylic acid derivatives, terphenyl ligands, proteins, etc.). Most of the complexes investigated emit red or green light (Eu$^{3+}$ and Tb$^{3+}$ luminescence, respectively). However, there are also complexes of different Ln$^{3+}$ ions that luminesce in other spectral regions: the near-IR (Yb$^{3+}$, Nd$^{3+}$, Er$^{3+}$, orange (Sm$^{3+}$) yellow (Dy$^{3+}$, blue (Tm$^{3+}$), or the near-UV (Ce$^{3+}$, Gd$^{3+}$).

Efficient LCMDs may find several applications, such as luminescent probes in biomedical assays and time resolved microscopy, fluorescent lighting and luminescent sensors for chemical species (H$^+$, O$_2$, halide ions, OH$^-$), electroluminescent devices, UV dosimeters, or antireflection coatings for solar
cells. Beside the quantum yield of a LCMD, other aspects such as light output, solubility, volatility, and photo-, thermal- and thermodynamic stabilities may be critical to many applications, and must also be controlled. In addition, incorporation of RE complexes into sol-gel glasses increases their mechanical and photostability. Silicon inorganic-organic hybrids, synthesized through a sol-gel [14,15] process, have been successfully employed for many purposes, such as sequestrating agents, and it has shown that the sol-gel process could be used to produce silica glasses with trapped Eu(III) fluorescent compounds. Silicon hybrids have, as an advantage, their very low solubility in water and many polar and apolar solvents, as well as their high thermal stability [15].

We have seen the ways in which the electronic $f$ levels of RE ions are populated and depopulated by radiative and non-radiative transitions. As already mentioned, the population density of the luminescent levels is generally weak because of the low transition probabilities. However there are other possibilities to increase the luminescence, mainly by creating strongly absorbing species that will transfer the energy to the RE ion. The three main ways of such excitation are:

(I). Exciting closed shell transition metal complexes such as tungstates, molybdates, vanadates, titanates etc. This way of excitation and its transfer to the RE has been known since the late fifties. The method has been applied to phosphors for luminescent lamps and television screens. There is a vast literature and many reports by Philips, General Electric, Westinghouse, etc. The method is applied to solids melting at high temperatures.

(II) Energy transfer from a strongly absorbing RE due to $f$-$d$ transitions or charge transfer; the literature is very large.

(III) Energy transfer between the ligands and the RE ion in complexes.

As an example we can take [Eu(bpy)$_3$]$_{_{_{3}^{+}}}$ . This compound has a macrocyclic ligand containing three 2,2’ bipyrindine units joined together by two amino groups. In the crystalline phase, it has three anions to neutralize the charge. The Eu is located in the cage of the cryptate. Intermolecular energy transfer from the ligand to Eu has been recently calculated by Malta et al.[16] starting from the classical Fermi golden rule. According to this, within the Born-Oppenheimer approximation, the energy transfer rate, $W_{ET}$ is given by

$$W_{ET} = \frac{2\pi}{\hbar} \langle \psi' \phi | H | \psi \phi' \rangle^2 \cdot F$$

(28)

where $\psi$ and $\phi'$ are the initial electronic states of the lanthanide ion and of the ligand, respectively. After energy transfer has taken place, we deal with the electronic states $\psi'$ and $\phi$. The temperature dependent factor $F$ contains a sum
over Frank-Condon factors and the energy mismatch condition for the transfer process. The following expressions for the transfer rate have been obtained [16]:

\[
W_{ET} = \frac{2\pi}{\hbar} \frac{e^2 S_L}{(2J+1)G R_L^6} F \sum_\lambda \Omega_{\lambda}^{ed} < \alpha' J' | U^{(\lambda)} | \alpha J >^2
\]

(29)
corresponding to the dipole-dipole mechanism, also with \( \lambda = 2, 4 \) and 6 and

\[
W_{ET} = \frac{8\pi}{3\hbar} \frac{e^2 (1-\sigma_0)^2}{(2J+1)R_L^4} F < \alpha' J' | S | \alpha J >^2 \sum_m \left( \phi \sum_k \mu_z(k) s_m(k) \phi' \right)^2
\]

(30)
corresponding to the exchange mechanism. In the above equations, \( J \) is the total angular momentum quantum number of the lanthanide ion and \( \alpha \) specifies the 4f spectroscopic term. \( G \) is the multiplicity of the ligand initial state and \( S_L \) the dipole strength associated with the transition \( \phi i_0 \rightarrow \phi' \) in the ligand. \( U^{(\lambda)} \) is the same unit tensor operator, the reduced matrix elements of which are given in the intermediate coupling scheme, and \( R_L \) is the distance from the lanthanide ion to the region of the ligand molecule in which the ligand donor (acceptor) state is localized. The quantities \( \Omega_{\lambda}^{ed} \) are the well-known Judd-Ofelt intensity parameters (for forced electric dipole contributions only).

In Eq. (30), \( S \) is the total spin operator of the lanthanide ion, \( \mu \) is the \( z \)-component of the electric dipole operator, \( s_m \) \((m = 0, \pm 1)\) is a spherical component of the spin operator and the index \( k \) runs over the electrons of the ligand. \( \sigma_0 \) represents a screening factor. The matrix element involving the coupled operators \( m_z \) and \( s_m \) can be treated by a quantum chemical method. The definition of \( R_L \) is

\[
R_L = \frac{\sum_i c_i^2 R_L(i)}{\sum_i c_i^2}
\]

(31)

A complete theoretical model to calculate the luminescent properties of lanthanide coordination compounds is used to analyze the emission quantum yield of the \([\text{Eu(bpy)}_3]^{3+}\) and \([\text{Eu(bpy)}_3]^{3+} \cdot \text{H}_2\text{O}\) compounds. This theoretical model includes the calculation of the molecular structure, of the ligand electronic structure, of the ligand-lanthanide energy-transfer, of the temporal
dependence of the ligand and lanthanide populations, which lead to the emission quantum yield, relative emission intensity and lifetime of the emitting state. This theoretical approach was used to ascertain the presence of a ligand-to-metal charge-transfer (LMCT) state in these compounds. In addition, this approach has provided indications of the location of the LMCT state, as well as of the magnitudes of the energy-transfer rates [16,17].

The molecular structure of the \([\text{Eu(bpy)}_3]^{3+}\) species has been calculated [16]. The overall structure agrees quite well with similar crystallographic structures presenting a helicoidal C₃ symmetry. The distances between the coordinated nitrogen atoms and the Eu(III) ion are relatively short, namely, an average of 2.53 Å for the bpy·bpy·bpy nitrogen atoms and 2.99 Å for the amino nitrogen atoms. These short distances favor the shielding of the encapsulated ion from the environment. The energy-transfer rates have a strong dependence on the ligand-to-metal distances \((R_L)\). Thus, any small increase in \(R_L\) would cause a significant decrease in the energy-transfer rates. This is coupled to the fact that the O-H oscillators are important luminescence suppression pathways, making the hydrated compound a poor candidate for an efficient light converter.

The calculations of the singlet and triplet states of both the \([\text{Eu(bpy)}_3]^{3+}\) and \([\text{Eu(bpy)}_3]^{3+}·2\text{H}_2\text{O}\) species agree quite well with the experimental data. Namely, the calculated singlet state is about 30100 cm⁻¹ compared to the experimental value of 31800 cm⁻¹; the triplet state is calculated to 19500 cm⁻¹ and the experimental value is about 20300 cm⁻¹. It should be noted that the experimental value for the singlet state was obtained from the absorption spectrum of the \([\text{Eu(bpy)}_3]^{3+}\) compound, and the triplet state from the emission spectrum of the \([\text{Na(bpy)}_3]^{3+}\) compound. From these calculated energy levels it has been possible to establish the most important states involved in the energy-transfer process.

There are five \(4f\) levels of these Eu compounds that are in quasi-resonance conditions with the ligand excited states. These states are then used to calculate the energy-transfer rates using the theoretical model. In order to obtain transfer rates several parameters are needed, which have been obtained from the structure and spectroscopic calculations. For the \([\text{Eu(bpy-bpy-bpy)}]^{3+}\) compound the following data were used to obtain the energy-transfer rates: \(R_L = 3.5\ \text{Å}\), triplet = 4100 cm⁻¹, \(\text{A}_{\text{rad}} = 1000\ \text{s}^{-1}\), which is the sum of the spontaneous emission coefficients of the transitions \(^5\text{D}_0 \rightarrow ^7\text{F}_{0,1,2,4}\) and the theoretical value of the z-component of the electric dipole matrix element is \(1.02x10^{-36}\ \text{esu}^2\ \text{cm}^2\). In addition, the value of 1053 s⁻¹ has been assumed for the inverse of the lifetime of the emitting state \(^5\text{D}_0\). The dipole-dipole contribution for the transfer rates was calculated by using the following theoretical values for \(W_j\) (in units of \(10^{-20}\ \text{cm}^2\)): \(W_2 = 0.16, W_4 = 0.50\) and \(W_6 = 0.4\).
A value of $10^{-1}$ s$^{-1}$ was assumed for the non-radiative decay rates between the 4f-4f transitions. Some of the most important energy-transfer rates were calculated.

It can be seen that the energy-transfer rates are larger for the $^5D_0$ and $^5D_1$ states, where the exchange interaction dominates, than for the higher excited 4f states, where the multipolar interactions are the most important ones.

An example of experimental results of ligand to Eu energy (or charge transfer), showing the intensification of Eu emission is presented in fig. 2 [19]. The schematic representation of charge or energy transfer from the cryptate complex to Eu is presented in fig. 3.
10. Summary

In this paper, I have outlined the theoretical approaches by which electronic levels of trivalent rare earths can be calculated. Radiative transitions between the levels are obtained from the matrix elements of the two relevant levels, which are similar for a given RE but dependent on the host material, and the three intensity parameters which are specific for a given ion. The non-radiative transitions between the emitting level and the lower levels depend on the number of lattice phonons connecting the emitting level and the next lower level.

The energy transfer mechanisms are presented for a transfer between two RE ions, between strongly absorbing charge transfer bands of host matrices and between strongly absorbing ligand states of complexes to the RE ion. Applications in nanotechnology, optics, television screens, sensors and biology were outlined.

References

## APPENDIX:

**Table 4.** Rare earth luminescence emissions of R.E. observed in minerals

<table>
<thead>
<tr>
<th>Center</th>
<th>$\lambda_{\text{em}}$ nm</th>
<th>$\lambda_{\text{ex}}$ nm</th>
<th>$\tau$ $\mu$s</th>
<th>Transition</th>
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<td>0.02</td>
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1. Introduction

The integration of a biological system and a solid state device requires information to be passed across the biological - non-biological interface, in order to sense a change or effect. For such devices to be “intelligent”, they must also be able to respond to those changes and effects, and this requires the transduction of information back from the biological system to the solid state device (for realization of devices to replace damaged tissue in the human body - the ear, eye, skin or nasal cavity). Biosensors that use silicon based devices are available for in vitro applications. However, for in vivo applications, information about the biocompatibility of the silicon is required.

The compatibility of inorganic materials with living tissues and biological compounds is crucial in many areas, such as pharmaceutics, medical diagnostics, surgery, biosensing etc. In particular, a combination of biological compounds with semiconductor-based microelectronics opens up a wide field for novel medical and sensor applications. Thus, the electrical properties of the cells, DNA and other organic materials could be conveniently monitored and controlled. For these purposes, however, a direct, reproducible and stable coupling of semiconductors and biomolecules at the interface has to be achieved.

Si and Si based materials (thin films of a-Si, a-SiC, a-SiOₓ or porous Si) possess physical properties that make them favorable candidates for advanced biological applications. Thin Si films can be deposited over large areas at low temperatures on almost any substrate material, by various methods that are compatible with established silicon technology. Properties such as their optical transparency and electrical conductivity can be changed over a wide range, by means of appropriate alloying or doping and thermal annealing. Amorphous and polycrystalline Si films offer some unique advantages over their crystalline
counterparts, and are widely used in commercial applications, including thin film transistors in active-matrix flat panel displays and photovoltaic solar cells. The ability to functionalize a-Si:H and poly-Si will enable the creation of new thin film electronic devices that sense or otherwise interact with biological molecules and cells. Porous silicon (PS) has been shown to be an excellent candidate biomaterial, following studies showing its biostability and non-toxicity [1]. These favorable properties, coupled with the ease of its topographical manipulation and its optoelectronic properties, make it an ideal material for the design of biologically active devices. PS has been studied for different bio-applications for the last 3-5 years [2, 3]. However, the use of thin films of a-Si:H, a-SiOx:H and polycrystalline Si as substrates for bio-functionalisation is still in its infancy.

A review of the first attempts to characterize thin amorphous and polycrystalline Si based films as materials for bio-applications is presented. The possibility for using PS and other semiconductors as substrate materials for bone implants is also discussed.

2. Biocompatibility of a-SiOx:H and a-Si:H

The majority of advanced biological applications rely on the ability of the inorganic material to directly interface with living cells, DNA and other organic materials. The integration of the biological system and solid state devices requires information to be passed across the biological - non-biological interface, in order to sense a change or effect. In order to achieve this, however, a direct reproducible and stable coupling of semiconductors and biomolecules at the interface has to be obtained.

A key element of biosensitive electronic device research is the controlled modification of the electronically active semiconductor or insulator surface, to permit selective and controlled adhesion of the biomaterial or cell under study. In the past few years, several researchers have studied the surface modification of semiconductor and insulator surfaces, to pattern cell adhesion and proliferation [4, 5]. Initial research on surface modification to control biomaterial interaction has focused almost exclusively on conventional semiconductors, including crystalline silicon, germanium and gallium arsenide [6, 7]. However, other semiconductor materials, including thin films of amorphous Si and its alloys, are also available, and the first attempts to study their biocompatibility have also been reported [8, 9].

The macroscopic biocompatibility of a solid surface is strongly linked to its specific wetting behavior with respect to water. For the purposes of hydrosilylation and selective cell adhesion, chemical surface modifications and their effects on the properties of amorphous hydrogenated silicon (a-Si:H) and silicon suboxide (a-SiOx:H) have been performed, in order to prepare a
hydrophobic/hydrophilic contrast on the sample surfaces [9]. Wafers of c-Si were also treated, for comparison.

Thin films of a-SiO\textsubscript{x}:H were deposited on glass substrates by PECVD in an atmosphere of SiH\textsubscript{4}+H\textsubscript{2}+CO\textsubscript{2} [10]. Films of a-Si:H were prepared by PECVD and magnetron sputtering [11-13]. Initially, all samples were cleaned by dipping in acetone and isopropanol, followed by drying in a stream of N\textsubscript{2}. The native oxide was removed by means of a 10% HF dip for 30 sec. followed by rinsing in water and drying. This procedure resulted in a hydrogen-terminated hydrophobic surface, as monitored by contact angle measurements. For the preparation of a hydrophilic surface, pre-cleaned samples were exposed to a stream of ozone (O\textsubscript{3}), typically for 10 min at temperatures between 20 and 110\textdegreeC.

The hydrophobicity and hydrophilicity of a sample can be characterized by the wetting behavior of water on its surface. The value of the static contact angle, \( \theta \), using de-ionised water, is a measure of this. According to [14], large static contact angles of around 90\textdegree are known for H\textsubscript{2}O drops on a hydrophobic Si surface. In contrast, \( \theta \) is close to 0\textdegree for a hydrophilic SiO\textsubscript{2} oxide surface.

Measurements of the dependence of the static contact angle for a-SiO\textsubscript{x}:H films with different O contents from 0 to 44 \% show that it is rather weak - the surface is mainly hydrophobic and the values of \( \theta \) are between 60\textdegree and 80\textdegree (figure 1). The hydrogen-rich growth conditions are likely to result in the formation of excess Si-H bonds, which render the surface of all as-deposited silicon suboxide samples prevalently hydrophobic. No significant variations of \( \theta \) were observed after storage in vacuum (10\textsuperscript{-2} mbar) for 14 days.

Figure 1. Water wetting angle of hydrogenated amorphous silicon suboxides in the as-deposited state (solid squares) and after storage in an inert nitrogen atmosphere for 14 days (open squares).
The influence of different surface treatments and cleaning procedures on the wetting angle of different samples - a-Si:H deposited by PECVD or magnetron sputtering, a-SiO\textsubscript{x}:H with 40% oxygen and c-Si, for comparison, is analyzed in figure 2. The static contact angles of these samples were determined in the as-deposited state and after the following treatments: dipping in 10 % HF for 30 sec, cleaning in acetone followed by washing in isopropanol for 10 min, “RCA” cleaning for 10 min, and ozonization for 10 min at 300 or 380 K. The results are quite similar for all samples. The most hydrophobic surfaces were obtained after hydrogen termination by exposure to HF. This even works best for the suboxide sample. All other chemical treatments or ozonization at room temperature gave rise to intermediate contact angles of 20 to 70°. However, a brief ozonization at 100°C for 10 min rendered all surfaces completely hydrophilic, with contact angles below 10° and very little dispersion among the different samples.

The influence of the ozonization temperature on the contact angle for an a-SiO\textsubscript{x}:H sample with 40% oxygen is shown in figure 3. Starting from a $\phi$ of 65° in the as-deposited state, HF-etching increases the contact angle to more than 90°. Ozonization for 10 min at higher temperatures gives rise to a rapid decrease in the wetting angle, which stabilizes at approximately 5° for ozonization above 70°C.

As summarized in figure 4, the same behavior is also obtained for crystalline Si and pure a-Si:H, so ozonization is a gentle, convenient and low temperature process for the reliable hydrophilization of a large variety of different silicon surfaces. Preliminary cell adhesion tests of T3T fibroblast cell survival were performed, and indicate a significantly higher cell survival rate during a period of three days for the hydrophilic, ozonized surfaces of a-Si:H and a-SiO\textsubscript{x}:H, as compared to the hydrophobic surface obtained after HF exposure.
The a-SiOx:H with a higher oxygen content (40%) exhibits the largest fibroblast adhesion, but also the strongest decay during three days of observation (figure 5) [15]. The results demonstrate that hydrophilic oxidized surfaces, as well as a large oxygen concentration in a bulk sample, seem to be favorable for enhanced adhesion of a biological cell.

Figure 3. Dependence of the wetting angle of water on a-SiOx:H with an oxygen content of 40 at. % on ozonization temperature. Ozonization was performed for 10 min. with an oxygen flow of 100 l/h. The inset shows photographs of the wetting droplets.

Figure 4. Wetting angle vs. ozonization temperature for the four samples of Figure 2.
Successful functionalization of a-Si:H by hydrosilylation with methyl acrylate has also been reported [9]. A hydrosilylation reaction proceeds, as indicated in figure 6. Starting from a fully hydrogen-terminated silicon surface, thermally or optical induced dissociation of an a-Si:H bond at the surface gives rise to a reactive Si dangling bond, which can form an a-SiC bond with the C,C double bond at the end of an alkane. The ensuing transformation of the double to a single C-C bond gives rise to the appearance of a carbon dangling bond orbital at the second carbon atom of the former C = C bond, which can extract a neighboring hydrogen atom from the hydrogenated silicon surface, giving rise to a new Si dangling bond at the surface. In this way, the hydrosilylation reaction proceeds serially across the Si-H surface, and thus can be expected to be very sensitive to local disturbances, e.g. those caused by weak oxidation of the surface. Successful hydrosilylation of the a-Si:H surface was achieved by simple methyl acrylate treatment. These molecules consist of an anchor group with a C,C double bond for hydrosilylation, followed by a spacer group and a specific cyclic “RDG” peptide group, which is known to promote the adhesion of cells.

Hydrophobic surfaces have been obtained after exposure to a vapor of octyltrichlorosilane CH 3(CH 2) 7SiCl 3, (OTS) of pretreated by UV/O 3 a-Si:H films deposited by PECVD on quartz substrates [8]. The resulting surface was strongly hydrophobic, with an advancing contact angle with water, > 106° - the organic monolayer produces a strongly hydrophobic CH 3–terminated surface.
This organic surface was masked, to reserve areas of the un-coated hydrophilic substrate (it has become hydrophilic after UV/O3 treatment), and was placed in a cell culture (a BHK-21 cell) to observe cell adhesion and proliferation (figure 7). A high degree of cell attachment was observed on the UV/O3 treated surface (~400 cells/mm² compared to 450 cells/mm² on the culture dish control surface, indicating cell proliferation and growth). Little cell adhesion occurred on the hydrophobic organic-coated surface (~ 40 cells/mm²), and cells remained round and only minimally attached. On a masked surface, the organic-free areas showed dense, well-adhered cell growth, while the coated areas showed much fewer and rounded cells.

Figure 7. BHK-21 cells on surface-modified amorphous Si (a) cell adhesion and spreading is inhibited on a patterned alkane monolayer surface; (b) control cell culture dish [8].
These results suggest a means for selectively controlling cell adhesion to thin film electronic device surfaces, through the patterning of hydrophobic surface coatings.

3. Biocompatibility of Porous Si

In order to quantify the effect of the substrate surface topography on the cellular behavior, different planar and micro-textured silicon surface substrates were produced and made suitable for cell culture [16,17]. The effect of the nerve growth factor on the morphology of B50 cells in culture was studied, using PS as a biologically applicable material [18].

The porous silicon was fabricated from 20 Ω.cm p-type silicon, using anodization conditions of 20 mA.cm⁻², for 10-30 min and a standard based HF 1:2:1 etch. The patterned substrates were prepared by KOH etching of the silicon prior to HF-etching, using positive photoresist and a mask of parallel lines of 100 μm width and spacing. Patterned substrates were used to assess the preference of B50 cells to various surface microstructures - i.e. whether the cells showed a tendency to adhere to troughs, ridges or plateaux on the same porous silicon substrate. A typical SEM side-on view of a B50 neuron on a porous Si substrate is shown in figure 8. The morphology of the cell is typical of functioning neurons, with axons, dendrites, and intercellular connections. Also, there are regions where contacts down to the substrate surface are made, and they are thought to be composed of an extra-cellular matrix. Furthermore,

\[ \text{Figure 8. SEM side-on view of a B50 cell at 72 h after seeding on PS [18].} \]

\[ \text{Figure 9. Fura 3 dye image of a B50 neuron superimposed on the image of the substrate. The image size is 100 x 100 μm [18].} \]
the distance from this matrix to the PS surface is less than 100 nm. Although such SEM images are very clear, this technique provides information on cells which are not living.

Typical contact points of B50 cells living on PS, probed using confocal microscopy, are shown in figure 9 (two frames taken at different heights from an image set of the same area, one superimposed upon the other). The background image is the silicon bed on which the cells have been cultured. The fluorescence is due to photoluminescence stimulated by the confocal light source. The lighter skeletal structure shows the distribution of surface calcium ions throughout the cell, as probed using a Molecular Probes Fura 3 calcium dye. This gives an indication of the density, shape, size and position of the contact points, and how the cell moulds to the surface topography. The studies indicate that the main body of the cell sits about 100 nm above the substrate surface, on a layer of extra-cellular matrix connected at various points into the PS. This work implies that direct signal transduction to and from the cell is more likely to be possible through the contact media, axons and/or dendrites, rather that through the cell body.

These preliminary results demonstrate that porous silicon is one of the most promising biomaterials. To cultivate the cell, no pretreatment (either chemical modification, or modification of the topography) of the PS surface is required.

The response of the PS material with respect to sodium ion concentrations with regard to its porosity, its pore morphology and PS thickness has also been studied [19]. The potentiometric technique provides a calibration of the functionalized PS sample response, as a function of the concentration of the injected sodium ions. Figure 10 presents the calibration graph of functionalized PS samples with different porosities. These results show the possible use of PS material as a large sensitive transducer for chemical sensor applications.

Figure 10. Calibration of the functionalized PS samples, prepared from heavily doped silicon material, $\rho = 0.02 \Omega \cdot \text{cm}$, as a function of the Na concentration [19].
4. Porous Si as a Substrate for Medical Implants

Most of the materials currently used in medical implants are bio-inert - they do not interact with living systems. This is ideal for mechanical substitutes for replaced body parts, such as artificial hips. Titanium substrates have been used till now for tooth and bone implants. For devices to be “intelligent”, semiconducting materials are very promising, because of their optical and optoelectronic properties.

Of the essential elements required by living organisms, silicon is a common constituent of biological minerals, together with Ca, P, Mg, Mn, Fe, S, C, O and H. Si is considered to be an essential element, although its biochemistry has not been elucidated in any detail. The widespread occurrence of silicaceous biominerals as structural elements in lower plants and animals suggests a role for Si in the production and maintenance of connective tissue in higher organisms, although this function has not been clearly established [20].

Recently, a wide variety of porous and amorphous materials (Ta, Ti, Al₂O₃, Si, and silica) have been investigated for biomedical applications [21,22]. Porous silicon has been shown to be an excellent candidate biomaterial, following studies establishing its biostability and non-toxicity [18]. It looks attractive to explore further the potential of PS as a substrate for preparing biologically useful silicon implant surfaces by coating with hydroxyapatite (HA). Porous structures have been found to allow fast deposition of HA layers with strong bonds to the surface and good osteo-integration when implanted [23].

It is considered that an ideal bioactive surface for bone-bonding material, such as HA, might be a surface with a porous structure which could induce the rapid formation of physiologically stable HA after immersion in an artificial fluid which resembles the body liquids, known as simulated body fluid (SBF), or even in real body fluid [24]. In reference [25], a PS layer (PSL) prepared by electrochemical etching was used as a substrate for inducing HA growth by two methods: a simple soaking process in SBF and a Laser-Liquid-Solid Interaction (LLSI) process.

PSL preparation includes electrochemical etching (ECE) of n-type (P-doped) Si wafers, with (100) orientation and 4-6 $\Omega\cdot$cm electrical resistivity, in a HF:C₂H₅OH:H₂O = 2:1:1 electrolyte under illumination [26]. Methods of HA growth used in the study involved

(i) a simple soaking process, i.e. immersion of the samples (horizontally and vertically) in a deposition system of 400 ml total volume of SBF for 15 h at 37°C [27,28] and

(ii) LLSI, which allows interaction between a scanning laser and the PS substrate immersed in the SBF. A CuBr vapor pulsed laser ($\lambda = 578.2$ nm,
average power 470 mW, pulse duration 30 ns, and repetition rate 19 kHz) was used. At the edge of each sample, the scanning laser beam formed a surface design of seven squares situated one inside the other at a distance of 200 μm. After LLSI, the samples were positioned horizontally and vertically in the SBF, following a simple soaking process for 15 hours at 37°C. Topographical and microstructural characterizations of the studied structures were investigated by light microscopy (LM, Nicon SMZ 1500), X-ray diffraction (XRD, Cu Kα1 X-ray source, λ = 1.54 Å), and electron microprobe analysis (EMPA, CAMECA, SX 100).

On a (100) Si plane, the surface morphology studied by SEM shows a porous network structure of star-like shapes (figure 11a). Figure 11b shows a LM image of the HA topography of a vertically positioned PS substrate. It was observed that, independently of the substrate position in the solution, the grown layers have a similar topography, and are dense and homogeneously distributed over the whole surface. This result shows that the PS substrate is able to induce HA formation, thus being bioactive. The PS samples also induce the deposition of HA when applying LLSI. The backscattered electron signal carries information about sample composition through the brightness of the image (brighter areas correspond to heavier average atomic masses): in figure 11c, the brighter areas correspond to Ca. The darker areas and dark points correspond to the porous network of Si. An elemental distribution image obtained by EMPA yields the distribution of the main components Si, O, Ca and P of the grown structures. Ca and P mapping (data not presented) shows that these elements are concentrated in areas randomly distributed on the network structure of the PSL. Quantitative analysis by EMPA was also obtained (elemental concentrations measured in weight %). Ca and P signals (3.59 and 3.28 respectively), as well as strong O (49.2) and Si (38) signals, were detected. The Ca:P ratio calculated in our experiment was 1.10.

Figure 11. a) SEM image of PSL in plan view; b) LM image of HA layers grown by a simple soaking process on PSL placed vertically in SBF; c) Backscattered electron image of the horizontally placed sample, obtained by the method of laser-liquid solid interaction [25].
Other elements, such as K (0.01), Cl (0.03), Mg (0.25), Na (0.08) and S (0.12), were also present in the spectra. EMPA shows that the layer grown after applying LLSI, independently of sample position in the SBF, as well as areas irradiated or non-irradiated by the laser, consisted of a thin layer of Ca- and P-containing compounds and clusters of HA, randomly distributed over the whole surface of the PSL.

The reported method of LLSI is based on the simultaneous interaction between a scanning laser beam and a solid substrate. The previous results on HA growth using LLSI [29] lead us to conclude that the irradiation of substrates immersed in SBF leads to a promotion and enhancement of the HA nucleation process, probably due to a synergistic effect of the simultaneous use of the laser light, the SBF and the substrate. Thus, the process of LLSI offers an attractive alternative to conventional time-consuming methods. It has been shown that PSL prepared by ECE of a n-Si (P-doped) substrate with (100) orientation induces the deposition of HA after the PS samples have been immersed (horizontally or vertically) in SBF using two methods (a simple soaking process and the LLSI). Layers grown by the simple soaking process are dense and homogeneously distributed, while those grown using LLSI consist of a thin layer of Ca- and P-containing compounds and clusters of HA, randomly distributed over the whole surface of the PSL. Using laser interaction, the electrical or electrochemical parameters of the PSL, such as resistance and capacitance, can be changed. As discussed in [16], this can be directly related to the nucleation and growth of apatite.

5. Conclusions

The first results of the study of the thin-film semiconductor materials a-Si:H, a-SiOx:H and porous Si demonstrate that these materials offer prospects for the creation of semiconductor bioelectronic devices for biosensor monitoring and human body implants. The demonstration of successful thin film semiconductor bio-devices could be the first step toward a new class of low-cost devices for a wide range of biomedical and biochemical applications. Although the true integration of a biological system with an electronic circuit has not been achieved, current research in the preparation of semiconductor materials suitable for this application is providing encouraging results. Some of the most promising materials for this purpose are silicon based thin films.

References


1. Introduction

This survey comprises the first of three articles on the structural characterization of nanoparticles by transmission electron microscopy (TEM), a powerful and versatile tool offering a wide range of methods to study different features of nanoparticles [1-4]. Here, more generally, TEM will be introduced including the basic principles of the electron beam interaction with inorganic matter, imaging and diffraction modes, preparation methods, high-resolution electron microscopy, image processing and image contrast calculation. Only by an appropriate combination of methods will it be possible to extract information on particle size, shape, composition, arrangement, crystal lattice peculiarities and orientation relationships. While a large diversity and amount of literature is available in respect of the general electron microscopy of inorganic materials, demonstration by means of instructive examples may enable one to make use of this knowledge for the specific issues of nanoparticulate matter.

2. Electron Beam Interaction with Inorganic Matter

The interaction of an incident beam of primary electrons of 100 or several 100 keV energy with a specimen of inorganic matter, thin enough to allow for considerable transmission, preferentially consists of elastic scattering. Besides this electron scattering in the forward direction governed by the atomic number and lattice parameter of the material, the primary electron impact produces not only a certain portion of backscattered electrons, but also secondary electrons and X-rays. Inelastic interaction processes are utilized for material composition analysis via electron energy loss spectroscopy (EELS) and energy dispersive X-ray spectroscopy (EDXS) as well as energy-filtered electron imaging and X-ray mapping in analytical TEM devices equipped with a scanning transmission addition. These interactions are schematically represented in Fig. 1. For conventional TEM investigation of nanoparticulate matter, the atomic number contrast due to
3. Imaging and Diffraction Modes

Structural information on nanoparticles by means of TEM can be obtained in the imaging mode using bright-field (BF) or dark-field (DF) specimen illumination or in the selected area electron diffraction (SAED) mode from the intensity distribution in the back focal plane of the objective lens, i.e. the diffraction pattern. This diffraction pattern, related via a Fourier transform to the electron wave function at the specimen exit surface, enables selection, by size and position of the objective lens aperture, of one, two, or several beams for image formation. In the BF mode, only the undiffracted beam contributes to the image where contrasts are determined by differences in thickness and/or atomic number as well as crystal lattice diffraction effects. In the DF mode, only one or more diffracted beams contribute to the image. This enables selective imaging of specimen areas of common orientation and/or a common lattice, and gives better resolution for thickness changes or lattice defect imaging. The SAED pattern, imaged in the observation plane, reveals, at least partly, the symmetry and structure of the specimen lattice, from which the conditions for HREM imaging can be derived, with contrasts resulting from the controlled interference of undiffracted and diffracted beams.

Most important for the investigation of nanoparticle morphology is the periodic intensity modulation with crystal thickness, resulting in characteristic fringes of equal thickness (thickness contours) for wedge shaped crystals. The spacings of such fringes are well suited for topographic imaging of nanoparticles only with beams of weak intensity in dark-field, i.e. the weak-beam dark-field (WBDF), mode [5]. Additional fringes from planar defects, inclined to the primary electron beam direction, improve the shape representation, as may be recognized from Fig. 2 where a particle of nearly...
Figure 2. Bright field and weak-beam dark-field images of a gold particle grown on AgBr.

A square profile with two crossed stacking faults imaged in BF and WBDF mode using diffracted beams of increasing intensity (DF1 to DF3) is shown.

Additionally to WBDF, particle shape features may be extracted from the spot fine structure of corresponding diffraction patterns, since the shape information is convolved to the diffraction spot intensity. The influence of the particle shape on the experimental electron diffraction spot fine structure has extensively been studied by crystal shape factor calculations based on a general algebraic expression for any crystal polyhedron [6]. Fig. 3 shows as an example a TEM image and SAED pattern (upper and lower left) of a Pd particle of tetrahedral shape together with two slightly off-symmetrical excited spots.

Figure 3. Diffraction spot fine structure of a tetrahedral Pd particle and calculated shape factor.
of this pattern (lower right and center) compared to two off-center cross-sections of the corresponding calculated crystal shape factor (upper right and center).

4. Specimen Preparation Methods

The choice of an appropriate specimen preparation technique depends on the origin and configuration of the nanoparticles. While colloid-disperse solutions, simply sprayed onto carbon-coated microgrids, are ready for investigation just after evaporation of the solvent, dry powders first need to be transferred into solution, and embedded particles require disintegration or dissolution of the respective matrix, e.g., by means of grinding and/or ultrasonic agitation [7]. Sometimes, it is of interest to get information on the spatial distribution of nanoparticles in a matrix or thin film, e.g., to record a depth profile of their size and number density. Imaging of nanoparticles within the matrix requires target-directed or cross-section preparation of the composite by mechanical and/or chemical thinning, including ion beam etching [8]. Alternatively, the composite material may be incorporated into epoxy and subsequently cut into thin enough slices using ultramicrotomy. Nanoparticles situated on a substrate surface may be prepared for TEM investigation by Pt-C shadow casting, to form enveloping shells or replicas that carry the particles when extracted from the substrate [9].

5. High-Resolution Electron Microscopy

In HREM imaging for structural characterization down to the atomic scale by the interference of undiffracted and diffracted beams, the resulting phase contrasts are influenced by (i) interaction of the incident electron wave with the specimen, leading to modifications of amplitude and phase, and (ii) modification of the image plane intensity distribution due to the contrast aperture setting, spherical aberration, beam divergence and objective lens defocus. In this two-step process, the specimen-independent properties of the image forming system are reflected by the contrast transfer function that describes how the objective lens acts as a filter on the spatial frequency spectrum of the specimen.

Depending on the imaging conditions, HREM results in lattice plane imaging with one or more sets of lattice plane fringes of a certain zone axis orientation, from which lateral extension of the crystal and also the presence of some lattice defects can be deduced, or structure imaging with characteristic image contrasts reflecting the respective lattice symmetry. As an example, Fig. 4 shows a HREM image of nanocrystalline Ge in <110> orientation. It contains some twin boundaries oriented perpendicular to the image plane, marked by arrows, and some regions of unusual contrast features, marked by circles. In the twinned image region bright dots correspond to the characteristic channels
Figure 4. HREM image of nanocrystalline Ge in a <110> orientation. Twin boundaries are marked by arrows and unusual contrast features by circles [10]. Inset: diffractogram (FFT).

of the diamond cubic lattice in the <110> zone axis orientation, while dark dots correspond to columns of atom pairs, as drawn schematically in the model of Fig. 5, where some lattice directions are also indicated.

Besides contributions from the image forming system mentioned above, particular image contrast contributions from nanoparticles concern surfaces, interfaces, stoichiometry variations, lattice distortions, specimen tilt, thickness changes, and deviations from the bulk lattice symmetry. These issues, and the characteristics of the imaging process, limit straightforward and intuitive interpretation of HREM image contrasts. Mostly, for comparison with experimental images and to meet the imaging conditions applied, image contrast simulations, based on appropriate atomic models, by means of multi-slice calculations of amplitude and phase modification are required.

6. Image Processing and Contrast Calculation

HREM image contrasts of nanoparticles are frequently degraded by superposition with amorphous support or matrix contrast, as well as by deviations from favorable orientations of the particles. Then, image improvement, e.g., by contrast enhancement, may be achieved by means of image processing techniques applied to digitized selections of electron micrographs. Image processing of experimental contrasts can also be employed
for other purposes, such as image analysis to evaluate nanoparticle features like size and shape, structure analysis to determine crystal lattice characteristics, and comparison to calculated image contrasts, respectively. As a rather useful tool in image processing, the Fourier transform (diffractogram) that exhibits the spectrum of the spatial frequencies present in HREM images is widely applied in diffractogram analysis of structural features and Fourier filtering. Diffractogram modification by filter operation and subsequent back transformation enables selective representation of image details. The inset of Fig. 4 shows the diffractogram of the image where the spots reflect the orientation and spacing of the corresponding lattice plane fringes, mostly \{111\}, and indicate the presence of several regions of <110> zone axis orientation that are azimuthally rotated relative to each other.

The application of contrast simulation to twin boundaries in nanocrystalline Ge thin films of <110> orientation, imaged end-on in Fig. 4, is demonstrated in Fig. 5. According to the model shown on the left, calculated image contrasts for typical parameters of a 400 kV HREM at 3 defocus values near the optimum setting (50, 55 and 60 nm) are presented on the right for a 6 nm (top) and a 14 nm (bottom) thick supercell of Ge in <110> orientation. Besides variation of contrast fine details with changing defocus and thickness one may recognize the typical appearance of a first-order twin boundary representing a mirror plane for the lattice of both adjacent crystallites.

Different contrast features are expected if the boundary between such twins is not perpendicular, but inclined to the image plane since then the electron beam penetrates two lattice regions of different orientation. Superposition of twins of various orientation relation to each other results in a kind of super-structures as those in Fig. 4 marked by circles [10]. Image contrast simulations using a superposition model of two twins with first-order boundary, structurally...
Figure 6. Model (upper left) and HREM image contrast calculation for 0 to –60 nm defocus of a first-order twin superposition structure of Ge. Supercell thickness: 4 nm.

related by azimuthal rotation of 70.53° within a supercell of 4 nm thickness, are shown together with the model (upper left) in Fig. 6. Already from visual inspection of the model, one can get the impression of linear superstructures. The simulation for a series of defocus values (0 to –60 nm) clearly demonstrates how these linear superstructures change appearance (e.g., contrast reversal when passing from –10 to –30 nm) with varying defocus. The image calculated for –30 nm appears to be most similar to the linear superstructures in Fig. 4 (see, e.g., the lower circle). These superstructures exhibit a threefold period of \{111\} lattice plane fringes parallel to the common <110> direction of both lattices.

Circular superstructures due to superposition of twin-related crystallites are expected if the twin boundary is not of first-order structure or if more than two twin units are overlapping. It needs extensive image contrast simulations according to different models in order to find the appropriate one, together with the right imaging conditions that fit well in an image matching comparison of experimental and calculated contrasts. As an example, Fig. 7 shows contrast calculations for a superposition model (upper left) of two twins with a second-order twin boundary, structurally related by azimuthal rotation of 109.47° within a supercell of 4 nm.

Figure 7. Model (upper left) and HREM image contrast calculations for 0 to –60 nm defocus of a second-order twin superposition structure. Supercell thickness: 4 nm.
thickness. Visual inspection of the model gives the impression of circular superstructures that are differently reflected by simulated contrast features in the defocus series (0 to –60 nm). Here again, the image calculated for –30 nm appears to be most similar to the circular superstructures in Fig. 4 (see, e.g., upper circle). Sometimes, the circular superstructures exhibit fivefold pseudo-symmetry, which makes direct interpretation in terms of the crystal lattice structure rather difficult since such symmetries are also found in multiply cyclic twinned nanoparticles [11].

References

1. Introduction

This survey comprises the second of three articles on structural characterization of nanoparticles by electron microscopy. It is devoted to TEM investigation of nanoparticles embedded in a matrix so as to form a composite of unique properties closely related not only to their nanoscale dimensions, but also to structural characteristics and dielectric properties of the surrounding medium. By presenting results of studies on selected examples, electron microscopy techniques directed to the particular issue of the respective material shall be imparted. These examples are (i) silica-supported Ag catalyst nanoparticles [1] from a sol-gel route of synthesis, (ii) Si [2] and CdSe [3] nanoparticles in silicon suboxide, produced both by physical vapor deposition (PVD) and thermal processing, and (iii) Ag nanoparticles in glass fabricated by multiple processing of commercial float glass [4].

2. Silica-Supported Ag Catalyst Nanoparticles from Sol-Gel Synthesis

The structural characteristics of metal nanoparticles become the more important the more they are employed in structure-sensitive processes such as heterogeneous catalysis. For particle sizes well below 10 nm, colloidal routes of synthesis produce a great variety of particle shapes accompanied by variations of the internal structure. To study this phenomenon, high-resolution electron microscopy (HREM) was applied to Ag nanoparticles formed in an acidic route of silica sol-gel synthesis modified by AgNO$_3$ addition and finished by forming treatment at elevated temperatures [5]. Preparation for TEM was done by ultrasound-assisted disintegration and dispersion in propanol to remove Ag nanoparticles from the silica matrix and transfer them to carbon supporting films on copper micro-grids. Digital image processing was used to calculate the Fourier transform (diffractogram) of digitized selections of electron micrographs recorded under optimum imaging conditions.
These particles may be divided into single crystalline (marked COP in Fig. 1), single twinned (marked STP) and multiply twinned particles (marked MTP), respectively. The HREM image plus the corresponding diffractogram reveal a clear signature (‘fingerprint’) of the particle structure. Some examples are shown in Fig. 2.
shown together with a particle scheme in Figs. 2 and 3. Single crystalline Ag particles may exhibit the shape of a cuboctahedron or a truncated octahedron (see Figs. 2a & 2b), common growth forms of noble metal particles that are found also for single twinned particles.

Multiply twinned particles occur in two configurations, the decahedron being a pentagonal bipyramid (see Figs. 2c & 2d), and the icosahedron approaching most effectively a spherical shape (see Figs. 3a – 3d), both composed of tetrahedral sub-units in twin relation and stacked around axes of fivefold symmetry [6]. The decahedron in 2(c) is imaged with the fivefold axis parallel to the image plane, while in 2(d) the fivefold axis is viewed end-on. This way, one may recognize distinct grooving where the twin boundaries emerge to the particle surface. Fig. 3 reveals how the particle appearance changes in various positions if, from (a) to (d), a 3-fold, 2-fold, 5-fold axis, or one between 2-fold and 5-fold, is parallel to the electron beam. The large number of particle configurations may be understood in terms of structural transformations during growth [6].

3. Si and CdSe Nanoparticles in SiO<sub>x</sub> by PVD and Thermal Processing

Silicon suboxide thin films fabricated by PVD of SiO in vacuum at defined oxygen partial pressures have been established as versatile approaches to transparent matrices for embedded semiconductor nanoparticles. Such nanoparticles exhibit peculiar optoelectronic properties closely related to their
size and internal structure, as well as the dielectric properties of the surrounding medium. One main issue in these studies is the objective of tuning the photoluminescence emission wavelength and efficiency, by controlling the nanoparticles' size and spatial arrangement [2,7]. TEM investigation of such materials is directed to the formation of nanoparticles during synthesis and processing, as well as to the evolution of their internal structure. For both Si and CdSe nanoparticles, the easy way of making SiO films by evaporation is utilized, either in an experimental set-up with two SiO evaporation sources, or with a SiO source and a CdSe source, allowing the deposition of single layer, sandwich, or multilayer films on Si wafers.
The formation of Si nanoparticles in a SiO\textsubscript{x} matrix is achieved by thermally induced phase separation of the suboxide at about 1000 °C. They are uniformly distributed in the SiO\textsubscript{x} matrix, have a nearly spherical shape and frequently exhibit planar lattice defects. These are twin boundaries, either in parallel or in a cyclic arrangement, as can be seen from the HREM images of Fig. 4. Fig. 5 demonstrates for a single twinned particle the different appearance of the crystal lattice and twin boundary in real space (HREM image) and reciprocal space (diffractogram). With the stoichiometry parameter \( x \) varying from 1.17 to 1.63, the mean size decreases from 4.29 to 2.96 nm.

The formation of CdSe nanoparticles in the SiO\textsubscript{x} matrix is achieved by sequential deposition of SiO and CdSe, where in a self-organized process their spatial arrangement (see Fig. 6) is directed by the surface roughness of the first SiO\textsubscript{x} layer. The mean size and crystallinity of the nearly spherical CdSe particles increase upon thermal processing at 400°C. HREM images as shown in Fig.7 reveal that this change involves a gradual transition from the hexagonal

![Figure 6](image)

*Figure 6.* TEM image of a cross-section through SiO\textsubscript{x}/CdSe/SiO\textsubscript{x} on a Si substrate (wafer). The particle arrangement follows the wavy SiO\textsubscript{x} surface.

![Figure 7](image)

*Figure 7.* HREM images of CdSe particles in SiO\textsubscript{x}, as-deposited, with wurtzite lattice in (00.1) orientation (left), and upon annealing, with a sphalerite lattice in (011) orientation (right).
wurtzite lattice of bulk CdSe to the cubic sphalerite lattice type. This transition is accompanied by a certain disorder in the stacking of close-packed planes that can be recognized as twin boundaries (marked by arrows). At these twin boundaries the sphalerite lattice locally obeys the wurtzite lattice stacking sequence [8] which may influence the optoelectronic properties of the material.

4. Non-Spherical Ag Nanoparticles by Multiple Processing of Float Glass

Nearly spherical metal particles of nanometer dimensions embedded in soda-lime silicate glass can be fabricated by several means. Their optical properties, promising for potential applications, depend on the concentration, size, shape, spatial arrangement and configuration of the nanoparticles. Conventional experimental routes of synthesis like, e.g., $Na^+/Ag^+$–ion exchange plus thermal processing, enable only minor variations of these structural characteristics. Particles of non-spherical shape are of particular interest. Spherical Ag particles in float glass can be deformed via stretching at elevated temperatures, so as to assume the shape of prolate spheroids. Parallel arrangement of their long axes results in different absorption of linear polarized light according to the polarization direction ($\perp$ or $\parallel$ to the long axes). The color effect and polarization efficiency can be adjusted by choosing the initial particle size or the extent of glass stretching, as well as by thermally induced shape relaxation. To initiate, promote or modify metal particle formation in glass, irradiation-assisted techniques may also be applied.

Figure 8. Spherical Ag particles in glass, produced by ion exchange and thermal processing.

Figure 9. Prolate deformation of spherical Ag particles in glass, produced by thermomechanical processing.
TEM investigation of such materials is required to elucidate the hidden structure related to their optical properties. From Fig. 8, a size distribution in the initial sample of spherical particles can be recognized. It is interesting to note that after stretching, the Ag particles below a certain size remain spherical, but above this threshold their elongation depends on the previous radius (see Fig. 9). In addition, the response of the particles to the tensile stress is influenced to some degree by the crystal lattice orientation with respect to the stretching direction [8].

Similar prolate deformation of spherical Ag nanoparticles in glass can be achieved by ultra-short laser pulses of high intensity, using linear polarized laser light of a wavelength corresponding to the spectral absorption by surface plasmon resonance of these particles [9]. As can be seen from Fig. 10, the deformed particles are uniformly arranged with their long axis determined by the polarization direction. This deformation is caused by the strong electrostatic field built-up. Simultaneously, ejection of electrons and Ag$^+$ ion desorption into

Figure 10. Prolate deformation of spherical Ag particles in glass, produced by laser irradiation processing.

Figure 11. Halo of secondary Ag nanoparticles around a deformed primary particle
the matrix is induced, where they recombine and precipitate in a certain distance from the primary particles so as to form a halo of secondary particles, as shown at larger magnification in Fig. 11 [10]. This interpretation of the experimental findings is mainly based on the results of HREM analysis of such complex nanoparticle structures, that revealed for the halo particles a crystal lattice of the same symmetry and spacing as that of the primary particles. Mass balance considerations based on particle size measurements and comparison of volumes of halo particles, primary deformed particles and initially spherical particles confirm the concept of irradiation-induced mass loss. The presence of a cloud of secondary Ag nanoparticles around the deformed primary ones also allows reasonable interpretation and modeling of the optical spectra of these materials, that differ distinctly from those of Ag nanoparticles in glass subjected to thermomechanical processing.

References

1. Introduction

This survey comprises the third of three articles on the structural characterization of nanoparticles by electron microscopy. It is focused on strategies for fabricating one-dimensional nanostructures and the contribution of electron microscopy to this aim. To introduce this field, a short overview on approaches to anisotropic growth will be given and growth mechanisms such as seed-mediated growth, template-directed synthesis and defect-mediated growth will be explained. In particular, growth promotion by twin formation and multiple twinning [1] will be discussed by means of examples like metal nanorods and Si nanowires of various origin. Structural characterization of these one-dimensional (1-D) nanostructures, composed of several subunits, by TEM using special techniques such as specimen tilting (rotation around a rod axis) and image processing (diffractogram analysis and Fourier filtering), has been aimed at understanding how twinning, in particular multiple cyclic twinning, may promote nucleation and anisotropic growth.

2. Approaches to Anisotropic Growth and Related Growth Mechanisms

The issue of 1-D nanostructures has attracted tremendous attention in the recent years, and a whole family of such objects like fibers, whiskers, wires, rods, tubes, and belts, all with ‘nano’ in their names, can be formed of nearly all technologically important materials like metals, alloys, elemental semiconductors, compound semiconductors, and semiconducting as well as insulating oxides. Various kinds of strategy for fabricating 1-D nanostructures have been explored. These include (i) size reduction in two dimensions, e.g., the elongation of spherical nanoparticles in glass by tensile stress applied to the matrix, (ii) linear self assembly, e.g., the preferred nucleation and growth of nanoparticles at surface steps of a crystal, and (iii) anisotropic growth, i.e. the unidirectional, axial growth due to inhibition of radial growth. TEM images of some examples are shown in Fig. 1(a) to illustrate the above terms.

Various routes of anisotropic growth, e.g., of dendrites, whiskers and needle-shaped crystals have been known for decades. Some new techniques have been invented recently, or are being developed now. They may be classified as (i) promoter-free growth, (ii) seed-mediated growth, or (iii) template-directed growth. Promoter-free growth includes the natural 1-D growth of linear chains due to anisotropic bonding, e.g., in molybdenum chalcogenides, the natural tendency of scroll formation in lamellar materials like layer minerals, as well as the kinetic control of growth habit mainly via supersaturation and impurities that causes whisker growth of Co, Ni, Fe, Pt and B and may also explain the oxide-assisted vapor-solid growth of semiconductor nanowires. To illustrate these routes TEM images of some examples are shown in Fig. 1b.
Seed-mediated growth makes use of metal nanoparticles serving as sinks for atomic or molecular nanowire species from solution or vapor phase, where upon exceeding a certain supersaturation 1-D crystallization takes place. This method enables large scale nanowire formation of elemental (Si, Ge) and compound semiconductors (SiC, GaAs, GaN, GaP, InAs, InN, InP), as well as semiconducting oxides (ZnO, CdO, Ga$_2$O$_3$, In$_2$O$_3$) with thickness control by adjusting the size of the seeds, and arrangement control by providing defined arrays of seed particles on a substrate surface. For Si nanowires, it has been proven to work with gas phase supply of the Si species, not only by SiO evaporation [2] and Si molecular beam deposition [3] as shown in Fig. 2, but also by Si pulsed laser deposition and silane chemical vapor deposition (CVD).

Template-directed growth makes use of shaping aids of nanometer dimensions, to achieve 1-D nanostructures in tube or rod configuration. Such shaping aids may be soft templates like micelles or inverted micelles of cylindrical shape, formed by surfactant molecules or diblock copolymers. Attaching precursors of the desired material to the interior or exterior micelle surface and subsequent thermochemical processing results in the fabrication of nanorods and nanotubes of various metals, compound semiconductors and oxidic materials. Hard templates like mesoporous membranes, nanorods or nanotubes are shaping aids that are accessible to complex physical and chemical procedures. Carbon nanotubes, for example, can be employed as templates for filling and coating procedures as well as confined and substitution reactions, respectively, to form new fibers, tubes and 1-D core-shell nanostructures. Accordingly, nanowires can be used as templates for coating procedures as well as confined reactions.

Of similar complexity are the possibilities to utilize porous materials like track-etched polycarbonate, porous silicon, porous alumina membranes, mesoporous silica and alumosilicate as hard templates to fabricate fibers, tubes and heterostructures. For filling of the pores or coating of pore walls various
techniques like CVD, electrodeposition, sputtering, liquid injection, electrophoresis, and polymer wetting can be applied [4-6]. Since porous alumina membranes can nowadays be fabricated as highly ordered arrays [7], as may be recognized from Fig. 3, this ordering holds also for the 1-D nanostructures obtained using the above techniques. It may be employed for ordering-related magnetic or optoelectronic properties.

3. Promotion of Anisotropic Growth by Multiple Twinning

While seed-mediated and, in particular, template-directed formation of 1-D nanostructures are not so much sensitive to the application of strictly anisotropic growth conditions, the promoter-free formation of such objects usually requires low supersaturation that favors defect-mediated growth where screw dislocations or twin boundaries enable unidirectional growth at reasonable rates. Screw dislocations need to be embedded in a certain volume of material. Therefore, they are rarely observed in nanoparticles or nanowires, whereas twin boundaries even occur in nanoparticles only a very few nanometers size [8].

Defect-mediated growth with twin boundaries in materials having face-centered cubic or diamond cubic lattices, respectively, is based on the effect of twin boundaries and twin junctions to enable considerable growth rates at low supersaturation. The first step is mis-stacking of atoms in twin positions on a growing close-packed plane, leading to accelerated growth along the twin boundary thus formed, since its configuration allows simplified nucleation. Multiple twin junctions appear if during growth twin formation on coplanar planes occurs. According to the ratio of the growth rate of cube faces to that of octahedron faces, various forms of multiply twinned particles with one fivefold twin junction may result, as shown schematically in Fig. 4. The ideal decahedron is composed of 5 tetrahedra. However, the growth shapes may exhibit different building units like octahedra (star decahedron), truncated octahedra (facet decahedron), cuboctahedra (prism decahedron), and cubes (cube decahedron). Axial growth along the fivefold twin junction takes place
where, because of a distinct growth rate anisotropy or some kind of surface modification (reconstruction), only negligible radial growth may happen. Fivefold twinned rod-like structures, mainly of transition metals, Si, Ge, diamond and TiN, have been known for a very long time [9] and can interestingly be found resulting not only from promoter-free, but also from seed-mediated as well as from soft template-directed routes of synthesis [1].

As an example of truly defect-mediated growth, Fig. 5 shows an Ag nanorod and the corresponding model, a prism decahedron. Such nanorods of length to diameter ratios of 2 to 6 and length variations between 20 and 130 nm have been fabricated by an inert-gas aggregation technique [10]. HREM revealed that the contrast appearance of the nanorods sensitively depends on their respective orientations. By means of specimen tilting, i.e. rotation around the rod axis, a rotational periodicity of 36° of two characteristic contrast patterns, separated from each other by 18°, has been established. One of them (Fig. 6 (a)), exhibits

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**Figure 4.** Overview of different growth shapes of fivefold twinned decahedra.

**Figure 5.** TEM image of an Ag nanorod (left) and the corresponding fivefold twinned rod model (right).
Figure 6. Characteristic image contrast of a Ag nanorod: (a) orientation A and (b) orientation B.

a symmetric contrast around a dark core, corresponding to a prism decahedron with the electron beam perpendicular to one of its prism faces. The other (Fig. 6(b)), exhibits a non-symmetric contrast corresponding to the prism decahedron with the electron beam parallel to one of its prism faces. In both images, the courses of fringes of \{111\} and \{220\} lattice planes are marked, together with Moiré fringes \{M\} occurring in orientation A. These Moiré fringes appear in the dark core region corresponding to the subunit with a prism face perpendicular to the electron beam. They result from superposition with two adjacent subunits, whose common twin boundary is situated parallel to the electron beam, and obscure lattice plane imaging. In contrast to this, orientation B exhibits 2 sets of \{111\} lattice plane fringes in one half of the nanorod image that result from the subunit with a prism face parallel to the electron beam. In the other half of the nanorod, the electron beam passes through two adjacent subunits of equal orientation, with their common twin boundary.

Figure 7. Diffractogram of a HREM image of a multiply twinned Ag nanorod in orientation A.
perpendicular to the beam direction, where only one set of \(\{220\}\) lattice plane fringes is seen.

The unclear HREM image contrast appearance due to superimposed contributions in orientation A can be clarified by Fourier-filtered image reconstruction. The corresponding diffractogram shown in Fig. 7 contains two sets of reflections, one marked by circles on a net of dotted lines and the other by circles on a net of dash-dotted lines. Moiré type extra reflections are indicated by \(M(i)\). The reflections on the dash-dotted net are due to the \(<001>\) zone axis orientation of the twin subunit with a prism face perpendicular to the electron beam. The image reconstruction by inverse Fourier transformation using only this type of spots is shown in Fig. 8(a). It reveals two sets of \(\{200\}\) lattice plane fringes restricted to the core region of the particle. The reflections on the dotted net due to the \(<112>\) zone axis orientation of two twin subunits with a common twin boundary parallel to the electron beam result in the uniform appearance of \(\{111\}\) lattice plane fringes across the whole particle upon Fourier-filtered image reconstruction, as shown in Fig. 8(b).

A quantitative confirmation of the above interpretation of HREM image contrasts and image reconstructions is found by identifying the Moiré reflections as result of double diffraction at superimposed twin subunits, according to the equations given below [11]. They may be due to \((i)\) subunits having parallel lattice planes of different spacings \(d_1\) and \(d_2\) (parallel Moiré \(M_p\)) as M1 and M2:

\[
M_p = \frac{d_1 \cdot d_2}{d_1 - d_2}
\]
or to (ii) subunits having an azimuthal rotation $\beta$ between lattice planes of equal spacings $d$ (rotation Moiré $M_r$):

$$M_r = \frac{d}{2\sin(\beta/2)}$$

or to (iii) subunits having an azimuthal rotation $\beta$ between lattice planes of different spacings $d_1$ and $d_2$ (mixed Moiré $M_m$) as M3 and M4:

$$M_m = \frac{d_1 \cdot d_2}{\sqrt{d_1^2 + d_2^2 - d_1 \cdot d_2 \cdot 2\cos\beta}}$$

Since Moiré fringe characteristics very sensitively reflect lattice plane spacings, they are rather useful for detecting deviations from the bulk lattice.

References


1. Introduction

For more than 30 years, the family of materials known as the transparent conducting oxides (TCOs) have been widely applied in many passive and active electronic and optoelectronic devices. The most notable applications are for the transparent front electrodes in solar cells, light emitting diodes, sensing devices and for flat panel displays.

2. TCO for Solar Cells, Light Emitting Diodes (LED) and Display Applications

The first report of transparent conducting materials was devoted to CdO films prepared by the thermal oxidation of sputtered Cd [1]. Since then, the technological interest in transparent conductors has grown tremendously. This is motivated by the increasing coated-area requirements of several very large volume applications such as photovoltaic modules, flat-panel displays, heat-reflecting coatings and architectural windows. As the area increases, there is a need for reduce the sheet resistance to avoid impairing performance. Increasing the thickness of the films causes increased optical absorption, and may also cause undesirable stresses to develop in the films, possibly leading to cracking and de-lamination. Therefore, reducing the sheet resistance may only achieved by reducing the resistivity, which may be achieved either by an increase in the carrier concentration or the carrier mobility. Increasing the former simply increases the free-carrier absorption. Therefore, developing new materials with higher mobility is more desirable.

The required condition for the application of materials as transparent electrodes in solar cells, flat panel displays and LEDs is the simultaneous
occurrence of a high optical transparency, T, (more than 80%) in the visible region and a high electrical conductivity, \( \sigma \), \((\sim 10^3 \ \Omega^{-1} \cdot \text{cm}^{-1})\). This is not possible in an intrinsic stoichiometric material. Partial transparency and fairly good conductivity may be obtained in thin films of a variety of materials. The only way to obtain good transparent conductors is to create electron degeneration in wideband (> 3 eV) oxides by controllably introducing non-stoichiometric oxides of Sn, In, Cd, Zn and their alloys in thin film form, prepared by a number of deposition techniques and/or by doping with metals (usually Al, Ga) which decrease the resistivity while retaining a good transparency.

Indium tin oxide (In\(_2\)O\(_3\):Sn or ITO) has been the standard transparent front conductor of choice for current applications in display and solar cells, because of its low electrical resistivity (5 x 10\(^{-4}\) \(\Omega\).cm), high optical transparency in the visible region and well established processing technology [2]. However, ITO has been recognized by users to have problems, such as insufficient conductivity in high density applications, instability in a hydrogen plasma, lack of repeatability during sputtering and annealing processing, and degradation during high temperature operation [3]. It has been reported [4, 5] that from the ITO or SnO\(_x\) contact, reduced In or Sn migrates into the a-Si:H. As consequence of the highly reducing silane plasma, a SiO\(_x\) barrier is then formed at the interface between the TCO and the a-Si:H. This promotes reduction of the metal oxide and silicon is bonded to excess oxygen. The conditions at the interface surely degrade the transport properties of charge carriers in the amorphous silicon, and will severely reduce the amount of light penetration to the active layers of the solar cells. Migration of the In and Sn could be prevented by deposition of a blocking layer of ZnO [6,7]. Recently ZnO has been recognized as being more appropriate for a transparent front electrode and anti-reflection coating for a-Si and CuInSe\(_2\) (CIS) solar cells [8]. ZnO offers some advantages: i) it consists of cheap, abundant and non-toxic elements, ii) it can be produced for large scale coatings, iii) it allows tailoring of the ultraviolet absorption; iv) it has a high stability in a hydrogen plasma, because it is able to tolerate reducing chemical environments, v) it can be deposited at a low growth temperature.

The most frequently used method of preparation is sputtering of a ZnO target and a ZnO target doped with Al, In or Ga, reactive evaporation of Zn in an atmosphere of O\(_2\), CVD, spray pyrolysis, laser deposition, screen printing, etc. [9-13].

The substrate can have a significant influence on the properties of the films. Glass substrates are most commonly used. Low temperature processes such as magnetron sputtering and ion beam sputtering allow the deposition of the oxide films onto polymer substrates such as plastic, Mylar and poly(ethylene-terephthalate). In processes which involve high deposition temperatures, the effect of the diffusion of alkali ions from the glass substrate to the films becomes extremely important [14].
2.1 ZnO FILMS AS TRANSPARENT ELECTRODES.

ZnO is an n-type semiconductor (due to the O vacancies) with a direct optical band gap of approximately 3.3 eV at room temperature [15]. Doping with group III metals (Al, In, Ga) causes an increase in the conductivity of n-type ZnO. It has proven to be difficult to dope it as p-type. A theoretical prediction for the realisation of p-type ZnO by co-doping with Ga and N in the ratio N/Ga = 2:1 has been proposed [16]. The formation of clusters consisting of acceptor-donor-acceptor groups that occupy nearest neighbor sites or second-nearest ones is energetically favorable (due to the strong attractive interaction between the N acceptors and Ga donors), which are used as co-dopants at high doping levels. The subsequent confirmation of the suitability of co-doping for the production of p-type ZnO was demonstrated and reported in [17]. They confirmed the p-type conductivity (by Hall and Seebeck coefficient measurements) and observed a resistivity of 2 $\Omega \cdot$cm at room temperature and a hole concentration of $4 \times 10^{19}$ cm$^{-3}$ using co-doping (N + Ga). They also obtained very high resistivity p-type ZnO by doping with active N alone.

ZnO films retain the bulk wurtzite structure, and are composed of columnar crystallites with grain sizes in the range 50 - 300 Å. Sputtered ZnO films have a strong c-axis orientation, perpendicular or parallel to the substrate depending mainly on the substrate material, while the degree of preferred orientation depends on the deposition parameters. Undoped ZnO films deposited using r.f. magnetron sputtering in an Ar+$H_2$ mixture at a substrate temperature of 750$^\circ$C had a typical as-deposited resistivity, $\rho$, of about $2 \times 10^{-3}$ $\Omega$ cm and a transmission coefficient, $T$, ~ 90%. The sprayed films, after annealing at about 400$^\circ$C in an H$_2$ ambient or vacuum, have $\rho$ ~ $10^{-3}$ - $10^{-2}$ $\Omega$cm and $T$ ~ 80% - 90% [13, 18].

Very high transparencies and high conductivities have been obtained in ZnO films doped with Al deposited by magnetron sputtering [19]. Figure 1a shows the r.f. power dependence of $\rho$, $\mu$ (the mobility) and n (the carrier concentration). The resistivity decreases when the r.f. power is less than 150 W. At higher powers, it does not change. Similar behaviour was reported for Ga doped ZnO films, by Choi et al. [20]. The free carrier concentration n and the mobility decrease with the r.f. power, and at values of 150 W they reach saturation. The increase in resistivity with r.f. power could be related to the increase in concentration of defects in the film, due to the fast growth rate and bombardment of energetic ion and neutral species during deposition, and hence to the increased electron trapping at the grain boundaries that can reduce the mobility and free carrier concentration and thereby limit the conductivity of the films [21, 22].

Figure 1a shows the dependence of the resistivity, Hall mobility and carrier concentration on the r.f. power during deposition, for ZnO:Al films with thicknesses of about 400 nm on glass substrates. Figure 1b shows the corresponding transmission spectra.
The transmission in the visible region is high (85 - 90% from the substrate transmission), and it does not depend on the r.f. power. An increase in r.f. power leads to a decrease in the transmission in the IR region. This is probably due to defects created by fast energetic species during the deposition at high power densities, as was the case in the r.f. power dependency of the resistivity of the same films (Figure 1a). The transmission edge of the films does not appear to depend on the r.f. power. The estimated optical width of the band gap is about 3.3 eV, which means that the films are colorless. An important parameter for the TCO is a figure of merit: $F_m = - R \ln(T)$, where $R$ is the resistivity and $T$ the transmittance of the films. The lower is this value, the better are the films for application as TCO. It has been shown [19] that thicker films deposited at lower r.f. powers, i.e. under less harsh conditions and lower deposition rates, exhibit better properties.

Figure 1. (a) - R.f. power dependencies of the film resistivity, $\rho$, mobility, $\mu$, and concentration of free carriers, $n$, for ZnO:Al films with thicknesses of about 400 nm, deposited by r.f. magnetron sputtering [19]. (b) - The corresponding transmission spectra [19].

Figure 2. AFM pictures of a ZnO:AL film, deposited by magnetron sputtering [19] The scale sizes are in $\mu$m. The brightest color in b) corresponds to 30 nm.
The surface morphology observed by AFM is presented in figure 2. As seen, the size of the grains is about 300-400 nm. It has been observed by TEM study that the habitus of the microcrystallites forming the texture depends on the Al doping (Figure 3) [23]. Films of undoped ZnO have a texture axis parallel to the substrate. The ZnO:Al films, instead, show a columnar texture with a texture axis perpendicular to the substrate. Analysis of diffraction patterns has shown that for both types of films the fundamental cells have a wurtzite structure.

It has been recognized that the conversion efficiency of solar cells can be improved by using textured TCO [24]. The large surface roughness, or large grain size resulting from the grain growth leads to strong scattering of incident light. Milky transparent conducting ZnO films with a textured surface have been prepared by techniques such as a MOCVD [25] and d.c. magnetron sputtering [26]. Figure 4 shows SEM photographs of the textured surface of ZnO:Al films with different thickness (T_s = 300°C and Ar pressure 8 Pa). At a higher sputter pressure of 80 Pa, milky ZnO films with sheet resistances as low as 4 Ω/cm have been deposited at a lower T_s = 200°C [27].

A very interesting approach has been proposed by Eisele et al. [28, 29]. In contrast to the statistically rough light-trapping structure, the authors used a periodically coupled grating (Figure 5). They employed such periodically structured TCO (SnO_2 and ZnO) for light trapping structures in thin film solar cells. For the case of microcrystalline silicon solar cells, the indirect band gap leads to a low absorption and the application of the efficient light trapping structures are essential to achieve good efficiencies.

Figure 3. RHEED patterns of ZnO films (a) undoped and (b) doped with Al [23].
Figure 4. SEM photographs of the surfaces of ZnO:Al films with different thicknesses: a) 0.5, b) 10 and c) 2.0 μm. The scale size is 0.5 μm in all of the photographs [26].

Figure 5. Typical surface topography (AFM) of a periodically structured ZnO:Al layer: a) a line grating with a period of 795 nm etched in ZnO:Al; b) a dot grating with the same period.; c) the profile across the lines in a diagonal direction for the dot grating. [29].

Figure 5 demonstrates the typical surface topography of a periodic line (a) and dot structured (b) ZnO:Al layer. Figure 6a shows a schematic drawing of a thin film solar cell with a periodic grating as the light-trapping structure. The ZnO:Al film deposited on glass is periodically structured. The a-Si:H and μc-Si:H solar cells were prepared as p-i-n structures.

Figure 6. (a) Schematic drawing of a thin film solar cell with a periodic grating as the light-trapping structure. (b) The reverse side of a 1μm thick μc-Si:H solar cell deposited on top of a ZnO:Al dot grating [29].
The reverse side of a 1 μm thick μc-Si:H solar cell deposited on top of a ZnO:Al grating is shown in Figure 6b. The periodic gratings are generated by holographic laser (Nd:YAG) interference illumination of photoresist deposited on the surface of a smooth ZnO:Al film. After the exposure for 8 nsec (a single shot of the pulsed laser), the photoresist is processed and diluted hydrochloric acid is used to etch grooves into the ZnO:Al. A standard p-i-n diode is then deposited on top of this grating. The periodic structure is preserved after deposition of the solar cell. Therefore the aluminium back contact acts as a periodic reflection grating for the incident light. A comparison of the reflection of the solar cells with dot and line gratings of 795 nm period is given in Figure 7. Data for the smooth solar cell are shown for comparison. Up to 700 nm, the reflection is the same for both types of grating. For longer wavelengths, when light trapping becomes more important, the dot grating is more efficient.

2.2 APPLICATION OF ZnO FILMS IN DIODE HETEROSTRUCTURES

ZnO films have been applied not only as a TCO in a-Si solar cells, but also to form heterojunction structures with n-type and p-type c-Si for photodetectors [30-32], InP [33], p-type NiO [34] and porous Si [35].

Al doped ZnO films were deposited by RF magnetron sputtering on a c-Si substrate, to form a ZnO:Al/n-Si heterojunction.[30]. Ohmic contacts to the samples were made by vacuum evaporation of Ti (30 nm) and then Al (800 nm) onto the back surface of the Si wafer, and by vacuum evaporation of a comb-like Al grid (thickness ~ 800 nm) onto the ZnO:Al layer. The resulting XRD pattern indicated the highly oriented crystal growth of ZnO films with c-axes perpendicular to the substrate surface. TEM showed evidence of a thin (~1.2 nm), unintentionally grown, silicon oxide layer between the ZnO and the Si, probably caused by natural oxidation during the pump-down period prior to the ZnO deposition (Figure 8a). The I-V characteristics of a ZnO:Al/n-Si heterojunction
Figure 8. a) Cross-sectional TEM bright-field image of a ZnO:Al/Si heterojunction. A 1.2 nm thick SiOx tunnel oxide layer exists between the ZnO film and the Si wafer substrate. b) Current-voltage characteristic of a ZnO:Al/Si heterojunction [30].

measured in the dark demonstrate good rectification (Figure 8b), the ideality factors are 2.7 (for $V < 0.25$ V) and 1.62 (for $V > 0.25$ V). The diode turn-on voltage is in the range 0.2-0.4 V, the junction built-in potential (from C-V measurements) is 0.56V. The heterojunction behaves similarly to a Si MIS diode. Temperature-dependent dark forward current vs. voltage measurements suggest that trap-assisted multi-step tunneling in the Si space charge region is the dominant carrier transport mechanism in this heterojunction.

Heterojunctions consisting of ZnO thin films prepared by chemical vapor deposition from the metallo-organic compound (Zn(C5H7O2)2) on n-type Si and p-type InP were prepare for large area photodetectors [33]. The ZnO film has a high transmittance ($> 80\%$), low roughness ($< 5$ nm) and low resistivity.

Figure 9. Quantum efficiency (1) and responsivity (2) of a ZnO/InP heterojunction [33].
(\(\rho \sim 3 \times 10^{-4} \ \Omega \cdot \text{cm}\)). Figure 9 shows the measured spectral characteristics and external quantum efficiency, \(\eta\), determined from a ZnO/InP photodiode. A maximum can be observed at 0.85 \(\mu\)m and an abrupt decrease for \(\lambda < 0.4 \ \mu\)m and \(\lambda > 1 \ \mu\)m. The measured values for the main parameters are 0.52 V for \(V_{oc}\), 120 \(\mu\)A for \(I_{sc}\) at \(E_v = 1 \ \text{Klx}\), and an external quantum efficiency of over 70%. These demonstrate that ZnO/Si and ZnO/InP heterojunctions can be used for detection applications.

The influence of the substrate temperature during the deposition of ZnO films on p-type Si wafers by magnetron sputtering in an Ar+O\(_2\) gas mixture has also been studied [31]. It has been observed that diodes prepared at \(T_s < 600^0\text{C}\) show strong rectifying behavior in the I-V characteristics measured in the dark (Figure 10). Photoelectric effects have been exhibited under illumination using monochromatic red light (670 nm). High levels of photocurrent or responsivity were obtained under reverse bias conditions, when the stoichiometry of n-ZnO films was improved by optimizing the process conditions, such as \(T_s\) and the Ar/O\(_2\) ratio. Structures prepared at 300\(^0\text{C}\) were found to exhibit only a small photoeffect, because the ZnO film contained a high density of deep-level defects caused by poor stoichiometry. A heterojunction diode with n-ZnO deposited at 600\(^0\text{C}\) was also found to be unsuitable, because the dark leakage current was too high, even though the crystalline quality of the ZnO film of the diode appeared to be the best among all the samples (figure 9).

The fabrication of a heterojunction photodiode for the visible range that consist of a transparent insulation ZnO overlayer and a transparent semiconducting n-ZnO layer on p-Si has also been reported [32]. For device
isolation, Si\(^{+}\) ions were implanted into the n-ZnO layer. A wide-range spectral responsivity was obtained, which showed a maximum quantum efficiency of 70\% at 650 nm and a minimum of 10\% at 420 nm. The ion-beam-induced isolation considerably reduced the dark leakage current in the device when the fluency of Si\(^{+}\) was as high as 5\times10^{15} \text{ cm}^{2}.

2.3 APPLICATION OF ZNO FILMS IN LEDs.

ZnO films have found applications in different opto-electronic devices, mainly as transparent electrodes in light-emitting diodes [35-38] and liquid crystal displays [31]. ZnO thin films doped with Al, Ga, or Zr were used as anode contacts for Organic LEDs (OLEDs). The films were deposited on glass substrates by pulsed laser deposition. The device structure consisted of a hole transport layer of N,N’-di(naphthalene-1-yl)-N, N’-diphenyl-benzidine and an electron transport/ emitting layer of tris (8-hydroxyquinolinolato) aluminium. The I-V characteristics and luminance efficiency are presented in Figure 11. The cathode contact deposited on top was an alloy of Mg/Ag. Luminance efficiencies of 0.1-0.9 lm/W were measured at a light output of 100 cd/m².

![Figure 11](image)

*Figure 11. a) Current density (J) vs. voltage (V) and b) luminance (L) vs. Voltage (V) characteristics for OLED devices fabricated on ZnO, doped with Al, Ga, Zr and commercial ITO films [36].*

ZnO:Al was used for the preparation of EL structures with the participation of porous Si [38]. The PS heterostructures were prepared on p-type c-Si with 1.5–2.5 \(\Omega\cdot\text{cm}\) resistivity, by stain etching of the c-Si covered with 200 nm of Al, in a solution of HF:HNO\(_3\):H\(_2\)O=1:3:5 for 1 min [37]. ZnO, doped with Al, was deposited by magnetron sputtering of sintered ZnO+Al\(_2\)O\(_3\) powder [19].
The transport mechanism of the diode was investigated using the current–voltage characteristics (I–V) measured at different temperatures (296–380 K). A model based upon the multi-step tunneling of the carriers under reverse and low forward bias ( < 1V) and for field-assisted tunneling across a narrow barrier under higher forward bias (> 1.5 V) was proposed. A band-gap diagram was proposed for the ZnO/PS/c-Si heterostructure. The electron affinity of the quantum-confined Si was determined to be 3.70 eV. Electroluminescence from the device structure in the visible region was detected under forward bias conditions, when the field-assisted tunneling mechanism was observed (Figure 12).

3. Gas Sensors

The increasing interest in areas such as pollution control, detection of hazardous gases and monitoring of combustion processes has lent prominence to gas-sensing devices. Recently, the application range of semiconductor gas sensors using metal oxides such as ZnO, TiO$_2$, SnO$_2$ and In$_2$O$_3$ has spread rapidly, to include the detection of pollutants, toxic gases, alcohol, food freshness and food (olive oil) quality [39-42].

The sensing mechanism of ZnO thin film gas sensors is usually based on the surface properties of the material. At elevated temperatures, adsorption of atmospheric oxygen takes place. This extracts the conduction electrons from the surface region of the ZnO grains, leaving positively-charged donor ions behind. A carrier depletion region is formed due to the extraction of the electrons, because of the presence of lattice defects and impurities. An electric field is developed between the positively-charged donor ions and the negatively charged oxygen...
ions ($O^{2-}$, $O^-$ or $O_2^-$) on the surface. The more of these there are, the higher the potential barrier and therefore the higher the resistance. When an inflammable or reducing gas interacts with the absorbed oxygen on the surface of the oxide, the amount of adsorbed oxygen decreases. This causes a reduction of the potential barrier and an increase in the carrier density, by releasing electrons back into the matrix.

Detailed studies of oxygen adsorption in ZnO indicates that reactions involving the carbon impurity commonly present in it have a role [43, 44]. In particular, it has been reported that the $CO_2^-$ ion is produced by the adsorption of oxygen onto carbon sites, accompanied by electron capture with the consequent formation of a depletion region around the crystallite boundary. Photo-desorption then appears to involve the neutralization of the ions by photogenerated holes and subsequent desorption of molecular $CO_2$. These phenomena have been reviewed in [45, 46].

The room temperature ozone sensing properties of undoped ZnO films have been reported [42]. The as-grown films were brought to a higher conducting state through a reversible photo-reduction process by UV light exposure. They were subsequently exposed to ozone, resulting in a strong resistivity increase caused by re-oxidation. The magnitude of the effect was largest for films deposited by sputtering, which exhibited resistivity changes of more than 8 orders of magnitude. Figure 13 demonstrates a typical result of four cycles of photo-reduction and oxidation for r.f. sputtered ZnO [42]. It was reported that the sensor response, $S$, of the ZnO films decreases with increasing grain size.

![Figure 13. Photoconductivity and oxygen cycles of an r.f. sputtered ZnO film [42].](image)

It has been demonstrated that the surface functionalisation of ZnO with RuO$_2$ gives better sensitivity for ammonia ($S = 440$) as compared to pure ZnO ($S = 1.5$) [41]. The amount and distribution of the RuO$_2$ species (0.48%) seems to
be the most critical parameter in order to get the maximum sensitivity (figure 14). A comparison of the micrographs of pure and ruthenated samples with various concentrations of Ru species (figure 15) shows some interesting changes. The pure sample has large (500 nm) grains of ZnO, segregated non-uniformly. The ruthenated samples show a uniform distribution of small (200 nm) particles between the grains of ZnO. Comparison of the micrographs with 0.17, 0.48 and 2.74 at.% Ru indicates the importance of the amount and distribution of it on the surface of the ZnO for obtaining maximum sensitivity. The results strongly suggest that the ZnO surface can be tailored to improve the gas sensing properties, as revealed by the high sensitivity and selectivity of surface ruthenated ZnO to ammonia.

The results of different authors show that to increase the gas sensitivity and selectivity for a particular gas, ZnO has to be doped with catalysts such as Au-, Ag-, Pd-, Pt-, Ru- and Rh, and some other dopants such as Al, Ti, V [40, 41, 47]. A very high sensitivity and selectivity to trimethylamine gas (which is emitted during the decomposition of fishes) at 300°C of the ZnO films doped with 4 wt% Al₂O₃, 1 wt% TiO₂ and 0.2 wt% V₂O₅ is obtained after annealing of the films at 700°C in oxygen [40]. These sensors could trace the deterioration of mackerel during storage.

The detection of hydrogen by ZnO films has also been investigated [48]. An undoped device-quality ZnO thin film was deposited on p-type Si, and a Pd/ZnO/p-Si heterojunction was fabricated. Its I-V characteristics, when the heterojunction was placed in air and in air with different concentrations (2,000 - 20,000 ppm) of hydrogen was performed. This revealed that the device could be used as a room temperature hydrogen sensor, down to levels below that of its explosive mixture with air. At 20,000 ppm H₂ in air, the sensitivity was found to be 5 x 10². The increase of the surface conductivity of ZnO at the Pd/ZnO interface, due to the absorption and chemical interactions of hydrogen, was found to play a key role in the sensing.

Figure 14. Variation of the sensitivity with the amount of Ru on the surface of ZnO, when exposed to 1000 ppm of NH₃ at 300°C [41].
Figure 15. Micrographs of (a) pure and ruthenated ZnO with (b) 0.17 at.% (c) 0.48 at.% and (d) 2.74 at.% Ru on the surface [41].

Figure 16. Ideal schematic diagram of the cross-section of the gas-sensing material and the corresponding circuit. (.) Catalyst dispersed; R_s - surface resistance; R_b, bulk (inner film) resistance, R_n the neck resistance of the grains.

The ideal model of the circuit corresponding to the conductivity of the polycrystalline ZnO, due to the interaction of gas and oxide films, is thought to be as shown in Figure 16 [49]. Although it is hard to estimate how much the conductivities of the bulk, surface and grain boundaries contributed to the total conductivity of the film, it is easy to understand how to increase the gas sensitivity from the following relation for the resistance:

\[ R = \frac{1}{\left(\frac{1}{R_s} + \frac{1}{R_b}\right)} + R_n, \]

where \( R_s \), \( R_b \) and \( R_n \) are the resistances of the surface, bulk (inner film), and neck of the grains, respectively. When the electrical resistance of the bulk is very large, i.e. \( R_s << R_b \), then

\[ R = R_s + R_n. \]

Thus, it is very important to make a thinner sensing film, or to make a thick film with a very high resistance and to control the electrical resistance in the neck of the grain boundary by, for example, the dispersion of catalyst in order to increase the sensitivity toward inflammable and other gases.
4. Conclusions

Although the interrelated electrical and optical properties of transparent oxide semiconductors like ZnO films can be tailored to suit the whole range of applications, a more significant challenge is to obtain metallic conductivity without sacrificing the optical transparency. This means that it is necessary to have a much better understanding of the scattering processes, and the roles of dopants, trap states, grain boundaries and the microstructure.

Although ZnO thin films have been an object of scientific study for more than 50 years, they will continue to play an increasingly important role in electronic and optoelectronic devices and sensors. Recent results [50] demonstrate the possibility of obtaining laser emission from ZnO films and LEDs with electroluminescence from rare earth ions (Tm$^{3+}$, Eu$^{3+}$ and Er$^{3+}$) in ZnO based varistor-type structures. Further efforts are required to introduce such dopants and impurities, and to tailor the grain size and development of the surface, which make it responsive to electric fields, illumination and gas exposure. It may well be necessary to develop a new technology for this purpose.

References


ION BEAM NANOSTRUCTURING OF MATERIALS

J.-C. PIVIN
CSNSM, CNRS-IN2P3, Bâtiment 108, 91405 Orsay Campus, France

1. Introduction

Nanostructured materials are presently the topics of many conferences and publications because their extremely small size and large surface-to-volume ratio lead to differences in their chemical and physical properties compared to bulk materials of the same chemical composition or to molecular clusters. The critical size range of the nano-domains with particular properties are quite well defined on the basis of relevant dimensions in each field of physics, such as the Bohr radius of excitons in semiconductors or the correlation length of spins in magnets.

Ions penetrating into a solid lose their energy in collisions with nuclei and in electronic excitations. The latter induce no significant deflection of the ion path and, in the absence of collision cascades, the perturbed tracks are cylinders of radii ranging from 1 to 20 nm, depending on the target structure (organic, metal, semiconductor, etc.) and on the ion nature. The spatial extension of cascades is significantly broader because of their subdivision by secondary projectiles. The mean size of nano-domains created by ions is correlated to those of the tracks and secondary cascades. These parameters can be varied via a proper choice of the ion mass and energy, which determine the densities \( S_e(r,t) \) and \( S_n(r,t) \) of the energy transferred by the ion to electrons and nuclei. The system perturbation lasts a very short time, typically \( 10^{-13} \) s for the cascade and \( 10^{-12} \) to \( 10^{-10} \) s for the relaxation of the lattice and electron gas. Transient melting or vaporization of the target material may occur beyond a threshold of energy transfer to the electronic system. For this reason, such events are more characteristic of swift heavy ion irradiation (S.H.I.). In contrast, because the displacement number density decreases with the ion velocity, low energy ion beams are generally used for producing topography changes resulting from the sputtering of surface atoms and for disordering superficial layers (disorder leading in some cases to target amorphization). Changes of local composition are also induced by the migration of displaced atoms and by electronic spikes. A radiation-induced...
diffusion of atomic defects over distances limited to the cascade extent occurs during the ballistic perturbation, then a radiation-enhanced diffusion occurs when the defects are mobile at the temperature of the experiment. These two types of diffusion have for effect a variety of chemical and structural changes, which are often similar to those obtained by thermal treatments, such as the mixing of superimposed layers, and the segregation and precipitation of some species in metastable systems. However, the synergic effects of displacements and lattice excitations also induce some modifications which are specific to ion beam processing.

These considerations of a general nature give good reasons for believing that ion irradiation is a suitable means for synthesizing nanostructures with well controlled sizes and metastable phases. Ion beam induced modifications of materials are localized either in a controlled range of depth, correlated to the ion implantation depth, or in a defined number of cylindrical tracks. In addition, the nano-patterning of thin films can be achieved by scanning a focused and pulsed beam. On the other hand, the major drawback of ion beam treatments is their cost, so that potential applications in the field of the solar energy conversion are very few. Therefore, most of the examples given in this overview of nanostructures produced by ion beams are the results of research performed for fundamental purposes or for fabricating more sophisticated devices and biomaterials. After a short summary of the ion-solid interaction physics, structures will be sorted on basis of the slowing down regime and of the nature of the bonds in the material. Ballistic disorder can for instance lead to the amorphization of metals, semiconductors or covalent compounds, while ionic crystals are more sensitive to high densities of electronic excitations. The effects of electronic excitations in dielectrics will be emphasized because these materials absorb little of the energy of visible laser beams and consequently an ion beam treatment constitutes an alternative route.

2. Physical Bases

The purpose of this section is to provide general concepts of ion interaction with solids, useful for the understanding of the phenomena described hereafter. Fine reviews already exist on the subject of energy loss and fundamental expressions can be found in handbooks [1-3]. They are briefly summarized in the appendix.

2.1. THE SLOWING DOWN PROCESS

First let me start with tutorial definitions and a description of the stopping process. Ions lose their energy in a series of collisions with nuclei, screened by their electron shells, and with electrons in various localized orbitals and in the
conduction band. The nuclear and electronic stopping powers of the target can be expressed as integrals of energy transfers, $T$, occurring for given impact conditions, weighted by the probability $d\sigma$ of these events. This probability has the dimension of a section because it is determined by the distance $p$ of the atom or electron at rest projected upon the ion path, called the impact parameter. For simplifying the problem of summing the energy lost to various atoms in compound targets, the travelled thickness (range $R$) is generally defined under the form of a number of target atoms per unit area and the unit of energy loss is a number of eV/atoms/cm$^2$. The advantage of this unit is that the Bragg rule can be applied to the calculated or measured stopping powers of elements (under different physical states), without having to assume a density value for compound targets.

An important simplification made for solving the transport equations consists of considering nuclear and electronic stopping as independent processes. This hypothesis is justified by the fact that the slowing down of the projectile due to electronic excitations is similar to the friction of an electron gas (with local fluctuations of gas density, which can be modelled by a Hartree Fock Slater distribution). The interest of this simplification can be easily understood when remembering that although the electronic stopping is always substantial, the projectile loses little energy in each electronic collision and does not deviate significantly from its original path. In contrast, its trajectory and residual energy vary stochastically during each nuclear collision, depending on the impact parameter $p$. The energy transfer $T(E_0, p)$ is determined by the screened repulsion potential $V(r, E_0, Z_1, Z_2)$ of colliding atoms, which has the simple form of a Coulomb potential for short distances of closest approach $r$. A universal expression for any $r$ value has been established for solving transport equations or performing Monte Carlo simulations of binary collisions in solids (the basis of the Stopping and Range of Ion in Matter program (SRIM) [1]). The dependence of the nuclear stopping power $S_n$ on the ion energy $E_0$, before penetrating into the target, on the masses $M$ and atomic numbers $Z$ of the ion (1) and target atoms (2) are given in the Appendix. $S_n$ goes through a maximum at the same energy for all combinations of ions and targets (0.3 keV) when using reduced energy units as defined in the Appendix. This value corresponds to absolute energies $E_0$ in the range 1keV to 1 MeV, depending on the ion mass, while $S_e$ is maximum at energies 2 to 3 orders of magnitude larger. Schematically, the electronic stopping power $S_e$ increases as the product of the ion velocity by the cube root of the electron gas density up to the Bohr velocity $v_B$ (corresponding to an energy of 25 keV/nucleon), then more steeply up to a critical velocity $Z_1v_B$, and it decreases in inverse proportion to $E_0$ when the ion becomes stripped of its electrons [2,3].
2.2. SPATIAL DISTRIBUTION OF DAMAGES IN THE COLLISIONAL REGIME

In most cases the atom set in motion during a primary collision with the incident ion (primary recoil) produces secondary collisions, which don't interfere with those resulting from other primary collisions. This regime of linear cascade, i.e. of independent sub-cascades (which is the basic assumption of SRIM calculations) takes place when the density of moving atoms is much smaller than the atomic density. In such a case, the depth distribution of secondary recoils is roughly the same as the distribution of primary recoils, because of the short mean free path of the formers. When the collision density exceeds a threshold, either because of the low incident energy or high ion mass, a collision spike occurs instead of a linear cascade [4]. Atoms which do not collide with the ion or a recoil atom acquire nevertheless a momentum under the effect of electronic interactions with moving neighbours. These ballistic spikes have some common features with the thermal spikes produced by high densities of electronic excitations under the impact of swift ions (partially or completely stripped of their electrons) or by illumination with a laser, in the respect that they are modelled by using the same transport equations as those for heat (see paragraph 2.4). However, the expressions for the concentration of atoms set in motion and for the temperature at the end of the energy impulse are different, and the heat is dissipated in part by a transfer from phonons to the electronic system in the case of ballistic spikes, instead of the reverse in electronic spikes [4,5].

The basic quantity defining the concentration of displaced atoms $N_d(R)$ and the threshold value for the occurrence of a collision spike is the ratio of the density of the nuclear energy transfer to the displacement energy $E_d$. The latter is the minimal energy which a recoil must receive in order that the formed Frenkel pair is not annihilated by direct recombination with the associated vacancy, located at a few interatomic distances, or by relaxation of the lattice. $E_d$ depends on the crystallographic orientation of the displacement, because replacement collisions are favoured along dense atomic rows and the binding energy is anisotropic (on the average, it is correlated to the cohesion energy of the crystal). This anisotropy contributes to various phenomena, such as the preferential sputtering and disordering of some crystals in a polycrystalline target. Since nuclear collisions don't necessarily lead to effective displacements, the part of the primary energy, $E_0$, which is converted into defect energy, $F_d(E_0)$, amounts to only 20 to 50% (according to the model used) of the energy transferred to nuclei over the whole ion path, $v(E_0)$. According to the earliest estimate by Kinchin-Pease [6], the number of stable Frenkel pairs created by each ion is:

$$N_d = \frac{v(E_0)}{2E_d}$$  \hfill (1)
The most probable ranges of ions, \(<R_1>\) and of defects, \(<R_d>\), can be derived directly from mean values of energy losses given in tables by writing:

\[
<R_1> = \int_0^{E_0} \frac{1}{N_{at} S_n + S_e} dE
\]

(2)

\[
\text{and } <R_d> = \int_{E_d}^{E_0} \frac{1}{N_{at} S_n} dE
\]

(3)

where \(N_{at}\) is the atomic density of the target.

Due to the stochastic nature of the nuclear stopping process, the depth distributions of implanted atoms and of energy transferred to nuclei, \(f_i(E_1, R)\) by ions having a residual energy \(E_1\) at depth \(R\) (which is the derivative of \(v(E_0)\) also labelled \(F_i(E_0)\)), can be approximated by Gaussian functions in the case of amorphous or polycrystalline targets. These distributions are, however, estimated more accurately by using the transport equations defined by Lindhart [1] and computing Monte Carlo simulations of binary collision cascades with the SRIM code. Molecular dynamics simulations attract more and more interest with the increasing speed of computers for their ability to simulate spikes and crystallographic effects which are randomized in Monte Carlo simulations.

2.3. COOPERATIVE EFFECTS OF CASCADES

The overlap of cascades produces a random walk of target atoms called radiation induced-diffusion (RID also called ballistic diffusion, or cascade mixing). Note that the anisotropic relocation of primary recoils must be distinguished from this RID in the analysis of transport processes such as the mixing of overimposed layers, especially when these layers are composed of atoms with very different masses [7]. In addition to RID, a migration of point defects occurs after the cascade when the temperature is sufficiently high (radiation-enhanced diffusion, RED). RID and RED lead in some cases to the segregation of an atomic species (one of the target components or the implanted ions), either due to its lower mass or its lower binding energy or its tendency to form complexes with defects [8-10]. Another factor to take into account in the analysis of diffusion fluxes is that a vacancy-rich zone is formed in the core of cascades, and interstitials are more numerous at their periphery. As a result, a given atomic species diffuses towards \(R_d\) or interfaces, depending on its stability and mobility on interstitial and substitutional sites, and point defects segregate into dislocation loops.
Another effect of the cascade overlap is the progressive change of surface geometry and composition related to sputtering. Let's just give here the Sigmund analytical expression for the sputtering yield $Y$ [11], obtained by applying the Boltzmann transport equation to describe the flux of particles. The Sigmund equation is less accurate but more useful than simulations to outline the effects of the mass and binding energy of target atoms and of the beam orientation with respect to the surface normal on the yield $Y$ and on surface modifications. An overview of these effects was given in [12] and a compilation of experimental data in [13]. The sputtering yield is proportional to the fraction $F_d$ of the ion energy used to displace atoms in the outermost layers (which includes displacements by all projectiles) and to the probability $\Lambda$ that these displaced atoms escape to the surface. $F_d$ differs from the energy deposited by the ion in the escape depth range $R_e$ (close to zero, so that $F_1(R_e) = S_n$) by a factor $\alpha$. This factor represents the influences of the mass ratio $M_2/M_1$ and of the incidence angle $\theta$ on the anisotropy of ion scattering in the outer layers of an amorphous or polycrystalline target. Its value, $\alpha_N$, for normal incidence is a slowly varying function of $M_2/M_1$, increasing from 0.2 to 1, and the exponent $f$ of the angular factor $\cos \theta^f$ is equal to 5/3 for not too heavy target atoms. The escape probability is inversely proportional to the Born-Mayer screening factor of the interaction potential $C_0$ ($3/4\pi^2C_0 = 0.042$) for slow recoil atoms and to the surface energy barrier $U_s$ (half the binding energy of the target atoms).

$$Y = \Lambda F_d(R_e) = \frac{3}{4\pi^2} \frac{1}{C_0 U_s} \alpha_N \cos \theta^{-f} S_n(E_o).$$ (4)

Here, $Y$ presents the same periodic variation with $Z_2$ in elemental targets, as does the surface binding energy, with the result that volatile elements (H$_2$, O$_2$, N$_2$, etc.) are preferentially sputtered from compound targets. When the binding energies of the target components are comparable, a superficial impoverishment in the lighter element is usually observed. The escape depth $R_e$ of the sputtered atoms is of the order of 2 atomic distances [6], but the target composition is modified from the surface to the mean range of defects $<R_{vd}>$. The surface topography changes progressively, due to statistical fluctuations in the number of atoms ejected from each point and to the differential sputtering of dislocation loops, or of precipitates in composite targets. Cones topped with precipitates are formed when their sputtering yield is lower than that of the matrix and the precipitate number density changes in all cases.

The depth profile of the implanted atoms also changes with the implanted fluence, under the combined effects of lattice swelling and sputtering (disregarding the casualty of a segregation). Schematically, the surface moves outward at a rate proportional to the ion fluence $\phi$, for keeping approximately constant the target atomic density when ions come to rest on substitutional sites,
while sputtering induces an inward motion of the surface. The concentration profile becomes an error function with a plateau value equal to $\phi/N_{at}(1+Y)$ close to the surface.

At this point, mention must be made of the channeling phenomenon, which consists of a slightly oscillating path of ions and considerably increased penetration depth when their incident direction is parallel to dense packing planes and rows of a crystal. The lessening of the scattering cross section is related to a large and constant impact parameter, on the average. Channeling affects not only the depth profiles of implanted ions and defects in single crystals, but also their sputtering yield. In polycrystalline targets, the different sputtering yields of grains, according to their orientation, induces a surface relief.

In some cases, residual defects segregate under the form of amorphous clusters instead of dislocation loops, because the configuration energy over short distance is lower in the amorphous state. This process is particularly efficient in all semiconductors and covalent compounds (such as quartz). The amorphization occurs locally when the amount of disorder exceeds a threshold value, either in the core of sub-cascades, when their density is sufficiently high, or by a statistical process of cascade overlap. On the contrary, ionic crystals are amorphized with difficulty because displacements produce two types of charged Frenkel pair, which exhibit a stronger tendency to recombine than in covalent systems for minimizing the space charge.

2.4. ELECTRONIC DAMAGING IN ISOLATED TRACKS PRODUCED BY SWIFT HEAVY IONS

Beside the linear density of energy transferred to the electronic system (the product of $S_e$ by the atomic density), another parameter to take into account in the damaging process is the radial distribution of this energy in tracks, as long as they don't overlap. One generally distinguishes two regions: a high density of electronic excitations is produced in the track core extending over 1-3 nm and the energy is transported by fast secondary electrons ($\delta$-electrons) in a track halo with a radius of some hundreds of nm. For the same $S_e$ value, the energy deposition is smeared out into a larger radius for high velocity projectiles [14]. The reason for this velocity effect is that the maximum energy transferred to the $\delta$ electrons is $T_{\text{max}} = 2 \ m_e \ V_{\text{ion}}^2$. The swifter the ion, the higher the fraction of the ion energy swept away from the core by these electrons for a given $S_e$ value. Polymers are sensitive essentially to ionizations produced in the core, while damaging in metals results from lattice vibrations induced by elastic collisions of $\delta$ electrons outside the core. The damaging mechanisms of semiconductors and inorganic insulators are more intricate, since they involve various processes of electron-hole recombination and charge transfer.
For most inorganic materials, there exists a threshold value of $S_e$ above which the damaging of crystalline targets increases dramatically (figure 1) or on the contrary crystalline order is reconstructed in some amorphous targets [15-17]. The threshold effect is particularly clear for metals, in which electronic excitations cause a partial annihilation of the defects created by atomic collisions at low energies. Two different mechanisms have been proposed for the steep increase of damaging: ion explosion spikes and thermal spikes.

In the ion explosion spike theory, one considers that the ion creates in its wake a cylinder of highly ionized matter which is very unstable due to Coulomb repulsion between electrostatic charges. Several models were derived from this theory; these being the core-plasma model, the shock-wave model, and the modified lattice potential model [18]). In fact, damage creation via electronic excitations in metals was considered for some time as unrealistic due to the high mobility of conduction electrons which rapidly smear out the deposited energy and very efficiently screen the atoms that were ionized in the ion wake. However, a shock-wave mechanism is pertinent in the case of metals with a low phonon frequency. Moreover, even if the charge neutrality is re-established in the track core, the interatomic potentials remain over some time different from the equilibrium potentials, setting atoms in motion and producing an athermal melting of the track. On the other hand, insulators mainly are sensitive to Coulomb explosion spikes in the strict sense of the term [19]. Thermal spikes occurring thereafter in the same material may anneal their effect, because the returning time of electrons expelled from the track core in a Coulomb
explosion is $10^{-14}$ to $10^{-13}$ s and the spreading of the energy in a thermal spike is much slower ($10^{-13}$ to $10^{-12}$ s depending on the electron mobility).

In the thermal spike model, the transfer of energy from the bombarding ion to the lattice is a two-step process [20, 21]: thermalisation of the energy deposited in the electronic system via electron-electron interactions and transfer of this energy to the lattice via electron-phonon interactions. Since the electronic system and the lattice are not in thermal equilibrium with each other, their temperatures, $T_e$ and $T_a$ respectively, are governed by a set of coupled nonlinear differential equations:

$$C_e(T_e)\frac{\partial T_e}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left[ rK_e(T_e)\frac{\partial T_e}{\partial r} \right] - g(T_e - T_a) + E(r,t)$$  \hspace{1cm} (5)

$$C_a(T_a)\frac{\partial T_a}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left[ rK_a(T_a)\frac{\partial T_a}{\partial r} \right] + g(T_e - T_a)$$  \hspace{1cm} (6)

where $T_{e(a)}$, $C_{e(a)}$, and $K_{e(a)}$ are the temperature, the specific heat, and the thermal conductivity for the electronic ($e$) and lattice ($a$) subsystem, respectively. $E(r,t)$ is the radial density of energy transferred to electrons. The electron-phonon coupling constant $g$ is directly linked to the electron mean free path $\lambda$: $\lambda = K_e/g$. The difference in sensitivity between metals and insulators is that in metals energy can be transferred from the hot lattice back to the electrons when $T_a > T_e$, while this transfer is inhibited in insulators.

The damaging of materials by electronic excitations may lead to their amorphization (Fig. 1), but those which are easily amorphized by collision cascades (such as Si) are little sensitive to electronic damaging. The reason for this difference is that the transient disordered phase formed within swift ion tracks tends to reconstruct epitaxially with the surrounding matrix in the case of semiconductors or covalent compounds. The recovery of structural order is less easy in ionic compounds containing charged defects. Moreover, defects on one of the ionic systems may combine to form a gaseous species, as for instance in alkali halides, and consequently metal atoms in excess segregate [22]. Note that pure metals (apart from Ga, Bi) are disordered but not amorphized [23] and the topological order just changes over a short range in metallic glasses.

3. Ballistic Effects

3.1 IMPLANTATION

Applications of ion implantation to the doping of semiconductors or of other materials (for chemical applications in catalysis, detection of gases, etc.) are
beyond the scope of this paper. Beside this undeniable interest of the ion implantation technique, it is also one of the most versatile means to create a supersaturated solid solution in the near-surface region of a solid. With regard to nanostructures, a precipitation may occur under the effect of radiation-induced diffusion during implantation, when the local concentration of implanted atoms is much larger than the solubility limit at equilibrium. It is, for instance, the case for noble metals in oxides, for concentrations over 1 at.% [24, 25] (figure 2). The radiation-enhanced diffusion of interstitials is also effective in many matrices at room temperature (RT). However that may be, implantations are often followed by annealing treatments at high temperatures (or implantations performed at elevated temperatures), in order to induce a maximum yield of precipitation and to eliminate defects in the host lattice. This combination of treatments has been called Ion Beam Synthesis.

![Figure 2. TEM images of silica implanted with 150 keV Ag⁺ ions at fluences of (a) 10¹⁶ and (b) 10¹⁷/cm² (3 and 28 at.% at the mean range) [24]](image)

3.1.1. Concentration Gradients in Implantation Layers

In addition to the lattice damaging, the inhomogeneous depth gradient of the concentration in implantation layers complicates the interpretation of their properties and may limit their performances. Multi-implantation at several energies permits one to overcome this problem, with more or less success because diffusion processes are not taken into account in SRIM simulations. Other types of dynamic changes in the target composition induced by sputtering, ballistic mixing and lattice swelling are taken into account in simulations with other codes such as TRIDYN [26]. Variations in the displacement and binding energies of target atoms with the composition are also considered in the inputs to these simulations.
The narrow depth distribution of ions implanted at a single energy is nevertheless interesting for some applications, as for instance in the fabrication of non volatile memories based on nanocrystals (NCs) embedded in the gate oxide of MOS transistors [27, 28]. By low energy Si+ implantation, NCs of Si can be formed a few nm above the SiO₂/Si interface. This allows charging of the NCs by direct electron tunnelling, which is a prerequisite for low operation voltages. Kinetic Monte Carlo Simulations (KMCS) [27] were developed for studying the process of phase separation in these systems, by a sequence of nucleation and growth at the expense of the Si supersaturated solution, then by Ostwald ripening of the Si NCs and, at higher Si concentrations, by spinodal decomposition. The simulations permit one to predict the Si concentration threshold of percolation (which process hampers the charging of the NCs) and the optimal temperature range of implantation or post-annealing treatment, in which the trapping of Si solute atoms at the substrate interface together with a controlled growth of the NCs leads to a self alignment suitable for the fabrication of non volatile memories.

An argument put forward by many authors to praise the usefulness of the IBS technique is that it permits one to obtain high filling factors of particles close to the surface [29-31]. In fact this characteristic is generally detrimental to the performances of nanocomposite systems, because of the well known effect of dipolar interactions in optics and magnetism. The plasmon resonance in the visible of Ag particles shown in figure 2 becomes broader with the increasing Ag fluence, under the combined effects of the increase in their size scattering and in their interaction [24]. In current magnetic recording media, the written bits are comprised of an ensemble of weakly interacting magnetic grains, contrary to what is obtained in insulators implanted with high concentrations of 3d metals (chosen high in fact, in order to compensate for the shallow range of doping) [30,31]. The confinement of excitons in semiconductors deteriorates also with the gathering of particles.

Beside their usefulness for charge injection in MOS structures, Si NCs are also interesting for their luminescence or for activating rare earth elements with an excited level at an energy close that of excitons in the NCs [32-35]. Once again, the criterion of quality is a narrow size distribution of the NCs, in the range of 2-3 nm, so that their gap fits the excitation energy of the Er³⁺ ⁴I⁹/₂ state for instance. The sensitization of Er ions implanted sequentially with Si has been extensively studied and the results constitute an excellent example of the difficulty of obtaining simultaneously: (i) Si clusters of a suitable size, (ii) Er atoms in solid solution in the oxide instead of in silicide particles [34], (iii) both of these at the same depth [36]. However, some useful devices seem to have been fabricated [37-39]
3.1.2. Variety of Obtained Structures and IBS Conditions

IBS has been used to create a wide variety of nanocrystals and quantum dots made of a single element or of a compound, by sequential implantation [32, 40-42]. The nature of the precipitation may depend on the implantation sequence [40, 43]. Implantation of two metals, with the aim of obtaining alloyed particles with a controlled plasmon resonance energy, may result in the formation of core-shell particles after annealing, when the 2 elements exhibit a solubility gap [43]. NCs of almost all semiconductors have been synthesized in silica, alumina and silicon [32]. The ionicity of the host affects the crystalline nature of the formed phases. As an example, it is possible to produce CdS and CdSe crystals with the hexagonal wurtzite or the cubic zincblende structure in $\alpha$-$\text{Al}_2\text{O}_3$ by modifying the implantation conditions, because this matrix has a low sensitivity to ballistic damaging. When implantation is carried out at a moderate temperature (~600°C), dynamic annealing keeps the alumina crystalline and epitaxial relationships favour the formation of NCs with the hexagonal structure. In contrast, when implantation is carried out at low temperatures (liquid N$_2$), the near surface region of the alumina is amorphized. Upon annealing, the amorphous layer first crystallises with the metastable $\gamma$-$\text{Al}_2\text{O}_3$ cubic structure embedding NCs with the same symmetry (zincblende). Particles with the latter structure are formed whatever the implantation temperature in silica. Another example of structure change correlated to the greater or lesser efficiency of dynamic annealing is that of $\beta$-FeSi$_2$ synthesis in Si single crystals. When implanting Fe atoms in silicon at a sufficiently high temperature (about 400°C), precipitates of $\beta$-FeSi$_2$ with their [100] axis aligned parallel to the [110] axis of Si are obtained [44]. Randomly oriented particles are formed when implanting Fe at lower temperatures. After further annealing at 800°C or more, the structure of the Si single crystal is restored perfectly in the latter case, while a large number of dislocation loops remains in the crystal containing particles in epitaxy. Given that $\beta$-FeSi$_2$ is often mentioned as a potential candidate for solar energy conversion, it may be worth noting that these dislocations are more luminescent than the semiconducting compound and at a close wavelength.

Implantation in channeling conditions permits one to increase significantly the ion range and to limit the damage to the host material. In connection with the increase in the range, the implanted species undergoes less self-sputtering and is more protected against oxidation. Buried layers of FeSi$_2$ or ErSi$_2$ have been grown in such conditions [45].

Rare gas atoms usually form bubbles at high fluences in all materials, and this effect is the origin of the blistering of the walls of ion guns or reactors. These cavities can be used as preferential nucleation sites for particles, formed for instance from layers evaporated thereafter on the surface and mixed by means of further heat or irradiation treatment. Let's mention for its exotic nature the formation of cubic porosities in MgO crystals, which were used as templates for fabricating cubic Ag and Au particles in this material [46, 47].
3.2. SPUTTERING

3.2.1. Cleaning and Roughening of Surfaces for Improving Coatings
The growth of "good quality" films (adherence, homogeneity and eventually epitaxy) owes its success to an appropriate surface cleaning step prior to deposition. Among the few techniques available, sputtering is attractive for its simplicity and insensitivity to the nature of the contaminants. However, the damage caused by ions can affect the epitaxy of subsequently grown films on crystalline substrates and must be repaired by \textit{in-situ} thermal annealing. Technological studies show that the optimal energy of Ar ions, commonly used in sputtering experiments for removing the native oxide and adsorbed molecules on Si substrates without extensive damaging, is of the order of 150-200 eV (while $S_n$ is maximum at 14 keV).

3.2.2. Surface Relief Induced by the Combined Effects of Erosion and Diffusion
The stochastic nature of sputtering implies that the surface roughness would increase monotonically if this statistical effect was not balanced by the local change of ion incidence and by radiation-enhanced diffusion. Experimental studies on amorphous materials and on semiconductors (amorphized by the bombardment) show that off-normal sputtering generates a more significant relief and an anisotropic modulation of the surface. Depending on the ion incidence angle $\theta$, the ripples can be either parallel ($\theta$ close to grazing) or perpendicular ($\theta$ close to normal) to the projection of the ion beam direction on the surface plane, while for normal incidence ($\theta = 0$) a periodic modulation of the topography is generally not observed. These results have been explained, on the basis of the Sigmund theory, in terms of a linear instability caused by the surface curvature dependence of the sputtering yield (equation 4), which dominates the smoothing due to the thermal surface diffusion \cite{48}. Schematically, the tops of crests are eroded faster than the bottoms of the trenches dug by ions at oblique incidence, and the change in the ripple orientation is related to the ratio of interlayer/superficial diffusion induced by collision cascades. On the contrary, at temperatures where thermal diffusion is noticeable, ion sputtering of single crystal metals produces features that reflect the substrate symmetry, without any relationship to the ion beam direction \cite{49,50}: square pits have been observed on Cu(001) and Ag(001) or hexagonal ones on Pt(111), Au(111) and Cu(111). This relief is ascribed to the coalescence of vacancies under the surface. In a critical range of temperature and ion flux, interlayer diffusion occurs along preferential directions ($<110>$ in fcc crystals) and ripples are formed parallel to a direction of the same family in the surface plane, independently of the beam orientation with respect to the normal to the surface and to the $<110>$ directions in the plane, at least for $\theta < 30^\circ$. At lower temperatures, the relief formation is controlled by erosion and depends on $\theta$. 
Ripples of smaller amplitude are formed as on semiconductors. The ripples with a crystalline orientation formed at intermediate temperatures find for example applications in the nano-patterning of epitaxial layers. The magnetic anisotropy of thin Co layers can be forced to be parallel to the <100> axis by modulation of the film thickness perpendicular to this direction [51].

Arrays of asperities with a conical or sinusoidal shape were observed recently at the surfaces of InP, GaSb, InAs and InSb sputtered at normal incidence, or at oblique incidence with simultaneous sample rotation [52]. A theory for their formation has not yet been developed. They are characterized by a uniform size distribution (around 100 nm) and a large degree of spatial ordering. They self-organize in hexagonal or square close-packed patterns, depending on the incidence angle and temperature (in the range 280 to 330 K).

3.3. ION BEAM ASSISTED DEPOSITION (IBAD)

Similar effects of diffusion occur during the vapour deposition of thin films. Adatoms diffuse faster along dense directions at moderate temperatures and interlayer diffusion takes place at high substrate temperatures. Shadowing of hollows for the atom flux plays the same role as for ions in sputtering experiments. As a result, different regimes of deposition can be distinguished as a function of the temperature, T: (i) at low T where the grain growth is controlled by the transport geometry, the coating exhibits a columnar structure and porosities; (ii) at intermediate T, the structure densifies and the columnar grains become coarser, with their axes oriented preferentially parallel to the dense packing direction; (iii) a fully dense and equiaxed structure is formed at high T [53]. In the case of magnetron sputtering deposition, increasing the plasma pressure has the same effect on the structure as increasing T [54].

Now, ion beams can be used to modify this texture through the effect of ion channeling. Molecular dynamics simulations predict the preferential growth of crystals with channeling directions parallel to the beam, due to the reduced sputtering and damaging [55]. The energy stored in the form of lattice defects leads to a migration of grain boundaries, towards the most damaged grains. This effect can be used to favour the epitaxial growth of some coatings or to alter their natural growth anisotropy. For instance, ion bombardment at normal incidence of a fcc metal film will cause a shift from a <111> texture favoured by surface energy considerations to a <110> texture, because the easiest channeling direction is <110> for simple fcc crystals and the sputtering decreases by 2 to 5 times when the beam is parallel to these directions. MgO films, which naturally grow in the form of islands with a <001> axis perpendicular to the surface, can be forced to grow with, in addition to the <001> texture, a preferential orientation of one of their <110> axes parallel to the ion beam if $\theta = 45^\circ$ [56].
The ion bombardment tends also to improve the film density and adhesion [57-59]. The adhesion improvement may be due in part to the mixing of interfacial layers or in other cases to the formation of precipitates anchoring the coating. Indeed, huge increases of resistance to indentation cracking and wear of diamond-like carbon coatings are obtained for instance by pre-implantation of C in the substrate, resulting in the formation of carbide nanoparticles, or by irradiation throughout the coating thickness (taking care not to destroy the diamond-like pilling of atoms by cascades) [60, 61].

When implantation is performed at very low energies (some hundreds of eV to a few keV), the concentration of implanted atoms tends progressively towards 100%, if their coefficient of self-sputtering is lower than 1. Their segregation by REP at the surface is facilitated by the shallow implantation depth when their solubility in the host material is limited. This ion beam deposition technique (IBD), shows common features with IBAD, in the respect that in both cases the structure of the deposited layers is affected by erosion and diffusion effects. However, the ratio of the ion/deposited atom fluxes in IBD experiments is unity, so that the outermost layers are strongly shaken and eventually frozen in and out of the equilibrium state, providing them with some ultimate properties. Films of pure amorphous diamond, with a proportion of sp³ bonds larger than 80% and a hardness close to 100 GPa have been grown by this method [62, 63]. There is no upper limit to their thickness (apart from a reasonable implantation time) and they are found to be indestructible in friction tests [60].

3.4. CLUSTER BEAMS

Beside other interests which are beyond the scope of this paper, the use of a cluster beam allows an easier control of the kinetic energy of atoms impinging upon a target than in the case of of monoatomic ions. Indeed, the energy of the cluster ions is shared between the atoms when they break during the collision with the target atoms. If the energy per atom is below the cohesion energy, the clusters can be deposited on the surface without destroying the structure. Nanostructured silicon films with controlled particle size obtained by cluster beam deposition (CBD) show a higher photoluminescence yield than porous silicon [64]. The proportion of sp² rings in C clusters is intrinsically connected to their size, so that the size selection of cluster beams permits one to grow coatings with various degrees of diamond-like hybridization [65]. Composite materials characterized by a monodisperse size and a homogeneous spatial distribution of particles, which constitute quality criteria for applications in opto-electronics and magnetism, have also been obtained by combining CBD with the evaporation of matrix atoms [66, 67]. B₁₀H₁₄ clusters were used to fabricate shallow (7 nm) junctions in p-type Si, which cannot be obtained by atom beam implantation due to boron enhanced diffusion [68].
3.5. MIXING

The ion beam mixing of superimposed layers of different materials under the effects of RID and RED deserves a place in the synthesis of nanostructures due to the fact that the thickness of the formed alloys or compounds is often nanometric (when the target is not made of multiple layers). One can put forward several advantages of using mixing instead of ion implantation for synthesizing compound layers:

-Alloying to high concentrations by ion implantation is time consuming and uneconomical.

-The maximum concentration that can be reached in the surface region is generally limited by sputtering.

-Ion implantation is not well suited to obtaining flat concentration profiles, even when using multi-energy implantation, or to forming alloys over thicknesses larger than a few hundreds of nanometers

-Implantation also requires the use of a different ion source in each case.

These limitations are in principle overcome by using the alternative route of ion beam mixing. A good illustration is the mixing of metal/silicon systems, which was extensively studied in the 1980s because of technological interest for the fabrication of electronic components. Simply making use of noble gas ions selected for their mass, Xe, with an energy of the order of 100 keV, about $10^{17}$ atoms/cm$^2$ can be mixed with Xe fluences as low as $10^{15}$/cm$^2$. The indicated value of mixing yield corresponds to a silicide thickness of 20 nm, and in many cases the composition of the formed silicide is homogeneous, because the enhanced-diffusion of Si atoms in metals is efficient at room temperature [69-72]. In the case of metal implantation in Si at the same energy, the sputtering yield is of the same order of magnitude as the implanted dose.

An advantage of mixing over fast annealing by laser or electron beams may come from the fact that ions transfer kinetic energy to target atoms without necessarily involving melting. Thus, one may expect to be able to form metastable alloys with zero solubility in the liquid state. In fact, numerous experiments have shown that the concentrations of crystalline solid solutions formed from superimposed layers of two metals are generally extended to the detriment of intermetallic phases, and the result of mixing is the formation of a metallic glass when the metals are not miscible at high T [73]. Several authors argued that in many metal-metal or metal-silicon systems, mixing occurs in the thermalizing stage of the ion-solid interaction after the cascade (for a comprehensive review of models see [74]). Indeed, they estimated the mean kinetic energy of atoms during the time wherein mixing occurs to be $kT_{eff} = 1-2$ eV, from a fit to experimental diffusion rates [75]. If this was true, there should not be much advantage over laser or electron beam heating (other than
that transparent materials cannot be heated with a laser beam), since ion mixing would involve melting. However, other experiments give evidence of a dependency of the mixing rate on the temperature of the experiment and of a diffusion anisotropy which can be explained by the occurrence of RED or of recoil implantation, but certainly not by thermal spikes.

Whatever the collisional regime, linear cascades, localized or global spikes all along the ion path [74], the mixing extent is correlated to the heat of alloying in most systems. This phenomenological law was verified for silicides [76] as well as for metals in covalent compounds and insulators [77]. The metal silicide formed by mixing of a single metal layer on silicon is generally the stable phase that lies near an eutectic composition and its composition is forced by the ratio of the layer thicknesses in multilayers. In a regime of low displacement density (linear cascades), the mixing rate may be controlled by recoil implantation, diffusion or an interfacial reaction, according to the system. A diffusion controlled kinetics is characterized by a variation of the number of mixed atoms \( N \) and a widening of the interfaces \( W = \sqrt{2Dt} \) as \( \phi^{1/2} \) (\( D \) being the effective diffusion coefficient and \( t \) the equivalent time, equal to the ratio of the fluence \( \phi \) to the flux), while in the two other cases \( N \) and \( W \) vary as \( \phi \) (examples are given in [72]).

The above mentioned enthalpy rule is of little use for predicting the mixing efficiency in the most insulating materials, such as alumina, because the charged defects which are formed in the oxide are unstable, so that displaced atoms tend to move back to the interface [77, 78]. On the other hand, when insoluble metal atoms are pushed into an insulator with a sufficient velocity (by primary collisions with ions of comparable mass), they migrate over a short range before precipitating in the form of nanoparticles. Given this, when the interface energy of metal layers embedded in oxides or on their surface is high, they spheroidize under irradiation as they do during heat treatments. Therefore, complex structures are obtained, made of large particles surrounded by a halo of smaller particles created by the mixing-reprecipitation process (figure 3). Particles of noble metals with this bimodal distribution of sizes in silica exhibit a plasmon-related resonance peak in the visible which is abnormally narrow, compared to the same ensemble of particles that are separated from each other. The effect is ascribed to a screening by nanoparticles arranged in a halo around each large particle of the polarization induced by other large particles (nanoparticles contributing directly to the optical absorption by less than 10%). The strong dipolar interaction between particles in implantation systems of the same nature has an opposite effect, because of their random distribution of size and spatial arrangement [24, 79].
3.6. AMORPHIZATION AND RECRYSTALLIZATION

A discussion of amorphization and recrystallization mechanisms under ion irradiation may appear irrelevant in a review concerning nanostructures. It finds its justification from the fact that amorphization is the most probable change of structure in semiconductors and insulators, and it proceeds from the coalescence of amorphous nuclei. This particular type of precipitation was studied first, and most others obey the same kinetic laws. On the other hand, the recrystallization of semiconductors after implantation treatments is a topic of major importance for applications in electronics, and an understanding of the recrystallization mechanism of bulk semiconductors under irradiation (IBIEC) is needed for applying the same principles to the formation of heterostructures.

Experiments on semiconductors and metallic compounds presenting an amorphous counterpart (like Ni₃B, NiAl, NiTi) showed that amorphization can occur by two different mechanisms, depending on the energy density deposited in nuclear collisions. In the case of a displacement spike regime, amorphous clusters are formed under the impact of each ion, while the number of displacements per atom (dpa) must be accumulated until it reaches locally a critical value in a linear cascade regime. Consequently, the amorphization kinetics is a linear function of the fluence in the former case and presents a sigmoidal shape in the latter, described by the following law [80, 81]:

\[
\alpha = \sum_{n=0}^{\infty} P_n = \sum_{n=0}^{\infty} \frac{(\sigma\phi)^n}{n!} \exp(-\sigma\phi)
\]  

\( (7) \)
The probability, $P_n$, of cluster formation is proportional to that for an area of the target $\sigma$ to be perturbed by $n$ impacts, and $n_c$ is the critical number of impacts to obtain a stable nucleus. In fact, $\sigma$ is the cross section of damaging, i.e. the product of the stopping power by its efficiency. The same law applies to many precipitation processes in the regimes of nuclear or electronic stopping.

Ion implantation at high ion fluences in pure metals has also been used for synthesizing amorphous alloys, generally of the same nature as those obtained by quenching from the melt, but interesting for their high purity [82]. The study of amorphization kinetics has shown that the decisive parameter is the chemical ordering due to the change in composition, to the detriment of the structural ordering of the host lattice. The role of cascades in the process is only to shake up the implanted layer, to allow the system to relax into the equilibrium configuration (the amorphous state on short range) [80, 83]. At low $T$, where the implanted atoms are not mobile, clusters are formed where the local concentration of implanted atoms exceeds a threshold value and the amorphization kinetics obeys the Poisson law given above (equation 7). At higher $T$, the short range diffusion of implanted atoms favours the formation of clusters for very low concentrations of implanted atoms, so that the kinetics is a linear function of the fluence.

Epitaxial recrystallization of amorphous implantation layers may be promoted by ion irradiation at lower $T$ than purely thermal recrystallization (called solid phase epitaxial regrowth). The ion-beam-induced epitaxial crystallization (IBIEC) is not an effect of beam heating, and numerous experiments have demonstrated that only the defects which are created at the a-c interface contribute to the process [84]. Each ion produces in the vicinity of the interface the amorphization of some atoms, and in the meantime kink-like defects (along [110] ledges connecting two (111) terraces in Si). IBIEC and ion-beam-induced interfacial amorphization (IBIIA) are competing processes and the direction and rate of the a-c interface motion depend on the temperature and ion flux: (i) at low $T$ and/or at high flux, a planar layer-by-layer amorphization occurs; (ii) IBIIA and IBIEC are in balance at a critical temperature $T_r$ and (iii) the IBIEC rate increases above $T_r$. A residual amorphous layer often remains close to the surface, and planar growth is blocked at too high temperatures by the formation of crystallites inside the amorphous layer [85]. Dopants such as B, P and As enhance the IBIEC rate, while C, O, F produce a retardation by pinning interfacial defects. The recrystallization of implanted layers can be obtained by subsequent irradiation with an energetic ion beam having an implantation range well beyond the a-c interface, or by a proper choice of implantation flux and $T$ (a self-annealing process). Besides the technological interest of IBIEC for lowering the crystallization temperature of implanted layers in Si, it has found applications in the fabrication of epitaxial heterostructures [84]. The maximum thickness of strained layers free of dislocation networks is increased, and the interface is more planar than by crystallization in a furnace. Higher temperatures must also be used for growing films of the same composition by molecular beam epitaxy.
Dynamic annealing is also used for curing implantation defects in polycrystalline layers of semiconductors, as for instance solar cells made of CdS films, implanted with N or Ar for increasing their conductivity [86]

3.7. PATTERNING

A number of patterning methods have been used, for instance to obtain single magnetic domains with as small sizes as possible but exhibiting no spontaneous reversal of magnetization. One involves creating arrays of soft regions with a longitudinal magnetization in a film of higher coercivity, with a perpendicular anisotropy, by ion beam irradiation through a mask, as for other types of patterned films. However a coupling remains between strongly magnetized bits and noise in disordered regions. The ideal material is one in which magnetism is either created or destroyed upon exposure to a low ion fluence. One technique consists of creating discrete islands of a magnetic phase by digging trenches with a focused ion beam (FIB) in a continuous thin film and, in addition, poisoning the magnetic order in the trenches by incorporation of implanted ions or by mixing with an overcoating [87]. Collimators with diameters smaller than 100 nm are commonly available for this purpose.

Focused ion beams also provide a means for fabricating channel waveguides and laser gratings by localized mixing of semiconductor multilayers.

4. Electronic Effects

4.1. RADIOLYSIS AND CONVERSION OF POLYMERS

Polymers are the most sensitive of all materials to radiation damaging, so that photons, electrons or ions may all be used for promoting the crosslinking or decomposition of thin polymeric films. One of the interests of using ion beams for this purpose lies in the much higher radiolytic efficiency of ions [88-90]. The short range order in amorphous ceramic films obtained by ion irradiation is also very different from that in polymers converted into ceramics by means of other treatments. Moreover, irradiation with low ion fluences permits patterning of the surface with isolated cylindrical tracks, which may thereafter be etched and filled with other materials. This use of tracks as templates is discussed below. Un-etched tracks also constitute interesting nanostructures with particular chemical properties, which will first be summarized.

4.1.1. Organic Polymers

The final product of the crosslinking process is a three-dimensional amorphous network composed principally of C, O and N atoms. The bond scission under
the effect of nuclear collisions is supposed to favour the formation of a network where C atoms exhibit a high degree of sp² hybridization [88-91]. However, collision cascades do not affect significantly the physical properties of this network, as long as ions lose as much energy in electronic excitations as in collisions. This has been shown by performing experiments with ions of energy in the range 20 to 100 keV/nucleon on polymers with alliphatic or cyclic structures [92, 93]. The measured values of the optical gap $E_g$ (larger than 0.5 eV) and the hardness $H$ (5 times that of turbostratic graphite) of polymer films irradiated in such conditions indicate that they exhibit a noticeable degree of diamond-like hybridization. In addition, variations of $E_g$, $H$ [92] and other properties [88-90] show that the efficiency of ionizations in crosslinking the structure increases with $S_e$, most probably because the ability of formed radicals to combine increases.

Let's get down to tracks formed in the purely electronic stopping regime by saying that fullerenes clusters seem to be formed in the core of tracks when $S_e$ exceeds a threshold value. This fact suggests the occurrence of thermal spikes, since this allotrope of C is stable at high T [94-97]. In milder conditions of irradiation, phenyl rings (even in alliphatic polymers) and other types of unsaturated bonds are formed at low fluences [98, 99] before C clusters. The nature of the observed moieties differs in many cases from those formed in polymers submitted to other types of ionizing radiation. They constitute grafting sites for other macromolecules or inorganic ions, which attract the interest of chemists [100]. It is also worth noting that the linearity of swift ions tracks facilitates the diffusion of dopants, and tracks decorated with alkaline or halogen elements can be used as nanometric electric contacts.

4.1.2. Semi-Organic Polymers and Gels
Given that ion irradiation of organic polymers produces carbon-rich amorphous phases (at high fluences) with more interesting physical properties than those of pyrolyzed polymers, and also with less change in the content of other elements than hydrogen, experiments were carried out on semi-organic polymers and gels. These materials made of an inorganic backbone and organic side groups are particularly useful as precursors of ceramic coatings, foams and fibers. Experiments on silicon-based polymers and gels with various ions show that, as in organic polymers, hydrogen is released selectively [101], with the same kinetic laws [102], and the molecular structure is crosslinked then transformed into a glassy ceramic. Physical properties such as the density and hardness increase with the same slope as a function of the transferred energy, $S_e \times \phi$, as does the amount of H release. Nuclear collisions appear once again to play no significant role in the conversion process, and don't affect the chemical order in the fluence range useful for the conversion into ceramics.

The C content in the ceramics generally exceeds the maximum value in homogeneous glasses $\text{SiO}_{2-x}\text{C}_{x/2}$ ($x \leq 2$), and the C excess segregates in
polysiloxanes with a Si-O- backbone as well as in polycarbosilanes with a Si-CH2-backbone. Energy filtered TEM images of the C distribution in cross sections of the irradiated films provide evidence that C atoms or CHx radicals migrate in the structure to form clusters with diameters of 3 to 7 nm, depending on the C content and the Se value (figure 4) [103]. In the case of phenyl-substituted precursors, clusters are also supposed to form on the spot of the radiolytic reaction [104]. C clusters are aligned along tracks or exhibit a more random distribution when ions also undergo nuclear scattering. Assuming that continuous wires may be obtained above a threshold of Se or C concentration, they would find applications as field emission tips or electric contacts with a well-defined and nanometric section. Raman analyses show that, whatever their arrangement, isolated C particles formed at low ion fluences exhibit a noticeable degree of tetragonal hybridization, while C clusters which are also formed in films of the same nature by annealing in vacuum are made of turbostratic graphite. The semiconducting particles formed under irradiation emit a yellow-green luminescence, in contrast to those formed in annealed films. The PL emission wavelength and yield are the same for spherical, randomly distributed, clusters and for discontinuous cylinders obtained at high energy, for a given value of energy transfer, Se × φ. The PL peak shows a red shift and broadening with the increasing Se × φ, ascribed to the growth of parts of the clusters (in matrices where percolation is unlikely, due to the low C excess). Rings of C atoms with a sp2 hybridization state are known to form at the periphery of C clusters when their size increases, and this graphitic state is the one stable at equilibrium (which factor explains the nature of clusters in annealed samples). Beside interesting optical properties, the tetragonal hybridization of C clusters give irradiated films hardness values 2-3 times higher than those of heat-treated films, as shown by nanoindentation tests: The hardness of irradiated polycarbosilanes reaches that of bulk SiC [101].

Figure 4: Energy filtered images of cross sections of methyltriethoxysilane gel ([Si(OH)(CH3)-O]-) films irradiated with 3 MeV and 100 MeV Au ions at fluences of 10^15 and 10^13/cm² respectively [103]
Similarly to C in gels and polymers containing C in excess, Si precipitates under irradiation in the suboxide with stoichiometry SiO$_{1.5}$ derived from the triethoxysilane gel (the ethoxide precursor has the formula SiH(OC$_2$H$_5$)$_3$) and the semiconducting clusters show a red luminescence, at a wavelength which is correlated to the particle size (~1 nm) [105]. When the same gel is mixed with metal salts, SiH hydrido groups react with the metal ions, forming metal nanoparticles [106]. Their distribution is relatively narrow (of Gaussian type with a standard deviation/mean size ratio of 25%) contrary to that of particles formed in films heat-treated in vacuum. In addition, the evolution of gases leads to the formation of ovoid porosities in annealed films, and the particles are segregated on the pore walls. An investigation of the precipitation kinetics, by means of electron spin resonance in the case of magnetic metals or of optical absorption for noble metals, shows that the driving force is the formation of Si$^*$ free radicals under the effect of ionizations, and clusters are formed when the number of neutralized metal atoms exceeds locally a threshold value for the building of a stable nucleus. The volume of metal phase therefore increases as the cumulative function of a Poisson distribution (equation 7), like that of amorphous clusters formed in semiconductors or metals in the ballistic regime of slowing down.

4.2. FORMATION OF COMPOSITES AND PHASE CHANGES IN OTHER MATERIALS

4.2.1. Demixing of Out of Equilibrium Solid Solutions
Irradiation of metastable solid solutions, such as silicate glasses containing noble metals, at energies below the threshold of matrix damaging by electronic excitations, may lead to precipitation. By varying the ratio of electronic to nuclear energy transfer, for instance via the mass of the ions, it has been demonstrated that displacements contribute to the precipitation only when the dissipated power is high enough to induce substantial target heating [107]. Otherwise, the nucleation yield varies in proportion to the energy transferred to electrons $S_e \times \phi$ [108, 109]. The kinetic law of precipitation may be the cumulative function of a Poisson distribution when tracks must overlap to form nuclei of a stable size [109], or a linear function of $S_e \times \phi$ when stable nuclei are very small [108]. Their size remains constant as long as the source of metal ions in solid solution is not exhausted and the clusters can be as small as 0.5 nm. Particles with such a size undergo a very high compressive stress due to their interface energy. Contractions of the order of 10% of the lattice parameter, $a$, were calculated for Ag particles in silica on the basis of the observed blue shift of their plasmon resonance.

4.2.2. Growth of Particles
When pursuing the irradiation of the same targets, or irradiating composites containing very few atoms of noble metal in solid solution, obtained by means
of another technique, a growth of the particles is observed when the energy density $S_e$ is not too high \[110\]. The linear increase of the particle size with the fluence indicates that the rate controlling process is the desorption of the noble metal atoms from the surface of pre-existing particles. These desorbed atoms diffuse over a short distance and are adsorbed at another particle surface. Thus, some particles grow at the expense of others, as long as the density of excitations remains low.

Above a given $S_e$ value, in the range 5 to 10 keV/nm, the size of the same particles decreases. A detailed investigation of the density effect is still needed for defining if the critical parameter is the ratio of the desorption/adsorption rates or the threshold of matrix damaging. On the contrary, a growth of Co particles formed by ion implantation in silica has been observed when they were submitted subsequently to electronic excitations with as high a density (of about 20 keV/nm) \[111\]. Given that the particles became elongated parallel to the beam direction and the density of energy transfer was 10 times larger than the threshold of silica damaging, the authors ascribed the structural transformation to a thermal spike effect. However the increasing elongation of the particles which was observed with the track overlap seems to indicate that the relaxation of energy in the transient disordered phase was so fast that a thermal equilibrium could not be reached. The occurrence of Coulomb explosions or an increase in the readsorption/desorption rates ratio in the case of a particle ensemble with a very high filling factor (compared to ion exchanged glasses and other colloids studied in \[110\]) cannot be excluded. From a practical point of view, the Co particle elongations had the interesting effect of tilting their easy magnetization axis perpendicular to the film surface.

4.3. LATENT TRACKS

Since tracks in some materials can be chemically revealed, the initial damage is also called latent tracks. Fission fragments from nuclear accelerators are sometimes used instead of ion beam accelerators for producing tracks. Latent tracks are formed in most materials above a $S_e$ threshold. This threshold is one order of magnitude larger in crystalline metals than in quartz, and tracks have been observed only in pure metals with a low phonon frequency and exhibiting a displacive transformation (of martensitic type) such as Fe, Ti, Zr \[18\]. The formation threshold is also much higher in Si or Ge than in compound semiconductors, and the ions must have a low velocity (together with a high stopping power, which combination is possible for cluster beams), probably because the crystalline order is more easily restored after melting of the track core when atoms are of the same nature and the core diameter small. In other terms, monoatomic semiconductors of type IV are probably not amorphized as long as the rate of power dissipation $dE_e/dt$ in the track core does not exceed that of epitaxial reconstruction \[15\]. The quantity $dE_e/dt$ may be more significant than the
linear density $S_e$ ($dE_e/dR$) in the modeling of transformations, since these depend on the lifetime of the transient disorder and on the structural parameters mentioned above. The track morphology is, however, correlated to the magnitude of $S_e$. Close to the $S_e$ threshold, the track consists of extended spherical defects. Increasing $S_e$ leads to the percolation of these defects in the form of a discontinuous cylinder of the same radius, then to the homogenization of the damaged radius.

4.3.1. Changes in Magnetic Ordering

Latent tracks have a wide range of applications linked to their anisotropy. The radial stress in magnetic oxides leads to an anisotropic orientation of the magnetic internal field. This orientation can be parallel or perpendicular to the track axis, depending on the sign and strength of the magnetostriction effect [112-114]. Paramagnetic phases may exhibit a permanent magnetization after irradiation, due to their disordering and related either to site exchanges between cations (ZnFe$_2$O$_4$, NiFe$_2$O$_4$) [115,116] or to the localization of d electrons in the amorphized structure, such as in the case of YCo$_2$ [117]. Amorphous tracks are insulating in high $T_c$ superconductors and, since their size is comparable to the coherence length of spins, they pin lines of magnetic flux [118], leading to an increase in the critical current by more than one order of magnitude. The pinning of walls by amorphous tracks also tends to increase the coercivity of the matrix in other magnetic materials [119]. As well as carbon cylinders formed in polymers, conducting cylinders formed by damaging diamond-like carbon films [120] may be useful as nanometric field emitters.

4.3.2. Filters and Templates

Chemical etching becomes very efficient, whatever the material, when track radii are larger than 2-3 nm. To date, commercial ion track membranes made of polymers, crystalline insulators (micas) and glasses with calibrated pore diameters between 15 nm and several µm are available [121,122]. Research is aimed at even smaller pore openings (around 2 nm). They find many applications as biosensors, filters for controlling drug delivery on wounds [122] or filters with pores sizes changing as a function of the external conditions, $T$ and $P$ (intelligent materials).

Using electrochemical or electroless deposition, pores can be filled with metals or semiconductors, to fabricate micro or nanometric needles, wires or tubes [121, 123-132] (figure 5). This replication technique is very simple and the wires or tubes can be removed from the membranes (by chemical etching or using adhesive tape) or used as an ensemble protruding from the membrane surface as the bristles of a brush. The template synthesis requires very low ion fluences ($\sim 10^6$ to $10^8$/cm$^2$). Nanostructures with extraordinary low and monodisperse diameters are obtained, which are difficult to manufacture using lithographic techniques. In the case of galvanic deposition, one has control over the filled length of the pores and can fabricate axially structured wires,
Figure 5: Example of a structure obtained by filling tracks with a metal: left Ag nanowires and right Cu-Ni concentric tubes, after Fink [126, 127].

consisting for instance of Co/Cu multilayers with a giant magnetoresistance perpendicular to the membrane plane [132] or of Cu/Se resonant tunneling diodes [128]. Radially structured tubes and wires can also be fabricated by electrochemical or electroless deposition with a catalyst on the pore walls. CdSe/CdTe nanodiode arrays obtained by this technique act as retinal photocells, resembling those in the human eye [126]. Metal tubes may be used as microchannel plates or anodes in batteries.

5. Conclusions

During their very short passage through the target, ions induce stochastic atom displacements and/or electronic excitations within tubular tracks of nanometric radius, depending on their velocity. The two processes of energy transfer may lead to a redistribution of atomic species and to structural transformations by mechanisms involving either solid state diffusion or relaxation of kinetic energy in a liquid-like, short lifetime, phase.

Ballistic effects are localized within a given depth range and the displacement density can be varied by means of the ion mass and velocity. In addition, other parameters such as the damaging resistance of the matrix, epitaxy relationships, ion channeling, ion flux and irradiation temperature may be used to modify the dynamic annealing of damage. Provided these irradiation conditions are judiciously chosen, on the basis of empirical studies and Monte Carlo dynamic simulations, the nature and the nucleation and growth rate of nanoparticles synthesized by ion implantation can be predicted and controlled. Ion beam mixing of heterostructures constitutes an interesting alternative for getting rid of implantation physical limitations (sputtering, depth gradients) and for decreasing the ion fluences needed to obtain compound layers and colloids. One can also take advantage of the crystallographic anisotropy of atomic displacements and sputtering for modifying the surface topography and the texture of PVD films.

Electronic excitations in swift ion tracks permit one to localize the energy deposition along the transverse direction (with respect to ballistic interactions) and the electron-lattice coupling to create cylindrical structures. Some are obtained
directly through the migration of radicals and secondary ions in materials particularly sensitive to electronic excitations, such as polymers and out of equilibrium solid solutions in insulators. Atomic rearrangements during the lattice relaxation also produce changes of density or crystalline structure with interesting effects on the magnetization anisotropy of thin films. Finally, latent tracks can be easily etched in many materials to obtain pore filters and templates for the fabrication of nanowires and tubes of various natures by a chemical deposition process. This use of tracks is particularly attractive for the extraordinarily low and monodisperse diameter of the pores and for their controlled density.

A large variety of planar or cylindrical structures have been synthesized by using ion beams, with applications as waveguides, nanodiode arrays, magnetic memories, electrical contacts, field emitters, transparent metallic structures, gas sensors and separators, and mimics of biological systems.

References

Appendix: Basic Formulae of Ion Stopping

1- The energies in the laboratory frame of the recoil $E_2$ and scattered particle $E_1$, after an elastic collision, are given by following formula:

$$E_2 = \frac{4M_1M_2}{(M_1 + M_2)^2} E_0 \cos^2 \zeta = \gamma E_0 \cos^2 \zeta$$  \hspace{1cm} (8)

$$E_1 = \frac{M_1^2}{(M_1 + M_2)^2} \left[ \cos \psi + \left( \frac{M_2}{M_1} \right)^2 \sin^2 \psi \right]^2 E_0$$ \hspace{1cm} (9)

$$\sin \zeta = \left( \frac{M_1 E_1}{M_2 E_2} \right)^{1/2} \sin \psi$$ \hspace{1cm} (10)

where $\zeta$ is the recoil angle and $\psi$ the scattering angle of the projectile. The scattering factor $k$, useful for instance in the Rutherford backscattering formula, is defined as the ratio of $E_1/E_0$ and $E_2=(1-k)E_0$.

2- Calculation of the nuclear scattering cross section:
Assuming that the force between the 2 particles acts only along the line joining them, the use of center of mass (CM) coordinates reduces the problem to a one-body problem, namely the interaction of a particle with mass $M_{CM}$ (or $\mu$) and velocity $v_{CM}$ with a static potential field $V(r)$ centered at the origin of the CM coordinates. This is because the total linear momentum of the particles is always zero in this frame.

$$\frac{1}{\mu} = \frac{1}{M_1} + \frac{1}{M_2}$$ \hspace{1cm} (11)

$$E_{CM} = \frac{1}{2} \mu v_0^2 = E_0 \frac{M_2}{M_1 + M_2}$$ \hspace{1cm} (12)

The scattering angle of the projectile in this frame is a function of the impact parameter $p$ (projected offset of the original path of the projectile (1) from the atom at rest (2)):

$$\theta = \pi - 2 \int_{r_{\text{min}}}^{\infty} \frac{pdr}{r^2 \left[ 1 - \frac{V(r)}{E_{CM} \frac{p^2}{r^2}} \right]^{1/2}}$$ \hspace{1cm} (13)
The transferred energy $E_2$, also denoted as $T$, is equal to:

$$T = \gamma E_0 \sin^2 \frac{\theta}{2}$$  \hspace{1cm} (14)

The choice of a proper interaction potential $V(r)$ during the collision is needed for calculating values of $\theta(p)$ and $T(p)$ used in transport equations or Monte Carlo simulations of ion impacts and the value of energy transferred per unit length of the ion path, $N_S n$ (where $N$ is the atomic density), averaged over all impact parameters $p$. This potential is of the form:

$$V(r) = \frac{Z_1 Z_2 e}{r} \Phi\left(\frac{r}{a}\right)$$ \hspace{1cm} (15)

where $\Phi(r)$ is a screening function and $a$ is a characteristic screening length. The unscreened potential of Rutherford collisions is valid for short $r$ (energetic collisions). The earliest screening functions proposed by Bohr and Thomas-Fermi are:

$$\Phi_B = \exp(-x) \quad \text{and} \quad \Phi_{TF} = \left[1 + \left(\frac{x}{144}\right)^{1/3}\right]^{-2.4}$$ \hspace{1cm} (16)

$x$ being a reduced approach radius $= r/a$, with

$$a_B = \frac{a_0}{Z} = \frac{\hbar^2}{m e^2 Z} \quad \text{and} \quad a_{TF} = \frac{1}{2} \left(\frac{3\pi}{4}\right)^{2/3} a_0 \frac{1}{Z}$$ \hspace{1cm} (17)

In these expressions $Z$ is the charge of the quasi-molecule formed during the overlap of electron shells and $a_0$ (0.0528 nm) is the Bohr radius. Different averaging processes were proposed by Bohr and Thomas-Fermi, giving:

$$Z_B = (Z_1^{2/3} + Z_2^{2/3})^{1/2} \quad \text{and} \quad Z_{TF} = (Z_1^{1/2} + Z_2^{1/2})^{2/3}$$ \hspace{1cm} (18)

Lindhard used the $a_{TF}$ expression with the Bohr equation for $Z$. On the basis of Hartree-Fock-Slater calculations for a large number of quasi molecules, a universal potential is now used in most calculations:

$$\Phi_u = 0.1818 e^{-3.2x} + 0.5099 e^{-0.9423x} + 0.2802 e^{-0.4028x} + 0.0282 e^{-0.202x}$$ \hspace{1cm} (19)

with $a_u = \frac{0.8854 a_0}{(Z_1^{0.23} + Z_2^{0.23})}$  \hspace{1cm} (20)
To be able to give universal expressions for the scattering angle $\theta$ as a function of the impact parameter $p$, it is useful to normalize $p$ to $a$, as also the center of mass energy $E_{CM}$ and the range $R$ of the projectile:

$$b = \frac{p}{a}, \quad \varepsilon = E_{CM} \frac{a}{(Z_1 Z_2 e^2)} \quad (21a)$$

$$\rho = \frac{2 N \pi a_U^2 \gamma R_s}{a} \quad (21c)$$

Finally, the nuclear stopping power $S_n(\varepsilon)$ is the integrated product of the transferred energy $T(E_0, p)$ in each collision by the probability $d\sigma(p)$ for a collision with an impact parameter $p$. $\sigma$ is the impact cross section $\pi p^2$:

$$S_n(E_0) = \int_0^\infty T d\sigma = \int_0^\infty T(E_0, p) \frac{2\pi p}{2} d\sigma = 2\pi T_{\max} \int_0^{p_{\max}} E_0 \int_0^{\frac{\theta}{2}} \sin^2 \theta d\theta dp \quad (22a)$$

or in reduced units:

$$S_n(\varepsilon) = \varepsilon \int_0^\infty \sin^2 \frac{\theta}{2} d\sigma \quad (22b)$$

Calculations with the universal potential were fitted by an analytic expression of the form:

$$S_n(\varepsilon) = \frac{\ln(a + b\varepsilon)}{2(\varepsilon + c\varepsilon^d + e\varepsilon^{0.5})} \quad (23)$$

in which $a=1$, $b=1.14$, $c=0.01$, $d=0.21$, $e=0.20$ for $\varepsilon<30$, $a=0$, $b=1.0$, $c=d=e=0$ for $\varepsilon>30$ (i.e. case of unscreened stopping)

3- Calculation of the electronic stopping power $S_e(\varepsilon$ or $E$):

The earliest expression proposed in the 1930's for the energy loss per unit length (labelled $S_e$ in this section but strictly speaking equal to the product of the atomic density $N$ by the stopping power $S_e$ per atom), of slow particles in an electron plasma is the product of the ion velocity, $v$, by the cube root of the electronic density of the medium, $N_e$. Lindhard introduced a stopping interaction function $I(v, N_e)$ taking into account the local density fluctuation of $\rho_e$ and the perturbation of this density by the ion (individual and collective excitations):
\[ S_e = \int I(v, \rho_e) Z_i^2 N_e \, dV, \quad (24) \]

\( V \) being the volume of each element of the target. \( I \) is a flat function when the ion is going much faster than the mean electron density and it decreases almost linearly with \( N_e \) when \( v \) becomes equal to the Fermi velocity \( v_F \) of the target electrons:

\[ v_F = \left( \frac{\hbar}{m_e} \right) \left( 3\pi^2 N_e \right)^{1/3} \quad (25) \]

Low velocity ions (with an initial velocity \( v_0 \)) are neutralized when penetrating into the target and their stopping power is:

\[ S_e = 8\pi N e^2 a_0 Z_i^{1/6} \frac{Z_i Z_2}{(Z_1^{2/3} + Z_2^{2/3})^{3/2}} \frac{v_0}{v_B} \quad (26) \]

which is proportional to \( N_e^{1/3} \) as \( v_0 (\approx v_F). v_B \) is the Bohr velocity of H electrons: \( v_B = e^2/\eta_l \).

High velocity ions are stripped of all electrons whose classical orbital velocities are less than the ion velocity. Their effective charge is \( \gamma Z_1 \) with:

\[ \gamma = 1 - \exp - \frac{v_0}{v_B Z_i^{2/3}} \quad (27) \]

For \( v_0 > v_B Z_i^{2/3} \), \( S_e \) is proportional to \( 1/E_0 \) and \( Z_2 \). The Bethe expression for \( S_e \) corrected for the partial stripping of electrons at intermediate energies and for the change of density and mass at relativistic energies is:

\[ S_e = \frac{4\pi Z_2 Z_i^2 e^4}{m_e v_0^2} \left[ \ln \left( \frac{2m_e v_0^2}{I} \right) - \ln \left( 1 - \frac{v_0^2}{c^2} \right) - \frac{v_0^2}{c^2} - \frac{c}{Z_2} - \frac{\delta}{2} \right] \quad (28) \]

with a mean ionization and excitation energy \( I \) of target atoms: \( I \approx 10eV \times Z_2 \).
POROUS SILICON FOR SENSOR APPLICATIONS

A. G. NASSIOPOULOU
IMEL/NCSR Demokritos, Terma Patriarchou Grigoriou,
15310 Aghia Paraskevi, Athens, Greece, www.imel.demokritos.gr

1. Introduction

Porous silicon is a nanostructured material intensively investigated in the early nineties in view of its application in silicon based integrated optoelectronics [1, 2]. For this application, different types of light emitting diodes (LEDs) [3,4] waveguides [5,6], photodetectors [7], electro-optic devices [8] and high quality porous silicon microcavities [9] were fabricated and tested. In parallel, the material properties (structural, optical, electrical, mechanical, thermal, etc.) were also investigated, and interesting other applications were derived from the better material knowledge. An interesting example is the field of Si sensors and other silicon-based micro-electro-mechanical (MEMs) devices. The compatibility of porous silicon with conventional silicon microelectronics fabrication technologies make it very attractive for these applications, since it offers possibilities for miniaturization, batch fabrication and cost lowering. Many applications of porous silicon in sensor technology have been proposed, based on conductivity [10], capacitance [11], or photoluminescence [12] changes of the material upon adsorption of molecules for gas, moisture, PH or biological sensing, thermo-optic properties for active optical component fabrication [13], and others.

In this paper, we will present in more detail two key applications of porous silicon and its use in thermal sensors: a) its application as a sacrificial material for silicon micromachining and b) its use as a low thermal conductivity material for local thermal isolation on bulk crystalline silicon.

2. Fabrication and Structure of Porous Silicon

2.1. FABRICATION

Porous silicon (PS) is formed during the electrochemical dissolution of bulk crystalline silicon, mainly in aqueous or ethanoic HF solutions. The material
obtained after anodization depends strongly on the type and resistivity of the original silicon substrate, and on the electrochemical parameters used during the anodization process. The porosity, pore size and pore distribution in the material are essential parameters for its structural characterization.

Different mechanisms have been proposed for the dissolution chemistries [14,15], which involve holes from the silicon substrate at the dissolution front. The silicon/HF solution interface behaves like a solid state Schottky contact [16]. The spatial distribution of holes depends on the doping level and type of the material, and is affected by potential inhomogeneities or defects at the silicon surface. In the case of p-type Si, the necessary holes are generated by thermionic emission over the potential barrier in the space charge region. For n-type silicon, where holes are the minority carriers, the electrochemical dissolution is promoted by hole/electron pair generation by illumination. When lightly doped (carrier concentration below ~ $10^{18}$ cm$^{-3}$) n-type silicon is anodized in the dark, the formation of porous silicon is observed only at high voltages (> 5V). In this case, breakdown and impact ionization processes are supposed to provide the holes required for the dissolution step.

The structure and morphology of porous silicon depend on the type and doping of the silicon substrate. Highly doped p-type (001) silicon yields a mesoporous structure, with pores in a range around 10 nm elongated along the [001] direction and presenting a characteristic branching “fir-tree-like” morphology. Lightly doped p-type (001) silicon yields finer, less regular pores, with a “coral-like” microporous microstructure on a scale of 2 nm [17]. Highly doped n-type silicon also yields mesoporous material, similar to that of highly doped p-type silicon, while lightly doped n-type silicon, anodized under illumination, gives pores of up to 100 nm or greater diameter (macropores) [17]. Thus, depending on the application, the structure of the material may be tuned to meet the corresponding requirements. Macropores are of great importance in VLSI trench and via formation, and in galvanic isolation for power devices, while in most of the other applications microporous or mesoporous material is used, with a very high internal surface area.

Depending on the pore size, we characterize porous silicon as “microporous” if the pore diameter is less than ~ 2 nm, as “mesoporous” if the pore diameter is in the range of 2-50 nm and as “macroporous” if the pore diameter is larger than 50 nm [18].

Anodization of porous silicon is usually performed at a constant current density. A typical current density-voltage curve [19-21] shows an initial rising part for a current density lower than a critical value $J_{\text{critical}}$, at which a small sharp "electropolishing" peak appears. Above this peak, a different slope in the J-V curve is observed. Pore formation occurs in the initial rising part of the curve and the porosity of the material depends on the current density used. For a current density above $J_{\text{critical}}$, electropolishing takes place.
The change of porosity with anodization current density and the switching to electropolishing for current densities above the critical value $J_{\text{critical}}$ are interesting for many applications, including buried channel formation in bulk silicon [22, 23] and multilayer porous structure formation [24, 25].

2.2 DRYING OF POROUS SILICON

The drying of porous silicon is a crucial step in the fabrication process, especially in the case of highly porous material. Cracking of the layer is systematically observed in thick or highly porous layers, if we water is allowed to evaporate out of the pores [26]. The origin of the cracking is the large capillary stresses associated with the nanometric size of the pores. Simple considerations based on the mechanical properties of porous silicon and X-ray diffraction data showed that there is a critical thickness $t_c$ above which cracking occurs [27]. This thickness depends on the porosity of the layer and on the surface tension of the drying liquid. An estimation of $t_c$ is obtained by the following formula [28]:

$$t_c = \frac{(r/\gamma_{LV})^2 E_{Si} (1-P)^3}{\gamma_{Si}}, \quad (1)$$

where $r$ is the pore radius, $\gamma_{LV}$ the surface tension of the pore liquid, $P$ the porosity of the layer, $\gamma_{Si}$ is the surface energy (~1 J/m²) and $E_{Si}$ the Young’s modulus of bulk silicon. For a 90% porosity, when the drying liquid is water, $t_c$ is of the order of 1µm, while it is of the order of 10 µm for an 80% porosity [28]. It is therefore obvious that water has to be avoided in the drying and rinsing process if we want to fabricate thick uniform PS layers of high porosity.

Different drying methods have been proposed in the literature, including freeze drying [29], drying with pentane or ethane (the critical thickness for cracking is significantly increased, compared with the use of water [28]) and drying at a slow evaporation rate [28]. However, the most efficient drying method was found to be supercritical drying [30], in which the removal of the pore liquid (generally CO₂) occurs above the critical conditions that permit one to avoid any interfacial tension. For sensor applications, slow drying in ethanol was found to be sufficient for avoiding cracking.

2.3 AGING OF POROUS SILICON. SURFACE MODIFICATION AND CAPPING

Due to the very large internal surface of highly porous silicon, any surface modification has an important impact on the material properties. These are significantly influenced not only by the fabrication and drying conditions, but also
by the reaction with the environment: the surrounding ambient or the containment vessel [31]. In order to minimize storage effects, different solutions have been proposed, including pore impregnation with different materials, internal surface modification or isolation of the internal surface by capping [32].

The technique mainly used in sensor and micromachining applications of PS is to intentionally oxidize the internal porous silicon surface [33,34]. In this way, passivation and stabilization against moisture and other environmental gases is achieved. High temperature stability is also obtained.

3. Local Formation and Patterning of Porous Silicon

In many applications it is interesting to form porous silicon on predefined areas of a silicon substrate. For this, there are several ways to proceed [35]; the most important being:

a. Local anodization of silicon through a masking layer or through a patterned etch stop and
b. Patterning of large area porous silicon films using lithography and etching techniques.

For the local anodization of silicon, different masking materials have been proposed [35]. Polymeric materials that are commonly used as lithographic films do not withstand an ethanoic HF solution for a long time. Thus, they can be used only for the local formation of very thin porous silicon layers unless a special very thick photoresist is used (SU₈ photoresist with a thickness of several micrometers [36]). Other masking materials proposed in the literature include silicon dioxide, silicon nitride and silicon carbide. With silicon dioxide the anodization time is limited to a few minutes, while stoichiometric silicon nitride and silicon carbide show a little higher maximum anodization time depending on mask thickness. However, they also show problems related to stresses induced by the mask, which cause PS cracking. These stresses increase with increasing film thickness. Better behavior (reduced stress) is obtained in the case of non-stoichiometric silicon nitride. In this case, stress within the film is reduced and a thickness of 1-2 µm is enough to withstand the anodization solution for a long time.

The best masking material, which shows important advantages compared with all the above, is a bilayer of silicon dioxide and polycrystalline silicon (polysilicon) [33,34]. Both films are fully compatible with silicon processing, and under certain optimum conditions they show negligible stress. Polycrystalline silicon, which is the top layer, shows an almost zero etch rate in an HF ethanoic electrochemical solution. Polycrystalline silicon may be used alone, but it has been shown [34] that in this case porous silicon formation is
initiated under the polycrystalline layer. This is stopped by the silicon dioxide layer, which electrically isolates the polysilicon film.

Instead of using a deposited layer, different etch stops may be created locally on a silicon substrate, which act as masking layers for anodization. A typical etch stop in the case of p-type silicon is an n-type area on the same silicon substrate. Under the same electrochemical conditions and without illumination, the n-type areas stay intact during anodization. Selected areas with different doping levels are produced on a silicon substrate by ion implantation through a mask.

4. Front Side Bulk Silicon Micromachining Using Porous Silicon Technology

![Process flow chart for the fabrication of suspended polycrystalline silicon membranes on bulk silicon](image)

Porous silicon is an ideal material for use as a sacrificial material for microstructuring of a silicon substrate, due to the ease of producing very thick porous silicon layers, which are then etched in order to produce deep trenches, lines or more complicated patterns into silicon. Suspended membranes in the form of thin films on top of cavities or other more complicated channels may also be fabricated. Processes compatible with silicon processing may be used in this respect. One such process was presented in [34] for the fabrication of polycrystalline silicon membranes in the form of bridges or cantilevers over deep cavities. The process flow chart used is illustrated in figure 1. A porous
silicon film is first grown locally on a p-type silicon substrate through a polysilicon/SiO₂ mask. The mask is then removed and a polysilicon layer is deposited on the wafer, which is patterned in order to define the membrane area. After this, the porous silicon underneath is removed by chemical etching, thus leaving the polycrystalline silicon membrane suspended over a cavity. Figure 2 shows different free standing polycrystalline silicon structures fabricated using this process. The surface area of a structure may be very large. It is also very flat provided that the stress within the polysilicon film is minimized [34,37,38].

![Figure 2. Suspended polysilicon membranes fabricated by using porous silicon as a sacrificial material (process flow of figure 1)](image)

5. Porous Silicon Technology for the Fabrication of Sealed Microchannels on a Silicon Substrate

Self-sealed microchannels of different geometries, buried into silicon, may be fabricated on a silicon substrate using a two-step electrochemical process, which combines PS formation and electropolishing, as illustrated in figure 3 [22,23,39]. As a first step, a masking polysilicon/SiO₂ bilayer is grown and patterned so as to define the membrane area (figure 3a). A PS layer of the desired membrane thickness is then formed (figure 3b) at the predefined area. In the following step, anodization is switched to the electrochemical dissolution regime by increasing the anodization current above the critical value, J_{critical}. Thus electropolishing is initiated and a cavity is formed beneath the PS layer. Fig. 3 ((d), (e)) shows SEM images of cross sections parallel and perpendicular to such a channel in silicon.
Figure 3. Process steps (a, b, c) for the fabrication of sealed microchannels on a silicon substrate. The first step (a) is the patterning of the masking bilayer. A porous silicon layer is then formed through the mask (b), followed by electropolishing, in order to form a cavity under the suspended porous silicon membrane (c). (d) and (e) show examples of cross sectional scanning electron microscopy (SEM) images of a channel, fabricated on a silicon wafer by the above process. (d) is an image of a cross section perpendicular to the channel and (e) one of a cross section parallel to the microchannel. This technology has interesting potential applications in microfluidics for drug delivery and controlled fluid flow.

6. Micro-Hotplate Technology based on Porous Silicon

Miniaturized silicon thermal sensors use local thermal isolation on predefined areas of a silicon substrate. This permits a local rise of the temperature of several hundreds of degrees, while neighboring areas remain at room temperature. Such miniature thermally isolated areas on a silicon substrate are called micro-hotplates. The basic requirement in micro-hotplate technology is the minimization of thermal losses, so as to get the desired temperature on the micro-hotplate with the minimum power consumption. Different types of micro-hotplate on silicon substrates have been reported in the literature: a) suspended membranes fabricated by back side silicon etching [40], where the membrane is released by etching bulk silicon from the backside of the wafer over a predefined area. The main disadvantage of this technique is that in general the etched silicon region has a conical shape; the top of the cone being
the suspended membrane. Thus the sacrificial area needed is quite large, and this constitutes a drawback towards miniaturization. Another disadvantage is the double side lithography needed. b) Another type of micro-hotplate is made of front side closed-type or suspended-type membranes made of different materials, over a cavity etched in the silicon substrate [41]. In both of the above cases, the thickness of the free-standing membranes made of silicon oxide or silicon nitride is of the order of a few micrometers. Thicker flat layers are difficult to fabricate because of cracking problems related to internal stresses. It is necessary, in order to achieve the desired thermal isolation, to make these films free-standing. An alternative approach is that of porous silicon micro-hotplate technology, since it is possible to fabricate thick PS layers locally on the wafer, without cracking problems [42].

Porous silicon technology offers significant advantages in micro-hotplate technology. It may be used in different ways, as follows:

6.1. COMPACT THICK POROUS SILICON MICRO-HOTPLATES ON A SILICON SUBSTRATE.

The thermal conductivity of porous silicon depends strongly on the porosity and morphology of the material. For a 65% porosity resulting from the anodization of p-type silicon with resistivity in the range of 1-10 $\Omega \cdot cm$, the thermal conductivity is of the order of 1.2 W/m.K [42]. This is similar to that of silicon dioxide (1.1 W/m.K) and 120 times smaller than that of bulk crystalline silicon (145 W/m.K). Compared to silicon dioxide, the advantage of porous silicon is that we can easily fabricate very thick layers, of a thickness of several hundreds of micrometers, locally on a silicon substrate. We can thus achieve the desired thermal isolation by monitoring the PS layer thickness.

A thick porous silicon layer on a predefined area of a silicon substrate constitutes a simple, efficient and reliable micro-hotplate [42-45] (see figure 4a), which offers thermal isolation similar to that provided by complicated membrane microstructures, bridge-type or membranes over cavity. The main advantage of this kind of micro-hotplate is its compatibility with CMOS processing and the planar technology with a compact structure.

The reproducibility in the fabrication and reliability of the structure is much higher than in the case of membrane technologies.

6.2. PS CLOSED-TYPE MEMBRANE OVER CAVITY MICRO-HOTPLATES, FABRICATED IN A SINGLE ANODIZATION PROCESS.

Compact thick PS micro-hotplate technology may be further improved by fabricating a cavity beneath the porous silicon layer, in the same anodization process, using a second step of electropolishing after PS formation. This
technology was described above for the fabrication of sealed microchannels on silicon [23,39,46] (see figure 4b). It has been applied successfully for the fabrication of a silicon micromachined gas flow sensor, as described in [22].

6.3. OPEN-TYPE MEMBRANE OVER CAVITY MICRO-HOTPLATES USING POROUS SILICON AS A SACRIFICIAL LAYER

![Diagram](image)

Figure 4. (a) (b) and (c) show schematic representations of the cross sections of different types of PS micro-hotplate on silicon substrates. (a): Thick compact porous silicon layer, (b): PS layer over a cavity (closed-type membrane), (c): bridge-type PS membrane, (d): Planar view of a suspended PS membrane with supporting beams over an open cavity.

Different designs of thin membranes suspended over a cavity may by fabricated using porous silicon as a sacrificial layer (see figures 4c and 4d). The membrane material may be silicon nitride [47], or polycrystalline silicon [33,34]. The process includes deposition and patterning of a masking layer, local porous silicon formation, deposition and patterning of the membrane material and removal of porous silicon. A critical step in the fabrication process is the minimization of the internal stress within the membrane material, in order to avoid cracking of the membranes. This poses limits on membrane thickness, especially in the case of silicon nitride membranes.

6.4. SUSPENDED POROUS SILICON MICRO-HOTPLATES.

Suspended membranes over an open cavity offer in general minimization of thermal losses and are very appropriate for cases where minimum power consumption is needed for heating a resistor on the micro-hotplate. One such case is that of gas sensors designed to work in an explosive environment. For this application, suspended porous silicon membranes may be fabricated, which are less fragile and more reliable than silicon nitride ones.
A process for the fabrication of suspended porous silicon membranes of different designs has been described [48,49]. It uses the following steps: a) growth of a porous silicon layer locally on the silicon substrate, b) deposition of a lithographic photoresist layer and patterning to open windows around the porous layer, c) isotropic etching of silicon under the PS layer, so as to release the structure and d) photoresist removal. The process flow chart used is illustrated in figure 5. The main innovative step is silicon etching beneath the porous silicon, using a high-density plasma etching process with a high etch rate. Using this process, suspended PS membranes as large as 50x50 µm² have been fabricated, with supporting beams, 25 µm wide and 150 µm long. On top of these, an integrated Pt heater was deposited, and a temperature on the heater of more than 700°C was achieved with an electrical power below 35mW [49].
7. Silicon Thermal Sensors using Porous Silicon Micro-Hotplates

Porous silicon micro-hotplate technology has been used to fabricate silicon thermal sensors for different applications, such as gas flow sensing, gas sensing or acceleration measurements [44,45].

An example of a thermal flow sensor using a compact PS layer micro-hotplate is shown in figure 6. It comprises a porous silicon layer on bulk silicon, on top of which a polysilicon or Pt resistor is integrated. Two series of thermocouples are also integrated on the left and right sides of the heater. The hot contact of the thermocouples lies on the PS, while the cold contact lies on the bulk crystalline silicon.

A gas flow on top of the sensor in a direction perpendicular to the heater causes cooling of one thermopile and heating of the other. The temperature change is measured as a voltage change at the output of the thermopiles. Instead of using a compact PS micro-hotplate, porous silicon over a cavity [22] or suspended PS membrane micro-hotplates may be used with the same heater-thermopile sensor. For the evaluation of the thermal isolation provided by a 40 µm thick PS layer, a comparison of the resistance increase of two similar polysilicon heaters integrated respectively on porous silicon and on a neighboring area of bulk crystalline silicon, as a function of the applied electrical power, has been made [44]. A value of 3.16 Ω/mW was found on porous silicon, while on bulk silicon the rate of resistance increase with power was only 0.16 Ω/mW, i.e. 20 times lower. This is due to the much better thermal isolation provided by the porous silicon. An example of experimental results showing the temperature
Figure 7. Simulation results of the temperature distribution around a heater on bulk silicon (a), on a compact porous silicon micro-hotplate (b), and on a polycrystalline silicon membrane covered with SiO₂ over a cavity (c), after application of a constant heat flow of \(8.6 \times 10^6\) W/m² on a heater (at zero point of the x-axis). We see that on bulk silicon (a), the maximum temperature is \(\sim 38^\circ C\), while it is \(140^\circ C\) on PS (b) and \(\sim 600^\circ C\) on a suspended membrane (c). The form of the distribution is also different in each case.

Figure 8. Experimental results of the temperature of a polycrystalline silicon heater on a 40 µm thick PS micro-hotplate (Δ) and a 20 µm thick porous silicon membrane over a 20 µm deep air cavity (■) as a function of the applied electrical power on the heater.
distribution around a heater at point zero of the x-axis on bulk silicon (a), on a 40 µm thick PS micro-hotplate (b) and on a 2 µm thick polycrystalline silicon membrane covered with 0.5 µm TEOS oxide over a 10 µm deep cavity, as a function of the applied electrical power, is shown in figure 7. We see an important difference in the maximum temperature and the form of the temperature distribution around the heater between the case of bulk silicon, a compact porous silicon film and a free-standing polycrystalline silicon membrane. This is due to the differences in the thermal isolation between these three cases.

8. Conclusions

Porous silicon is a nanostructured material with variable properties tailored by changing the material porosity, the anodization conditions and the type of the anodized silicon wafer. By adequate porous silicon surface modification, the material may become either very reactive or totally passivated and stable with time.

The low thermal conductivity of highly porous silicon finds interesting applications in micro-hotplate technology and thermal sensors.

Porous silicon is also a powerful tool, as sacrificial material, in bulk silicon micromachining and the fabrication of different microstructures of very complicated designs on a silicon wafer. The fabrication of microfluidic channels sealed with porous silicon, using a single two-step anodization process, is also very challenging. This technology opens important possibilities for applications in medicine (drug delivery, controlled drug release, etc.).

9. References


LUMINESCENT NANOPARTICLES: COLLOIDAL SYNTHESIS AND EMISSION PROPERTIES

THIERRY GACOIN
Groupe de Chimie du Solide,
Laboratoire de Physique de la Matière Condensée,
Ecole Polytechnique - CNRS UMR 7643,
91128 Palaiseau, France.

1. Introduction

The aim of this paper is to give a basic understanding of researches performed in the field of nanoparticles. Luminescent nanoparticles will be taken as a representative example of the different strategies that can be used for the elaboration of well controlled particles with optimized properties. The impressive results obtained in this field over the last ten years can certainly be considered as being the base of most ideas that are now applied to elaborate many other systems.

2. Nanoparticles

Usually, the electronic and optical properties of solids do not depend on their dimensions, and the main properties are well described by classical theories of solid state physics. It is nevertheless now well known that this is no longer true when the dimensions of a material are decreased down to the nanometer scale, which is much smaller than many characteristic lengths of physical phenomena: mean free path of electrons, light wavelength, exciton diameter, magnetic cooperative interactions, etc. Although size effects have been known for a long time (e.g. the ruby color of gold colloids discovered by Faraday), the investigation of size effects in solids has received an increasing interest from scientists since the beginning of 1980 [1]. At that time, a lot of effort was devoted to understanding and quantitatively describing size effects in metal, magnetic and semiconductor nanoparticles, the latter case being focused on the understanding of quantum size effects in II-VI compounds [2]. Rapidly, two important observations were made [3]: first, nanometer sized particles cannot be described
simply as an excised fragment of a bulk solid with limited dimensions, mostly because a large fraction of the atoms are localized at the surface of the particles. As a consequence, the physical properties of the nanoparticles are greatly dependent on atoms with a distorted environment, very different from the ones located in the volume of the particles. Second, an investigation of the physical properties of materials in the nanometer size range is very dependent on the synthesis of particles with a very good control of the different parameters which are recognized as having an influence on their properties. The importance of these parameters of course depends on the system under investigation and its physical properties, but in most cases they are related to:
- The size of the particles
- Their shape
- Their surface state
- Their dispersion within a host media
- Their interactions with other systems (molecules, other particles, surrounding medium)

3. Colloidal Synthesis of Nanoparticles

In principle, the correct control of the parameters listed above implies that the particles should have a rather complex structure, corresponding both to the control of their surface states and functionalizations. A perfectly well controlled particle should then consist of a core material covered by two distinct shells (figure 1).

![Figure 1. Schematic representation of the “ideal” nanoparticle](image)

Many works have been devoted to the synthesis of nanoparticles. Nevertheless, good control of the structure can be achieved only on dispersion of particles in a solvent, which preserves the accessibility of their surfaces for further chemical treatments of passivation or functionalization. In this field, colloid chemistry has been shown in many different systems to be a very powerful tool for the elaboration of nanoparticles. Although this chemistry has
been known for a very long time, it is remarkable to notice that tremendous improvements have been achieved in the last ten years, opening new possibilities and large fields of investigation [4].

Colloidal synthesis of nanoparticles always relies on the precipitation of the material from dissolved precursors in solution [5]. Formation of the solid occurs when the concentration of its constituents goes beyond saturation, and follows the nucleation/growth process well described by the famous diagram of LaMer [6]. The main difficulty is the control of the size and dispersion state of the particles. Rapid aggregation of the particles occurs due to strong van der Waals (vdW) interactions, leading to a precipitate of aggregated nanoparticles. Two main strategies may be used against attractive vdW interactions. The first consists of using the electrostatic repulsion between the particles, resulting from the presence of ionic charges on their surfaces. These charges arise either from the ionization of surface groups (e.g. hydroxyls with acid/base properties) or from the surface complexation of the particles with ionic species (e.g. citrate salts). This strategy can only be achieved in dissociating solvents and with low ionic strengths. It is then used almost exclusively for aqueous syntheses, mostly in the case of oxide materials. The second strategy consists of complexing the surfaces of the particles with an organic agent, which will provide a steric hindrance between the particles keeping them far enough apart that vdW interactions are negligible. The nature of the surface complexing agent may be either a polymer or a surfactant molecule, or more generally any compound which may be grafted onto the surface of the particle and strongly coordinated by the solvent. The resulting thick coordinating sphere of solvent molecules around the particles also ensures steric hindrance and stability of the dispersion.

4. Luminescent Nanoparticles

Researches on luminescent nanoparticles were first achieved on II-VI compounds, but historically most studies on these compounds were devoted to the understanding of the quantum size effect and potential applications of the expected large third order susceptibilities in non-linear optics [3]. The latter property was expected to be enhanced due to the electronic structure of quantum sized nanoparticles, which behave as two level systems. It was nevertheless rapidly found that the non-linear optical properties of nanoparticles were much more dependent on excited states in which the charge carriers are trapped at the surface of the particles. It then became very important to study the recombination pathways of excited states in the nanoparticles, and of course luminescence was a good technique for this.

A large amount of work performed for the optimization of the luminescence properties of II-VI compounds led to the idea that these particles could find
applications for this specific property itself. The quantum yields of the optimized particles were indeed found to be competitive compared to usual light emitting dyes, while their inorganic nature made them expected to be much more stable toward photodegradation. These statements were the beginning of much more intensive researches for the elaboration of new luminescent nanoparticles, with the aim of using them for original applications such as light emitting diodes, transparent emitting devices or new biological labels.

5. II-VI Semiconductor Nanoparticles

Many colloidal syntheses of II-VI nanoparticles have been reported. Representative examples are the precipitation in the presence of a complexing molecule (for example a thiol), the precipitation in a microemulsion, and the precipitation in high boiling point complexing solvents (for example trioctylphosphine oxide) [7].

These techniques, and especially the latter one, allowed the production of nanoparticles with a very narrow size distribution in the 2-10 nm diameter range. This made possible the reliable determination of excitonic energies and the correct description of the quantum size effect through theoretical particle-in-a-box or tight binding calculations [8].

Concerning the luminescence properties of the particles, numerous spectra were reported in the abundant literature on the subject, which revealed large discrepancies from one sample to another. It rapidly became clear that the luminescence behavior of the particles is very dependent on their chemical environment. This is illustrated in the figure 2, which presents the luminescence
behavior of CdS particles in solutions containing different chemical species in excess. In the presence of sulfide ions, the emission intensity is very low, while an excess of cadmium salt increases the luminescence, the shape of which is a broad peak at a much lower energy than the band gap. Complexation of the surface cadmium ions with an amine still increases the luminescence intensity, and a blue shift is observed. In the presence of cadmium hydroxide, a new band appears, much closer to the absorption threshold.

All these results indicate a direct effect of the chemical structure of the surface on the luminescence energy and efficiency. Sulfide ions act as hole traps and non-radiative recombination centers, while cadmium ions are electron traps, the energy of which may be modulated by complexation. In the presence of hydroxyl groups, the increase of the energy of surface traps is high enough so that trapping is much less efficient and direct band gap recombination can occur.

The high sensitivity of the luminescence of the particles to the chemical nature of their surfaces is clearly a problem for the investigation of their physical properties, such as the dynamics of the electron/hole recombination, the optimization of the luminescence quantum yields, and the study of non-linear processes. The control of the surface of the particles is not an easy problem, since the atoms at the surface have a large distribution of environments and, more practically, any modification of the surface of the particles may affect their colloidal stability.

Two main strategies have nevertheless been studied for the control of the recombination pathways from the excited states. The first is a passivation of the surface of the particles through the elaboration of core/shell nanostructures. The second does not change the surface state of the particles, but aims to achieve an efficient energy transfer from the delocalized excited carriers to the localized electrons of a doping ion (rare earth or transition metal). These two strategies are shown schematically in figure 3.

Figure 3. Schematic representation of a core/shell nanostructure (left) and transfer of the excitation to a doping ion (right)
6. Core/Shell Nanostructures

Efficient surface passivation of the particles requires the elimination of both electron and hole traps located on their surfaces. As is well known in the case of bulk semiconductors, the best way to achieve maximum surface coverage by a passivating layer is to have it grown epitaxially on the substrate material. This requires that the deposited layer has a crystalline structure similar to that of the substrate material, with a limited lattice mismatch. Furthermore, the passivation efficiency depends on the relative energy of its electronic levels as compared to the bands of the core particle. The passivation effect may be obtained either by an increase of the energy of the trap levels, or by limiting the extension of the core electron and hole wavefunctions at the shell/solvent interface [9].

This strategy was first investigated in the case of CdSe colloids by Brus [10] and Guyot-Sionnest [11], who demonstrated that CdSe particles with high luminescent efficiencies and almost only band to band recombination could be prepared by depositing a thin shell of ZnS on the surfaces of the particles. The strategy was further successfully applied in the case of CdSe particles prepared in TOPO following the method of Bawendi [12-13]. Emission quantum yields up to 60% were then reported, with a variable emission color strongly dependent on the size of the core particles. It should nevertheless be noted that the efficiency of the passivation shell is not complete, since the transfer of the particles into water or protic solvents leads to a strong decrease of the emission yield, down to about 20% [14].

7. Doped II-VI Nanoparticles

The other possibility for decreasing non-radiative surface recombination consists of achieving an efficient energy transfer from the delocalized excited carriers to the localized electrons of a dopant (rare earth or transition metal). This strategy is commonly used in the case of bulk phosphor technology. In the case of II-VI compounds, it is already well known that Mn doping of CdS or ZnS results in a bright emission at around 600 nm, which is characteristic of the \( ^4T_1 - ^6A_1 \) transition of the Mn\(^{2+} \) 3d electrons. This emission occurs after formation of an exciton which transfers its excitation to the 3d electrons of the dopant. Return to the ground state then occurs with the emission of a photon of characteristic energy. Synthesis of CdS nanoparticles homogeneously doped with Mn was achieved by co-precipitation of a mixture of cadmium, manganese and sulfide salts under conditions similar to those used for undoped particles [15]. Incorporation of the Mn ions as a solid solution within the CdS lattice was found to be difficult, mostly due to the difference of solubility between MnS and CdS. Moreover, precise analysis of the number of Mn\(^{2+} \) ions located inside the particles required a careful EPR study, which showed that the maximum Mn content obtained by this method was no more than 5%.
The emission properties of the particles were found to be greatly dependant on their numbers of Mn$^{2+}$ ions. The highest emission yields were observed when the Mn content corresponded to an average of 1 Mn$^{2+}$ ion per particle. In this case, the quantum yield was about 20% and the emission spectrum corresponded to the classic emission from the Mn$^{2+}$ ions. Higher Mn$^{2+}$ contents lead to drastic decreases in the emission yields, as a consequence of Mn-Mn interactions. An interesting result is obtained when considering that due to the poor efficiency of the incorporation of Mn$^{2+}$ into the particles, there is a distribution of the number of ions within each particle of a given sample. For example, a sample with an average of one Mn$^{2+}$ ion per particle contains in fact particles with no Mn$^{2+}$, and particles with two or more Mn$^{2+}$ ions. Assuming a Poissonian distribution of the number of Mn$^{2+}$ ions within the particles, one can estimate that the emission yield of the particles which contain exactly one Mn$^{2+}$ ion is around 60%. This high value shows that energy transfer to the localized excited state of a doping ion is indeed a good strategy to avoid, to some extent, the negative effect of surface states, considering the fact that no specific surface treatment is required.

8. Rare Earth Doped Oxide Nanoparticles

Results obtained concerning the Mn$^{2+}$ doping of CdS nanoparticles show that surface recombination in semiconductors may be somewhat avoided by the rapid localization of the excited states in the volume of the particles. This strategy is in fact the basic idea used in the field of phosphor technology, which aims to synthesize emitting materials for display devices (lamps, TV screens,
scintillators for X-ray imaging, etc.) [16]. Doped chalcogenides are indeed a class a compounds which have been used in emitting devices, but the most commonly used phosphors are oxides, either doped with transition metals or rare earth ions.

Up to now, only a few studies have concerned the elaboration of luminescent oxide nanoparticles. The first reason is that the excellent emission properties of II-VI nanoparticles were discovered rather recently, so that practical applications of luminescent nanoparticles, justifying more extended research, were clearly identified only a few years ago. The second reason is that most of the well known oxide phosphors are prepared through conventional ceramic processing techniques and require high temperature treatments to ensure a good crystallinity of the final compounds. Such treatments are not compatible with the synthesis of well controlled particles, and usually lead to agglomerated powders with large distributions of grain sizes.

There are nevertheless a limited number of compounds that can be crystallized at low temperatures. Among them are vanadates and phosphates that can be prepared by precipitation from soluble precursors and which exhibit high emission efficiencies in the bulk state.

9. Rare Earth Doped Vanadate Nanoparticles: YVO₄:Eu

Yttrium vanadate is a well-known phosphor matrix which can easily be combined with many rare earth ions. Most applications in the bulk state concern Nd (laser crystals) and Eu (red phosphor). In the latter case, UV excitation is absorbed by the vanadates and the excitation is transferred by exchange interactions within the vanadate sub-lattice until it finally reaches the europium emitting ion (figure 5).

![Figure 5](image)

*Figure 5. (Left) Representation of energy transfers in YVO₄, leading to radiative Eu emission \( hν_{em} \) or non-radiative quenching (Q) after UV light absorption by vanadate groups \( hν_{ex} \). (Right) Characteristic emission and excitation spectra*
The optimum europium content in this compound is quite low (about 5%), which is a direct consequence of the efficiency of the energy transfer processes. Higher europium concentrations result in a strong decrease of the efficiency due to quenching effects resulting from Eu-Eu interactions (the so-called concentration quenching effect).

Colloidal synthesis of YVO$_4$:Eu nanoparticles can be achieved by the progressive thermal dissociation of a vanadate/yttrium/citrate complex [17]. The final colloidal suspension consists of well dispersed nanoparticles with an average size of about 8 nm.

![Graph](image)

*Figure 6. Evolution of the luminescence quantum yield as a function of the europium content for Y$_{1-x}$VO$_4$:Eu$_x$ nanoparticles after different chemical and thermal treatments (cp: crude nanoparticles, sp: silica capped nanoparticles, cpd: crude nanoparticles in deuterated water, cp600: crude particles annealed at 600°C, sp600: silica capped particles annealed at 600°C, bulk: YVO$_4$:Eu micronic crystalline powder).*

The emission spectra of the particles are roughly the same as those for the bulk material, except for a slight broadening which is attributed to distortions within the particles. The main differences are in fact observed considering the quantum yield versus europium content curve (curves cp and bulk of figure 6). Firstly, the optimum quantum yield is reduced to about 20%, and secondly the optimum europium content is now in the 20-30% range. Two experiments show that both effects are related to the surfaces of the particles [18]. Firstly, transfer of the particles into deuterated water results in an increase of their emission efficiency by a factor of about 2 (curve cpd of figure 6). This shows that a large part of the non-radiative relaxation occurs through an energy transfer to OH groups, which are well known to quench the emission from rare earth ions [19]. Secondly, the deposition of a thin silica shell on the surface of the particles results in a decrease of the optimum europium content and thus an improvement.
of energy transfers between the vanadates (curve sp of figure 6). This shows that there are non radiative recombination pathways for the excited states of the vanadates, and the silica shell acts as a passivation layer.

Up to now, efficient passivation of the particles has been observed only after thermal treatment of the silicated particles at 600°C. In this case, the optimum europium content does not change compared to untreated particles, but the emission yield increases up to 50%. Such treatment achieved on crude particles, i.e. without a silica coating, leads to particles with a slightly lower emission yield (40%), but with more efficient energy transfers, as can be seen from the lower optimum Eu content. This shows that the silica coating of the particles enhances the removal of surface OH groups, but does not allow relaxation of the strains or defects that somewhat alter energy transfers within the vanadates.

10. Phospate Nanoparticles: LaPO₄:Ce, Tb

Similar colloidal synthesis was achieved in the case of the well known LaPO₄:Ce,Tb green luminescent phosphor [20]. The emission process in this compound is quite similar to that in the vanadates, except that in this case the UV excitation light is absorbed by cerium ions (and not by the phosphate groups of the matrix). Once absorbed, the energy is transferred from Ce to Ce until it is finally transferred to the Tb³⁺ ion.

The obtained nanoparticles have a rhabdophane hydrated structure, which differs from the monazite type of the bulk material obtained by high temperature treatments. The average particle size is around 7 nm.

![Image of excitation and emission spectra](image_url)

*Figure 7.* Excitation (em = 543 nm) and emission (ex = 272 nm) spectra of a LaPO₄:Ce₄5%, Tb₁5% colloid in water
Typical emission spectra are given in figure 7. As expected, the absorption and excitation spectra of the green luminescence (543 nm) are characteristic of the absorption of the 4f-4f5d bands of the cerium. The emission spectrum shows the typical line spectrum of the terbium $^5\text{D}_4 - ^7\text{F}_j$ transitions between 450 and 700 nm. A slight contribution (5% of the total) appears at 350 nm, due to cerium ions whose luminescence is not totally quenched. This spectroscopic behaviour does not show significant differences compared to that of the bulk monazite material. The emission quantum yield is 31% for the green luminescence of the terbium, and 43% if the cerium contribution is added. This is among the highest yields reported for luminescent nanoparticles. Nevertheless, deviations from the bulk behaviour are still noticed, either considering the lower emission efficiency than in the bulk, or the values of the optimum Ce and Tb contents. As in the case of the vanadates, this is interpreted in terms of the surface quenching of both terbium and cerium excited states, which is thought to occur from surface OH species and oxidized Ce ions respectively.

11. Conclusions

This paper has described the different strategies that can be used for the colloidal synthesis of luminescent nanoparticles. The first studies concerned the case of II-VI semiconductors, in which the luminescence is drastically affected by the surface trapping of excited carriers. Two strategies can be used to avoid surface trapping. The first consists of the elaboration of core/shell nanostructures by epitaxial growth of another semiconductor on the surface of the particles. This allows a limitation of the extension of the carrier’s wavefunction at the surface of the particles and leads to a tremendous improvement of the emission. Another possibility consists of doping the nanoparticles with a luminescent ion (CdS:Mn). Rapid transfer of the energy of the excited carriers to the localized electrons of the luminescent ion avoids non-radiative relaxation at the surface of the particles. High luminescent yields are also obtained, with an emission spectrum characteristic of the doping ion. The same strategy of using localized excited states is in fact commonly used for the elaboration of highly luminescent phosphors such as rare earth doped oxides. Recent investigations performed on YVO$_4$:Eu and LaPO$_4$:Ce,Tb show that nanoparticles exhibit high emission yields, which are nevertheless affected to some extent by the surface quenching species.

References


NANOPARTICLES: FUNCTIONALIZATION AND ELABORATION OF MATERIALS

THIERRY GACOIN

Groupe de Chimie du Solide,
Laboratoire de Physique de la Matière Condensée,
Ecole Polytechnique - CNRS UMR 7643,
91128 Palaiseau, France.

1. Introduction

Impressive progresses achieved in the last ten years for the synthesis of nanoparticles allows consideration of numerous original applications in many different fields such as catalysis, optics, magnetic recording or biology. As compared to bulk materials, the originality of nanoparticles comes first from their high surface area and their good optical transparency when they are well dispersed. But it is also now well known that depending on the chemical nature of the particles, new physical properties arise from their small size in the nanometer range as compared to the bulk materials: quantum confinement, plasmon excitation, superparamagnetism, the Coulomb blocking effect, etc.

Considering the case of colloidal nanoparticles, only a few applications can be achieved directly from the as-synthesized suspension, and further work has to be performed for the elaboration of materials. Many different systems may be synthesized, but the majority of the studies are performed on isolated particles, composite materials, or materials obtained by the direct assembly, organized or not, of the nanoparticles.

![Figure 1. Different interactions that may be controlled through surface functionalization of the particles](image-url)
In all cases, the key issue for the synthesis of materials is the control of the interactions between the particles and a host medium, a substrate or other individual species like molecules, other particles or biological systems (figure 1). This control is usually achieved through the so-called functionalization of the particles, which consists of the grafting onto their surfaces of molecules with specific chemical functions. These functions may be chosen either to just ensure the stabilization of the particles by playing on dispersion forces, or to allow their binding to more or less specific sites of the target substrate.

2. Functionalization of Nanoparticle Surfaces

The main issue of nanoparticle functionalization is to cover its surface with a molecule that possesses the appropriate $F$ functions depending on the interactions that are required for further processing (figure 2).

![Figure 2. Schematic representation of the functionalization of a particle in order to control its interactions with a substrate](image)

Post functionalization of the particles then requires the grafting, onto the surfaces of the particles, of a molecule having a structure which can be described as $C-R-F$. The $C$ group ensures the binding of the molecule at the surface, mainly in two different ways.
The first one is the direct grafting of the $C$-$R$-$F$ molecules by complexation of surface cations with the $C$ group (figure 3 left). For example, thiol, phosphine oxide, phosphonates or carboxylates groups have commonly been used in the case of chalcogenides, oxide nanoparticles and noble metal nanoparticles. The complexing strength of the $C$ group must be high enough to ensure maximum surface coverage. This is of particular importance, especially when the $C$-$R$-$F$ molecule is grafted in substitution to the complexing agents that have previously been used for the synthesis of the particles (e.g. TOPO molecules for CdSe nanoparticles). In that sense, it appears as very interesting to use polydentate ligands, like dithiols or oligomeric phosphines which bind much more strongly to the surfaces [1].

A second strategy consists of using a silane as the $C$ group. Hydrolysis/condensation reactions lead to the formation of a silane coating around the particles with a fraction of F groups outside (figure 3 right). This process has been used in many systems, mostly oxides [2], but it has also been investigated in the case of chalcogenides [3]. Its main advantage comes from the large number of commercially available silane coupling agents, the chemistry of which is well documented. Moreover, the core/shell structure ensures a strong binding of the functional groups with a high surface coverage. The main problem is that there must be an affinity between the silane and the surface of the particle to ensure that the precipitation of the silane coating occurs on the surfaces of the particles and not as isolated clusters. In all cases, special care must be taken for the elimination of such unavoidable clusters.

Other functionalization processes have also been used, among which the encapsulation with a polymer which possesses both the $C$ and the $F$ function. Another interesting approach has been developed recently in the case of TOPO capped CdSe/ZnS particles. It consists of keeping the TOPO molecules, and grafting a functionalization molecule in which the $C$ group is a long alkyl chain which interacts with the octyl groups through hydrophobic interactions [4,5].

Figure 3. Schematic representation of two strategies for the functionalization of nanoparticles: direct grafting (left) and encapsulation with a silane (right)
In all cases, it must be noted that functionalization of the particles necessarily yields a drastic change of their surfaces. The choice for the functionalization function must be a compromise between having the maximum number of $F$ groups and preserving the stability of the particles in their dispersion media. In some cases, colloidal stability may be improved by playing on the chemical nature of the linking R radical of the $c$-$R$-$F$ molecule. For example, it has been shown that the aqueous stability of CdSe nanoparticles can be greatly improved by using PEG functions [6].

Another point is that it is quite difficult to obtain a precise determination of the exact number of $F$ groups that are effectively attached to the surfaces of the particles. A large part of the work for the functionalization of nanoparticles is usually devoted to this problem. Many analytical techniques may provide complementary information (NMR, infra-red spectroscopy, thermogravimetric analysis), but non grafted molecules must be carefully removed.

3. Materials from Nanoparticles

3.1 SINGLE NANO PARTICLES

Because of the development of near field microscopy techniques and confocal microscopies, more and more studies are performed directly on single nanoparticles. The purpose was initially to get information on the physical properties of single nanoparticles, avoiding the inhomogeneous broadening of the signals coming from an assembly of particles. Recently, an original application of single nanoparticle optical microscopy is their use as fluorescent labels for the in-vitro or in-vivo tracking of the individual actions of biomolecules [7]. Organic fluorescent compounds have been extensively used for this purpose, but their application is severely limited by their rapid photobleaching. Promising results have been obtained using semiconductor quantum dots, despite the fact that their water solubilization is complex and that their use for long-term single-molecule tracking is hampered by their fluorescence intermittency [8].

Other systems have also been investigated more recently, among which are rare earth doped oxide nanoparticles. As an example, a recent study was devoted to the study of the localization of $Na^+$ channels in live cardiac myocytes [9]. Specific interactions are expected through the functionalization of the particles with guanidinium groups, which are the active parts of complex toxins (tetrodotoxin and saxitoxin) that are well known for specifically plugging the $Na^+$ channel mouths. The luminescent oxide particles used in this work are $YVO_3$:Eu nanocrystals prepared following a simple aqueous colloidal route [9]. Their emission spectra consist of narrow lines with a main contribution at
617 nm. Their emission yield is about 25% with an emission lifetime of 0.7 ms. Surface functionalization of the particles was achieved through the covalent grafting of guanidinium groups on a thin shell of polymerized silane-bearing epoxy groups (figure 4 left).

![Figure 4. Schematic description of nanoparticles functionalized with guanidinium groups (left) and an optical image of isolated nanoparticles deposited on a glass slide (right)](image)

The biological activity of the guanidinium-functionalized nanoparticles was compared to that of saxitoxin. Action potentials were recorded by means of intracellular microelectrode techniques. These experiments showed that functionalized nanoparticles do indeed block the Na\(^+\) channels similarly to saxitoxin, whereas no effect was measured using nanoparticles without guanidinium groups or with free guanidinium groups alone.

Optical detection of particles deposited on glass slides can be achieved quite easily by using wide field fluorescence microscopy (figure 4 right). Individual imaging of the nanoparticles on cardiac cell membranes confirmed the interactions measured previously by electrophysiology experiments. Moreover, the absence of particles bound to the membrane when the Na\(^+\) channels are previously blocked by the saxitoxin demonstrates the high specificity of the interactions between the particles and the channels. It may then be concluded that functionalized YVO\(_4\)::Eu nanoparticles mimic the blocking effect of the saxitoxin and behave as artificial toxins. Such particles then provide a versatile tool for long-term single-molecule tracking, allowing further work on the dynamic and the aggregation behaviour of Na\(^+\) channels on excitable cell membranes.

3.2 COMPOSITE MATERIALS

Many applications of colloidal nanoparticles require their incorporation within a solid polymer matrix. The main advantage is that it allows stabilization of the
particles in a solid material which can be further handled and used for the fabrication of devices. Depending on the volume fraction of particles, the host matrix can be seen either as a dispersing medium or simply as a binder, which is only devoted to ensuring the mechanical resistance of the composite material. Bulk monoliths (i.e. solids with dimensions of centimeters or more) may be synthesized. However, an increasing number of applications use thin films deposited on various substrates by spin, dip or pulverization coating. The main advantage of thin films (compared to bulk composite materials) is that the properties of the coating come in addition to those of the substrate (which can be not only mechanical, but also optical, electrical, etc.). Moreover, deposition of thin films can be achieved on large complex surfaces, using relatively small amounts of matter, which is of importance considering the high cost of colloidal synthesis on an industrial scale.

There are many examples of applications, such as the elaboration of magnetic recording media, optical filters, transparent luminescent materials, anti-reflective coatings, photocatalytic film, etc. Another important class of applications concerns the loading of polymers in order to improve their mechanical properties.

The main difficulty for the elaboration of composite materials is of course the dispersion of the particles within the host medium with a high volume fraction. In general, incorporation of the nanoparticles is achieved from colloidal suspension, and more rarely from dispersible powders. The host medium is an organic or inorganic polymer (e.g. sol-gel silica), and the incorporation of the particles is achieved into a liquid solution of at least partially polymerized precursors. The final composite material is further obtained either by letting the polymerization process going on or through the evaporation of the solvent. In most cases, the stability of the particles during the formation of the solid is preserved if there is a specific interaction between the particles and the polymeric network of the matrix. This interaction is controlled by specific chemical functions following the strategy described for the functionalization of the particles. In some cases, the host polymer itself bears chemical functions that can react with the surface of the particles, but more generally the particles have to be functionalized. For example, incorporation of chalcogenide nanoparticles in sol-gel silica matrices was successfully achieved using a preliminary functionalization of the particles with a silane bearing a thiol group. The silane can polymerize with the other silane precursors of the matrix, while the thiol group complexes the surface cations of the particles. The resulting strong interaction between the particles and the growing silica clusters allows one to obtain composite materials with high volume fractions of particles (up to 30%) [10]. The general process is summarized in figure 5.
Figure 5. Example of a process used for the incorporation of nanoparticles in a sol-gel silica matrix.

3.3 SOL-GEL MATERIALS FROM COLLOIDS

The colloidal processing of ceramics is an emerging field of research in materials science [11]. Controlled aggregation of highly concentrated colloids provides the opportunity to reliably produce ceramic films and bulk forms with optimized micro- or nano-structures. In this field, the elaboration of optically transparent materials represents the ultimate challenge, which has led to the development of new chemical processes such as sol-gel chemistry [12]. The synthesis of solid materials made from nanoparticles as building blocks involves the aggregation of the particles to form a solid network. A transparent material will be obtained, rather than a diffusive powder, only if the aggregation is sufficiently well controlled that the physical structure of the aggregates preserves the homogeneity of the material in the visible wavelength range.

Theoretical aspects of colloid aggregation have been the subject of a large number of investigations based on experimental results gathered from model systems such as gold [13] or silica [14] colloids. Most of these works use the formalism of fractal geometry to give a mathematical description of the morphology of the aggregates. Their main characteristics are then found in their fractal dimension $D_f$, which determines the variation of their mass, $m$, as a function of their radial dimension, $r$, through the relation $m = r^{D_f}$. A $D_f$ value of 3 corresponds to dense solids or solids with regular porosities, whereas lower values are found for lacunar aggregates.

The sol-gel processing of transparent materials relies on the controlled formation of such lacunar aggregates within the solution which is called a "sol". Percolation of the aggregates results either from rapid solvent evaporation (deposition of thin films by spin or dip-coating) or simply by their continuous
growth within the sol. This moment corresponds to the sol-gel transition, a gel being a rigid skeleton of particles enclosing a continuous liquid phase. The careful removal of the solvent from the liquid phase yields the final solid material. This can be an aerogel with a very low density if drying is achieved under supercritical conditions, or a dense xerogel if drying is made slowly at a low temperature (20-100°C) to avoid fractures from capillary stresses [12].

![Figure 6. Sol-gel aggregation of CdS nanoparticles through their controlled aggregation induced by the progressive removal of surface thiol groups.](image)

Until recently, sol-gel chemistry was restricted to a limited number of compounds, mostly oxides, and especially silica. The main barrier for the extension to other compounds stems from the difficulty of the synthesis of highly concentrated colloids with a controllable state of dispersion. Numerous works performed on the colloidal synthesis of chalcogenides have nevertheless allowed the synthesis of concentrated suspensions. For example, it has been shown that surface complexation of CdS nanoparticles with 4-Fluorophenylthiol allows one to stabilize highly concentrated suspensions in organic solvents such as acetone [15]. It is well known that thiol can be easily oxidized under soft conditions into disulfides. Controlled oxidation of the stabilization thiolates in concentrated CdS colloids leads to the slow aggregation of the particles. Fractal aggregates of particles are formed and continuously grow until the sol turns into a gel [16] (figure 6). In the case of concentrated sols, no visible light diffusion is observed while the sol turns into a gel, showing that the fractal aggregates do not have any characteristic structural dimensions of the order of the visible light wavelength.

Although large quantities of colloids would be required for the development of such synthetic processes, this study on chalcogenide nanoparticles could
open the way toward the development of sol-gel chemistry for the elaboration of bulk transparent chalcogenide materials.

### 3.4 ORGANIZED NETWORKS OF NANOPARTICLES

Many investigations have been performed in the last 20 years to understand the physical properties of nanoparticles considered as individual objects. Over the last few years, the question has been raised of how to study effects resulting from physical interactions between the particles, i.e. effects which depend on the distance between two particles when this distance is less than a few nanometers. It can be, for example, plasmon coupling between metallic nanoparticles, charge transport between semiconductor quantum dots, or magnetic interactions between magnetic particles.

As for the investigation of size effects, which was limited by the size distribution of the particles, the study of physical effects resulting from particle-particle interactions requires either the use of near field microscopies or the development of materials in which the particle-particle distance is well known and with a narrow distribution. In this context, there is an increased interest in the elaboration of periodic nanostructures, in which the particles are organized into 2D or 3D periodic networks with a lattice parameter that can be varied in the nanometer range.

Different strategies can be used for the realisation of such nanostructures. The template approach consists of forming the particle within a medium which already has a periodic structure. However, it is although known in some examples that colloidal nanoparticles can assemble themselves directly into periodic arrays, though a process known as self-organization which is similar to crystallization. Well known examples of such spontaneous arrangements are colloidal crystals [17], obtained from highly charged latex particles in solution, and artificial opals made through the slow decantation of silica particles [18]. In both cases, the important factors allowing self-organization of the particles is their high monodispersity and their high stability in the dispersion medium. Recent developments of colloid chemistry have allowed the synthesis of particles with a very good monodispersity, which are usually surface functionalized with long alkyl chains so that they can be stabilized in an organic solvent with high concentration [19]. It has been shown in many examples that the slow evaporation of the solvent leads to spontaneous formation of crystals of particles, either 2D [20] or 3D (figure 7) [21-22]. The main problem is that the dimensions of the organized domains are usually small (less than a few hundreds of nanometers). As for classical crystal growth, improvement may be obtained through the careful control of the nucleation/growth of the structure, which can be optimized to some extent by playing on the experimental conditions, and especially the evaporation rate of the solvent and the surface
functionalization of the substrate. As in the work reported by Lin et al. [20] on gold particles, it is then possible to obtain 2D structures with an almost perfect organization over several microns.

![2D superlattice of gold nanoparticles](image1.png)

**Figure 7.** (left) 2D superlattice of gold nanoparticles (after Lin et al. [20]); (right) colloidal crystals of CoPt$_3$ nanoparticles (after Shevchenko et al. [19])

4. Conclusions

Most applications of colloidal nanoparticles require the control of their interactions with a host medium, a substrate or other individual species (molecule, particles, etc.). This control is usually obtained through the surface functionalization of the particle, which consists of the grafting of a chemical function $F$ that will determine the nature and the strength of the interactions. Once functionalized, the particles may be used either directly (for example in biological labeling), or for the development of different materials: composites are obtained through dispersion in the host medium; transparent gels and xerogels are formed through controlled aggregation of the particles, and organized networks from their self assembly.

References

ORGANIZED MESOPOROUS THIN FILMS

THIERRY GACOIN
Groupe de Chimie du Solide,
Laboratoire de Physique de la Matière Condensée,
Ecole Polytechnique - CNRS UMR 7643,
91128 Palaiseau, France.

1. Introduction

Sol-gel chemistry is now a well-known method for the development of materials through “soft chemistry” routes. Its basic principle relies on the controlled polymerization or precipitation of inorganic materials from molecular precursors in solution [1]. Also many oxide compounds have been synthesized. Silica remains one of the most important, mostly because the chemical properties of silicon allow a remarkable control of the polymerization processes. Moreover, a large number of silicon precursors are known, and the stability of the Si-C chemical bond opens up the way towards inorganic/organic materials.

Sol-gel synthesis of silica is usually achieved from alkoxides through hydrolysis/condensation reactions of polymerization (figure 1).

Figure 1. Schematic description of the sol-gel synthesis of transparent silica matrices
The structure of the obtained solid depends strongly on the pH of the water used for hydrolysis, which governs the relative kinetics of hydrolysis and condensation reactions. Basic media allow the synthesis of remarkable silica particles such as described in the famous Stöber Process [2], while acid hydrolysis leads to homogeneous polymerization which allows the synthesis of transparent materials. As they are synthesized at low temperature, these latter materials have found numerous applications as host matrices for many organic molecules, in particular dyes with specific optical properties [3].

Within the last ten years, and starting with the pioneering work of Kresger and co-workers [4], a new field of applications concerns the association of sol-gel chemistry and surfactant assemblies. Surfactant molecules have an amphiphilic structure, which means that one part of the molecule is hydrophilic (anionic, cationic or neutral) and the other one is hydrophobic (hydrocarbon chains or polyalkyl ethers). It has been known for a long time that such molecules self assemble in the presence of water and oil (usually a hydrocarbon) to form different structures depending on the composition in a ternary phase diagram. Some of these structures present a remarkably high degree of organization (figure 2).

![Diagram of classic structures](image)

*Figure 2. Classic structures that have been identified in many surfactant/water/oil phase diagrams with a low concentration of oil and an increasing concentration of surfactant from left to right.*

The idea is then to stabilize surfactant assemblies by achieving the sol-gel polymerization of an inorganic compound around the micelles. After complete drying of the material, the surfactant may be withdrawn (for example by calcination at 450°C) so that the final material presents a porosity which is the replica of the initial surfactant structure. Until now, most work has been devoted to silica, but many other oxides have also been investigated, such as TiO₂ and ZrO₂.
Organized mesoporous materials are then characterized by a porous structure with the following general characteristics:
- There are two kinds of pores: micropores and mesopores.
- Micropores are located within the oxide walls between the mesopores. They result from the incomplete condensation of the oxide precursor. Their dimensions are typically of the order of a few angstroms.
- Mesopores are the negative structure of the micellar organization existing just after the synthesis of the material.
- The dimensions of the mesopores are typically in the 3-10 nm range. They may represent more than 30% of the total volume of the material.
- The mesopores are organized through a periodic network, with a textured structure which depends on the experimental conditions used for the synthesis of the material and the nature of the surfactant which has been used.

The original structure of organized mesoporous material forms the basis of a huge number of works in the last ten years, motivated by numerous applications, most of which aim to take advantage of the very high specific surface of the materials and the original structure of the pores. Material processing may be achieved to use the properties of the materials in many different forms such as powders, fibers, thin films or monoliths [5].

Thin films of organized mesoporous silica may find numerous applications for the surface functionalization of various substrates (glass, fibers, plastics, semiconductors, etc.). One class of applications concerns the use of the very high specific surface of the mesoporous films. This allows the chemical grafting with a very high density of species with a specific activity (catalysis, stain, hydrophobic coating, etc.). A second class of applications concerns the property of the porous coating to have a very low dielectric constant and refractive index. Finally, ordered mesoporous films may be used as templates for the elaboration of periodic networks of particles which are grown inside each pore. This case allows more fundamental research on collective effects in the physical properties of periodically assembled nanoparticles of metals, semiconductors or magnetic materials.

2. Organized Mesoporous Thin Films

The elaboration of mesoporous silica films has been the subject of many investigations, mainly using spin or dip-coating methods of deposition [6-8]. In a typical procedure, a silica sol is prepared by acidic hydrolysis of tetraethoxysilane (TEOS) in ethanol, and further aging to achieve a partial condensation to form silica aggregates. The surfactant is added into this sol just
before its deposition, with a concentration corresponding to a given surfactant/silicon molar ratio. The obtained solution is deposited on the substrate, for example by spin or dip coating (figure 3). During the deposition process, the ethanol evaporates so that the volume fractions of both the surfactant and the silica aggregates increase. As the silica phase is polar and contains water, micellar aggregation of the surfactant occurs, followed by self assembly of the micelles. As evaporation goes on, the structure evolves due to the increase of the surfactant volume fraction, until the moment when the structure is fixed by the sol-gel transition of the percolating silica aggregates. After complete drying of the film at moderate temperature, the surfactant may be withdrawn by calcinations at typically 450°C.

![Surfactant](image)

*Figure 3. Spin coating deposition of a mesoporous thin film*

Structural characterization of the porous structure may be achieved by using X ray diffraction, grazing incidence small angle X ray scattering, and electron microscopy. In the particular case when the surfactant used is the classic CTAB (cetyltrimethyammonium bromide), it was found that the structure of the films strongly depends on the surfactant/silica molar ratio, and the time for which the silica sol has been aged before deposition. A diagram of the different phases obtained was established, showing unsurprisingly that the structure depends on the relative volume fraction of the surfactant and the silica phase [9] (figure 4). This relative volume fraction depends on the surfactant/silicon molar ratio, and on the size of the silica aggregates, which determines the volume fraction of the polar phase at the moment of their percolation. The vapour pressure in the environment of the films during the deposition and drying steps was also found to be a parameter determining the quality of the structure, probably since it determines the amount of water in the film at the sol-gel transition and so the volume fraction of the polar phase [10].

Three different structures were obtained: the cubic and the hexagonal ones were classically observed in thermodynamically stable surfactant assemblies in solution, but the 3D hexagonal one appears to be almost original, and its formation is directly related to the stabilization of a transient association of micelles. In all cases, the structures are textured. For example, the c axis of the
3D hexagonal phase is always perpendicular to the surface of the substrate. The structure of the film is almost perfect for thicknesses less than around 400 nm, and in the plane domains extend for a few hundreds of nanometers.

![Diagram of phases obtained using CTAB as a surfactant template](image1)

**Figure 4.** (a) Diagram of the phases obtained using CTAB as a surfactant template (diamonds: 3D hexagonal, squares: cubic, triangles: 2D hexagonal). (b) Cross sectional view by electron microscopy of a film with the 3D hexagonal pore structure. (Inset, c) Power spectrum of the same picture

The same method of elaboration may be achieved with other surfactant templates, among which are block copolymers such as PPO-PEO-PPO (PPO = polypropylene oxide, PEO = polyethyleneoxide). As an example, perfectly organized films with an orthorhombic pore structure were obtained using pluronic PE6800 [11] (figure 5).

![Transmission electron microscopy image of a film made with the triblock PPO-PEO-PPO PE6800 copolymer](image2)

**Figure 5.** Transmission electron microscopy image of a film made with the triblock PPO-PEO-PPO PE6800 copolymer.
3. **Application of Organized Mesoporous Thin Films as Templates for the Elaboration of 3D Arrays of Nanoparticles**

It is now well known that the physical properties of materials may be drastically modified when considering particles with sizes in the nanometer range. A huge amount of work has been achieved in the last 30 years for the synthesis of nanoparticles with a tunable size and a narrow size distribution. This allowed a good physical description of many size effects such as plasmon resonance in metal particles, the quantum size effect in semiconductors and superparamagnetism in magnetic oxides or metals.

In the last few years, an increasing amount of work has been devoted to the study of new effects that may result from the collective interactions of nanoparticles separated by less than a few nanometers. Experimental results may be obtained only on materials containing monodisperse nanoparticles separated by a controlled distance. The ideal structures for such studies are then 2D or 3D organized networks of particles.

Up to now, most methods for the elaboration of such structures rely on the self assembly of monodisperse colloidal nanoparticles. Nice results have thus been obtained, for example on gold [12], CdSe [13] or CoPt₃ [14]. Nevertheless, such processes are still limited to a few compounds for which the synthesis is very well controlled. Moreover, the coherence length of the structures is usually small, typically of the order of a few hundreds of nanometers.

Another strategy consists of taking systems that are well known to form organized networks, and using them as templates for the elaboration of ordered arrays of nanoparticles. Many different systems have been investigated, such as artificial opals [15], ferritin [16] or anodized aluminium [17]. Mesoporous thin films are also good candidates for this purpose, since their elaboration may be achieved quite easily over large surfaces. Moreover, their structures and pore sizes and shapes may be varied by playing on the different parameters of their synthesis.

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![Figure 6](image_url). Principle of the use of mesoporous thin films as templates for the elaboration of ordered networks of particles (left). Porous structure of the film, showing its meso and micro porosity (right).
The basic principle is then to achieve the precipitation of nanoparticles in the mesopores of a silica film synthesized as previously described. Formation of the particles should be achieved after the impregnation of the films with precursors that are allowed to diffuse over all the film thickness thanks to both meso and micropores (figure 6). The precipitation process has to be optimized so that each pore is finally filled with one particle, within all the film thickness.

3.1 3D ARRAY OF CdS NANOPARTICLES

CdS nanoparticles have been widely investigated, and their optical properties are well understood in term of quantum confinement [18]. Size effects are clearly visible from the absorption spectra of the particles, in which the absorption threshold changes from 530 nm for particles with diameters larger than 8 nm, down to 350 nm for 1 nm particles [19].

Precipitation of CdS within the pores of the films may be achieved in a three step process [20]: (a) impregnation of the film with a solution of Cd$^{2+}$ ions; the pH of which was optimized to ensure their complexation by the silanol groups; (b) washing the film to remove any excess Cd$^{2+}$ ions; and (c) precipitation of the CdS particles by rapid injection of H$_2$S into the vessel containing the films. This cycle is repeated until the film is saturated, as monitored by its absorbance spectra.

![Diagram](image-url)

*Figure 7. Evolution of the X ray diffraction diagram (left) and absorbance spectra (right) of a mesoporous film after each cycle of CdS precipitation. Inset: Evolution of the size of the particles as deduced from their onset of absorption.*
After each cycle, the film is studied by X ray diffraction. The main peak is characteristic of the periodic porous structure [7]. Its intensity strongly decreases during the first cycle, and then slowly increases again. This is attributed to an inversion of the electronic contrast of diffraction, due to the fact that the pores are progressively replaced by CdS, which has a higher electron density than the sol-gel silica walls around the pores. The evolution of the absorbance spectra of the same film clearly shows the typical spectra from quantum confined CdS particles. The absorption onset shifts to the red after each cycle of impregnation, which attests for the growth of the particle. The particle size may be quantified using well-established size/gap correlations [17], which shows that saturation is observed when the particles have a diameter of about 3.5 nm. This size corresponds well with the dimension of the mesopores in the empty film. Transmission electron microscopy imaging of the empty and filled films in transverse section confirms that each pore is filled with a CdS particle of roughly the same size. The same effect of contrast inversion is observed as for X ray scattering experiments, since for a given defocalization of the microscope, the CdS particles appear as black dots (figure 8, right), while empty pores correspond to white dots (figure 8, left). Note that the contrast of the CdS particles comes both from their electronic density and their diffraction.

Figure 8. Transmission electron microscopy image of an empty (left) and a CdS filled (right) film (transverse section). The scale bar corresponds to 30 nm. Inset: high resolution image of a few CdS particles.

3.2 3D ARRAY OF METAL NANOPARTICLES

The same process as for CdS nanoparticles was adopted for gold and silver. Reduction of the Ag⁺ was achieved by thermal treatment of the films at 100°C under a dilute atmosphere of hydrogen [21]. The first results clearly showed that the nanoparticles were localized anywhere in the film without any relation to the mesoporous structure (figure 9a). Moreover, their size distribution was broad, and no saturation could be observed (i.e. the absorbance of the film grew continuously after all impregnation cycles).
This problem is attributed to a high mobility of the silver ions within the film, and the difficulty of having one silver particle nucleating in each pore. In fact, it is the basic principle of photography [22] that the reduction potential of silver ions at the surface of existing particles ($E^0[Ag^+/Ag_{bulk}] = +0.8 \text{ V/NHE}$) is much more favorable than the reduction of silver ions to silver atoms or very small aggregates of silver atoms ($E^0[Ag^+/Ag_0]=-1.8 \text{ V/NHE}$).

Improvement of the material could be obtained by decreasing the mobility of the silver ions in order to limit the growth rate of the particles. Diffusion of Ag$^+$ ions occurs mainly through the silanol groups located at the surface and inside the silica walls around the mesopores. Grafting of trimethylsilyl groups (SiOH → Si-O-Si(CH$_3$)$_3$) was achieved just after the first impregnation with the silver ions in order to both reduce the number of silanols and create a hydrophobic barrier between the mesopores. Such grafting is easily made by just letting the films in the presence of hexamethyldisilazane vapors [19]. After this treatment, the size distribution of the Ag particles appears much narrower than in the untreated films and almost all particles are clearly located on the initial mesopores. Meanwhile, not all the pores are filled with a silver particle after the first reduction process, and further impregnation steps (still possible using hydro-alcoholic solutions because the film is hydrophobic) only leads to the growth of already existing particles. Improvement must then be found for this process, especially in order to increase the silver loading in the film after the first impregnation.

4. Conclusions

This paper gives an overview of research in the field of organized mesoporous thin films. Such films are synthesized by sol-gel polymerization of an oxide network (especially silica) around highly organized micellar assemblies. The
removal of the surfactant template after the complete drying of the films leads to an organized porous network which is a replica of the initial micellar template. The sizes of the pores, their shapes, and their periodic arrangements depend strongly on the nature of the surfactant which has been used, as well as on the experimental conditions of synthesis. Such films may be used either for their high specific surface to functionalize substrates, for their optical properties (low refractive index) or as templates for the elaboration of 3D ordered networks of nanoparticles.

References

PHOTOVOLTAICS IN THE WORLD

STANISLAW M. PIETRUSZKO
Centre of Photovoltaics
Warsaw University of Technology
IMiO PW, Koszykowa 75, 00-662 Warsaw, Poland
E-mail: pietruszko@imio.pw.edu.pl

1. Introduction

Photovoltaics is positioned to meet the energy-sector demands worldwide in the coming 20 years. It has significant values: it is an inexhaustible resource, available anywhere, clean and noiseless. Today, the cost of PV electricity is too high for bulk power production. The use of renewable energy sources combined with a rational use of energy represents a fundamental vector of a responsible energy policy for the future. Because of their sustainable character, renewable energy technologies are capable of preserving resources, of ensuring security and diversity of energy supply and providing energy services, virtually without any environmental impact. It becomes more and more obvious that the use of renewable energy sources, in combination with very ambitious energy conservation schemes, will be required very soon by environmental concerns rather than by the exhaustion of fossil fuel reserves, although that will be also a problem to consider several decades from now.

With the current technology and business evolution path, solar photovoltaics (PV) will have considerable impacts on the environment, energy security, and economy - the three prevailing drivers to renewables considerations and investments in our 21st century world. Positive impacts on the environment (including CO₂ mitigation), economic values (industry size), employment opportunities (jobs), and energy contributions (gigawatt significance, market sectors) are forecast [1].

Today, the cost of photovoltaic (PV) electricity is still too high for bulk power production in utility grids. However, for peak power applications and local grid support, PV electricity may become cost-effective in the near future, especially in southern Europe and the USA. PV electricity already has an important natural market in world-wide off-grid applications. This market has been quickly expanding in recent years.
2. Status of the World's Photovoltaics

Photovoltaic systems were the first used commercially in the late 1950's, for powering satellites for space applications. The need for a highly reliable, lightweight power source for satellites was an important driving force in the early evolution of PV systems, and the tremendous technological progress made during the 1960s helped to establish their credibility for terrestrial applications. Despite these advances, photovoltaics in the 1970s was still too expensive for most terrestrial uses. However, in the mid-1970s, rising energy costs, sparked by a world oil crisis, renewed interest in making PV technology more affordable. Since that time, the costs of photovoltaic devices have fallen considerably, and the range of terrestrial PV applications has grown accordingly.

The prices (in US$/W) of PV modules have shown a sharp fall since the 1970s, and an exponential increase in their production. The world market for photovoltaics is growing rapidly, at about 35% annually over the last five years. Total production of PV modules worldwide reached 742 MW in 2003, jumping 32% from 562 MW in 2002 (Fig. 1) [2].

![Figure 1. PV Cell/Module production in 2003.](image)

This reflects very strong growth in virtually all PV markets, such as telecommunications, remote power, utilities, agriculture and building integrated PV. The average growth of the photovoltaics market is comparable to the growth of the microelectronics market in its early stages of development. The latest top-ten ranking producers are Sharp, Kyocera, BP Solar, Shell Solar, RWE (ASE), Mitsubishi, Isophoton, Sanyo, Astropower and Q-Cells (Fig. 2) [2].
In the countries belonging to the International Energy Agency (IEA), almost 1.3 GW of PV power had been installed by the end of 2002. The majority of the rise in the installed power is due to the continued dramatic increases in Japan, being joined by a significant increase in Germany. The continued high rate of installation in Japan promotes this country to that with the highest installed power per capita (5.0 W/capita), above Germany (3.37 W/capita) [3]. The rapid growth in grid-connected distributed applications is driven mainly by the large, government or utility supported, programmes with financial incentives in Japan, Germany, the USA and the Netherlands, which generally focus on PV in the urban environment.

Photovoltaic devices are used in four principal areas: consumer products, stand alone systems, utility applications and space applications. Millions of small PV systems (producing from a few miliwatts to a few watts) currently power watches, calculators, toys, radios, portable TVs and a great variety of other consumer goods. Solar cells in these systems are typically made using thin-film amorphous silicon.

Until 1998, the greatest percentage of PV systems installed were for off-grid applications producing from a few watt-hours to a few thousand watt-hours. They are mainly used in isolated sites, where all means of power generation are expensive, and where PV offers a clean, silent and very reliable power supply. Stand-alone PV systems are used in automated applications such as highway lighting, navigational buoys, lighthouses, telecommunication repeater stations, and weather stations. These stand-alone
PV systems have proven to be reliable, maintenance-free, and cost-effective power sources. Also, tens of thousands of stand-alone homes world-wide now rely on PV systems for most or all of their electrical needs. Solar electricity provides power for water pumps, refrigerators, communications, etc.

The costs of PV systems range from 6 US$/W to over 12 US$/W, giving life-cycle costs for PV-generated electricity from 0.25 US$/kWh to over 1 US$/kWh, depending on the available insolation and financing schemes. These costs make PV an economically advantageous choice for a large range of applications where the electric grid are not readily available, replacing batteries and small engine generator sets in applications from telecom repeaters to rural households.

Photovoltaics is very much a global market. World annual module production is forecast at 2.4 GWp by 2010. Reaching this annual production goal would generate direct employment of several tens of thousands of man-years. Between now and 2010, demand side requirements are expected to change so that a far higher proportion of PV sales will be for grid-connected applications.

The number of worldwide PV installations is steadily growing, due to improvements in the technology and reductions in the cost. The target for installed PV power in Japan in 2010 amounts to 4.8 GW. The US PV Roadmap assumes 3 GW of installed power in 2010, and 15 GW in 2020. The target for the cumulative photovoltaic systems capacity installed in the European Union by 2010 is 3 GW [4].

3. Technology

The workhorse of the photovoltaic industry over the past decades has been bulk crystalline silicon solar cells. Recent investments in the research and development of monocrystalline and multicrystalline silicon wafer-based technologies, as well as in related silicon ribbon and sheet approaches, ensure that this role will be continued in the future. Currently, all silicon technologies together have a market share of about 97%. The remaining 3% is divided between thin films not involving silicon, especially cells based on the chalcogenides Te and Se in the form of polycrystalline thin-films of CdTe and CuInSe2 (Fig. 3) [5].

3.1 MONOCRYSTALLINE AND POLYCRYSTALLINE SILICON

Crystalline silicon technology is a well-established one. This means that technical progress can be taken-to-market faster than in any other photovoltaic technology. Crystalline silicon (x-Si), Czochralski-material (CZ), and multicrystalline cast (m-Si) have been the major contribution to the market. Although the basic design of crystalline devices has remained essentially the same for 20 years, the vast growth of the photovoltaic market during the last
2-3 years is directly related to the major and dominant presence of more efficient and reliable m-Si modules. This increasing share of crystalline silicon in recent years is in contradiction to the expectations until the mid-1990s that thin-film technology would be dominant by the middle of the present decade. Following in the direction of improving the efficiency of silicon solar cells, new high-efficiency technologies were invented and currently are being developed and introduced into the market.

For example, Saturn solar cells produced by BP are based on a "Laser Grooved Buried Contact" technology, invented and developed by Martin Green from the University of New South Wales [6]. The feature of this technology is that contacts are not printed on the cell surface as in conventional solar cells, but are placed in grooves obtained by laser cutting into the cell surface. First, the grooves are strongly n-doped in a diffusion furnace. Then they are coated in a chemical bath with nickel and finally with copper. The thin nickel layer is used as a protective coating against copper penetration into the silicon, which would support the undesirable recombination of charge carriers. Saturn cells absorb 5% more light than conventional cells, because the 20 µm wide contact grooves cause less shadowing than conventional contacts. The surface of the Saturn cell is structured in the form of small pyramids, to increase light absorption. The combination of the pyramid structure and the anti-reflection layer of silicon nitride causes the amount of light which is totally reflected to be reduced to less than 3%. The back surface of the cell, which is covered by an alloy of nickel and copper, serves as a kind of mirror for photons that would normally pass through the cell. It thus causes better absorption in the red and infrared areas of the solar spectrum.
Another new high efficiency technology is "Point-Contact" from the SunPower Company. This comprises a backside contact cell with a top surface structured into tiny chemically etched pyramids. Such a surface allows reduction of the light reflection and improved cell efficiency. The cell has a non-conductive SiO$_2$ layer created on the back surface of the wafer. This reduces the recombination of electrons and holes on the upper surface of the cell’s back side, and reflects photons back into the cell [7].

The present status of cell and module energy conversion efficiencies achieved in the laboratory for different silicon technologies are presented in Table 1.

Table 1: Energy conversion efficiencies achieved in the laboratory for different photovoltaic silicon based technologies.

<table>
<thead>
<tr>
<th>Silicon Technology</th>
<th>Cell Efficiency (%)</th>
<th>Module Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Float-Zone</td>
<td>25</td>
<td>21</td>
</tr>
<tr>
<td>Czochralski</td>
<td>22</td>
<td>18</td>
</tr>
<tr>
<td>Cast polysilicon</td>
<td>18</td>
<td>15</td>
</tr>
<tr>
<td>Thin-Si on Si-substrate</td>
<td>17</td>
<td>10</td>
</tr>
<tr>
<td>EFG Ribbon</td>
<td>15</td>
<td>12</td>
</tr>
<tr>
<td>String Ribbon</td>
<td>15-17</td>
<td>12</td>
</tr>
<tr>
<td>Lift-off techniques</td>
<td>12-17</td>
<td>-</td>
</tr>
</tbody>
</table>

3.2 THIN FILM SOLAR CELLS

Reductions in the cost of the photovoltaic systems have been achieved during the last twenty years of development of thin film solar cells. After years of research and technology development, the thin film technology is now in a transition from pilot to industrial production. The efficiency of thin-film solar cells is presented in Table 2. Equally competitive technologies are amorphous silicon, CdTe and Cu(In,Ga)Se.

Table 2: Energy conversion efficiencies achieved in the laboratory for different photovoltaic thin-film technologies.

<table>
<thead>
<tr>
<th>Technology</th>
<th>Cell Efficiency (%)</th>
<th>Module Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thin Silicon High-T process</td>
<td>12</td>
<td>8</td>
</tr>
<tr>
<td>Thin Silicon Low-T process</td>
<td>10</td>
<td>-</td>
</tr>
<tr>
<td>Thin amorphous Si (a-Si)</td>
<td>13</td>
<td>8</td>
</tr>
<tr>
<td>Chalcopyrites (CIGS)</td>
<td>19</td>
<td>12</td>
</tr>
<tr>
<td>Cadmium Telluride (CdTe)</td>
<td>16</td>
<td>10</td>
</tr>
</tbody>
</table>
Application of thin film semiconductor materials as active layers in photovoltaic devices offers the promise of low utilisation of raw materials and the use of manufacturing technologies already demonstrated in other industries. The oldest and still the most important thin film solar material is amorphous silicon. Initially, it was used mostly in consumer items like pocket calculators and watches. With increasing efficiencies, amorphous silicon modules gained a share in the market for consumer power (<50 W) and building integrated systems, particularly in facades. A major advantage of amorphous silicon technology is the potential of low-cost mass production, the good availability of silicon and the excellent environmental profile.

At present, amorphous silicon based devices are the most important thin-film solar cells. Three different processes are used:

- The Chronar process, which is simple and low cost, but gives a moderate 5% efficiency.
- The triple-junction process, which is expensive and gives about 7% efficiency.
- A third, hybrid, approach which gives above 10% efficiency.

It can be expected that the µ-Si/a-Si solar modules will reach efficiencies of 12-15% by 2010. The research goal is that thin-film silicon solar cells will reach 20% efficiency by 2020 [6].

In 1997, Sanyo Solar presented HIT (Heterojunction with Intrinsic Thin-layer) solar cell. This cell combines both crystalline and amorphous silicon in the one structure. It is composed of a textured n-type c-Si wafer (solar grade CZ-Si) sandwiched between a p/i a-Si:H film on the illuminated side and an i/n a-Si:H film as a back surface field structure on the rear face. Films are deposited by plasma enhanced chemical vapor deposition (plasma CVD). The 200 W market-available HIT modules have a cell conversion efficiency of 19.5% and a module efficiency of 17%, which is the best result on the market. A second feature is very good temperature characteristics. In most solar cells, output power decreases with increasing temperature. However, the temperature dependence of the conversion efficiency of a HIT solar cell is smaller than that of conventional crystalline silicon solar cells. According to SANYO simulations, HIT solar cell modules can generate 43% more electricity annually than conventional solar cells. Other features are the thin wafer (an advantage for the silicon feed stock problem), and the low temperature process (less detrimental to the environment) [7].

Chalcopyrites, or more specifically the Cu(In,Ga)(Se,S)₂ family of compounds, have achieved the highest efficiencies of any polycrystalline thin-film material. A record cell efficiency of 19% has been reported. Large-area modules (120 x 60 cm) were produced at a pilot scale, with efficiencies of up to
10.4%. The ultimate potential performance of this material has not yet been achieved, with efficiencies beyond 20% being expected in the near future.

For both CIS and CdTe technologies, in-line processing for high throughput has been developed. Efforts were made to make use of as much standard equipment as possible. However, many process steps are very specific for these products, making the development of special equipment inevitable.

The main barriers for thin film technologies are:

- A poor image from the first, amorphous silicon, prototypes
- A still relatively low efficiency for commercial modules
- The expected lifetime
- A low yield in production.

### 3.3 HIGH EFFICIENCY SOLAR CELLS

High efficiency solar cells are based on multijunction solar cells with materials from the III-V group of semiconductor compounds. The goal is to achieve efficiencies higher than 40% by the utilisation of tandem structures of up to four-junction devices.

III-V solar cells are now applied in space satellites, owing to their high performance, reliability and radiation resistance. Some companies produce large quantities of cells with efficiencies of around 25%. The disadvantage of GaAs for terrestrial applications is the cost of the wafers - two orders of magnitude higher than for silicon, with efficiencies not much higher than for silicon devices.

GaInP/GaAs monolithic structures have reached efficiencies as high as 32%. Improved structures of GaInP/GaAs/Ge have reached a 32.3% efficiency under 566 suns, without open-circuit voltage losses. The GaInP/GaInAs/Ge triple-junction cell presented in July 2003 by Spectrolab Inc. has a world record efficiency of 36.9%, reached under 308 times concentrated sunlight. This was achieved by adjusting the bandgaps of the middle and the top cells to terrestrial conditions of radiation [8]. Also, GaAs single-junctions have reached efficiencies of about 30% at 1000 suns. These values of efficiency at the level of concentrations reported mean that they reach the requirements for commercial applications.

### 3.4 NEW CONCEPTS

In order to move the prices of photovoltaic electricity to those required to be competitive with other power sources, basic research to explore new materials for photovoltaics and new cell concepts is needed. Among the new promising ideas and concepts are: dye-sensitised photochemical solar cells, conducting polymer cells and quantum solar cells.
Dye-sensitised photochemical solar cells use basically cheap nanocrystalline titanium dioxide with a large effective area and organic dyes, in order to enhance the solar spectrum absorption when immersed in an electrolyte. Dye-cells have achieved 11% efficiency on small areas (0.25 cm$^2$). The main advantage of dye-cells is that they can be produced from inexpensive materials, by a simple production technology. However, the major challenge is development of cells and modules for power applications, since presently the major application of these solar cells is in “pocket” applications.

Conducting polymer cells are based on the property of some organic materials to be conductive - “plastic cells”. Among the conductive polymers investigated, the most promising ones are fullerene (C$_{60}$) based structures. Evident advantages of this technology are the expected low-cost fabrication and the possibility of make solar cells by tailoring the required properties by modifications of the organic molecules. However it is necessary to increase cell efficiencies and stability, avoiding degradation under solar exposition.

The basic principle for quantum solar cells is the utilisation on the nanoscale range of quantum confinement, for controlling band gaps to utilize a broad part of the solar spectrum. The actual status of these cells is theoretical, but the potential for increasing the possible maximum efficiencies leads to the study of material candidates and the realisation of the first devices.

4. Summary

With the current technology and business evolution path, solar photovoltaics will continue to grow in response to requirements for clean, reliable on-demand electricity worldwide over the coming decades. On the environmental side, compared to fossil-fuel electricity generation, each kW of installed solar PV power annually saves up to 16 kg of NO$_x$ and 9 kg of SO$_x$, and offsets between 600 and 2300 kg of CO$_2$, depending on the fuel mix and solar insolation.

New concepts of solar cells - improving the efficiency and reducing the cost of photovoltaic systems - mean that photovoltaics has bright prospects for becoming a significant partner in the world-energy mix for 2020 and beyond. However, to meet the assumed goals further improvements in efficiency and cost are necessary. The intensification of research is needed to overcome existing barriers and to advance the development. On the political side, dissemination of photovoltaics needs support from governments.

References

1. Introduction

Mankind is using increasing amounts of energy, and especially in the fast developing Asian countries, such as China and India, the use of fossil fuels is expected to increase from about 14 million barrels of oil per day to over 30 million barrels per day in 2025 [1]. Limited resources and especially environmental pollution caused by the combustion of fossil fuels, such as petrol, natural gas and coal, call for renewable and sustainable alternatives for the energy economy [2].

The focus is on new energy carriers and novel technologies for a future clean and sustainable energy economy. With regard to electricity and hydrogen, it is anticipated that both energy carriers will indeed become principal interchangeable energy carriers for the future. Their combined use provides a unique pathway towards a decreased dependency on fossil fuels, reduced greenhouse gas and pollutant emissions, and an increased contribution of renewable energy resources. In the long term, hydrogen may play a key role in adapting energy supply to energy demand, as it has the potential for large-scale, even seasonal, energy storage.

To date, hydrogen is manufactured industrially from steam reforming of natural gas, thereby producing CO₂. Electricity from photovoltaic solar cells or wind energy can be used to produce sustainable hydrogen via electrolysis of water. While the current state-of-the-art solar cells are mainly based on silicon, novel and especially cheaper solar cells are being developed, as well as the direct photo-electrolysis of water using new photoelectrochemical devices.

A major obstacle to the conversion to a Hydrogen Economy is the problem of safe and cheap storage of hydrogen. Nano-structured hydride-forming metals and alloys are attracting global attention. Safety requirements and social acceptance of a Hydrogen Economy also necessitate the non-destructive detection of hydrogen, for example with solid state hydrogen sensors.
In this paper, we present an overview of several recent studies on nanostructured materials, with emphasis on thin films, for novel solar cells and for Photo-Electrochemical Cells (PECs), and on hydrogen storage and detection.

2. Thin-Film Techniques for Nano-Structured Materials

Since the introduction of the dye-sensitized Grätzel solar cell [3,4], highly porous, nano-structured anatase TiO$_2$ substrates have been used to design novel three-dimensional (3D) solid-state solar cells. While these substrates are usually prepared using screen-printing [5] or by using a doctor-blade process with commercial nano-sized anatase powders of TiO$_2$ [6], gas-phase and aerosol deposition techniques offer the possibility for creating specific surface morphologies for such cells. Several prime examples will be presented here.

2.1. CHEMICAL VAPOUR DEPOSITION

Among the proposals for new designs for photovoltaic cells is the Extremely Thin Absorber (ETA) solar cell [5,7]. A highly structured, transparent to visible light, substrate layer, i.e., n-type anatase TiO$_2$, is covered with a very thin layer of a visible-light absorbing material, i.e., CuInS$_2$, by Ion Layer Gas Reaction (ILGAR) [5]. The solar cell is completed by depositing a thin film of transparent p-type CuSCN, using electro-deposition [5]. In a further study CdTe, obtained by electro-deposition, is used as an absorber layer [7]. In addition to screen-printing, spray pyrolysis of anatase TiO$_2$ has been used to increase the effective surface area by a factor of 10 to 60 [5,7]. As a consequence, the film thickness of the absorber layer can be as small as ~150 nm [7]. The ETA solar cell concept is presented schematically in figure 1. To date, ETA solar cells exhibit an energy conversion efficiency of around 2%.

Figure 1. Structure of an ETA solar cell. The cell is deposited on a glass substrate coated with a transparent conducting oxide, i.e., fluoride-doped SnO$_2$ [5,7].
In the ETA solar cell concept, several different deposition techniques are used. Recently, it has been shown that with Metal-Organic Chemical Vapour Deposition (MO-CVD), fractal surface morphologies of anatase TiO$_2$ can be deposited [8]. As precursors, mixtures of titanium tetrachloride, titanium-tetra-isopropoxide, oxygen, and water vapour have been used. These structures have been explored for solar cells using organic p-type conducting zinc phthalocyanines [6] and for photocatalytic conversion of mixtures of CO$_2$ and water vapour to methanol and O$_2$ [9]. Conversion efficiencies are <1%. Figure 2 presents the fractal surface morphology of the MO-CVD deposited TiO$_2$ layers.

2.2. ATOMIC LAYER DEPOSITION

While in CVD all precursors are introduced into the deposition chamber at the same time and process conditions are selected such as to deposit smooth or structured layers, in Atomic Layer Deposition (ALD) the precursors are introduced into the deposition chamber sequentially. This leads to a self-limiting growth mechanism while gas-phase reactions are inhibited due to the sequential introduction of the precursors. By carefully tuning the relevant process parameters, i.e., pulse length, reactor chamber pressure, deposition temperature, and number of deposition cycles, thin films of high purity and a well-defined thickness are obtained [10,11].

Highly porous, nano-structured anatase TiO$_2$ layers are the basis for 3D TiO$_2$-CuInS$_2$ hetero-junction solar cells. Here, the pores of the n-type substrate are infiltrated with p-type CuInS$_2$ using ALD to form the solar cell [12,13]. Figure 3 presents this hetero-junction solar cell.
This solar cell exhibits an open-circuit voltage of 0.5 V, a short-circuit current of 18 mA/cm², a fill factor of 0.45, and an overall energy conversion efficiency of 4% (all measured under AM 1.5 irradiation from a calibrated solar simulator) [13]. An in-depth presentation of ALD and 3D solar cell materials will be presented in the accompanying paper “Nano-Structured Materials for Conversion of Sustainable Energy” [14].

3. Photo-Electrolysis

While the silicon-based and the novel 3D solar cells can be coupled to an electrolyser to split water into oxygen and hydrogen, the direct photo-electrolysis of water appears to be the most efficient route to small-scale decentralised production of sustainable hydrogen. In 1972, Fujishima and Honda reported photo-electrolysis, using TiO₂ [15]. Since then, stable materials have been found that can split water but show insufficient visible light absorption, such as TiO₂ that absorbs only in the near UV. Efficient visible-light absorbing materials, such as Si and GaAs, suffer from photo-corrosion, energetically unfavourable band edge positions, or recombination and low electrical conductivity.

Doping of TiO₂ to increase visible-light absorption can only be effective if the electron hole diffusion length is as short as possible, thus preventing recombination, and this requires nano-structured morphologies. Such morphologies will also optimise light absorption through scattering and possibly also light trapping. Kahn et al. reported that anion doping with carbon improves the conversion of solar energy more than eightfold, to 8.35%, at an applied voltage of 0.3V [16,17]. Although this claim has been disputed, and the actual efficiency is more likely to be ~1.4% [18], other recent reports also indicate that carbon doping does seem to significantly enhance the visible light absorption of TiO₂ [19,20].

Figure 3. Structure of an inorganic 3D hetero-junction solar cell [13].
Using our research on 3D TiO$_2$|CuInS$_2$ hetero-junction solar cells (viz. 2.2), MO-CVD of anatase TiO$_2$ (viz. 2.1), the Electrostatic Spray Deposition (ESD) technique for reticular surface morphologies [14,21], and the anion-doping effect, a new concept for photo-electrolysis for the production of hydrogen is being studied. Figure 4 presents this PEC concept.

![Figure 4. The Delft Monolithic Multi-Junction Photo-Electrochemical Cell concept.](image)

This multi-junction device, comprising anion-doped anatase TiO$_{2-x}$C$_x$ and CuInS$_2$, absorbs blue/green light and red light, respectively. The doped metal oxide also acts as a protective material for CuInS$_2$. One of the main challenges for this concept is to find a metal oxide that fulfils the following requirements: i) sufficient visible light absorption, ii) suitable band edge positions, iii) stability against photo-corrosion, iv) fast charge transport and absence of recombination, and v) a high surface catalytic activity. To design such a material, one needs to have a detailed understanding of and control over its defect chemistry. Our approach is to study these materials in the form of thin, dense films, which allows us to determine key intrinsic parameters, such as the optical absorption, the donor density, and the energy levels of the various defects. We recently reported some initial results on thin film carbon-doped anatase TiO$_2$ films [22]. Due to the low carbon content, no visible light photoresponse could be detected. However, the effect of the carbon was to increase the UV photoresponse while at the same time an increase in the donor density was observed. To explain these apparently contradictory results, further studies on the defect properties of this material are necessary.

4. Hydrogen Storage and Chemical Sensing

For the introduction of a Hydrogen Economy, a cheap and safe storage technology, along with accurate detection of hydrogen, are prime prerequisites.
There are basically three ways to store hydrogen, i.e., 1) storage in a pressure tank, 2) storage as a liquid, and 3) storage via absorption. Containing the lightest gas in the universe on board a car presents an enormous challenge [23]. For a normal-sized car with an average driving range of 500 km, about 6 kg of hydrogen fuel needs to be stored on board. At atmospheric pressure, the energy density per unit volume of hydrogen gas is ~3000 times smaller than that of gasoline, so even state-of-the-art fibre-reinforced gas cylinders containing H₂ compressed to 800 bar take up too much space. Liquefied hydrogen needs to be kept at -253°C (20K), which requires extremely well-insulated and, therefore, expensive storage tanks. Even in current state-of-the-art tanks, most of the hydrogen is lost in several weeks through pressure relief valves. A more attractive option that attracts global attention is absorption in a metal or an alloy. In the absorption process, a solid solution (MHₓ) is formed first. Then a compound (MHy) is formed according to the reaction:

\[ \text{MH}_x + \frac{1}{2}(y-x) \text{H}_2 \rightarrow \text{MHy} \]  

For M-H₂, the systems Fe-Ti-H₂ and La-Ni-H₂ have been studied widely. With a storage capacity of less than 2 wt% H₂, these alloys are too heavy for mobile applications. Therefore, the system Mg-H₂ is being studied, and can store up to 7.6 wt% of hydrogen. The kinetics of hydrogen absorption and desorption of this system are slow, but can be improved by decreasing the grain size into the nano-size regime. Furthermore, the addition of small amounts (<1%) of nano-sized transition metal oxide catalysts, for example TiO₂ or Cr₂O₃, improve the kinetics even more. The combined use of nano-sized hydrides and metal oxide catalysts results in ~100 times faster kinetics [24]. In these nano-sized catalyst particles, point defect densities differ from standard bulk defect densities. In order to understand this catalytic effect, enhanced defect densities in 3D-metal oxide catalysts and the influence thereof on the interaction with H₂ are currently under investigation. Under these highly reducing conditions, extensive ordering of oxide ion vacancies is expected to occur, which may even lead to the formation of stable Magneli phases [25].

Accurate detection of gaseous hydrogen or hydrogen absorbed in a metal hydride can be performed using a Nernst sensor. The sensing process is schematically represented as follows:

\[ \text{M}^1\text{H}_x \text{ (or Pt}^1(\text{H}_2)) / \text{Solid Electrolyte} / \text{M}^2\text{H}_y \text{ (or Pt}^2(\text{H}_2)) \].  

Here, M¹Hₓ or Pt¹(H₂) represent a sensing electrode and M²Hᵧ or Pt²(H₂) a reference electrode. The solid electrolyte is a proton-conducting material. For this sensor, the following Nernst equation can be written:
\[ \Delta E = \Delta E^0 + \frac{RT}{nF} \ln \frac{a_H(M^2)}{a_H(M^1)} \]  

Here, \(a_H\) stands for the activity of hydrogen in the metal hydride. In the case of gaseous hydrogen, \(a_H\) is replaced by the partial pressure. For M-H, \(\Delta E\) changes by 60 mV/decade at room temperature and 30 mV/decade for \(H_2\). The Nernst sensor is very selective, but has a low sensitivity. Several solid-state sensors have been studied in the past, with \(PdH_{y} (0.1 \leq y \leq 0.6)\) and \(H_{0.34}MoO_3\) as reference electrodes, and a variety of solid electrolytes: \(HUO_2PO_4\cdot4H_2O\), the zeolites \(HY\) and \(NH_2Y\), and \(H_3O^+\)-\(\beta''\)-alumina. In these studies, \(Pd\) and \(Pd_{1-x}Ag_x\) were generally used as sensing electrodes [26].

In our current research, protonated \(Li_4Ti_5O_{12}\), i.e., \(Li_{4-x}H_xTi_5O_{12}\), is studied as a solid electrolyte. The pristine material can insert three lithium atoms and is then used as an anode material in a rechargeable lithium-ion battery. With reference and sensing electrodes made of \(Pt(H_2)\), Nernst-type behaviour is obtained, indicating that this new protonated material can indeed reach equilibrium with hydrogen [27]. Further studies are under way.

5. Conclusions

In this paper, we have presented selected nano-structured materials for the conversion and storage of solar energy. Process conditions for CVD can be selected to deposit thin films of anatase \(TiO_2\) with fractal surface morphologies, which can be used for an ETA solar cell. ALD is an excellent tool to design novel nano-structured 3D solar cells. The presently-achieved conversion efficiency of 4% is double that of the current ETA solar cell. Nano-structured metal oxide catalysts improve the kinetics of hydrogen sorption in metal hydrides. The mechanism is yet not understood, but enhanced point defect densities play an important role. A new proton-conducting solid electrolyte has been tested in a Nernst hydrogen sensor.

6. References


NANO-STRUCTURED FUNCTIONAL MATERIALS: THE DEFECT CHEMISTRY

J. SCHOONMAN
Laboratory for Inorganic Chemistry, Delft Centre for Sustainable Energy, Delft University of Technology, Julianalaan 136, 2628BL Delft, The Netherlands

1. Introduction

Functional materials with specific electronic, electrical, optical, and optoelectronic properties are being studied widely for application in devices for the conversion and storage of (sustainable) energy, for chemical sensing, for electrochromic devices, and for the production and storage of hydrogen.

While the traditional length scales of materials are in the micron-size domain, recent attention has been focused more on the sub-micron and nanometre scales [1-6]. It has become apparent that microstructures based on nano-structured materials exhibit chemical and physical properties that no longer compare to those of traditional ceramic microstructures.

Ionic and electronic point defects determine, to a large extent the fundamental properties of functional materials. For instance, their concentrations and mobilities determine mass and charge transport processes in the above-mentioned devices, and are thus key parameters as regards chemical and electrochemical kinetics. The significance of nano-structured materials is two-fold: (i) the ratio of the interfacial area to volume increases substantially, and (ii) intrinsic size effects occur if the reduced spacing of the interfaces leads to local effects. We can thus distinguish between trivial and proper size effects on the defect chemistry of nano-structured materials, and hence their properties [7].

In this paper, the fundamental defect chemistry will be presented in detail, for materials with traditional and nanometre length scales.

2. Nanotechnology

Nanotechnology is the exploitation of novel and improved properties, phenomena, and processes specific to the intermediate scale, i.e., 0.1-100 nm,
between individual atoms/molecules and bulk behaviour. This size range implies a number of atoms per particle varying from several atoms to 10 million or more. For instance, particles with a diameter of 0.7 nm comprise 10 atoms, rising to $10^3$ atoms and $10^6$ atoms for diameters of 3.4 and 33.7 nm, respectively. Nano-structured microstructures have, therefore, large fractions of two-dimensional defects, i.e., grain boundaries, and hence large percentages of surface atoms. For close-packed spheres, the percentage of surface atoms is about 80% for a 50-atom particle, and is still 20% for a particle containing 2000 atoms. Hence, surface diffusion over the grain boundaries becomes more important in materials with a nano-structured microstructure. In principle, this is an extrinsic effect of the nano-scale. As point defect densities at curved surfaces deviate substantially from those at planar structures, enhanced point defect densities can occur in the space-charge regions of nano-sized particles [7, 8]. If the space-charge regions exhibit percolative diffusion, the ionic conductivity can be improved via two effects: (i) enhanced diffusion over the grain boundaries, which is an extrinsic effect and (ii) enhanced defect densities; this being an intrinsic effect of the nano scale.

If the particle size becomes of the order of the radius of an exciton, quantum confinement effects will occur. Quantized values of the electron wavelength translate into quantized energy levels, with the energy of the first excited state of the electron or electron hole shifted by

$$E_{1s} = \frac{\hbar^2}{8m_{\text{eff}}a^2}$$

from its energy in the bulk material. Here, $\hbar$ is Planck’s constant, $m_{\text{eff}}$ the effective mass of the electron or hole, and $a$ the particle size. The energy shifts, and therefore the band gap of the nano-sized material increases with decreasing size, as $1/a^2$. Because the effective mass of an electron differs from that of an hole, the contribution to this “blue shift” of the valence band edge differs from that of the conduction band edge. This strong size dependence is a practical advantage in the use of nano-materials for luminescence.

3. **Defect Chemistry**

3.1 **KRÖGER-VINK DEFECT NOTATION**

In defect chemistry, the standard notation of point defects, defect associates, and defect clusters is the Kröger-Vink notation. In principle, the notation for a point defect is $S_{p}^C$, where $S$ is the symbol for the point defect. The subscript denotes the site which the point defect occupies in the crystal lattice, and the superscript identifies the effective charge of the point defect relative to the
perfect crystal lattice. For this part of the notation, dots (·) represent effective positive charges, dashes (‘) represent effective negative charges, and (×) represents an effective zero charge.

Some examples are: vacancy V, metal ion (M⁺) vacancy Vₘ⁺, metal ion interstitial Mᵢ⁺, empty interstitial site Vᵢ⁺, oxide ion vacancy Vₒ⁻, magnesium ion vacancy Vₘg⁺, magnesium ion on a regular lattice site Mₘg⁻.

3.2 INTRINSIC POINT DEFECTS

Starting with a perfect crystal at zero temperature, point defects can only form with an expenditure of (usually) thermal energy. The increased energy and amplitude of lattice vibrations at finite temperatures increase the probability that an atom or ion will be displaced from its lattice position. Thus, the formation of point defects is a thermally activated process, in which the formation energy represents the activation barrier. In many ceramic systems, significant defect densities are generated only at temperatures well beyond half the melting point (9).

The most common types of thermally generated intrinsic disorder are Schottky disorder, Frenkel disorder and anti-Frenkel disorder. These usually occur in ionic materials. Their thermal generation can be represented as follows,

\[
\text{Schottky disorder for, e.g. KCl: } \quad \text{O} \leftrightarrow V_K^+ + V_{Cl^-} \quad (2)
\]

Here O indicates the thermal generation of point defects from a perfect lattice.

\[
\text{Frenkel disorder for, e.g. AgCl: } \quad \text{Ag}^x_{Ag} + V^x_{i} \leftrightarrow \text{Ag}^i_{i} + V_{Ag}^+ \quad (3)
\]

\[
\text{Anti-Frenkel disorder, e.g. CaF}_2: \quad F^x_{F} + V^x_{i} \leftrightarrow F^i_{i} + V_{F}^- \quad (4)
\]

In the different types of disorder, the point defects are formed in a stoichiometric ratio, in order to preserve electroneutrality. Thus, in KCl and MgO, a cation vacancy and an anion vacancy are formed simultaneously, while in TiO₂ a titanium ion vacancy and two oxide ion vacancies are formed. Upon the formation of Schottky disorder, the total number of lattice sites is increased by one formula unit, unlike Frenkel and anti-Frenkel disorder, which conserve the number of lattice sites. Hence, Schottky disorder is generated at one- or two-dimensional defects, i.e., a dislocation or a surface, respectively. Frenkel and anti-Frenkel disorder can occur throughout the crystal lattice. As a consequence, the kinetics of generation and annihilation of Schottky defects is much slower than that of Frenkel and anti-Frenkel disorder. Schottky disorder usually prevails in close-packed crystal structures.

The thermal generation of the intrinsic point defects is given in the form of a chemical reaction for which there is an equilibrium constant, governed by the law of mass action. Hence, the respective mass-action equilibrium constants are,
The brackets denote the concentration, which is usually given in mole fraction units. Here, we consider only dilute defect concentrations (<< 1%), without defect-defect interactions. In the case of defect-defect interactions concentrations should be replaced by activities. The equilibrium constant is a function of temperature only. This means that for intrinsic defects generated according to a Schottky mechanism, the product of the cation and anion vacancy concentrations is a constant at a fixed temperature, and that these concentrations are equal for charge neutrality, i.e., in the case of KCl:

\[ \text{K}_S = [\text{V}_{K}'] [\text{V}_{\text{Cl}}'] \]

\[ \text{K}_F = [\text{Ag}_{\text{Ag}}'] [\text{V}_{\text{Ag}}'] \]

\[ \text{K}_{aF} = [\text{F}_i'] [\text{V}_F'] \]

Here, \( \Delta g_s \) is the free energy of formation of a set of Schottky point defects. Similar relations hold for the temperature dependence of the concentrations of a set of Frenkel point defects and anti-Frenkel point defects.

3.3 EXTRINSIC POINT DEFECTS

Extrinsic point defects result from doping, from deviations from stoichiometry, and from deviations from molecularity. In cases where a material is doped with isovalent dopants, the defect chemistry is not affected, but the material is no longer pure. The concentrations of the intrinsic point defects are affected by aliovalent dopants at not too high temperatures. For example, the defect chemical reaction for the dissolution of CaO in MgO is given by

\[ \text{CaO} \rightarrow \text{Ca}_{\text{Mg}}^x + \text{O}_x^\cdot \]

assuming substitutional dissolution. It does not involve the formation of point defects with an effective charge. Hence, intrinsic defect concentrations are not affected.

As a second example, the dissolution of K₂O in MgO is considered. The defect chemical reaction is given, assuming substitutional incorporation, by

\[ \text{K}_2\text{O} \rightarrow 2 \text{K}_{\text{Mg}}' + \text{O}_x^\cdot + \text{V}_o^\cdot. \]
The electroneutrality condition is

$$[K_{Mg}'] = 2 [V_{O^-}].$$  \hspace{1cm} (11)$$

MgO exhibits intrinsic Schottky disorder. Hence, in the extrinsic region, the $K_2O$ concentration determines the concentration of the oxide ion vacancy concentration, which is then temperature invariant. The magnesium ion vacancy concentration exhibits a temperature-dependence in the extrinsic region, given by:

$$[V_{Mg}^-] = K_S/\frac{1}{2}[K_{Mg}'] = K_S/[K_2O]$$  \hspace{1cm} (12)

in order to comply with the Schottky equilibrium constant. Beyond a certain temperature, the thermally generated concentrations of the intrinsic point defects take over, and the material behaves as a quasi-pure intrinsic material.

Deviations from stoichiometry usually lead to a combination of ionic and electronic point defects. As examples we present here the reduction and oxidation reactions of metal oxides.

The reduction of a metal oxide can be written as the removal of oxide ions from the metal oxide as oxygen to the gas phase, thereby leaving oxide-ion vacancies in the metal oxide. The effective charge of an oxide ion vacancy is charge-compensated by two electrons, showing that deviations from stoichiometry lead to a combination of ionic and electronic point defects. The defect chemical reaction describing reduction is:

$$O_{O^x} \leftrightarrow \frac{1}{2}O_2 (g) + V_{O^-} + 2 \text{e}^-.$$  \hspace{1cm} (13)

The equilibrium constant for this reduction reaction is given by

$$K_R = [\text{e}^-]^2 [V_{O^-}] P_{O_2}^{1/2} = \exp (-\Delta G_R/kT),$$  \hspace{1cm} (14)

where $\Delta G_R$ is the free energy for the reduction of the metal oxide and it is assumed that the defect concentrations are small.

Oxidation can be written as the consumption of oxide-ion vacancies, with the formation of two hole carriers for charge compensation, i.e.

$$\frac{1}{2}O_2 (g) + V_{O^-} \leftrightarrow O_{O^x} + 2\text{h}^+,$$  \hspace{1cm} (15)

with an equilibrium constant

$$K_O = [\text{h}^+]^2 [V_{O^-}]^{-1} P_{O_2}^{-1/2} = \exp (-\Delta G_O/kT).$$  \hspace{1cm} (16)
Here, $\Delta G_O$ is the free energy of oxidation of the metal oxide. In general, metal oxides in which the valence state of the cation is fixed, such as $\text{Ba}^{2+}$, $\text{Al}^{3+}$, or $\text{Zr}^{4+}$, exhibit a large free energy for reduction and oxidation, and hence very small deviations from stoichiometry. In contrast, metal oxides that contain multivalent cations, such as the transition metal ions, exhibit large deviations from stoichiometry. For instance, $\text{Fe}_{1-x}\text{O}$ cannot be made stoichiometric, i.e., as $\text{FeO}$, because it has a minimum cation deficiency of 0.05 [9]. In $\text{TiO}_{2-x}$ with a substantial deviation from stoichiometry, extensive ordering of oxide-ion vacancies occurs and stable Magnéli phases are formed [10]. These phases have a high electronic conductivity and are used as support for commercial electrolysis electrodes.

The optical or thermal generation of an electron hole-electron pair requires excitation across the band-gap of the material and the formation of intrinsic electronic disorder is represented by

$$\text{O} \leftrightarrow \text{e}^\prime + \text{h}^\prime.$$  \hspace{1cm} (17)

The equilibrium constant is

$$K_{el} = [\text{e}^\prime] [\text{h}^\prime] = \exp(-E_g/kT)$$  \hspace{1cm} (18)

Here, $E_g$ represents the bandgap energy. It can easily be shown that the oxidation and reduction processes are not independent, as from the equilibrium constants (15), (17), and (19) it follows that

$$K_R \times K_O = K_{el}^2$$  \hspace{1cm} (19)

A deviation from molecularity always leads to a combination of extrinsic ionic defects. For example, $\text{BaTiO}_3$ with a slight excess of $\text{TiO}_2$ leads to the defect combination $\text{V}_{\text{Ba}}^-$ and $\text{V}_\text{O}^{\cdot\cdot}$, while an excess of $\text{BaO}$ leads to the defect combination $\text{V}_{\text{Ti}}^{\cdot\cdot\cdot}$ and $2\text{V}_\text{O}^{\cdot\cdot}$. The difference in the defect structures of these two compositions of $\text{BaTiO}_3$ with a deviation from molecularity indicates that the solubility of $\text{TiO}_2$ is larger than that of $\text{BaO}$ in $\text{BaTiO}_3$, because a smaller number of defects with a lower effective charge is created in $\text{TiO}_2$-rich $\text{BaTiO}_3$.

### 3.4 THE BROUWER DIAGRAM

In large bandgap materials, the intrinsic ionic disorder is usually predominant, and electronic defects are minority charge carriers. However, because the mobility of electronic charge carriers is usually much larger than that of ionic defect species, mixed ionic and electronic conductivity may occur in materials with small deviations from stoichiometry. It is, therefore, important to know the
dependence of the point defect concentrations on temperature, dopant concentration and ambient gas partial pressure. In the case of metal oxides, the last of these parameters is the oxygen partial pressure. In small bandgap materials, electronic disorder will prevail. However, in diffusional processes, minority ionic defects remain important.

If the case of deviations from stoichiometry in a material MX with Frenkel disorder is considered, the total electroneutrality condition reads,

\[ [V_M^+] + [e^-] = [M_i^+] + [h^+] \] (20)

In order to obtain an expression for each defect as a function of the partial pressure of X₂, we use the equilibrium constants for oxidation and reduction reactions under the assumption that intrinsic thermally generated electronic disorder can be ignored, due to a large band gap energy. In using the full electroneutrality condition, rather cumbersome equations would be obtained. In the Brouwer approximation, reduced electroneutrality conditions are used, i.e.

\[ [M_i^+] = [e^-] \] (21)
\[ [M_i^+] = [V_M^+] \] (22)
\[ [V_M^+] = [h^+] \] (23)

These can be used to obtain the dependences of the ionic and electronic defect concentrations on the partial pressure of X₂. In general, we find for the concentrations \([j]\) of the ionic and electronic point defects the following expression:

\[ [j] = P_{X_2}^{n/2} \Pi K_i^s \] (24)

Here, \(n\) and \(s\) represent characteristic values for each ionic or electronic point defect, and the values of \(n\) determine the slope of the dependence of \(\log[j]\) upon \(P_{O_2}\) in the Brouwer diagram. For the example of the non-stoichiometric Frenkel disordered material, MX the Brouwer diagram is presented in Figure 1.

Usually, the ionic regime is used to determine the electrolytic domain, i.e., the domain in which the material can be used as a solid electrolyte in a solid rechargeable lithium-ion battery, a solid oxide fuel cell, a chemical Nernst-type gas sensor, or a smart window. A characteristic of the material in its electrolytic domain is the fact that the electrical transport is carried only by ionic species. Because, in general, the mobilities of electronic defect charge carriers are much larger than these of ionic defect charge carriers, the electrolytic domain is observed in a much smaller pressure regime than indicated by the Brouwer ionic regime. In addition, the nano-length scale can also exert a dramatic influence on the electrolytic domain.
The preceding section presents the classical defect chemistry of bulk materials. Nano-structured materials are distinguished from the conventional polycrystalline materials by the size of the structural units that comprise them, and they often exhibit properties that are drastically different from those of conventional materials, due the large fraction of grain boundaries and hence of surface atoms. A size range of 1-100 nm implies a number of atoms per particle varying from several to 10 million or more (Section 2). Due to the large interfacial surface area, bulk properties can become governed by surface properties. This represents the trivial, extrinsic effect of the nano scale and a wide variety of examples are presented in the recent literature [1-4, 11]. In the case of a ceramic rechargeable lithium-ion battery, studies of the defect chemistry of a lithium-doped BPO₄ solid electrolyte, i.e., LiₓBPO₄ [12-14], reveal that the defect chemistry of LiₓBPO₄ is represented by the equilibrium,

\[ V_{B}^{"} + Li^{+} \rightleftharpoons Li_{B}^{"} \]  

(25)

The ionic conductivity of this solid electrolyte is dependent on the primary particle size in the microstructure of the densified solid electrolyte. This has been established from studies of the ionic conductivity of these samples,
densified by room-temperature magnetic pulse dynamic compaction which produces a nano-structured microstructure based on the particle size of the starting powder [1]. The total electrical conductivity of these compacted materials comprises the bulk and grain boundary conductivities. Combined with Scanning Electron Microscopy and X-Ray Diffraction results, a trend between the primary grain size and the ionic conductivity is apparent, i.e., the total ionic conductivity increases with decreasing grain size. Hence, the grain boundary conductivity is the main conduction mechanism, and this represents a trivial effect of the nanostructure [12-14].

Chiang et al. [15, 16] have reported that unique transport properties and defect thermodynamics result for fully dense cerium oxide nanocrystals of approximately 10 nm grain size. Besides the observation that the electrolytic domain for coarsened material exhibits an extrinsic ionic conductivity, independent of the partial oxygen pressure, the nano-structured material exhibits an enhanced n-type electronic conductivity that is improved by a factor of $10^4$ and requires less than one-half the reduction enthalpy of the coarse-grained counterparts. In addition, it is observed that the ionic conductivity regime for the coarsened material is transformed to an n-type semi-conducting regime for the nano-structured material. Here, the nano-structured approach does not improve the properties of the oxide-ion conducting solid electrolyte for an Intermediate-Temperature Solid Oxide Fuel Cell (IT-SOFC), as mixed ionic-electronic conductivity in the solid electrolyte reduces the load-circuit voltage, and hence the performance of an IT-SOFC.

Undoped alkaline earth fluorides and anion-excess solid solutions based on fluoride-ion conducting materials like Ba$_{1-x}$La$_x$F$_{2+x}$ have attracted widespread attention in recent decades. The alkaline-earth fluorides exhibit intrinsically anti-Frenkel disorder, and can accommodate large concentrations of fluoride-ion vacancies and fluoride interstitials. In the anion-excess solid solutions, extended defect clustering occurs and room-temperature ionic conductivities increase by a factor of $10^8$ to $10^{10}$, as explained by the Enhanced Ionic Motion model of Wapenaar and Schoonman [17,18]. Similar conductivity enhancements can be realized with nano-structured alkaline-earth fluorides. The increase in mobile ionic defects in the space-charge regions accounts for substantial conductivity increases, as has been shown for nano-structured calcium fluoride [19], using the space-charge model of Saito and Maier [20], taking the increased interfacial area of the nano-structured material into account. Chiang et al. [8] have presented the detailed equations for the spatial dependences of the oxide–ion and the magnesium-ion vacancy concentrations in nano-structured MgO with intrinsic Schottky disorder. In this model, it is assumed that the surface of the MgO has a positive charge, and that this is compensated by a spatially-dependent magnesium-ion vacancy concentration
with a larger value at the surface. Likewise, the oxide-ion vacancy concentration exhibits a much smaller value at the surface. Beyond the Debye length, both defect concentrations are equal, as required for intrinsic MgO.

An additional enhancement factor must be considered if the microstructure contains grains with sizes that are smaller than four times the Debye length, i.e., the width of the space charge region [21]. While this is not the case for the nano-structured CaF$_2$ study referred to above [19], the recent work of Sata et al. [22] presents this additional enhancement of the ionic conductivity of planar hetero-junctions of CaF$_2$ and BaF$_2$. With Molecular Beam Epitaxy, heterostructures with varying periodicity and thickness were obtained at a growth rate of about 1nm/min. Individual layer thicknesses varied between 2 and 500 nm. The ionic conductivity parallel to the CaF$_2$-BaF$_2$ interfaces increased linearly with the ratio of the number of hetero-junctions and the thickness of the laminar composite. It was shown that the space charge layers in BaF$_2$ determine the overall parallel ionic conductivity, concordant with the better BaF$_2$ anti-Frenkel ionic defect dynamics, as compared to the defect dynamics of CaF$_2$. If, however, the individual layers of the alkaline earth fluoride layers become so thin that the regime of overlapping space-charge regions is reached, the layers loose their individual duality and the laminar composite structure transforms into an artificial super-ionic conducting system, since in this composite the ionic conductivity perpendicular to the space-charge regions is also enhanced substantially.

5. Concluding Remarks

The field of nano-structured materials is very broad and involves a wide spectrum of disciplines [23]. The field has a very high degree of actuality and cross-fertilization leads to new avenues in materials science and technology.

The examples presented here reveal that decreasing the length scale to the nanometer range leads to different properties of ionic and electronic charge carriers in functional materials, such as materials for rechargeable advanced lithium-ion batteries and ceramic fuel cells for the Hydrogen Economy. The Hydrogen Economy also requires hydrogen production using sustainable energy sources, i.e., solar and wind energy. Solid-state electrochemical cells for the conversion and storage of electricity and hydrogen require materials that can be designed only if a profound knowledge of the relations that exist between the structure, defect chemistry, microstructure and properties of the functional materials is available. Therefore, this paper has been focused on the more classical defect chemistry of functional materials, and describes for several selected materials trivial and proper size effects on the defect chemistry.
6. References

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1. Introduction

The ever-growing worldwide consumption of fossil fuels and the concomitant emission of greenhouse gases, as well as the limited availability of fossil fuels, have led to a growing interest in the application of renewable energy sources. The increased general awareness of the negative environmental impact of the use of fossil fuels demands that alternative energy sources are sustainable, i.e., for instance, solar energy, wind energy, hydropower, and tidal wave energy. A Common Rule, issued by the European Union in October 2001, states that the share of sustainable energy should increase to 12% in 2010. This target seems rather modest for European countries. However, when one realizes that, for example, in 2000 only about 1% of the total electricity consumption in The Netherlands is produced by sustainable energy sources, it is clear that considerable effort has to be invested to achieve this goal.

The newly industrialized countries of Asia and Latin America are experiencing very rapid economic growth that is bringing modern society’s environmental problems, including air and water pollution and waste problems, to wider areas of our planet. Merkel [1] has discussed the role of science in sustainable development, and has stressed that the key technologies of sustainable development include new energy and propulsion technologies that will help reduce emissions of climate-damaging greenhouse gases.

The direct conversion of solar energy into electrical energy is very promising, as the world’s energy consumption in 1999 was about $4 \times 10^{20}$ J, while the amount of solar energy that reaches the earth is $5.4 \times 10^{24}$ J per year [2,3].

Indeed, photovoltaics has enjoyed substantial growth during the last few years, with overall growth rates between 30% and 40% making further increase...
of production facilities an attractive investment. However, different solar cell
technologies have grown at different rates, and over 85% of the current
production is based on silicon wafer or silicon ribbon technology [4].

In this paper nano-structured materials for new generations of solar cells
will be presented, but will be preceded by several aspects of wind power
systems.

2. Wind Energy

Wind energy stands out as one of the most promising new sources of electrical
power in the near future, and many countries promote wind-power technology
by national programmes and market incentives.

The first use of wind power was to sail ships in the Nile some 5000 years
ago. The Europeans used wind power to grind grains and pump water in the
1700 and 1800s, and the first windmills to generate electrical power in rural
areas of the USA. were installed in 1890 [5]. Now, these types of windmills are
merely attractions for tourists. The modern average wind turbine size has been
300 kW until the recent past. To date, the newer wind turbines have a capacity
of 500 to 1,000 kW. Improved wind turbine design and plant utilization have
contributed to a decline in large-scale wind energy generation costs in the
period 1980 - 2000, such that wind energy power has become one of the least-
cost sustainable energy sources [5]. The major factors that have accelerated the
wind-power technology development are related to materials, i.e., high-strength
fiber composites for the construction of large low-cost turbine blades and falling
prices of power electronics. In addition, the economies-of-scale of these
increases have contributed to this acceleration. Recently, wind turbine parks in
Denmark and Norway have not only been connected to the electricity grid, but
also to commercial electrolysers. If grid-instabilities were to occur, the
electrical energy is used in part to electrolyze water to form hydrogen and
oxygen. When stored, the hydrogen can be converted into electrical energy on
demand, using a fuel cell with water vapor as the emission product.

3. Silicon Photo-Voltaics

The photovoltaic (PV) power technology mainly uses silicon-based
semiconductor cells. From a solid-state physics point of view, the solar cell
comprises a large-area p-n diode with the junction positioned close to the top
surface. The schematics of this p-n junction device are given in Figure 1.
Figure 1. Principle of a silicon or thin-film solar cell

It comprises a phosphorus (P)-doped n-type silicon layer connected to a boron (B)-doped p-type silicon layer. The space-charge layer at the p-n junction facilitates the separation of the optically excited charge carriers. The blue color of silicon-based PV solar cells is a result of the anti-reflection TiO₂ coating. Depending on the thickness of this coating, gold colored and red colored silicon-based solar cells can be obtained, but the optimal thickness leads to the blue color.

Solar cells can be divided into several categories. These are, including the efficiency of commercial cells and efficiency in the laboratory, respectively: Single Crystalline Si (13-16%, 24.7%), Polycrystalline Si (12-15%, 19.8%), Amorphous Si (4-7%, 10.1%), III/V GaAs, (Ga)InP (21%, 25.1%), II/VI CdTe, ZnSe, CdS (5%, 16.5%), I/III/VI CuInS₂, Cu(In,Ga)(S,Se)₂ (in combination with ZnO and CdS) (12%, 19%), Dye Sensitized (7%, 11.4%), and Solid-State Nano-structured Heterojunction, for which only the laboratory efficiency has been established, i.e. 5.1% [3]. Microcrystalline and proto-crystalline Si are also under development for solar cells.

A detailed discussion of all silicon-based solar cell materials is beyond the scope of this paper. Here, we will discuss several aspects of microcrystalline and amorphous silicon-based solar cells. The successful doping of hydrogenated amorphous Si (a-Si:H), which is an alloy of silicon and hydrogen, has initiated global interest in this material for solar cell applications. In addition, the preparation of microcrystalline films of Si (µc-Si:H) instead of amorphous ones, as reported by Usui and Kikuchi [6], has stimulated many researchers to investigate these films for solar cell applications. Schropp and Zeman [7] have presented definitions for various morphologies of thin-film Si materials.

Hydrogenated amorphous silicon (a-Si:H) is a single-phase material. Hydrogenated microcrystalline silicon (µc-Si:H) is a two-phase amorphous and
crystalline material that comprises crystallite sizes < 20 nm, and hydrogenated polycrystalline silicon (poly-Si:H) is a single-phase crystalline material with grain boundaries, and the smallest crystallite size exceeds 20 nm. Amorphous and microcrystalline thin films of Si are applied in solar cells and many other electronic devices, like the thin-film transistor (TFT), a switching device that is applied in commercially available liquid crystal displays (LCDs). Microcrystalline silicon layers are often combined with amorphous layers in TFTs and solar cells [7]. Schropp and Zeman also present superstrate solar cells, where the carrier on which the various thin films are deposited serves as the window to the solar cell. Both superstrate single junction and tandem solar cells are described. A recent overview of amorphous and thin-film silicon technologies has been reported by Jäger-Waldau [4].

Thin films of the II/VI semiconductors CdS and CdTe and the chalcopyrite I/III/VI semiconductors Cu(In,Ga)(S,Se)₂ (CIGS) are ideal candidates for thin-film solar cells. The most common CdTe-based solar cell is an n-CdS/p-CdTe heterojunction with an efficiency of about 12%, where the CdS thin film is deposited on a transparent conductive oxide (TCO), like SnO₂:F coated glass [4]. The chalcopyrites form interesting material systems that offer the possibility to tailor the bandgap between 1.01 eV for CuInSe₂ to 1.68 eV for CuGaSe₂ or 2.40 eV for CuGaS₂ by substituting indium with gallium and selenium with sulphur. This makes chalcopyrites not only interesting for single-junction devices, but also opens the route to a possible tandem structure solar cell device made from the same class of materials [2,4]. An example of a thin-film solar cell based on CIGS and CdS is presented in Figure 2. In this solar cell only the thickness of the thin-film of CdS is in the nanometer range [8].

![Figure 2. The structure of a Mo/CIGS/CdS/ZnO solar cell [8].](image-url)
These types of heterojunction based on the chalcopyrites CIGS in combination with ZnO and CdS exhibit efficiencies varying between 12% for CuInS₂ and 21.5% for Cu(In,Ga)Se₂.

Solar cells based on a-Si:H and on CdTe are already commercially available, while several CIGS-based solar cells, while commercially available, are mainly in the pilot plant stage. Unfortunately, several of these solar cell systems contain either poisonous, e.g. Cd, Te, and Se, or rare elements, like Ga and In.

To date, only 18% of the worldwide sales of thin-film solar cells in 2002 (43.8 MW) was based on CdTe (indoor 4%, outdoor 7%) and on CIGS (7%), with the remaining fraction being Si-based [4]. It should be mentioned that it takes many (2-8) years, using existing production methods, before the different Si-based solar cell systems have produced the energy that was used in the process of making them. This is a significant problem in using Si-based solar cells for the large-scale conversion of solar energy in electrical energy. Various new, promising and cheap solar cell techniques have been reported in recent years, and are currently being developed for the large-scale conversion of solar energy.

4. The Grätzel Solar Cell and Beyond

A novel way to harvest solar energy is based on a photo-electrochemical (PEC) approach, in which the essential region is the interface between a semiconductor and a liquid electrolyte. Regenerative PEC cells produce electrical energy, but the PEC cell can also generate a chemical fuel, hydrogen, through the photo-cleavage of water [9]. The potential applications of PEC cells for solar energy conversion by water splitting to form the energy carriers hydrogen and oxygen, were recognized some three decades ago [10] by using a TiO₂ photo-electrode. This electrode is, due to its band gap energy of 3.2 eV, only sensitive to the near UV part of the solar spectrum. Unfortunately, highly efficient PEC solar cells based on Si or GaAs, which absorb the visible part of the solar spectrum efficiently, suffer from passivation by the formation of a SiO₂ layer, or by dissolution of GaAs under visible-light irradiation, respectively.

An alternative approach is to use a stable semiconductor with a low solar light-to-electrical energy conversion efficiency, like TiO₂ or ZnO, and to sensitize it with a visible-light absorbing dye. The practical use of sensitized flat surfaces in regenerative PEC cells is, however, limited by the low light-harvesting efficiency obtained with a single monolayer of a dye molecule. The absorption by a monolayer of dye is weak, because the area occupied by one molecule is much larger than its optical cross section for light capture. An improved photovoltaic efficiency, therefore, cannot be obtained by the use of a
flat semiconductor surface, but rather by the use of a highly porous, nanostructured film of very high surface roughness. A major breakthrough on such a novel type of dye-sensitized solar cell was achieved by Grätzel and co-workers. They used nano-structured thin films of anatase-structured TiO$_2$ with an extremely large surface area [9,11,12]. The interconnections between the nanoparticles of TiO$_2$ allow for electronic conduction through the network, and the porous structure makes it possible to have a large interfacial area between a liquid electrolyte and a dye-sensitized wide bandgap semiconductor. This dye-sensitized solar cell is schematically presented in Figure 3.

![Figure 3](image)

Figure 3, Schematic presentation of the dye-sensitized Grätzel solar cell.

The wide band gap nano-porous n-type titanium dioxide with an anatase crystal structure is covered with a monolayer of a visible-light absorbing dye molecule, usually a ruthenium complex. Visible light is absorbed by the dye molecules, exciting an electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the dye molecule. Subsequently, the photo-excited electron is injected into the conduction band of the nano-structured TiO$_2$ photo-anode, through which it migrates to the metal back electrode, usually a TCO. An I$_3$/I$^{-}$ redox couple in acetonitril mediates the electron to the oxidized state of the dye molecule,
thereby closing the circuit by regeneration of the dye molecule. The maximum voltage $\Delta V$ that such a device can deliver corresponds to the difference between the redox potential of the mediator and the Fermi level of the semiconductor. The conversion efficiency of the dye-sensitized Grätzel cell is at present 11.4% [13].

The demands for visible-light absorbing dye molecules for the use in these hybrid solar cells are [3,12]:

1. The HOMO-LUMO energy difference must be small enough to absorb the visible part of the solar spectrum,
2. The absorption spectrum must have a large overlap with the solar spectrum, to absorb as much visible light as possible,
3. The absorption coefficient must be as high as possible to absorb sufficient visible light, while using only a thin film of the dye molecules,
4. The HOMO energy level must be higher than the conduction band edge (CB edge) of the selected n-type semiconductor,
5. The difference between the CB edge of the n-type semiconductor and the HOMO level of the dye molecule must be as large as possible, as it determines the open-circuit voltage of the solar cell,
6. Preferably, the dye should be cheap, non-toxic, and exhibiting flexible properties, like solubility. Furthermore, it must be stable under illumination and oxidation/reduction cycling,
7. The dye must be able to conduct the (bound) electron-hole pairs, excited upon irradiation, to the dye molecule/semiconductor interface, to inject the photoelectron into the conduction band of the n-type semiconductor. Here, the monolayer approach is very beneficial.

The liquid electrolyte, containing the mediator, can be replaced by a visible-light absorbing p-type inorganic [2,12], or p-type organic [3,12] semiconductor. In this case, a monolayer of a dye-sensitizer molecule is no longer required. Perniu et al. [14] have described thin-film techniques for novel three-dimensional (3D) solid-state solar cells, i.e. Chemical Vapor Deposition (CVD) and Atomic Layer Deposition (ALD). CVD is very beneficial for the manufacture of the Extremely Thin Absorber (ETA) solar cell [14,15], and ALD for TiO$_2$-CuInS$_2$ 3D hetero-junction solar cells. The 3D hetero-junction solar cells and their manufacture using ALD are described by Nanu et al. [16,17].

Atomic Layer Deposition, which is also known as Atomic Layer Epitaxy (ALE) and Atomic Layer Chemical Vapor Deposition (AL-CVD), has been developed for the fabrication of polycrystalline luminescent ZnS:Mn and
amorphous Al$_2$O$_3$ insulator films. Since the mid 1990s, ALD has been introduced in the field of IC-technology. The decreasing dimensions of IC-devices call for well-defined extremely thin films, of the order of 1-20 nm in thickness [2,18]. A schematic presentation of the principle of ALD is given in Figure 4.

![Principle of Atomic Layer Deposition](image)

Figure 4. Principle of Atomic Layer Deposition

When a binary compound is deposited, the ALD process comprises four steps. First, an excess of precursor A is introduced into the reactor chamber and one monolayer chemisorbs at the surface of the substrate and the excess of A is subsequently removed by an inert gas purge. Then precursor B is introduced into the reactor chamber, which reacts with adsorbed precursor A (step C) and a monolayer of film is formed (D). After reaction, the excess of precursor B and the volatile reaction products are removed by an inert gas purge.

In contrast to CVD, ALD precursors have to chemisorb self-limiting at the surface of the substrate, in that adsorption stops if one monolayer is adsorbed, hence the growth rate becomes independent of the pulse time of the precursor. In addition, all precursors should be stable at the deposition temperature, preventing decomposition upon chemisorption, which usually results in the loss of self-limitation. Finally, the reaction rates should be very high, in order to avoid long saturation pulse times [2]. ALD is currently being used very successfully for the manufacture of novel 3D nano-structured solar cells.
5. Conclusions

Nano-structured materials for silicon-based and non-silicon-based solar cells have furthered the pace of advance in developing advanced and novel solar cells. Especially of interest are doped amorphous and microcrystalline silicon. The dye-sensitized Grätzel and ETA solar cells have stimulated the development novel 3D nano-structured solid-state solar cells, for which Atomic Layer Deposition is a very efficient deposition technique. It is anticipated that these 3D solar cells will reach efficiencies of over 8% in the coming years, and will start to replace silicon-based solar cells.

6. References


DOUBLE-WALLED CARBON NANOTUBES: SYNTHESIS AND FILLING BY 1-D NANOCRYSTALS

E. FLAHAUT
CIRIMAT, UMR CNRS 5085, Université Paul Sabatier
31062 Toulouse Cedex 04, FRANCE
flahaut@chimie.ups-tlse.fr

1. Introduction

Double-walled carbon nanotubes (DWNTs) are at the frontier between single-walled carbon nanotubes (SWNTs) and multi-walled carbon nanotubes (MWNTs). The possibility to functionalise the outer wall is of key interest, because this will ensure the connections with the external environment, while retaining the remarkable mechanical and electronic properties of the inner nanotube. This may prove to be very useful for their integration into systems and composites.

Different strategies have been developed over the years to achieve the catalytic chemical vapour deposition (CCVD) synthesis of DWNTs. We will firstly provide a brief review of the synthesis of DWNTs by the arc-discharge process. Secondly, we will focus on the use of CCVD and will compare the different methods proposed in the literature in terms of yield, purity and selectivity.

The second part of this paper will briefly describe how 1D-nanocrystals have been prepared using carbon nanotubes (CNTs) as templates. The influence of the confinement and the interaction with the inner wall of the carbon nanotube on the crystal structure will be discussed.

2. Synthesis of DWNTs

2.1 SYNTHESIS OF DWNTs BY THE ARC-DISCHARGE METHOD

The first report of the synthesis of DWNTs by the arc-discharge process was by Hutchison et al. [1], in 2001. The DWNTs were prepared using a catalyst containing Ni, Co, Fe and S in an atmosphere of Ar and H₂. The DWNTs mainly formed as bundles and the sample contained some SWNTs. The authors found that the presence of hydrogen in the mixture was essential for the synthesis of DWNTs.
The raw product contained many carbon-encapsulated metal particles and the tubes were heavily coated by disorganized (amorphous-like) carbon. No indication of either the purity or the yield was given. More recently, Huang et al. [2] synthesized DWNTs without the use of hydrogen (using only a neutral atmosphere of He) and claimed 80% selectivity (meaning that the sample contained around 80% DWNTs together with some SWNTs and MWNTs). The catalyst was a mixture of Ni, Co and FeS. Numerous metal particles (almost 60 wt.% in the raw material) were present, but their proportion could be reduced to around 7 wt. % after a long purification (refluxing in dilute HNO₃ followed by repeated centrifuging and sonicating dispersing). 300 to 500 mg of raw product could be collected in 20 minutes in optimized conditions (meaning only 130-230 mg of DWNTs after purification). Sugai et al. [3] placed a furnace heated to above 1200°C in the arc-discharge rig and prepared DWNTs using a Ni/Y catalyst. The raw sample contained SWNTs, amorphous carbon and fullerenes, and required purification. The purified DWNTs were slightly damaged by the purification process and there was no information about either the purity or the yield.

2.2 SYNTHESIS OF DWNTs BY THE CCVD METHOD: REVIEW AND EXPERIMENTAL RESULTS

The different CCVD methods used for the synthesis of DWNTs can be classified into 3 different processes: (i) gas-phase synthesis; (ii) an impregnation technique and (iii) solid-solution-based catalysts. The gas-phase synthesis proposed by Wei et al. [4] used a mixture of ferrocene and sulphur as catalyst and CH₄ as the carbon source. The reaction occurred at 1150°C for 30 minutes and led to samples containing 70% CNTs (estimated from statistical analysis of 180 HRTEM images), but also almost 20% SWNTs together with triple- and four-walled CNTs. The raw product contained an important amount of catalyst particles (almost 70 wt.%), and required a long multi-step purification process to achieve a purity close to 90 wt.%. No yield was reported and amorphous carbon deposits were clearly present on the walls of the purified DWNTs. The same authors have recently [5] proposed the replacement of CH₄ by xylene, and have prepared long DWNT strands (up to 20 cm). The samples were much purer than when CH₄ was used as the carbon source, but there was unfortunately no indication of the chemical purity. The samples also contained some triple-walled CNTs (clearly visible in TEM images, although not described in the paper).

The impregnation technique is widely used for the CCVD synthesis of SWNTs. Lyu et al. [6] have impregnated an Al₂O₃ support with Fe and Mo, and used ethanol as the carbon source (reaction at 800°C for 10 minutes). The yield was around 2 wt.% (compared to the supported catalyst). The walls of the DWNTs were rather free of amorphous carbon deposits. This method is interesting, although the use of an Al₂O₃ support makes its removal (if required) difficult. Lyu et al. [7] have also
tried benzene as the carbon source, after reduction of the supported catalyst in an Ar-H₂ mixture. The selectivity towards DWNTs was claimed to be around 90% (only from visual observation by TEM) and the samples also contained SWNTs and MWNTs. The samples were claimed to be free of amorphous carbon deposits, but this was not obvious from the reported TEM images. Unfortunately, there was no information about either the purity or the yield. Zhu et al. [8] have impregnated mesoporous SiO₂ with Co and Fe. The carbon source was CH₄ (pure or with H₂) and the reaction was carried out at 800°C (for 10 minutes to 1 hour). The selectivity towards DWNTs was estimated to be around 50% (from visual observation of TEM images) and some wide DWNTs (inner diameter up to almost 4 nm) were produced. Again, there was no information about either the purity or the yield. Li et al. [9] impregnated MgO with Co and used CH₄ as the carbon source to prepare DWNTs at 1000°C. The yield was low (not detailed) and the sample contained some large carbon-encapsulated cobalt particles (up to 50 nm). No selectivity was indicated, but the authors reported the presence of SWNTs and MWNTs together with the DWNTs (giving no proportion). The samples were surprisingly rather free from amorphous carbon deposits (non-catalytic self-decomposition of CH₄ occurs spontaneously on MgO at 1000°C).

We have proposed an original CCVD method for the synthesis of DWNTs, which uses oxide solid solutions as catalysts. It was originally shown [10] that the reduction of these catalysts in a H₂-CH₄ atmosphere allows the use of the freshly formed surface metal nanoparticles to form the CNTs. CH₄ decomposes on the nanoparticles and supplies them with carbon, which accumulates until the saturation in carbon is reached. The nucleation and growth of CNTs then takes place, blocking the particle growth. The resulting composite powders contain an enormous amount of SWNTs and thin MWNTs (mainly less than four walls), with a very homogenous dispersion of the CNTs between the oxide grains. Incidentally, to the best of our knowledge, this was the first time that the formation of SWNTs by CCVD from a hydrocarbon has been reported [10].

Several parameters related to the starting oxide material have then been investigated in order to increase the proportion of CNTs with respect to the other carbon species (carbon nanofibres, graphitic shells, disordered carbon), and then to improve the selectivity of the process towards SWNTs or DWNTs. The control of the experimental CCVD parameters using Mg₀.₉₉(Coₓ,Moₓ)₀.₀₁O [11] solid solutions allowed us to obtain a rather good selectivity towards the number of walls of the CNTs, 80% of which were SWNTs and DWNTs. The CNTs were, again, very well dispersed within the oxide matrix grains, and their specific surface area could be as high as 980 m²/g [12]. Furthermore, it was also shown that when using MgO-based solid solutions, a simple soaking in HCl allows an easy separation of the CNTs from the metal and MgO matrix, without damaging them [11]. Molybdenum is often added to transition metals such as Fe and Co to increase the efficiency of catalysts. A systematic study of the ratio between Co and Mo in Mg₀.₉₉(Coₓ,Moₓ)₀.₀₁O catalysts...
was performed [13], and showed that a Co:Mo ratio of 3:1 significantly enhanced the yield while keeping the number of walls low (CNTs mainly double and triple-walled). Our latest results obtained with the MgO system [12] are very promising for the large-scale production of DWNTs, because we managed to prepare in one unique batch 1.3 g of CNTs (77% of which are DWNTs, only less than 5% triple-walled CNTs; purity around 98 at.% of carbon) from 10 g of Mg_{0.99}(Co_{0.0075}Mo_{0.0025})O [12]. This was achieved by keeping the Co:Mo ratio to 3:1 but modifying the catalyst preparation (use of citric acid instead of urea for the combustion synthesis). These DWNTs have been fully characterised [12,14], and Raman spectroscopy suggests that the inner and outer walls of some of the DWNTs could be observed separately (RBM peaks).

3. Filling CNTs to Prepare 1D-Nanocrystals

CNTs were filled by capillarity, by immersing the CNTs in a melted phase. This method was originally proposed by Ajayan [15]. The main effect of confinement inside a CNT of only a few nanometers diameter is to decrease the coordination (figure 1) of the atoms (or ions). This happens because the inserted material is often reduced to only a few atomic layers when observed in the direction perpendicular to the CNT axis, meaning that complete layers of atoms or ions are lacking when compared to the bulk structure. Confinement thus leads to 1D structures of atoms or ions of reduced coordination; the structure of which can either be or not be related to that of the bulk. We will now describe a series of examples to illustrate the effect of confinement.

\[ \text{KI} \rightarrow \text{KI} \text{ confined} \]

The first example [16] is that of KI@SWNT. KI has a face-centred cubic structure (a = 3.53 Å). The general methodology employed to determine the structure of the confined crystals is the following: (a) HRTEM observation; (b) Construction of a rough outline of the structural model from the HRTEM images; (c) Simulation of the HRTEM image from the proposed structural model and comparison with the experimental data. Images are simulated at different foci, in order to match the experimental images; (d) correction of the

![Figure 1. With KI, the coordination of the ions decreases from 6:6 in the bulk to 4:4 when confined inside a 1.4 nm diameter CNT.](image-url)
structural model and simulation until the fit with the experimental images is acceptable. In the case of KI@SWNT, the confined KI crystals retain a structure close to that of the bulk, but distortions are observed.

In the case of two-layer 4:4 co-ordinated KI crystals [16] confined within 1.4 nm single-walled carbon nanotubes, lattice distortions were observed perpendicular to the CNT axis: along the axis the d-spacing is 3.5 Å, as in the bulk; however, this spacing is increased to nearly 0.4 nm across the CNT axis (a 14% extension). In such a thin crystal, where all the ions are indeed "surface ions" (compared to the bulk), there is a strong interaction between the ions and the CNT inner wall. In the case of CNTs with larger diameters [17], the situation was a bit different, and slight distortions were observed both parallel and perpendicular to the CNT axis. The measure of such small distortions was made possible by the use of the phase image restoration technique.

Another example can be taken with lead iodide (PbI₂), which was also crystallised inside CNTs of different diameters [18]. Bulk PbI₂ has a layered structure, each layer being composed of edge-sharing PbI₆ octahedra. Slight distortions could be observed, and the orientations of the PbI₂ fragments with respect to the CNT axis were found to be strongly dependant on the diameter. Because there is a strong interaction between the confined-nanocrystals and the inner wall of the CNTs, the composite crystal@CNT may have new physical properties. For this reason, PbI₂ and other semiconductors such as Se, Te, SnSe, HgTe and Bi₂Te₃ have also recently been inserted into DWNTs (characterisation in progress).

4. Conclusions

CCVD is a very efficient method for growing DWNTs. The use of Mgₓ₋₅CoₓO solid solutions containing small additions of Mo allows the synthesis of gram-scale amounts of clean DWNTs, with an increased selectivity and with a low residual catalyst content, as long as the Co:Mo ratio remains high. SWNTs and DWNTs have been successfully used as templates to grow 1D-nanocrystals of semiconductor compounds such as PbI₂, and we have shown that some structural modifications occur due to the limited amount of space offered by the inner wall. This may lead to modifications of the physical properties of the nanocrystals, which are currently under investigation.

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References


1. Introduction

Active matrix liquid crystal displays (AMLCDs) employing thin film transistors (TFTs) based on hydrogenated amorphous silicon (a-Si:H) as the channel material currently lead the flat panel display market. This has been achieved through significant investment in this technology, which has resulted in a rapid increase in the size and resolution of AMLCDs. As a result, these displays are no longer only found in laptop computers, but are now a common desktop computer display and are also starting to encroach into the home television market – 40” displays are now available commercially. However, the limited carrier mobility and metastability of a-Si:H is now restricting AMLCD development [1]. Polycrystalline silicon (poly-Si) is an alternative TFT channel material that does not suffer from these limitations. As a thin film material, poly-Si consists of ordered regions of material (grains) which can be up to several micrometres in diameter, separated by disordered grain boundaries [2]. The field effect mobility of poly-Si is over 100 cm² V⁻¹ s⁻¹ and TFTs fabricated with this material do not exhibit metastable threshold voltage shifts.

Solid phase crystallisation (SPC) permits large areas of a-Si to be crystallised to produce poly-Si by simply heating the sample in a furnace [2, 3]. The nucleation and growth of crystalline grains is thermally activated, and consequently the time required for complete crystallisation decreases exponentially with increasing temperature with an activation energy of (3.0±0.25) eV [4]. Between 10 and 100 hours of annealing time are required for complete crystallisation at temperatures below 600° C. This annealing time and temperature may be reduced through the addition of a small quantity of a metal impurity to the a-Si [5, 6]. This is achieved by selectively depositing a thin film...
of the impurity metal onto the surface of the a-Si. Upon heating, the metal diffuses into the a-Si and catalyses a lateral crystallisation in the uncoated regions of material with low residual metal contamination in the bulk of the crystal grains. The application of an electric field during crystallisation further increases the metal induced crystallisation rate and can also lead to a preferential crystallisation direction. However, this directionality varies between studies, and in some cases the crystallisation rate is enhanced in all directions [7-9]. It is suspected that these inconsistencies are due to variations in the properties of the amorphous silicon precursor material. In this work, the effect of changing the hydrogen content of the a-Si:H precursor material upon the kinetics of field-aided lateral crystallisation (FALC) using a nickel catalyst is investigated. It is demonstrated that the presence of hydrogen has a strong influence upon the crystallisation process by controlling the charge on nickel ions at the crystallisation front and by limiting the diffusion and mobility of nickel through the silicon bulk.

2. Theory of Field-Aided Lateral Crystallisation

The production of poly-Si by both metal induced lateral crystallisation (MILC) in the absence of an electric field and FALC using nickel as the catalyst metal has been previously studied by the authors [10]. This study showed that, in both cases, growth of grains following nucleation is limited by a reaction between nickel and silicon at the growth front to form NiSi. Therefore, the MILC rate (in the absence of an electric field) is simply given by

$$\frac{dx}{dt} = 12K_0 \exp\left(-\frac{E_{AK}}{kT}\right).$$ (1)

where $E_{AK}$ is the activation energy of the reaction, $K_0$ is the pre-exponential factor, $k$ is the Boltzmann constant and $T$ is the annealing temperature. In the case of FALC, the electric field will cause nickel ions to move. This additional flux of nickel ions towards the crystallisation front will increase the NiSi reaction rate, and an additional ‘field enhancement’ term is required in the equation describing the crystallisation rate,

$$\frac{dx}{dt} = \left\{12K_0 \exp\left(-\frac{E_{AK}}{kT}\right)\right\} + \left\{12YD_0 \exp\left(-\frac{(E_{AD} + E_{AK})}{kT}\right)\right\} eE.$$ (2)

where $E_{AD}$ is the activation energy for the diffusion of nickel in silicon, which is
0.47 eV \[11\], \(D_0\) is the pre-exponential diffusion coefficient, which is \(2\times10^{-7}\) m² s⁻¹ \[12\], \(e\) is the electronic charge, \(E\) is the applied electric field strength and \(Y\) is a dimensionless constant. It should be noted that in the absence of an electric field, equation 2 reduces to equation 1, as expected.

### 3. Experimental Details

Samples of a-Si:H were deposited onto Corning 7059 glass substrates using a PlasmaTech DP80 capacitively coupled rf plasma enhanced chemical vapour deposition system (240 mm plate diameter, 40 mm plate separation) using pure silane gas (80 sccm flow rate, 300 mTorr pressure) and an applied rf power of 10 W at 13.56 MHz. Samples were deposited at varying substrate temperatures to yield material with different hydrogen contents (20 at.% at 200°C; 10 at.% at 300°C; 5 at.% at 400°C). In all cases, the deposition time was controlled to produce 50 nm thick samples. A 5 nm thick layer of nickel was then thermally evaporated onto the a-Si:H samples using an Edwards E306A Coating System through a shadow mask to produce a pattern of 0.5 mm diameter dots. Finally, a set of aluminium on chromium metal contact pads, 12.5 mm apart, were thermally evaporated onto either end of the sample to allow the application of an electric field during annealing. The final structure of the samples is shown in figure 1. Annealing was performed in air in a Thermco quartz tube furnace and an electric field was applied using a 0-600 V dc power supply. The current in the power supply circuit was monitored during annealing to confirm that a good electrical connection was made to the sample.
4. Results and Discussion

It has previously been demonstrated by the authors that the crystallisation of unhydrogenated a-Si using a nickel catalyst is accurately described by equation 2 [10]. Figure 2 shows the extracted crystallisation parameters (from equation 1) of a-Si:H with varying hydrogen content. Even without the application of an electric field, the presence of hydrogen has a profound influence on the crystallisation kinetics. It is clear that the activation energy of the nickel silicide formation reaction shows a marked increase with hydrogen content. It has already been reported that the formation of nickel silicide on a crystalline Si surface is suppressed if the surface is hydrogen terminated [13], and the activation energy of surface diffusion of Ni on Si(100) is also increased by ~0.3 eV in the presence of H [14]. A similar effect is also expected in bulk silicon. First principles calculations suggest that Ni tends to exist in interstitial sites in the silicon network [14]. Therefore, the presence of dangling bonds acts to assist Ni diffusion. However, hydrogen terminates most dangling bonds in a-Si:H, and this suppresses Ni diffusion and silicide formation which may then require a capture and release of an H atom by the Ni to proceed, resulting in an increase in the activation energy, as observed in figure 2.

The presence of hydrogen also affects the FALC of silicon using a nickel catalyst. Figure 3 shows the variation in FALC rate as a function of electric field for a-Si:H samples with varying hydrogen concentrations. At low hydrogen concentrations (~5 at.%) the electric field serves to reduce the influence of the electric field upon crystallisation. First principles calculations
for Ni atoms in crystalline silicon show that a strong charge transfer takes place between the bound Ni atom and the surrounding silicon lattice, with the Ni taking on a positive charge, but in the presence of H this charge transfer is suppressed [14]. It is not surprising, therefore, that the influence of the electric field is also reduced. At a hydrogen content of ~10 at.%, as found in device quality a-Si:H, the effect of the electric field is restored, with an increase in the crystallisation rate, particularly towards the positive electrode. This is an indication that there are negatively charged Ni ions at the crystallisation front. This is to be expected if a nickel atom is in the presence of excess hydrogen, as the electron affinity of nickel (1.156 eV) is greater than that of hydrogen (0.754 eV) [11]. At very high hydrogen contents (~20 at.%), the effect of moderate electric fields is to actively suppress crystallisation in all directions. It is known that, at these concentrations, hydrogen atoms tend to cluster in internal micro-voids in a-Si:H and there is a significant rise in the defect density [1], but it is not clear why this should lead to a reduced crystallisation rate in the presence of a moderate electric field. Neither is it apparent why a high electric field should be able to enhance crystallisation once more, and this is the subject of ongoing research.

5. Conclusions

It has been shown that nickel induced crystallisation of a-Si:H is strongly affected by the presence of hydrogen. In the absence of an electric field,
hydrogen acts to increase the activation energy of silicide formation. Low hydrogen concentrations also reduce charge transfer between nickel and silicon, thereby eliminating the influence of electric field upon crystallisation rate. The crystallisation rate is strongly enhanced towards the positive electrode at a higher hydrogen content of ~10 at.% as a result of the lower electron affinity of hydrogen relative to nickel. This work demonstrates that variations in the hydrogen concentration of the a-Si:H precursor material can indeed alter the direction of crystallisation, but further work is required to fully describe the mechanism by which this occurs.

References

SILICON THIN–FILM SOLAR CELLS

W. FUHS
Hahn-Meitner-Institut Berlin, Dep. Silizium-Photovoltaik,
Kekuléstraße 5, D-12489 Berlin, Germany

1. Introduction

Silicon thin-film solar cells are a particularly attractive option for a future photovoltaic technology. Among the various options, the technology of hydrogenated amorphous silicon, a-Si:H, is certainly the most advanced. Various companies manufacture modules with efficiencies of 6-8 % [1]. Crystalline silicon, in principle, has the potential for a higher cell efficiency. The various approaches may be ordered in the sequence of the process temperatures used. Below a growth temperature of T_S~300°C, micro-crystalline silicon (µc-Si:H) can be made using the same deposition techniques as for a-Si:H, namely plasma enhanced chemical vapor deposition (PECVD) or hot-wire deposition (HW). Characteristic of these materials is the incorporation of hydrogen, which enables very effective in-situ passivation. Polycrystalline silicon (poly-Si) films on glass substrates can be made by solid phase crystallisation of amorphous Si, at temperatures of 500-600°C. Recently, Pacific Solar [2] has announced that on the basis of this technique, module efficiencies of about 8 % have been obtained. Deposition of poly-Si films from the gas phase on foreign substrates results in general in very complex, heterogeneous morphologies which, due to their high densities of grain boundaries, are difficult to use in solar cells. This problem led to approaches where, as a first step, a thin polycrystalline seed layer is made. The absorber layer is then deposited epitaxially upon this, from the gas phase.

The low-temperature approach, working with glass substrates, is limited to T_S<600°C, because of the softening temperature of the glass. In this temperature range, the challenge is to achieve epitaxial growth of reasonable quality, by applying ion-assisted deposition methods [3]. For the high-temperature approaches at T_S>1100°C, epitaxial growth is much easier [4]. However, the problem here is to find inexpensive substrates which can stand the high process temperatures. The present report thus confines itself to the low temperature approaches.
2. Amorphous and Microcrystalline Silicon

The structural model for amorphous silicon is a random network, characterised by a complete loss of long-range order due to statistical changes in bond length and angle. Such a structure is characterised by a large number of broken (dangling) bonds, which constitute the most relevant electronically-active deep defect states. Progress in this field is strongly related to the ability to reduce the concentration of these defects, in particular by *in-situ* hydrogen passivation.

The optical absorption of a-Si:H in the visible spectral region is considerably greater than that of c-Si, enabling effective absorption of sunlight in a film which is only about 1 µm thick. In the most commonly used superstrate cell, the typical structure is glass/TCO/a-Si:H(p)/a-Si:H(i)/a-Si:H(n)/metal, and the light enters through the glass. The substrate cell uses stainless steel (ss) as a substrate, with an inverted layer sequence: ss/Ag-ZnO/p-SiC/a-Si:H(n)/a-Si:H(i)/a-Si:H(p)/metal grid. In both cases, the thickness of the undoped layer of a-Si:H(i) is about 0.5 µm. In these p-i-n devices, the electric field extends throughout the i-layer, and carrier collection therefore occurs predominantly by drift. Single junction cells have been developed to yield stable efficiencies of 9-10 % in the laboratory.

However, a major problem of the amorphous silicon technology has been the degradation of the electronic properties of films and devices under illumination. Considerable progress has been made concerning the increased stability of solar cells, predominantly by proper device engineering. The strategy is to use stacks of two or three p-i-n cells. Such an advanced device structure offers several advantages. In a stack, the thickness of the single cells is reduced, improving the stability by enhancing carrier collection through an increase in the internal electric field. In addition, by using materials with different bandgaps, a tandem structure can be made. Due to the selective use of sunlight, this reduces thermalisation losses and therefore gives a higher theoretical efficiency. In recent years, several companies have started commercial production of modules on the basis of this technology, with stabilized efficiencies in the range of 6-8 % [1]. The triple p-i-n junction solar cell produced by the United Solar System Corporation (USSC) led to the highest efficiency (per active area) reported so far for laboratory cells (A = 0.25 cm²) using a-Si:H and a-Si/Ge alloys: 15.2 % initial and 13 % stabilized [5].

At present, the challenges for research in this field are the development of materials which can be used in stacked tandem structures with a-Si:H, the enhancement of the deposition rate, and the improvement of the cell efficiencies and production yields. The optical absorption of µc-Si:H is very similar to that of crystalline silicon, which suggests the use of this material for a bottom cell in a tandem concept with a-Si:H (the micromorph concept). Fig.1 shows an
example of such a cell structure, made with a-Si:H p-i-n as the top cell, about 100 nm thick, and µc-Si:H-p-i-n as the bottom cell, with a thickness of a few µm.

It has to be emphasized that such a cell requires an excellent light trapping technology. In the work at the Forschungszentrum Jülich, this has been achieved by post-deposition chemical texturization of the ZnO window layer, combined with a back-reflector (a ZnO/metal double layer) [6]. The resulting quantum yield reveals the advantage of the tandem concept: The top cell uses the high energy photons, while the bottom cell uses the low energy photons. The results obtained with this technology are very promising: 9-10% conversion efficiency for large modules (Kaneka Corporation [7]), and 12 % for laboratory cells (various groups, e.g. [6,8]).

3. Polycrystalline Silicon Thin-Film Solar Cells on Glass

The basic problem in realising a polycrystalline silicon thin-film solar cell on an inexpensive substrate such as glass is the generation of a poly-Si film of large grain size at the low temperatures demanded by the nature of the substrate (T < 600°C). A suitable approach is solid phase crystallisation (SPC), in which amorphous silicon a-Si is annealed at temperatures close to the softening temperature of the glass substrate [2]. However, this approach requires unfavorably long annealing times, and the potential is limited by the fact that the grain size of the SPC poly-Si layers is of the order of the film thickness,
In order to achieve efficiencies of the order of 15%, the grain size should be considerably larger than the thickness of the electronically active absorber layer (a few µm). Therefore, alternative projects are being pursued in various laboratories. In the first step, a large grained poly-Si layer is generated by Al-induced crystallisation of amorphous silicon. In the second step, this is used as a template for the subsequent epitaxial growth of the absorber layer (e.g. [3]). The most important process steps are discussed below, for a glass/poly-Si(p+)/poly-Si(p)/a-Si:H(n+)/TCO solar cell structure.

The Al-induced layer exchange process (ALILE, see Fig. 2) transforms the layer sequence glass/Al/a-Si by a simple annealing step into a sequence glass/poly-Si/Al(Si). After wet chemical removal of the Al(Si), a poly-Si film with grains as large as 10-20 µm is left on the glass [9]. For this process to occur, a thin layer of Al2O3 on top of the Al is essential. It acts as a barrier layer and controls the mass transport across the interface [10]. The most important partial steps in this process are (1) dissociation of Si and transport across the barrier, (2) diffusion of Si within the Al, (3) nucleation of Si crystallites, (4) growth of crystallites, and (5) Al transport across the interface. If the nucleation rate is small, the grains growing out of one nucleus can reach large sizes. It is characteristic of this process that nucleation can be strongly suppressed by control of the mass transport across the interface [10]. It has been shown that the aluminium-induced layer exchange process provides large grained (> 10 µm) polycrystalline silicon layers, within short process times (< 2 h) at low temperatures (< 600°C), with a desired preferential (100) orientation on large areas (3” substrates) (pole diagram in Fig. 2). This makes ALILE a promising choice for the formation of seed layers for low temperature epitaxial thickening.
Silicon homoepitaxy by chemical vapor deposition at temperatures above 1000°C, is well established, and provides device-grade silicon films (the high-T-path). At low temperatures (T < 600°C, the low-T-path) it becomes necessary to apply deposition techniques which provide additional non-thermal energy to the surface of the growing film (ion-assisted deposition methods). In addition, the crystal orientation, quality of the surface, surface contamination and substrate temperature are much more critical for the low-T-path than for the high-T-path. According to present experience, a strong preferential (100) orientation of the seed layers and a high substrate temperature are required. The first successful depositions which showed local epitaxial growth on an ALILE seed layer were made with ion-assisted deposition (IAD) [11] and electron cyclotron resonance chemical vapor deposition (ECRCVD) [12].

The final step in the cell process is the deposition of a thin-film emitter from the gas phase. These emitters can be grown epitaxially or alternatively as heteroemitters, using a material with a large bandgap. At present, the most promising approach is the use of a heterostructure with hydrogenated amorphous silicon (a-Si:H/c-Si), which can be prepared by PECVD-deposition. This heterostructure technology has been introduced by the Sanyo Corporation. For the time being, it forms the basis for their production of HIT-modules. In the laboratory, efficiencies of up to 20.7% have been reached for the structure a-Si:H(p+)/c-Si(n) with monocrystalline silicon [13]. The inverse structure, a-Si:H(n+)/c-Si(p), has been far less successful. At present, the highest values that were obtained for flat FZ-Si(p) wafers range between 16 and 17% [14]. The detailed analysis of this cell led to the conclusion that the performance is not limited by the properties of the heterostructure interface, due to excellent in-situ passivation by hydrogen.

The first solar cell structures with an absorber thickness of 1.5-2.0 µm have been prepared on the basis of this concept, with open circuit voltages in the range 200-250 mV. These allow the identification of a number of problems that have to be solved. Clearly, epitaxial growth at low temperatures has to be improved, in order to improve the structural quality of thick (up to 2 µm) epitaxially grown absorber layers. The first material characterizations by photoluminescence and electrical defect spectroscopy (CV, DLTS) indicate the presence of high defect densities in the epitaxial layers. This may arise from structural defects, but also from contamination with O or N. Such results suggest that additional passivation of the absorbers will be required. In various laboratories, such projects have been launched with great expectations. It is clear that these long-term research projects are characterized by a substantial risk, due to many problems that are not yet solved. However, there is a large potential for cost reductions, in the case of success.
References

1. Introduction

Early observations of nanocavities produced by implantation of energetic ion or neutral species into solids were associated with the problems of swelling, exfoliation and release of gas that occurred in nuclear reactors, particle accelerators and the walls of experimental fusion devices. Of most concern was the implantation of insoluble inert species that formed small nanometer bubbles through a process of vacancy accumulation, although the processes involved were not well understood at that time. In 1961, Pugh [1] found such bubbles nucleating on dislocation lines, with heterogeneous nucleation and growth by vacancy diffusion and/or plastic deformation of the material matrix.

Later, Barnes [2] developed a theory of swelling and gas release for reactor materials, drawing attention particularly to the insolubility of inert gases and bodily migration of bubbles. Key parameters were the surface energy, surface self-diffusion coefficient, lattice parameter of the solid and a driving force believed to be related to line tension of dislocation lines. In 1965, Grant and Carter [3] described a similar process occurring in ion-pumps, with release of inert gases trapped as bubbles after pumping for prolonged periods. In 1973, studies were made of argon ions implanted into thin films. It was shown that the recoil implanted material formed discrete clusters within the substrate, and that argon entering silicon oxide formed bubbles [4].

The distribution of helium implanted into stainless steel was studied in 1978 by Choyke et al. [5]. In 1981, Jager and Roth [6] discussed the concept of helium trapping and the build up of pressure in nanometre size bubbles forming in nickel, stainless steel and amorphous alloys following room temperature implantation. The authors pointed out that in crystalline material the He bubbles arrange in ordered domains where they are preferentially aligned parallel to the \{111\} and \{220\} matrix planes, forming a “bubble lattice” with lattice
parameters $a_1 = 8 - 9$ nm. An important concept was put forward by Yadava in 1981 who showed how bubbles can grow by the action of the compressive strain fields surrounding bubbles, attracting vacancies and repelling interstitials [7]. In 1983, Paszti et al., as part of a study of flaking and blistering in helium implanted silicon wafers, broke the wafers open. They discovered a sponge-like structure with channels and large cavities observed in the region of the broken silicon, produced as cracks of interconnected He bubbles merging together [8]. Although not discussed in the paper, this observation can be seen in retrospect as suggesting future possibilities for thermal splitting of silicon wafers.

In 1987, Griffioen et al. [9] and Evans et al. [10] implanted helium into silicon with subsequent annealing to produce nano-sized cavity structures devoid of gas. Since this key work, many applications for nanocavities have been found in the fields of electronics, microelectronics and opto-electronics, ranging from gettering and trapping of impurities [11, 12] to splitting of silicon wafers [13] and strain relaxation layers for thin layer strained silicon devices [14]. These topics are the main subject of this review.

2. Production of Nanocavities

The nanocavities discussed here are formed by ion-implantation of hydrogen or helium with subsequent annealing, although other species may sometimes be used effectively and have been reported occasionally [15]. The importance of hydrogen and helium induced nanocavities for the splitting of silicon wafers to produce silicon-on-insulator (SOI) structures, and for layer transfer in general, cannot be over-emphasised. The subject of a great deal of research over the past fifteen years, the topic continues to be investigated as critical dimensions decrease with new challenges for performance improvement. The detailed processes involved are complex, and here it is only possible to give a brief outline of basic ideas in current thinking. For more detail, we recommend a comprehensive review by Cerofolini et al. [16] and more recent studies, for example those in references [17-21].

When a species is implanted, damage is produced and for a reactive species both chemical and physical interaction with the host lattice are possible, which will be affected by the distribution and nature of the damage. During annealing, a complex series of changes may be expected, dependent on both time and temperature. For an inert species like helium, chemical reactions are not possible and it is possible to study the differences of the mechanism for reactive and non-reactive species by co-implantation [22]. Some basic behaviours of helium and hydrogen implants are however similar to both species. Both gases dissolve endothermically in silicon and both produce damage predominantly of the vacancy type. When an excess of vacancy-like
defects exists, reorganisation proceeds so that the defects tend to form cavities in which the gas segregates. It is the interaction of the implanted species with vacancies and vacancy clusters that leads to the production of bubbles. Voids will be created when a sufficient density of vacancies is present (supersaturation) at the void nucleation temperature. However, if the voids produced are too small these will shrink and disappear as fast as they are formed. Only a sufficiently high concentration of vacancies will produce stable voids of over a critical size. Generally, vacancies will annihilate with interstitials and will diffuse from the damage region and be lost to the surface, if not trapped by the strain fields in the damaged region.

The interaction of implanted gas with the damaged silicon lattice is complex, but is easier to understand in the case of inert gases. For helium, Alatolo et al. [23], using a molecular dynamic approach, have shown that helium is dissolved at interstitial sites (solution enthalpy = 0.82 eV); even if present in a single vacancy it will diffuse out to be trapped interstitially. For a sufficiently raised temperature, diffusion without significant lattice re-arrangement will take place between interstitial sites via hexagonal sites, with an activation energy of 0.96 eV. However, for a vacancy cluster or void, the surrounding tensile strain-field will attract helium atoms which will accumulate there, since the helium-helium repulsive potential is relatively weak.

When silicon implanted with a sufficiently high fluence of helium is heated, then cavities are produced. The process starts with the mutual attraction of helium (in atomic or cluster form), and mobile vacancy clusters; this being caused by the compressive strain field around the helium and the tensile field around the vacancy clusters. The process leads initially to helium decorated vacancy clusters, but heating leads to re-organisation of vacancies in a central cavity with capture of the helium therein, a model described by Cerofolini et al. [16]. TEM studies can be useful in showing the evolution of cavity development with annealing temperature.

The results of studies made in our laboratories are shown in Figure 1, which shows the effect of annealing helium implanted <111> silicon wafer samples to various temperatures. Up to 300°C, only damage similar to as-implanted samples was observed. A significant change occurs at 400°C (Figure 1a), when voided platelet structures, appearing as light-coloured lines but interpreted from existing literature as platelets [24], can be observed. These are mostly parallel to the surface but are occasionally tilted, often producing a ‘daisy-chain’ pattern. Strain markings are much in evidence. At 500°C (Figure 1b), some annealing out of the damage region has occurred, and there are slightly less strain markings. The platelet formations up to 13 nm wide are more clearly defined, and these are beginning to break up into bubbles. At 600°C, Figure 1c, the transformation to bubbles is much further advanced, and parallel rows of bubbles can be seen between 50 and 100 nm apart. Further annealing
out of strain is in evidence. At 700°C, the bubbles begin a conversion process to lenticular-shaped cavities and the process continues to higher temperatures, until at 800°C the platelets have completely converted to spherical and lenticular-shaped bubble cavities of average size 20x30 nm, with a small number up to 30x60 nm. Facetting and tetrakaidecahedral [16] shapes can be observed. With further increase of temperature, the density of bubble cavities decreases and the size increases until at 1050°C, there are roughly equal numbers of spherical cavities (~30 nm) and lenticular shapes up to 50x100 nm, Figure 1d.

Hydrogen is highly reactive, and when implanted at low fluence into silicon at low temperatures is expected to take up a bond-centred configuration [25]. This is relatively unstable, so that with increase of temperature and higher fluences (implying higher density), hydrogen atoms will diffuse sufficiently to react with other hydrogen atoms or vacancies, leading to stabilized hydrogen decorated vacancy complexes and decoration of (111) crystal faces. The latter is strongly suggested by the TEM studies of Wang et al. [26], who also found a smaller number of (100) plane defects. In fact, IR measurements show that substantially all the implanted hydrogen is bonded to silicon and a wide distribution of Si-H bonds exists [13]. Annealing to temperatures of the order of 500°C leads to the destruction of Si-H bonds and the formation of H₂.

According to Wang et al. [26], the conglomerate of hydrogen on (111) planes leads to an amorphous layer, and the build up of H₂ in this layer leads to the cracking and flaking that is observed for high fluences. Platelets, one to two
atomic layers thick (0.3 to 0.6 nm) and 5 to 20 nm long, are observed in as-
implanted samples, and for annealing temperatures over 500°C these give way
to spherical voids which grow by exchange of vacancies from the smaller ones
to the larger ones. Above 700°C, no more hydrogen remains [24].

3. Applications of Nanocavities

New applications of nanocavities continue to be found. Here, the most
important are described and some future possibilities mentioned.

3.1 GETTERING OF IMPURITIES

Gettering can be an important process in the management of contamination in
semiconductor devices, and nanocavities have been shown to be particularly
effective for this purpose. Dangling bonds on the inside surface of the cavity
wall will trap contaminants by chemisorption, even for very low levels of metal
contamination. This was shown for example by Wong-Leung et al. [11] and
Mohadieri et al. [12], who studied gettering of fast diffusing metals to hydrogen
induced cavities. A study of Cu, Au, Co and Fe using silicides as a source was
made by Myers et al. [27], who showed using RBS and TEM that Cu and Au
would travel distances of the order of 1 µm to form monolayer coverage on the
cavity surfaces. With Co and Fe, less than a monolayer coverage was found.

Metals were also found to transfer between one cavity layer and another.
Williams et al. [28] showed that when the cavity walls were saturated, Au
would precipitate within the cavity itself, as had been shown previously for Cu
[29] and Ag [30]. It is of interest that Wong-Leung et al. [29] found that copper
silicide would form within these cavity structures. The power of cavity gettering
was well demonstrated in the lateral-gettering studies of Roqueta et al. [31],
who showed that the influence of cavities produced by helium implantation
could extend over millimeter distances to getter Pt and Fe, with applications in
power device technology. An interesting use of Cu gettering to study the
position of defects in 40 keV He ion implanted silicon was made by Peeva et al.
[32], who found with 10 min annealing times at 800°C, that gettering occurred
at half the projected range of the implant.

Related to gettering is the possible use of nanocavities in power devices,
as localized recombination centers to control minority carrier lifetimes. In
power device technology, 5d transition metals (Pt, Au) are used to control the
minority carrier lifetime and reduce the reverse recovery time in bipolar
structures. Rangan et al [33] showed that closely-spaced multi-layered cavities
can be produced in silicon by sequential helium implant and anneal cycles.
Deep level transient spectroscopy showed broad minority carrier peaks
attributed to the defect clusters. Metastable behaviour was observed, with energy shifts \( \sim 30 \text{ meV} \) with temperature cycling, suggesting a change in the structural configuration of the cavity defects.

### 3.2 STRAIN RELAXATION LAYERS

Strained silicon is of particular interest for high-speed devices like MOSFETS, which utilise the enhancement of electron mobility from bi-axially stretching the silicon lattice (typically \( \times 1.7 \) for a lattice mismatch of 0.84%). This is normally achieved with a series of compositionally graded buffer-layers of \( \text{Si}_{1-x}\text{Ge}_x \) grown on a silicon substrate, with the device layer of strained silicon grown on top of the final strain free silicon-germanium layer. The technique is necessary to prevent threading dislocations extending to the surface silicon and affecting device performance, as shown for example by Churchill et al. [34]. An alternative to the use of graded buffer layers is to deposit on a silicon substrate a single layer of relatively thick \( \text{Si}_{1-x}\text{Ge}_x \) with the required value of \( x \). Then to implant hydrogen or helium through this layer into the silicon substrate, followed by annealing to produce a layer of nanocavities. The cavity layer has the effect of relieving the local compressive strain in the silicon-germanium, allowing strained silicon to be grown directly on relaxed silicon-germanium of the required composition. Ideally, one would like values of \( x \) to approach 0.3. Hollander et al. [14] showed that it is possible to implant through a 250 \( \mu \text{m} \) silicon-germanium layer to about 70 \( \mu \text{m} \) below the interface with silicon, to achieve this effect. Although the misfit dislocation network was more dense and entangled compared to non-implanted graded samples, threading dislocations were minimal. The authors found that values of \( x \) of the order of 0.2 with H and 0.3 with He could be achieved.

### 3.3 THERMAL SPLITTING OF SILICON WAFERS

The use of nanovoids using the high internal pressure of implanted gases built up in the voids during annealing is a well established process to produce thermal splitting of bonded silicon wafers for Silicon-on-Insulator (SOI) substrates. The technology can be applied to a range of both semiconductor materials and substrates, and the mechanisms involved are still the subject of experiment and discussion [35]. The implanted gases are normally hydrogen [24], helium [36], or co-implanted hydrogen and helium [37], with hydrogen normally implanted first. Although the technology for SOI is well established, its limitations have been become apparent in recent years, as critical dimensions decrease and performance needs increase. This can be clearly seen in sub-micron SOI CMOS devices, where major gains are being made over bulk technology, with application for example to mixed signal and RF circuits. Even
greater potential for SOI CMOS exists in low power and communication circuits when scaled to less than 100 nm, but this also implies the controlled production of thin (100 nm) top layers. Chemical-mechanical polishing (CMP), or plasma-etching are possible techniques, but with these it is difficult with very thin layers to achieve satisfactory uniformity over a wafer surface [38].

An alternative is low energy implantation. However, this has problems since the damage layer and hence the thickness of the plane in depth where nanovoids are created is relatively greater and less sharply defined. At low energy, scattering collisions, sputtering and variations in the dynamics of splitting with different crystal faces all lead to uncertainties in the final split thickness [39]. A way forward is to use epitaxy to define the layer to be transferred, which is grown on the splitting layer. After splitting, the relatively rough split layer is removed by selective etching, to stop accurately on the transferred layer. This is a powerful and flexible technique which can be applied to single or multilayered films, typically Si, SiGe or Ge. When all layers are defined epitaxially, it gives precise control over the transferred layer(s). A good account of the method has been presented by Taraschi et al. [40]. The method is particularly applicable to splitting within a SiGe layer, which may be used as a base for growing strained silicon, as shown recently by IBM researchers who fabricated 19 nm strained silicon long-channel FETs [41].

Another approach proposed by Gaiduk et al. [15, 42, 43] is to use the strong non-uniform compressive strain existing around quantum-well (QW) structures of SiGe in Si to attract and trap vacancies in a controlled way. Thermal activation then leads to the production of nanovoids precisely positioned in the plane of the SiGe. The authors’ experiments were made with Ge ions implanted into multi-layered QW structures, but should apply in similar fashion to other implant species, thermal splitting then producing an accurate cut of low roughness.

3.4 MECHANICAL SPLITTING OF SILICON WAFERS.

This technique is used industrially with porous silicon as a splitting layer for layer transfer, and is particularly advantageous when it is necessary to avoid the high temperatures associated with thermal splitting. Mechanical splitting techniques are thus applicable to low temperature substrates like glass and polymers. It has been found that well-bonded oxide to silicon wafer pairs can be split mechanically by immersing in water and inserting blades that are slowly driven into the bonded region from four sides [44]. Currently, we are investigating this method to split wafer pairs which are weakened by nanovoids created by implantation and annealing. The method depends upon crack propagation from void to void, and a critical factor may be the degree of strain existing in the lattice around each void. Factors such as annealing time and
temperature, plus the size, shape and density of voids are expected to be important.

4. Conclusions

Nanovoids can be readily formed in silicon substrates by ion implantation of various species, followed by annealing. Although some understanding of the mechanisms of formation exists, there are many details unresolved and further studies are needed. The most important applications include gettering for power device technology, strain relaxation in strained-silicon devices and thermal or mechanical splitting for layer transfer to non-silicon substrates.

References


NANOCRYSTAL SUPERLATTICES OF COPPER, SILVER AND GOLD, BY NANOMACHINING

ALDO A. PONCE, AL SMETANA, SAVKA STOEVA, KENNETH J. KLABUNDE and CHRISTOPHER M. SORENSEN
Departments of Chemistry and Physics, Kansas State University, Manhattan Kansas 66506.

1. Introduction

Synthesis of metallic nanoparticles has captured the attention of scientists for decades, especially for their application in the area of catalysis, but more recently due to their unusual properties, different from those of the atomic or bulk metal. In addition, ordered structures of metallic nanoparticles display properties that lie between those of the isolated particles and the bulk material.

Nanoparticles can act as building blocks to form well-organized structures, known as nanocrystal superlattices (NCSL). A narrow particle size distribution is required to obtain long-range superlattice ordering. The collective properties of metallic NCSL can be engineered by controlling the particle size and the type of ligand used to stabilize the colloidal system. The most widely studied metallic systems have been the ones prepared using gold nanoparticles [1,2,3], but there are other studies where silver [4,5,6,7], and cobalt [8] have been used to prepare NCSL.

In this paper, we present for the first time the synthesis of NCSL by self-assembly of thiol stabilized copper nanoparticles, which have been prepared using the solvated metal atom dispersion (SMAD) method. The main advantage of the SMAD technique is that it allows us to prepare large quantities of the metal colloid, free of impurities. This is in great contrast to other techniques such as chemical reduction. A novel method discovered in our laboratories [9,10,11], called “digestive ripening” (i.e. allowing sufficient time and temperature (usually at the solvent’s boiling point) to attain a structural equilibrium.), has been used to attain a narrow particle size distribution. The same procedure as described here has previously been used to prepare NCSL from gold and silver colloids. Herein, it is shown to be applicable for copper as well.
2. **Experimental Details**

2.1 **SYNTHESIS OF LIGAND-STABILIZED COPPER NANOPARTICLES**

The copper colloids were prepared using the SMAD method [12]. The procedure is based on that described by Stoeva *et al.* [2].

The digestive ripening process was carried out by refluxing the colloid in a Schlenk flask under argon, at the boiling point of the solvent (\(\sim 191^\circ\text{C}\)). The time required to obtain a monodispersed system was 3 h.

2.2 **NANOCRYSTAL SUPERLATTICES**

Upon cooling, the monodispersed copper nanoparticles (colloids) readily crystallized into superlattices. In an attempt to show that NCSL behaved as molecular solids, two sets of colloids were studied. The first set contained the as-prepared colloid (100%) and two diluted as-prepared colloids, one having a concentration of 50% and the other one of 10% relative to the concentration of the as-prepared colloid. This set was digested afterwards. The second set was prepared by diluting a digested as-prepared colloid in order to have the same concentrations as the previous set. The colloids were kept hot during the preparation of these dilutions. Moreover, 20 ml of the as-prepared colloid was digested, allowed to cool down. After the formation of NCSL at the bottom of the flask, the supernatant was syringed out and replaced with 20 ml of the as-prepared colloid and then digested at reflux temperature. This colloid had a concentration of 200% relative to the as-prepared one.

Transmission electron microscopy (TEM) studies were carried out using a Phillips 201 TEM operated at 100 kV. In order to obtain dispersed particles on the grid (for measurement purposes), a drop of the hot colloid was placed onto a 200-mesh carbon coated copper grid, and some of the solvent removed by touching the grid with an absorbent paper. In order to obtain NCSL, 3\(\mu\)L of the hot colloid was placed onto the grid and allowed to dry in a desiccator. All the sampled grids were stored overnight under vacuum, before examining them in the microscope.

Dynamic light scattering (DLS) experiments were done using a 633 nm He-Ne laser, with a power output of 40mW. The laser beam was passed through the colloid, contained in a 10 mm diameter airtight tube, which was placed in a heating block attached to a temperature controller. The colloid in the tube was under an argon atmosphere. Scattered light was collected by a FW130 photomultiplier tube at 45° angle, and the signal passed to a ALV-5000 Langen correlator, where the homodyne-detected correlation function was calculated and the average particle size determined.
UV-VIS absorption spectra were obtained in a Cary 500 UV-VIS-NIR spectrophotometer, using the double beam mode and baseline subtraction. The colloids were placed in a 1 cm pathlength quartz cell, with a high-vacuum valve attached to it. The reference sample holder contained a cell filled with 4-tert-butyl toluene. Both sample holders were kept at 100°C, and the colloids were heated to ~191°C immediately before spectra were collected.

3. Results and Discussion

During the SMAD reaction, a dark blue matrix was formed on the inner walls of the reactor. Upon warm-up, gas evolution was observed as the matrix melted and mixed with the ligand rich solvent. These bubbles are thought to be hydrogen which is formed as the S–H bond of the ligand is cleaved, leaving the thiolate attached to the surfaces of the copper particles. Such gas evolution was not observed in previous work using Ag and Au. The product of the reaction is a black-colored dispersion. The as-prepared colloids were stable for at least five months under an argon atmosphere, but they flocculated and showed a yellow color when exposed to air.

As the samples were digested, a drastic color change was observed by transmitted light. This change was from black to red-wine or even yellow (depending on the concentration). As the digested colloids cooled down they formed a black precipitate. The rate of formation of this precipitate depended upon the concentration of the colloid. As in the case for molecular solids, if the system was heated again, the precipitate re-dissolved. A representative TEM micrograph of the digested samples is shown in Figure 1.

Figure 1. A representative TEM micrograph of the copper nanoparticles after digestive ripening.
The ligand stabilized particles were found to be spherical, with an interparticle separation of ~ 1.9 nm, which is indicative of a strong interdigitation of the alkyl chain (chain length ~ 1.6 nm). On examination of the TEM micrographs, the formation of both 2-D arrays of the particles and their stacking to form 3-D structures, which will eventually form NCSL, could be observed. Similar 2-D arrays were obtained by Lisiecki, et al. and Hambrock et al., for 7.5 nm copper nanoparticles [13, 14]. The result of digesting the as-prepared colloid is the formation of a mono-dispersed system with an average particle diameter of 6 nm and a standard deviation of ± 0.6 nm, independent of the concentration of the colloid.

DLS experiments showed that the digested system is mono-dispersed and contains single particles with an average size of 6 nm at the digesting temperature. This observation excludes the possibility that agglomeration of the particles in solution is the cause for the different colors observed for the colloids at different concentrations. Moreover, as can be seen in the UV-visible region, the normalized absorption spectra superimpose, remaining unchanged upon variation in concentration. Therefore, the color changes observed must be due simply to changes in concentration.

Formation of NCSL on the TEM grid was successful to a certain degree, since only small crystals (a couple of hundreds of nanometers) were formed. This was mainly due to the fast agglomeration rate of the particles when the temperature decreased abruptly.

The most striking results were obtained for the TEM samples collected from the bottom of the flask after digestion of the as-prepared (100%) and concentrated (200%) colloids. Figure 2 shows NCSL from the 100% colloid.

![Figure 2](image.png)

Figure 2. Representative TEM micrograph of the copper NCSL obtained from the bottom of the Schlenk tubes after cooling down the digestive colloids. a) NCSL obtained from a 100% colloid (inset: magnified micrograph, showing the organization of the particles within the NCS), and b) NCSL obtained from the 200% colloid.
Although irregular shapes were predominantly present, some triangular shapes were formed. The average side length for these triangles was 1.5 μm.

It can be observed in Figure 2 that larger NCSL were formed, including this time some hexagonally shaped ones. The average side length for the triangles in this case was 4 μm. In the light of these results, we can conclude that the size of the NCSL increases with the concentration of the digested colloid, and is inversely proportional to the cooling rate, as it is for molecular crystals.

It has been well documented that there is a relationship between the position of the plasmon absorption peak and the size and shape of the particle. It is also known that the peak profile is related to the particle size distribution [13,15]. Figure 3 shows the UV-VIS absorption spectra for the as-prepared colloid and for the digested colloid, at different concentrations at ~192°C. It can be observed that the as-prepared colloid shows a plasmon absorption at 560 nm, which closely agrees with the ones found in the literature for copper [8,13,15]. The broadness and low intensity of the peak is attributed to the small particle size and its poly-dispersity. In contrast, for the diluted digested colloids the plasmon absorption peak is absent.

![Figure 3. UV-VIS spectra of the as-prepared colloids and digested colloids, at three different concentrations. Inset: the absorption of the digested colloids, normalized to concentration.](image-url)
Similar observations were made by Chen and Sommers [16] for copper nanoparticles stabilized with alkenothiolates monolayers, but in this case they were attributed to the small particle size. The disappearance of the plasmon peak after digestion of the as-prepared colloids could be attributed to the formation of a large number of oxidized copper species on the surfaces of the nanoparticles, i.e. a core-shell like structure, with a zerovalent copper core and a shell formed by Cu\textsuperscript{n+} species.

Powder XRD of the NCSL is characterized by the lack of peaks from either copper or copper oxide species. This could be explained by the size reduction of the metallic core, which may contain even smaller crystallites, which are below the detection limit. Moreover, it has been demonstrated that the surface plasmon absorption is greatly affected by the species or material coating the surface of the nanoparticles [17,18]. As a result of this, damping of the plasmon absorption band takes place. In our case, the plasmon absorption disappears after digestion, indicating that the zerovalent copper available on the surface of the particle has reacted with the thiol to form a considerable layer of oxidized species on its surface, as proposed by Chen et al. [19]. These authors reported the oxidation of a series of alkanethiols to disulfides by copper nanoparticles with an average diameter of 50 ± 30 nm. The increase in reactivity with decreasing particle size has been related to a change in the redox potential of the metal, and this had been observed previously for silver nanoparticles by Kapoor [20], and stated previously by Horányi [21]. In our case, we have produced 6 nm copper particles for which the reactivity could be expected to be, if not the same, higher than those synthesized by Chen et al. In fact, NMR studies of the supernatant (after NCSL have precipitated) show the presence of dodecane disulfide, which is a further indication that an oxidation/reduction process has taken place.

4. Conclusions

We have successfully prepared a mono-dispersed system containing thiol-stabilized copper nanoparticles. The surfaces of these particles possess a layer of oxidized species which damp the plasmon absorption of the digested colloids. Dodecane disulfide was found to be present in the colloids as a result of the interaction between the thiol and the particles. It has been shown that the digestive ripening process yields copper particles with a narrow size distribution, as was the case for the Au and Ag systems previously studied in our laboratories. In addition, the SMAD technique is the method of choice to produce gram-scale metallic nanoparticles. Finally, these particles self-assemble into nanocrystal superlattices, which behave like molecular crystals with sizes that fall in the micron region.
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1. Introduction

Low-dimensional semiconductors attract much interest because many of their properties differ significantly from those of the corresponding bulk materials. They offer a great variety of attractive applications such as electronic, optoelectronic and optical devices, solar cells, sensors etc. Being sensitive to the crystal potential fluctuations and local atomic arrangement, Raman scattering (RS) is an excellent probe for studying nanostructured materials. Particle size and disorder in nanomaterials change the shapes and positions of Raman lines. This makes it possible to obtain valuable data about the crystallinity of nanoparticles, their size and shape, size distribution etc.

In this article, size-induced changes in the Raman spectrum of semiconductors are considered, and some RS results taken from nanostructures containing semiconductor nanoparticles or ultra-thin films are described.

2. Effects of Reduced Dimensionality

In the Raman scattering process in bulk (3D) crystalline materials, both the energy and the wave vector $k$ are conserved. The $k$-conservation rule requires that only phonons with $k \approx 0$ take part in the scattering process. This results in a single (first order optical) phonon band having a Lorentzian shape and a natural line width of around 3.5 cm$^{-1}$. In nanosized materials characterized by dimensions comparable with the phonon wavelength, phonon confinement introduces uncertainty in the wave vectors, and phonons with $k \neq 0$ can be involved in Raman scattering. As the optical phonon dispersion curves are in general not flat, new frequencies are introduced into the Raman spectra [1-4]. Assuming that the size reduction relaxes the Raman selection rules but does not modify significantly the phonon dispersion curves of the reference three-dimensional system, Raman bands will “red shift” and asymmetrically broaden
to the low-energy side of the band. Normally, the smaller the size, the stronger the shift and band asymmetry. Calculated 1TO (first order transverse optical) Raman bands for two ensembles of Si nanocrystals are shown in Figure 1. The size-induced “red shift” and broadening of the band are clearly seen. The figure also displays the influence of the nanocrystal size distribution $\sigma$ (half width at half maximum divided by average size) on the shape of the calculated Raman band. With increasing $\sigma$, the peak position remains nearly constant, but the full width at half maximum (FWHM) of the band, and its asymmetry, increase significantly. It has been calculated [1] that for large (> 10 nm) crystals, and/or small $\sigma$ values (< 10%), the effects of $\sigma$ variations are negligible.

Considering the phonon wave function to be partially confined to the volume of crystallites of three different shapes (thin film, column and spherical crystals) Campbell and Fauchet calculated [3] the relationship between the FWHM/Raman shift and the crystal size, as qualitatively presented in Figure 2. A clear distinction exists between the size effect in ultra-thin crystalline films, nanocolumns and nanospheres; the alterations of the Raman band position and shape are strongest for spherical nanoparticles, and marginal for ultra-thin films. For this reason, following the works of Richter et al. [2] and Campbell and Fauchet [3], several research groups have developed theoretical formalisms, mostly for calculation of the first order Raman scattering from nanocrystals. Along with the effect of the reduced size of a single nanoparticle [1,5-7], the nanoparticle shape and size distribution in an ensemble of small crystals has also been considered [8]. It has been argued that apart from superposition of the individual scattering from each single sphere, a collective scattering can exist by a coherent mode involving many spheres, unless their concentration is too small [8].

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Calculated 1TO Raman bands for two ensembles of Si nanocrystals with average sizes of 11 and 2.7 nm and several different size distributions, $\sigma$ [1].}
\end{figure}
Several relatively simple formulae can be found in the literature, giving the intensity of the first order Raman spectrum in nanocrystals. They have been used to determine the average sizes of ensembles of nanocrystals in nanocrystalline Si and Ge films [9-11] and of CdS, CdSe nanocrystals embedded in various matrices [12-14]. However, one should keep in mind that not only reduced dimensionality but also lattice disorder can cause Raman band broadening, and thus can have an appreciable influence on the average nanocrystal size determined.

3. Raman Scattering from Ultra-Thin Films

RS investigations of the effects of furnace and laser annealing on interface quality and lattice disorder of amorphous Se/CdSe multilayers with various layer thicknesses (3.5, 5, 6.5 and 10 nm) have been made. They showed [15] that after furnace annealing at temperatures $T < 360$ K, the intensity of all bands increases for all multilayers, implying an improvement in the interface quality. It has also been observed [15,16] that a gradual increase in the laser power density causes a decrease of the 256 cm$^{-1}$ band (due to amorphous Se) and a significant increase in the 237 cm$^{-1}$ band (due to crystalline Se) in the room temperature Raman spectra of Se/CdSe and Se/Se$_{100-x}$Te$_x$ multilayers. This observation is illustrated in Fig.3, and indicates that crystallization of the Se layers takes place. Based on the threshold laser power necessary for crystallization, it has been concluded that the crystallization temperature of ultra-thin Se films is significantly higher than that of bulk Se. Thus, the Raman scattering experiments confirmed the prediction of theoretical thermodynamic considerations for an increase of the crystallization temperatures of 2D amorphous materials when compared with those of the 3D material.
Raman scattering measurements have been carried out at low temperatures (to avoid heating of the samples and thermally-induced crystallization), in order to explore the photocrystallization of Se$_{70}$Te$_{30}$ layers in Se/Se$_{70}$Te$_{30}$ amorphous multilayers [16,17]. Spectra obtained for Se(4 nm)/Se$_{70}$Te$_{30}$ multilayers having Se$_{70}$Te$_{30}$ layer thicknesses of 3.5 and 7.0 nm are shown in Figure 4. It is seen that photocrystallization in the sample with a Se$_{70}$Te$_{30}$ layer thickness of 3.5 nm is significantly retarded, when compared with the sample with a layer thickness of 7 nm. Thus, the RS results have shown for the first time that photoinduced crystallization of ultra-thin amorphous films is strongly affected by the size reduction. Since Raman scattering is very sensitive to the composition of materials, it has been used to check interface alloying in ZnSe/CdSe multilayer structures [18]. Formation of ZnCdSe regions at the interfaces, with thicknesses that increase upon furnace annealing of the samples, has been established.

4. Raman Scattering from Ensembles of Nanocrystals

Phase separation of supersaturated solid solutions is frequently used for the preparation of semiconductor nanoparticles embedded in various glass matrices. Raman scattering can give information about the nanocrystal size and shape distribution, and it is often applied to control and optimize the parameters of the nanoparticle growth process. Figure 5 shows Raman spectra of SiO$_x$ films annealed at three different temperatures [19]. The spectrum of the sample annealed at 523 K displays only a narrow band that originates from the c-Si substrate. This indicates that no phase separation occurs upon such annealing. Upon annealing at 973 K, two wide bands at ~ 150 and ~ 480 cm$^{-1}$ are
observed. These are typical for amorphous Si and their appearance indicates that, at this temperature, phase separation occurs and regions of ‘pure’ amorphous silicon are formed. In the samples annealed at 1303 K, the 150 cm$^{-1}$ band was not observed. A low-frequency tail of the band from the c-Si substrate is seen, and can be related to scattering from Si nanocrystals. Figure 6 illustrates the possibility of observing coexisting amorphous and crystalline nanoparticles in the same sample. This is very important from a practical point of view. In these samples, the coexistence of amorphous and crystalline nanoparticles could be explained by assuming slight thermally-induced Si enrichment of the interface region of the quartz substrate, and the growth of extremely small amorphous Si clusters in this region.

Finally, in this context, we would like to mention the possibility of exploring internal strain and size-dependent lattice contraction in nanocrystals. It has been shown [20] that CdSe-like and CdS-like 1LO bands of CdS$_{1-x}$Se$_x$ nanocrystals embedded in a glass matrix exhibit a blue shift of the Raman band with respect to its position in bulk materials. Such a shift indicates that the nanocrystals suffer a compressive strain which increases with decreasing crystallite size. Raman measurements performed on CdSe nanocrystals of various sizes embedded in three different matrices (GeO$_2$, SiO$_2$, B$_2$O$_3$-SiO$_2$) have shown [21] that at the same nanocrystal size, both the 1LO band position and the magnitude of the size-induced red shift depend on the matrix composition. The strongest band shift has been observed in B$_2$O$_3$-SiO$_2$ samples, in which the samples with the largest nanocrystals showed an appreciable blue shift of the 1LO band of
CdSe. This indicates that there is a compressive strain in the B\textsubscript{2}O\textsubscript{3}-SiO\textsubscript{2} samples which is significantly greater than the stress in the other two composites.

In conclusion, the above consideration of off-resonance Raman scattering from nanosized semiconductors shows that reduced dimensionality causes significant changes in the first order Raman band. This is due to relaxation of the wave vector selection rule. The experimental results described illustrate that the Raman scattering technique can be successfully applied to nanosized materials. Valuable information can be obtained about: interface-induced disorder in multilayers, interface alloying, crystallization of ultra-thin amorphous films, phase separation in supersaturated solutions, the crystallinity of nanostructured materials, nanocrystal size and shape, lattice contraction, etc. Moreover, using resonance Raman scattering, not discussed here, one can also investigate [22] the electronic structure of low-dimensional semiconductors.

References

1. Introduction

Spherical metal nanoparticles embedded in glass can be fabricated using various techniques, so as to introduce distinct colors into the transparent material. Shape modifications of such particles, e.g., via an elongation procedure, have been found to be versatile tools to vary the color appearance. Stretching of the glass at elevated temperatures deforms the particles such that they assume the shape of prolate ellipsoids. A uniform arrangement of elongated nanoparticles within the glass induces polarization effects for a certain spectral range. This means different absorption of linear polarized light, depending on the polarization direction (perpendicular or parallel to the long axes) [1].

Tailoring of glass-based dichroic polarizers, e.g., for display application, requires a detailed knowledge of the relationships between optical absorption and structural features. The aspect ratio and size distribution of the elongated particles influence the bandwidth and maximum position of the absorption, and thus the color appearance and polarization efficiency. They may be controlled by the initial particle size, the extent of stretching, and the degree of thermally induced shape relaxation [2]. To monitor the stress state and defect configuration occurring in Ag nanoparticles of colored glass polarizers fabricated by a multistep procedure, electron microscopy has been applied down to the atomic scale of resolution.

2. Experimental Details

Spherical Ag nanoparticles, 7 to 70 nm in size, have been fabricated inside soda-lime silicate float glass by ion exchange in a NaNO\textsubscript{3}/AgNO\textsubscript{3} melt mixture,
and subsequent annealing in a hydrogen atmosphere at 580 °C, leading to a yellow-brownish color. Thermomechanical processing of this glass was performed in a furnace at 600°C, by applying a constant stress of 50–150 N/mm². This treatment changed the color to a dichroic cyan.

For microstructuration purposes, local energy admission by electron beam irradiation (60kV) was applied to induce partial shape relaxation of the elongated Ag nanoparticles, depending on the power density. This irradiation processing applied in stripe configurations of 130 µm width resulted in magenta and yellow dichroic colors.

The optical properties of the processed glass in the visible and near UV range have been investigated using a J&M microspectrometer. Thin slices of the glass, appropriately prepared for transmission electron microscopy (TEM), were examined using a JEM 1010 (100 kV) and JEM 4010 (400 kV), respectively.

3. Results and Discussion

The color appearance and polarization effect of the three different dichroic glass areas containing elongated nanoparticles of various mean aspect ratios, due to different degrees of shape relaxation, are demonstrated by the transmittance spectra recorded with linear polarized light, as shown in Figure 1. The corresponding TEM images shown in Figure 2 give an impression of the elongation, arrangement and size variation of the Ag nanoparticles that cause these optical effects. While in the cyan-colored base glass the elongated particles are characterized by a 54 nm mean major axis length and a mean aspect ratio of 3.0, upon irradiation-induced shape relaxation the mean major axis length and mean aspect ratio decrease to 35 nm and 1.7 in the magenta areas, and 26 nm and 1.2 in the yellow areas, respectively. The arrangement of the particles with their long axes parallel to each other, as well as their size distribution reflected by the broad transmittance bands, remain unchanged.

![Figure 1. Transmittance of dichroic colored glass upon multistep processing recorded with linear polarized light parallel (left) and perpendicular (right) to the long axis.](image-url)
For spherical nanoparticles with decreasing radius and large surface-to-volume ratio, a lattice contraction is expected that results from the hydrostatic pressure caused by the surface stress [3]. However, elongated ellipsoidal particles exhibit two different half axes $a$ and $b$ instead of one radius of curvature, and so an inhomogeneous lattice strain results. Regardless of the presence of planar defects, a lattice contraction of about 4% along the long axis direction has been measured from high resolution electron micrographs of nanoparticles of 2.5 mean aspect ratio. The aspect ratio of an elongated nanoparticle depends on its previous radius. Below a certain threshold, no deformation occurs since the external tensile stress is balanced by the internal capillary pressure. That is why the smallest Ag nanoparticles preserve their spherical shape throughout all processing steps.

*Figure 2.* TEM images of Ag-particles in dichroic colored glass upon multistep processing: a) cyan, b) magenta and c) yellow areas.

*Figure 3.* TEM images of Ag-particles in dichroic colored glass upon multistep processing: Change of the twin configuration from cyan (top) to yellow (bottom) areas.
Like their undeformed predecessors, elongated Ag nanoparticles frequently contain planar defects, mostly twin boundaries, that may be recognized in electron micrographs by characteristic bright-dark contrast features. In the as-deformed state, most frequently cyclic twin sectors arranged around a common axis are observed, as shown by some examples in the upper part of Figure 3. Upon partial shape relaxation by local electron beam heating, however, the frequency of cyclic multiple twins [4] is decreased, while more and more parallel twin lamellae occur that have different characteristic contrast features. This can be seen from the examples in the lower part of Figure 3.

This behaviour may shed some light on the kind of processes taking place during the multistep synthesis and processing of these colored glass polarizers. Firstly, cyclic multiple twinning occurs in spherical Ag nanoparticles formed by about 10 h of thermochemical processing (ion exchange and annealing in a H$_2$ atmosphere) at 580 °C. These twin configurations are widely conserved during thermomechanical processing (deformation), where the particles are exposed to about 600°C for nearly 1 min. The irradiation processing however, introduces heat that may raise the temperature up to about 850°C in a very short time interval.

4. Conclusions

Spherical silver nanoparticles embedded in commercial float glass have been fabricated and deformed to prolate ellipsoidal shapes in a multistep procedure that is completed by partial shape relaxation in well-defined regions, so as to obtain microstructuration of dichroic colors. Transmission electron microscopy has been used to monitor not only the size and shape evolution, but also the stress state and defect configuration of the nanoparticles that occur in the course of processing. As our main results, an inhomogeneous lattice strain in the elongated nanoparticles, as well as distinct changes in the defect configuration upon irradiation processing may be stated.

References

SYNTHESIS, CHARACTERIZATION, PHOTOCATALYTIC AND DIELECTRIC PROPERTIES OF NANOSIZED STRONTIUM AND BARIUM TITANATES

D.V. DEMYDOV and K.J. KLABUNDE
Chemistry Department, Kansas State University
Manhattan, KS 66506 USA

1. Introduction

Mixed metal oxides can be used as catalytic, photocatalytic, photoelectric, and dielectric materials for different applications. An aerogel method can be successfully applied for the production of these nanosized oxides of high purity [1]. This process involves the production of a gel of a three-dimensional polymeric network from alkoxides. Solvent removal by supercritical drying prevents the collapse of the network and preserves the unique properties of the product with a high porosity, small crystallite sizes, and a large surface area.

2. Synthesis

![Figure 1. Aerogel procedure for SrTiO₃ or BaTiO₃ synthesis.](Reprinted from [1] with permission from Elsevier).

The synthesis of aerogel prepared strontium and barium titanates (AP-SrTiO₃ and AP-BaTiO₃) consists of several stages, including the preparation of alkoxide mixtures in an alcohol–toluene solvent, hydrolysis, co-gelation of alkoxides, and solvent removal by a supercritical drying step.
A mixture of alcohol and toluene solvent is essential for obtaining mixed metal oxides with high surface areas and small crystallite sizes [2]. Toluene in the mixture reduces the surface tension at the gas-liquid interface, resulting in the formation of more open porous network products with higher surface areas. Alcohol is important for the prevention of phase separation of the alkoxide precursors.

Different alcohols mixed with toluene were used as solvents for synthesis. AP-SrTiO$_3$ and AP-BaTiO$_3$ were prepared in either an ethanol or isopropanol mixture with toluene in a toluene-to-alcohol volume-ratio of 1.5. The mixture of metal alkoxides and alcohol-toluene was hydrolyzed with water by a slow, dropwise addition, to transform it into a gel. Supercritical conditions were achieved by heating in an autoclave under a nitrogen atmosphere. The solvent vapors were removed by quick venting off, and the residual solvent in the prepared aerogel powders was removed by heat treatment (calcination in air for SrTiO$_3$, and calcination in oxygen for BaTiO$_3$).

3. Characterization

![Figure 2. Powder XRD patterns of commercial and synthesized SrTiO$_3$ and BaTiO$_3$ with different alcohols used in synthesis (CM – commercial, NCM – nanosized commercial, AP – aerogel prepared samples). (Reprinted from [1] with permission from Elsevier).]

The structural and texture properties were investigated by nitrogen adsorption at 77 K (BET analysis) and powder X-ray diffraction. The aerogel prepared SrTiO$_3$ and BaTiO$_3$ samples have smaller crystallite sizes and significantly higher surface areas in comparison with available commercial samples (from Sigma-Aldrich or Alfa-Aesar).
TABLE 1. Textural properties of different SrTiO$_3$ and BaTiO$_3$ samples

<table>
<thead>
<tr>
<th>SrTiO$_3$ sample (alcohol in solvent)</th>
<th>Average crystallite sizes (nm)</th>
<th>Surface area ($\text{m}^2 \text{ g}^{-1}$)</th>
<th>BaTiO$_3$ sample (alcohol in solvent)</th>
<th>Average crystallite sizes (nm)</th>
<th>Surface area ($\text{m}^2 \text{ g}^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial CM-SrTiO$_3$</td>
<td>145</td>
<td>1</td>
<td>Commercial CM-BaTiO$_3$</td>
<td>76</td>
<td>3</td>
</tr>
<tr>
<td>Nanosized NCM-SrTiO$_3$</td>
<td>25</td>
<td>17</td>
<td>Nanosized NCM-BaTiO$_3$</td>
<td>36</td>
<td>19</td>
</tr>
<tr>
<td>AP-SrTiO$_3$ (ethanol)</td>
<td>8</td>
<td>159</td>
<td>AP-BaTiO$_3$ (ethanol)</td>
<td>6</td>
<td>175</td>
</tr>
<tr>
<td>AP-SrTiO$_3$ (isopropanol)</td>
<td>20</td>
<td>121</td>
<td>AP-BaTiO$_3$ (isopropanol)</td>
<td>12</td>
<td>101</td>
</tr>
</tbody>
</table>

4. Photo-Oxidation of Acetaldehyde by Aerogel Prepared SrTiO$_3$

Strontium titanate is known as a material that can be applied for the photooxidation of volatile organic compounds under light irradiation. Acetaldehyde photo-oxidation has been studied on pure AP-SrTiO$_3$ and chromium ion-doped AP-SrTiO$_3$ under UV and visible light irradiation, and compared with the photoactivity of P25 TiO$_2$ (Degussa). The degradation of CH$_3$CHO over AP-SrTiO$_3$ is lower than that of P25 under UV. However, Cr-doped AP-SrTiO$_3$ shows a higher activity in the visible region of irradiation compared to P25 TiO$_2$.

TABLE 2. Initial rates of acetaldehyde oxidation and carbon dioxide evolution

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dopant</th>
<th>Light source</th>
<th>$k[\text{CH}_3\text{CHO}]$, min$^{-1}$</th>
<th>$k[\text{CO}_2]$, min$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$ Degussa</td>
<td>--</td>
<td>UV(&lt;380 nm)</td>
<td>-0.1023</td>
<td>0.01310</td>
</tr>
<tr>
<td>AP-SrTiO$_3$</td>
<td>--</td>
<td>UV(&lt;380 nm)</td>
<td>-0.0579</td>
<td>0.00240</td>
</tr>
<tr>
<td>AP-SrTiO$_3$</td>
<td>5% mol. Cr</td>
<td>UV(&lt;380 nm)</td>
<td>-0.0576</td>
<td>0.00134</td>
</tr>
<tr>
<td>TiO$_2$ Degussa</td>
<td>--</td>
<td>visible(&gt;420 nm)</td>
<td>-0.0147</td>
<td>0.00016</td>
</tr>
<tr>
<td>AP-SrTiO$_3$</td>
<td>--</td>
<td>visible(&gt;420 nm)</td>
<td>-0.0077</td>
<td>0.00021</td>
</tr>
<tr>
<td>AP-SrTiO$_3$</td>
<td>5% mol. Cr</td>
<td>visible(&gt;420 nm)</td>
<td>-0.0237</td>
<td>0.00053</td>
</tr>
</tbody>
</table>

Barium titanate is a well-known ferroelectric material with a high dielectric constant. The aerogel prepared BaTiO$_3$ bulk resistivity values were significantly lower than that of commercial BaTiO$_3$, by several orders of magnitude (Figure 3).

![Figure 3. Resistance and relative permittivity (o - commercial, * - AP- BaTiO$_3$).](image)

6. Conclusions

Aerogel prepared SrTiO$_3$ has a surface area of 159 m$^2$/g and a crystallite size of 8 nm, and aerogel prepared BaTiO$_3$ has a 175 m$^2$/g surface area and a 6 nm crystallite size. Ethanol mixed with toluene is the best solvent for production of high surface area SrTiO$_3$ and BaTiO$_3$ products.

The unique properties of these materials, such as high porosity, small crystallite size and large surface area can be utilized. SrTiO$_3$ can photocatalytically oxidize volatile organic compounds, and BaTiO$_3$ can be applied as a dielectric material for capacitors.

7. Acknowledgments

The support of the U.S. Army Research Office through a DARPA-sponsored MURI grant (DAAD-19-01-1-0619) is acknowledged with gratitude.

8. References

1. Introduction

The preparation of quantum structures (QS) by self-assembly is one of the most challenging tasks in solid state technology [1], owing to its scientific interest and possible technological importance [2]. Semiconducting $\beta$-FeSi$_2$ is a potential material for silicon-based optoelectronics, working at 1.5 $\mu$m, and for magnetic devices. Suemasu first reported the aggregation of monocrystalline $\beta$-FeSi$_2$ islands on Si(100) [3]. In previous works, we have investigated the properties of $\beta$-FeSi$_2$ QSs on Si [4,5,6].

In this work, we study these structures by new methods and investigate the QSs formed by RDE at different Fe layer thickness and deposition temperatures.

2. Sample Preparation

The n-type (001) Si substrates were cleaned by a standard chemical process and annealed in situ for 5 min at 800°C at $10^{-8}$ Torr to remove the native oxide. Fe (99.9%) was deposited by e-gun evaporation at a base pressure of $2\times10^{-8}$ Torr. The Fe was deposited onto room temperature (RT) substrates at a 0.02 nm/s deposition rate, and annealed in-situ at 600°C for 15 min, and by reactive deposition epitaxy (RDE) on 450, 500, 550 and 600°C substrates at a 0.015 nm/sec deposition rate. The in situ annealing time in the RDE samples was chosen to give a total of 15 minutes, including the time of deposition.
3. Results

Far infrared (FIR) measurements were carried out with a Bruker IFS 113v spectrophotometer operated under vacuum at room temperature in the 900-120 cm$^{-1}$ region with 4 cm$^{-1}$ resolution. Figure 1 shows typical reflectivity spectra of layers formed by depositing Fe in 2, 4 and 6 nm thicknesses onto RT substrates, and also that of a reference bulk $\beta$–FeSi$_2$ crystal. The five characteristic modes of $\beta$–FeSi$_2$ are indicated by shadowed areas in Figure 1. In the RDE samples, these phonon lines were not observed.

Transmission electron microscope (TEM) investigations were carried out in a JEOL-100 CX microscope at 100 kV. The planar-view bright field images (Figure 2a) of RT deposited 2 nm Fe shows linear, S-like, and circular structures, as indicated in the figure. The cross-sectional image (Figure 2b) shows a flat surface, the QSs are embedded in the Si. Thicker Fe at RT develops a 50 – 500 nm grain size polycrystalline layer, with rough interface and planar defects. Planar view images of the 3 nm Fe RDE sample (c) exhibit rod-like structures. The cross-sectional image (d) shows that the silicide grows into the silicon in platelets.

Scanning electron microscopy (SEM) was performed using a LEA Gemini 1540 SEM. In 3 nm RDE Fe at 600$^\circ$C, rod-like QS (left), and 5 nm RDE Fe QDs (right) are formed, as shown in Figure 3.

The samples RDE grown from 6 nm RDE Fe at 550$^\circ$C show rod-like QS. Diffusion of Fe in a surface layer may explain the QS formation. The markers and measuring parameters of the SEM images are shown in the insert.
Figure 2. Bright-field planar-view of the RT deposited 2nm Fe (a) and of the 600 °C RDE deposited 3 nm Fe (c). The cross-sectional images are shown in (b,d).

Figure 3. SEM images of the 3 (left) and 5 nm (right) RDE Fe prepared at 600°C.

Figure 4. AFM measurement on the RDE 5nm Fe sample.
An atomic force microscopy (AFM) image of the 5 nm RDE deposited at 600°C Fe sample is shown in Figure 4. The density of the QDs increases above 3 nm Fe thickness, while above 6 nm the QDs become irregular in size and shape.

4. Conclusions

QSs were grown by depositing Fe layers on RT and hot Si(001) in an ultra-high vacuum system, with in-situ annealing. FIR phonon lines show that the RT deposited Fe results in $\gamma$-FeSi$_2$, but this is not the case for the RDE Fe. In samples 3 nm RDE Fe at 600°C and in 6 nm RDE Fe at 550°C, platelets are grown into the silicon. Above 3 nm RDE Fe at 600°C, quantum dots grow onto the rod-like structure.

Acknowledgements

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References

1. Introduction

ZnO is a piezoelectric, semiconducting and magnetic material having potential applications in Surface Acoustic Wave (SAW) devices [1], varistors [2], gas sensors [3], etc. ZnO, being a II-VI semiconductor, has a wide band gap and large exciton binding energy. In 2001, Huang et al. [4] reported the room temperature lasing action of a highly oriented nanorod array of ZnO, thus demonstrating that the functional design of ZnO nanomaterials is crucial for the development of novel devices. Apart from the lasing property, Blue/UV light emitting devices [5], and solar cells [6] are other potential optoelectronic applications of ZnO.

The colloidal approach to ZnO nanowires is appealing, because of the low growth temperatures and good potential for scaling up. Vayssieres et al. [7] reported a method for creating highly oriented arrays of ZnO micro-rods in 2001, based on the epitaxial growth of ZnO on a substrate. This process was improved by Greene et al. [8] by fixing pre-synthesized ZnO particles on the substrate to act as seeds, resulting in the growth of ZnO nanorods/nanowires from the seeds. A high yield of nanowires, with average diameters of 40-80 nm diameters and lengths of 1.5-2 μm was reported.
We report an optimized scheme to create uniform ZnO nanowires of very high aspect ratio and excellent uniformity in diameters. The process is based on the technique of epitaxial growth of ZnO from seeds fixed on a substrate, and we have achieved nanowires of ~30 nm diameter and lengths more than 10 μm, yielding an aspect ratio of over 330.

2. Experimental Details

High aspect ratio nanowires were grown using a simple two-step process. Firstly, a suspension of homogenous ZnO nanoparticles was prepared, based on the method proposed by Spanhel and Anderson [9], forming roughly spherical ~ 30 nm diameter particles. The colloid was stored in a refrigerator at 4°C.

To grow nanowires, nanocrystals so prepared were centrifuged at 5000 rpm for 20 minutes for size selection, smeared evenly on a glass microscope slide to ensure a monodispersed layer, and oven-dried at 65°C for 12 hours, for proper fixation. This seeded glass substrate was fixed inverted in an open Petri-dish containing an equimolar solution of 1 mM zinc nitrate hydrate and hexamine. The growth process was carried out in an oven at 65°C for 12 to 24 hours. Compared to similar work reported in the literature [8], nanowires grown by this method were highly anisotropic. The length of the wires increased to over 10 μm. The wires grown were ~ 30 nm in diameter and showed excellent uniformity. Sample characterization involved SEM (JSM6301F) to confirm the morphology of the nanowires array and to estimate the overall aspect ratio of the nanostructure.

3. Results and Discussion

Fairly spherical nanocrystallites, ~ 30 nm in diameter, were obtained by hydrolysis of the zinc acetate solution. Figure 1(a) shows a SEM image of the nanocrystals after fixation onto a glass slide to act as seeds.

Nanowires grown from these seeds had a diameter of ~ 30 nm, hence demonstrating a high anisotropy in the hydrothermal growth process. Prolonging the growth period only increased the wire length, while the diameter was constant, resulting in an increase in the aspect ratio up to about 330 for samples grown for 12 hours.

According to similar work reported in the literature [8], after a period of time, the anisotropic growth decreases and epitaxial growth begins laterally. This results in a net decrease in the aspect ratio. There was evidence of agglomeration of individual wires to form larger structures in the samples grown for 12 hours (Figure 1c). However, no indication of any increase in the diameter of the wires was observed.
The high anisotropy observed can be attributed to the selection of the concentration of the crystallizing solution in which the seeded substrate was placed. This anisotropic growth of the nanowires occurs due to the lower surface energy at the tip compared to the sides, which leads to improper coverage of the tip, allowing the ions to aid the crystal growth [10]. Along the length of a growing wire, the surface energy is high, leading to the passivating ions completely covering the wire. In effect, this provides an effective shield from the surrounding precursor ions, thereby inducing anisotropy in the growth. The growth process of the wires depends strongly on the concentration of the precursor ions in the ‘crystallizing solution’. It can be disturbed in conditions of higher ion concentrations, leading to growth in lateral directions.

Figure 1. (a) SEM image of monodispersed ZnO crystals fixed on a glass substrate, showing fairly spherical particles ~30 nm in diameter; (b) Image of the wires grown for 12 hours. The wires are more than 10 µm long; (c) Magnified image; (d) The individual wires are ~30 nm in diameter.

4. Conclusions

In summary, we have demonstrated a technique to design nanowires of ZnO of high aspect ratios, typically above 300, with lengths and diameters that can be controlled by the growth conditions and the nature of the seeds used for the
process, respectively. The obtained nanowires were approximately 30 nm in diameter and average wire lengths well exceeded 10 μm. These highly anisotropic nanowires can find applications in most optoelectronic devices, as well as in gas sensors.

References

1. Introduction

In the last decade, the process of Aluminum Induced Crystallization (AIC) has attracted increasing scientific interest, because of the possible application of the resulting poly-Si films in solar cells, TFTs, image sensors, etc. [1]. Usually the crystallization of the bilayered structures is performed in air, vacuum or nitrogen [2-5]. The properties of the resulting polycrystalline Si films have been investigated by SEM, TEM, Raman scattering, electrical resistivity, Hall effect measurements, etc. This has mainly been in order to study the process of crystallization and the influence of the metal layer structure on it [1-5]. No attention has been focused on the influence of the atmosphere in which the crystallization is performed. In this work, we report a study of the influence of different annealing atmospheres on the structural properties of poly-Si films, obtained by AIC of a-Si films.

2. Experimental details

For the preparation of polycrystalline silicon films, glass/Al/a-Si structures were deposited. The films of Al were deposited on cleaned glass substrates by rf magnetron sputtering at a substrate temperature of $T_s = 250 \, ^\circ C$. They were kept for 24 hours in air before the deposition of a-Si films, for native aluminum oxide formation. Unhydrogenated a-Si layers were deposited by rf magnetron sputtering of a Cz c-Si target (Wacker, 9-12 $\Omega \cdot cm$) at $T_s = 250 \, ^\circ C$ in an Ar atmosphere, at 0.5 Pa. The thicknesses of the Al and a-Si layers were both 200 nm. The prepared glass/Al/a-Si samples were isothermally annealed at temperatures ranging from 480 to 530 $^\circ C$, for durations from 2 to 7 hours.
Different annealing atmospheres were used: N\textsubscript{2}, forming gas (N\textsubscript{2}+H\textsubscript{2}) and H\textsubscript{2}. The annealing was performed in a horizontal tube furnace at atmospheric pressure. The remaining Al layer on top was removed with a standard wet Al etch before the structural investigations of the films. The structure of the poly-Si films was studied by microprobe Raman scattering, optical microscopy (OM) and X-ray diffraction. Raman spectra were excited by the 514 nm line of an Ar\textsuperscript{+} laser with a 1 \mu m laser spot, using a Renishaw Ramascope. XRD measurements were performed on a TUR-M-62 diffractometer using Cu K\textalpha\ (\lambda = 1.5406 Å) radiation in a regular \theta-2\theta scan.

3. Results and Discussion

The optical micrographs of poly-Si thin films prepared by annealing in different atmospheres (H\textsubscript{2}, N\textsubscript{2}+H\textsubscript{2}, N\textsubscript{2}) of glass/Al/a-Si samples are shown in figure 1.

![Figure 1](image1.png)  
**Figure 1.** Optical images of poly-Si films prepared by AIC of glass/Al/a-Si samples at 500 °C in different atmospheres: N\textsubscript{2} for 6h (a); N\textsubscript{2}+H\textsubscript{2} for 5h (b); H\textsubscript{2} for 3h (c).

![Figure 2](image2.png)  
**Figure 2.** Microprobe Raman spectra of glass/Al/a-Si samples, measured at grain (1), and inter grain (2), positions, annealed in different atmospheres at 500 °C.

The poly-Si, obtained by annealing in N\textsubscript{2} (figure 1a) exhibits large grains (dendrites), 20-30 \mu m in size (figure 1a, arrow 1), separated by inter-crystallite spaces of about 10-20 \mu m (figure 1a, arrow 2). When annealing is performed in an atmosphere containing H\textsubscript{2} (figures 1b and 1c) the surface of the resulting poly-Si is very smooth. The grains are very closely packed and continuous poly-Si films are formed. The size of the inter-grain space decreases to about 2-3 \mu m. The poly-Si surface in these cases is more uniform.

In order to analyse the grain orientation, XRD measurements have been performed. They show that the preferential crystallographic orientation of the crystallites of the polysilicon thin films obtained by AIC is (111).
The crystallinity of the samples after the annealing was investigated by microprobe Raman spectroscopy. The Si-Si TO-like peak of a c-Si wafer, used as a reference, is observed at 521 cm$^{-1}$. Two spectra were measured for each sample – on the grain surface (1) and between the grains (2). All of the spectra of the annealed samples have a Si-Si TO-like phonon band centred in the range 520-521 cm$^{-1}$, showing the presence only of the Si crystalline phase. The most narrow Si-Si TO-like band centred at 521 cm$^{-1}$ with FWHM of 7 cm$^{-1}$ is demonstrated by the sample annealed in H$_2$, for both the grain and the inter-grain material.

An estimate of the grain size and the stress in the films can be deduced from the downshift and the FWHM of the Si-Si TO-like Raman peak [6]. It should be noted that accurate values for the grain size cannot be determined from the relationships described previously in the literature [6,7], as they depend on the structure of the grains and their boundaries. Despite this, comparisons between spectra obtained from similar materials are valid. The grain size is inversely proportional to the FWHM of the peak, so it can be deduced that the grain size increases when the annealing is performed in the presence of H$_2$. The downshift of the TO-like peak is related to the amount of stress in the polycrystalline films. From the results obtained, it can be concluded that annealing in the presence of H$_2$ results in stress-free poly-Si films.

The influence of the annealing duration and temperature in a N$_2$ atmosphere has been studied (figure 3). The spectra of the grains exhibits TO-like peaks, centred at 520 cm$^{-1}$, which is an indication of the presence of a weak tensile stress in the films. Spectra (1) show that when the annealing is performed at $T_{an} = 480$ °C for 5 h, the full crystallization of the a-Si film is not observed and the

Figure 3. Microprobe Raman spectra of samples glass/Al/a-Si annealed in N$_2$ atmosphere for different times at different temperatures measured at grain (1), and inter-grain (2), positions.

Figure 4. Microprobe Raman spectra of samples glass/Al/a-Si annealed in N$_2$+H$_2$ atmosphere for different times at different temperatures measured at grain (1), and inter-grain (2), positions.
inter-grain material remains amorphous. Even higher temperatures and the longer durations do not result in the full crystallization of the films.

The influence of the annealing duration and temperature in a $\text{N}_2+\text{H}_2$ atmosphere has also been studied (figure 4). Both spectra of the sample annealed at the lowest temperature exhibit a Si-Si TO-like band centred at 521 cm$^{-1}$. However the Si-Si TO-like band is broader and assymmetric, with a shoulder at 510-515 cm$^{-1}$. This intermediate band can be attributed to small-grained (nano-crystalline) Si, grain boundary defects or stress. Spectra (1) and (2) have a FWHM of 8.8 cm$^{-1}$ and 10.2 cm$^{-1}$, respectively. Increasing the annealing temperature results in a decrease of the FWHM. Full crystallisation of the structures is achieved when the two-step annealing technique is employed. No difference in the spectra (1) and (2) is observed in this case. The results demonstrate that annealing in forming gas yields stress-free poly-Si films with better structural quality compared to those annealed in nitrogen.

4. Conclusions

In this work, the structural properties of poly-Si films obtained by AIC in different atmospheres – $\text{N}_2$, $\text{N}_2+\text{H}_2$ and $\text{H}_2$ have been studied by microprobe Raman spectroscopy, optical microscopy and XRD analysis. The XRD measurements show that the preferential crystallographic orientation of the silicon crystallites is (111). The results indicate that the structure of the poly-Si films, obtained by AIC of a-Si, is improved when the annealing is performed in an atmosphere containing $\text{H}_2$. More significant improvement occurs for the inter-grain material. Full crystallization of the structure glass/Al/a-Si annealed in forming gas is achieved when a two-step annealing technique is employed.

References

1. Introduction

CuAlSe₂ is a wide band gap (~2.70 eV) chalcopyrite compound semiconductor with potential applications in light emitting devices such as light emitting diodes (LEDs) and lasers in the blue portion of the visible spectrum [1-2], and as a buffer layer in thin film solar cells [3]. CuAlSe₂ single crystals have previously been exclusively obtained by vapor transport methods [4-5] and various versions of chemical vapor deposition (CVD) techniques [6-7]. The physical vapor deposition (PVD) technique has rarely been used to grow this material. This work investigates properties of polycrystalline CuAlSe₂ thin films obtained by multisource PVD.

2. Experimental details

Cu, Al and Se were thermally co-evaporated from Knudsen type cells onto bare glass and molybdenum coated glass substrates at substrate temperatures of 450 and 530 °C. The first set of depositions was carried out for a target [Cu]/[Al] ratio of 1 to obtain stoichiometric CuAlSe₂. Subsequent depositions were carried out for [Cu]/[Al] ratios of 0.3, 0.5, 0.7, 0.9, 1.5 and 1.7. Depositions were carried out under various Se delivery conditions ranging from R_{Se}/R_{M} = 1 to R_{Se}/R_{M} = 30, where R_{Se} is the effusion rate of Se, and R_{M} is the sum of the effusion rates of Cu and Al, in mol/min. Energy dispersive spectroscopy (EDS) was used for composition analysis. The film structures were determined by x-ray diffraction (XRD) measurements, and optical measurements were carried out using a spectrophotometer.
3. Results

The following results fall into two categories: films obtained under R_{Se}/R_{M} ≤ 10, and those deposited under R_{Se}/R_{M} > 10. Films with [Cu]/[Al] < 0.9 deposited under R_{Se}/R_{M} ≤ 10 contained various Cu-Al intermetallics. At [Cu]/[Al] ~ 0.3, CuAl₂ was formed, for 0.3 < [Cu]/[Al] ≤ 0.5, a mixture of CuAl₂ and CuAl was obtained, and for films with 0.5 < [Cu]/[Al] ≤ 0.9 Cu₂Al was the predominant phase (see Figures 1 and 2). A mixture of Cu₂Al and CuAlSe₂ was formed in films with 0.9 < [Cu]/[Al] ≤ 1.0. As [Cu]/[Al] increased above 1.0, multiphase films containing CuAlSe₂, Cu_{2-x}Se and traces of Cu₂Al were obtained (Figure 3). All films with [Cu]/[Al] < 1.0 deposited under R_{Se}/R_{M} ≤ 10 contain oxygen levels ranging from 4 to 60 at. %, as shown in Table 1. The oxygen content increases as [Cu]/[Al] decreases, and there is a trade-off between the oxygen and Se as shown in Figure 4.

![Figure 1. Film with [Cu]/[Al] ~ 0.3 showing CuAl₂ (A) with traces of CuAl (B).](image1)

![Figure 2. Film with [Cu]/[Al] ~ 0.7 showing Cu₂Al (C).](image2)

![Figure 3. Film with [Cu]/[Al] ~ 1.7 showing CuAlSe₂ (E) and Cu_{2-x}Se (G).](image3)

![Figure 4. Increasing oxygen (●) and decreasing Se (▲) content in films as a function of [Cu]/[Al].](image4)
It is postulated that the oxygen comes from Al(OH)$_3$ and SeO$_2$ formed as a result of the hydrolysis of Al$_2$Se$_3$ present in the films before they are extracted from the chamber. Upon exposure to the atmosphere, Al$_2$Se$_3$ hydrolyzes according to the reaction:

\[
\text{Al}_2\text{Se}_3 \text{ (s)} + \frac{3}{2}\text{H}_2\text{O} \text{ (g)} + \frac{15}{4}\text{O}_2 \text{ (g)} \rightarrow 3\text{SeO}_2 \text{ (s)} + \text{Al(OH)}_3 \text{ (s)}
\]  

(1)

Table 1 Composition of films deposited under $R_{Se}/R_{M} \leq 10$

<table>
<thead>
<tr>
<th>Composition in at. % by EDS</th>
<th>Phases observed by XRD</th>
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<tbody>
<tr>
<td>[Cu]</td>
<td>[Al]</td>
</tr>
<tr>
<td>17.9</td>
<td>58.7</td>
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<tr>
<td>17.4</td>
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<td>23</td>
<td>33.9</td>
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<tr>
<td>17.7</td>
<td>20.8</td>
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<td>35.7</td>
<td>20.6</td>
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</table>

Films deposited under $R_{Se}/R_{M} > 10$ with [Cu]/[Al] < 0.9 contain an unidentified Cu$_x$Al$_y$Se$_z$ phase with traces of CuAlSe$_2$. Cu$_x$Al$_y$Se$_z$ is transformed into CuAlSe$_2$ after annealing under H$_2$Se, Ar and H$_2$/Ar at different annealing temperatures and times. This transformation is shown in Figure 5 for a Cu$_x$Al$_y$Se$_z$ film annealed under H$_2$Se at 450 °C for 30 minutes.

![Figure 5](image)

*Figure 5. Film with [Cu]/[Al] ~ 0.5 showing Cu$_x$Al$_y$Se$_z$ (I) and the transformation into CuAlSe$_2$ (E) upon annealing under H$_2$Se at 450 °C for 30 minutes.*

![Figure 6](image)

*Figure 6. Before (1) and after (2) optical transmission and reflection of the films shown in Figure 5. Data show that the transmission decreases after transformation due to the annealing.*

All films deposited under these conditions ($R_{Se}/R_{M} > 10$) with [Cu]/[Al] > 1.0 were CuAlSe$_2$ with traces of Cu$_x$Al$_y$Se$_z$, and contained Cu$_{2-x}$Se at higher
[Cu]/[Al] ratios. Cu$_x$Al$_y$Se$_z$ has a sub band gap transmission higher than 60% which decreases to < 50% after transformation into CuAlSe$_2$ (Figure 6). All films in this section contain less than 3 at. % oxygen (See Table 2).

<table>
<thead>
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<tbody>
<tr>
<td>[Cu]</td>
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</tr>
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<td>15.8</td>
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<tr>
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<td>25.1</td>
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<tr>
<td>32.2</td>
<td>21.7</td>
</tr>
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</table>

4. Conclusions

PVD grown CuAlSe$_2$ films with [Cu]/[Al] < 0.9 deposited under R$_{Se}$/R$_{M}$ < 10 contain various Cu-Al intermetallics that track with the Cu-Al binary phase diagram. These films also contain 4 to 60 at. % oxygen. This possibly results from the hydrolysis, upon exposure to the atmosphere, of Al$_2$Se$_3$ present in the films. Films with [Cu]/[Al] < 0.9 deposited under R$_{Se}$/R$_{M}$ > 10 contain an unidentified phase Cu$_x$Al$_y$Se$_z$ which transforms into CuAlSe$_2$ upon annealing under H$_2$Se, Ar and H$_2$/Ar atmospheres. It is postulated that Cu$_x$Al$_y$Se$_z$ is a previously undetected polymorph of CuAlSe$_2$.

References

1. Introduction

Crystalline silicon has the advantage of being one of the most abundant elements in nature, but still about the half the cost of a finished module is due to the material itself, and it needs to be reduced [1]. During recent years, scientists attention has been focused on thin film materials technologies, as they seem to be promising alternatives to bulk silicon materials, reducing the cost of PV module production. Due to this fact, an increased activity has taken place using liquid phase epitaxy (LPE), in particular epitaxial lateral overgrowth (ELO), to prepare silicon thin film materials for solar cells applications [2, 3].

2. Experimental Details

The experiments were carried out by means of LPE, using a sliding graphite boat system with ultra-pure H₂ as a process gas. The silicon substrates used were (111) oriented with the SiO₂ film (0.1 µm thick), deposited by oxidization in dry O₂ at 1000°C. Suitable 50 µm silicon open windows, oriented along the <110> or the <112> direction, were created in the SiO₂ layer through the mask that defined the parallel line pattern, using a conventional photolithography technique. Typically, the solution was saturated for 120 min at 1050°C, using Sn (5N) as a solvent [4]. The growth was carried out by an equilibrium cooling method at a rate of 0.5°C/min. Samples were then cleaned in aqua regia (3:1 HCl:HNO₃) in order to remove the remains of the solutions, and examined using a Scanning Electron Microscope (SEM). The width and the thickness of the ELO layers were determined from the SEM images.
3. Results and Discussion

On the basis of the data acquired, we managed to determine the dependencies of the width and thickness of the ELO layers on the time of growth (Figure 1 a, b).

![Graph a) Width of the ELO layer](image)

*Figure 1a.* Time dependencies of the width of the ELO layer.

![Graph b) Thickness of the ELO layer](image)

*Figure 1b.* Time dependencies of the thickness of the ELO layer.

These data show that in both cases the width and thickness increase with time up to the moment when they become stable, even if the time of growth becomes longer. However, there are noticeable differences between the values of width as well as thickness with the respective orientation of the seeding windows. As can be seen in Figure 1a, the width of the ELO stripes achieves higher values when the lines are oriented along the <112> direction than in the case of <1̅1̅0> orientation. For example, an ELO layer grown for 6 hours on silicon open windows oriented along the <112> direction is almost twice as wide as in case of <1̅1̅0> orientation, reaching 202 μm. Moreover, the ELO stripes are also thicker when the seeding lines are oriented along the <112> direction than in case of <1̅1̅0> orientation.
However, to determine the favourable conditions of growth resulting in the maximum width and minimum thickness of the ELO layer, the aspect ratio, defined as the ratio of the width to the thickness of the ELO layer, should be considered. The data plotted in Figure 2 show clearly that the maximum aspect ratio can be achieved after 60 min of growth in the case of $<1\bar{1}0>$ as well as $<11\bar{2}>$ orientation.

![Figure 2](image-url)  
*Figure 2. Aspect ratio of the ELO layers dependencies on time.*

A noticeable difference in the morphology of the layers exists with the respective orientation of the seeding windows. Comparing the images shown in Figures 3 a and 3b, it becomes clear that there is a strong dependence of the ELO layer formation upon the orientation of the silicon open windows.

![Figure 3](image-url)  
*Figure 3. SEM cross section images of the ELO layer for the seeding lines orientation along the a) $<1\bar{1}0>$ and b) $<11\bar{2}>$ direction.*

In the case of the lines positioned along $<1\bar{1}0>$ direction, the crystallization front is aligned to the seeding lines. The layer grows in plane-parallel manner, although it is difficult to achieve the coalescence of the
adjacent stripes (Figure 3a). In contrast, when the seeding windows are along the \(<1\overline{1}2\>\) direction, the stripes tends to coalescence but there are some perturbations in the growth. These result in irregularities of the growth front, and coalescence within the whole depth of the ELO layer is not possible (Figure 3b).

In the ELO technique, the SiO\(_2\) layer works as a filter that prevents the defects present in the substrate from propagating into the ELO layer. Thus, the defect density in the ELO layer is lower than that of a LPE layer grown directly on the Si substrate. We found that these two types of layer differ in defect density by an order of magnitude, reaching 2\(\times\)10\(^4\) cm\(^{-2}\) for a Si/Si layer and 3\(\times\)10\(^3\) cm\(^{-2}\) for Si/SiO\(_2\). Nevertheless, some defects are created during the growth. Apart from dislocations present in the substrate, we also found stacking faults in the ELO layer. However, the concentration was four times lower than in a LPE Si/Si layer. This makes the ELO technique a promising tool for reducing the defect density in thin silicon layers.

4. Conclusions

In this work, we studied the kinetics and morphology of silicon ELO layers grown on silicon substrates patterned with SiO\(_2\) masking films, for PV applications. It turned out that the mechanism and kinetics of silicon crystallization strongly depend on the orientation of the silicon open windows.

An effort to determine the most favourable conditions for ELO growth has also been made. We also confirmed the ELO technique as a promising tool for the fabrication of defect-free and good morphology silicon layers.

References

RECRYSTALLIZATION OF CdTe UNDER CONDITIONS OF HIGH TEMPERATURE AND PRESSURE

V. MIKLI and * J. HIIE
Centre for Materials Research, * Inst. of Materials Science, Tallinn University of Technology, Ehitajate tee 5, 19086 Tallinn, Estonia

1. Introduction

The low efficiency and reliability of polycrystalline thin film CdTe solar cells are mainly caused by imperfections in the structure of absorber layer. Large amounts of generated carriers are absorbed by defects like grain boundaries, dislocations, impurities and inclusions of residual phases as oxides and elemental tellurium [1]. To improve the quality of such cells, various chemical and physical treatment methods have been developed. The tradition in the sintering of II –VI type crystalline films is to use a liquid phase [2] (usually chlorides like CdCl₂ for Cd compounds) for acceleration of mass transfer at low temperatures, around 400°C. Heating of the heterostructure of CdTe/CdS at 400°C for 30 min in air in the presence of CdCl₂ increases the grain size of a CdTe film from 0.05 to 0.5 µm, and the end product (solar cell) efficiency from 3 to 12.4% [3].

Figure 1. Hot-pressed (200 MPa) bromide sodalite structure obtained via solid phase recrystallization; a - 950°C (0.6 Ts), b - 1150°C (0.75 Ts), c - 1250°C (0.8 Ts) [4].

The high temperature (near to the melting point) solid phase recrystallization (SPRC) of optoelectronic thin films has not previously been studied (Figure 1). The disadvantage of liquide-phase sintering is the formation of undesirable residuals like oxychloride of cadmium in the grain boundaries of
the recrystallized film [1]. In the case of the deformation aided SPRC process, crystal grains of the matter are exchanged with the crystals, which are more perfect (without defects), have the same phase and a lower total energy. An increase in crystal size of 10-100 times can be achieved [4]. The present study is devoted to obtaining dense polycrystalline CdTe films with large (> 5 µm) grains with a honeycomb–like structure, which is recrystallized under the SPRC crystal-growth conditions (Figure 1b). There is a considerable previous experience in the preparation of CdTe crystals and films. CdTe is the optimal material for solar cell applications, since the theoretical limit of a CdTe based solar cell efficiency is 40.7% [5], whereas only 16.5% has been achieved; CdTe is a simple chemical compound (the unknown phases will not form during high temperature treatment). This means that the results are more easily interpretable. In comparison with other solar cell materials, CdTe is relatively cheap and is stable over long-time use.

2. Materials and methods

![Figure 2. Schematic illustration of the hot-pressing experimental device.](image)

Our experiment was carried out with high purity CdTe powder and 100 µm thick Mo plates. The CdTe powder was mechanically refined and compressed into thin (50 µm) tablet form. Figure 2 shows a schematic illustration of the hot-pressing experimental device built up from a VUB-5 high vacuum system. Temperature was generated by a resistance-heating plate and measured from both sides of the sample with Pt-Pt(Rh) thermocouples. A temperature of 800°C was applied (bottom side) and 400°C was measured from the top side of the sample (the melting temperature of CdTe is 1050°C). A mechanical pressure of 5 N/cm² and a heating time 1 hour were used. Figure 2 shows the possibility
for using a spring instead of the weights. This allows adjustment of the load pressure on a large scale, but is not used in the current experiment.

The structures of the CdTe films were examined using a Jeol JSM-840A scanning electron microscope. The chemical composition and possible phase changes in the CdTe films were evaluated by a point EDS analysis method, using a Link Analytical AN10000 analyser. Electrical resistivity and I-V characteristics of the Mo/CdTe interface were measured with a Keithley 2400 SourceMeter. Indium dot contacts 1mm² area were applied to the CdTe surface.

3. Results and Discussion

As shown in Figure 2, the CdTe sample is situated in a high temperature gradient, which is caused by heat conduction from the hot plate through the Mo plates and CdTe tablet into the bulk, which has high radiation losses from its surface. By use of a temperature gradient in CdTe film preparation, two critical problems in high temperature treatment has been resolved: 1. the recrystallized film is joined to the surface of the upper low-temperature (400 °C) Mo disk, which reduces the problem of adhesion between the film and substrate; 2. the temperature gradient enables use of traditional and cheap substrate materials like Mo or ITO coated glass in high temperature processing. Figure 3 shows the results obtained from the hot-pressing SPRC treatment of a CdTe film. The shortcomings of this experiment were inhomogeneities in the particle size of the

![Figure 3. SEM micrographs of the investigated powders. a- initial, compressed CdTe powder material, b- hot-pressed CdTe film, c- freely (without pressure) grown crystals, d- crystals grown in the hot-pressing conditions.](image-url)
initial CdTe powder (Figure 3a) and variations in thicknesses over the compressed tablet, but also to too low a mechanical pressure. As the result, areas with different recrystallization structures appeared in the film (areas 1 and 2 in Figure 3b, which correspond to Figures 3c and d respectively).

Freely (without pressure) grown grains had sizes up to 30 µm (Figure 3c), but this process is not verifiable over large areas. Structures obtained under hot-pressing conditions had grain sizes of 1-5 µm (Figure 3d). Due to the low mechanical pressure and imperfections in the initial material, the obtained structure was porous, and the recrystallized grains were defective. It is characteristic for all areas of the tablet that CdTe crystals and compressed regions are firmly joined (stuck) to the upper low-temperature Mo plate. This results from the high temperature gradient across the sample. Linear ohmic contacts were seen on the Mo/CdTe back contact interface for the hot-pressed regions of CdTe specimens. The resistivities of the layers varied between $10^6$ and $10^7$ Ohm-cm. Freely grown regions had symmetrical nonlinearities of their I-V curves, indicating the porous polycrystalline character of the material.

It should be noted that this was a first step in this kind of CdTe film processing, and more accurate powder compacting could be achieved at higher mechanical pressures, for a finer and more homogeneous particle size in the initial powder.

4. Conclusions

The method of high temperature gradient in CdTe film preparation enabled us to join the recrystallized film to the upper low-temperature (400°C) surface of a Mo disk, and to achieve an ohmic linear contact between the Mo and CdTe, enabling one to use cheap substrates of Mo- or ITO-glass in high temperature vacuum hot-pressing.

Acknowledgements

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References

PROSPECTIVE INVESTIGATIONS OF BIOFUEL CELLS AS SOURCES FOR APPLICATIONS IN NANOBIO TECHNOLOGY

I. STAMATIN, A. MOROZAN, L. STAMATIN* and A. DUMITRU
University of Bucharest, Faculty of Physics, 3 Nano - SAE Res.Centre, MG-11, 077125, Bucharest-Magurele, Romania
Longhin Scarlat Hospital, Microbiology Laboratory, Serban Voda 94, Bucharest, Romania

1. Introduction

Nanobiotechnology describes the use of nanotechnology in biological systems, in the development of novel nanoscaled products. Nanoscaled power sources are critical to supply energy for nanodevices such as implantable electrically operated nanodevices which would take advantage of the natural fuel substances found in the body, and thus would continue to draw power for as long as the subject lives [1]. Bennetto and Daviss [2, 3] have demonstrated how various microorganisms, such as bacteria or yeast, can be used to convert a substrate into an electrical source, directly and efficiently. Microbial Fuel Cells (MFCs) offer specific advantages over other renewable energy conversion methods.

The present work proposes a novel biofuel cell configuration based on biocatalytic interface structures integrated with water soluble quantum dots (WSQD) as mediators, to check the microorganism activity (mediator reduction test) and reports the incipient results by comparison with a classical dye-test using methylene blue. We are investigating the design of bioanodes for biofuel cell applications based on the *Escherichia coli* bacterium. The results provide the basis for the development of a novel bioanode for a biofuel cell, and offer a source for nanobiotechnology applications.

2. Biofuel Cells - Status and Development

A biofuel cell is a device that directly converts microbial metabolic or enzyme catalytic energy into electricity, by using conventional electrochemical technology. Biocatalysts (microorganisms, enzymes) can be alternatives to the
use of transition metal catalysts in fuel cells. They can be used in one of two ways: they can generate the fuel substrates for the cell by biocatalyst transformations or metabolic processes; or they may participate in the electron transfer chain between the fuel substrates and the electrode surfaces [4]. One of the main obstacles in respect of enzyme-based biofuel cells has been to immobilize the enzyme in a membrane at the electrode surface. Typically, polymers used as ion conductors in H₂/O₂ regular fuel cells, have not been successful in immobilizing enzymes in biofuel cells, because they form an acidic membrane that decreases the lifetime and activity of the enzyme [5]. Molecular imprinted polymers provide the high physical and chemical stability needed to work with immobilized biomaterials in a biofuel cell [6]. In addition, quantum dots biocompatible with biomaterials can be a good aid in the identification of the mechanism that takes place at different interfaces in biofuels. Quantum dots take advantage of the quantum confinement effect, giving the nanoparticles unique optical and electronic properties [7].

The use of microorganisms as microreactors in fuel cells eliminates the need for the isolation of individual enzymse, although they can be difficult to handle and require particular conditions to remain alive. Thus, a wide variety of microorganisms have been tested in MFCs, in terms of their compatibility to various mediators, coulombic yield, electron transfer rate, and regenerative abilities. An electron mediator is required for electron transfer from a microbial electron carrier to an electrode to occur and to generate electrical current. Also, maintaining the anolyte and catholyte solutions in proper chemical balance, the mechanical design, and issues of suspension, waste removal and buffering are all equally important.

Actually, the results indicate that MFCs exhibit many of the desirable features, including: the ability to be recharged nearly to the original charged state following discharge, the ability to accept fast recharge, reasonable cycle life, and low capacity loss under open circuit conditions, as well as in prolonged storage under idle conditions. However, their applicability has been limited by several factors (the need to add electron mediator compounds, incomplete oxidation of the carbohydrates and lack of the long-term stability of the fuel cells [8]).

3. Experimental Details

3.1 SOURCE OF THE BACTERIA AND ACTIVITY TEST

*Escherichia coli* were grown from a stem on specific culture media at 37°C for 48h. The colonies were transferred in the buffer solution (pH=7). The density of the bacteria was estimated at 100.000/ml equivalent with 5 mg/ml sufficient to give a turbid suspension. Two types of mediator were used to test the bacteria
activity: methylene blue solution (10 mM) and WSQD (CdSe-ZnS stabilized by amines group micelle, excitation under 450 nm, emission in the yellow range around of 550-570 nm, concentration of 0.2 mg/ml).

*Case Methylene Blue:* A suspension of bacteria in buffer solution was placed in the tube to almost fill it, to mix the contents. 2-3 droplets of methylene blue solution were added. In the first step, the medium colour was blue ink, specific to the oxidized mediator. After 1h, it turned colourless, specific to its reduced form.

*Case WSQD:* In the same conditions as before, 1-2 droplets of WSQD were added in solution and exposed to radiation at 450 nm (Hg-lamp with a violet filter). In first stage without glucose, the emission spectra was yellow with a good brightness. Upon adding glucose, the colour turn to pale yellow, and the intensity vanished after 30 min. The response was faster than for methylene.

3.2 FUEL CELL CONFIGURATION

The biochemical fuel cell used spectroscopic graphite for electrodes, an ion exchange membrane type dialysis membrane as a separator between two half-cells, the soluble salt potassium ferricyanide, K₃Fe(CN)₆, *Escherichia coli* bacteria, the mediator methylene blue and WSQD in the configuration shown in Figure 1. This cell is similar to that in [9].

The oxidizing solution (catholyte) was a solution of potassium ferricyanide, 0.02 M, in a potassium phosphate buffer (pH=7). The cathode was immersed in this solution to form the oxidizing half-cell. The reducing solution (anolyte) was a solution of phosphate buffer (pH=7) with microorganisms, the mediator methylene blue and WSQD, and a small amount of glucose (1M). In this solution, that is contained in the purse, was immersed the anode. The purse and contents form the reducing half-cell.

3.3 MEASUREMENTS

The cell voltage was measured with a precision digital multimeter. An open circuit configuration was used to measure the potential, while the current was measured in the closed circuit configuration. The measurements were performed in two stages. Firstly without the mediator to establish the initial potential, and secondly with the mediator to establish the maximum performances that can be reached. The results are summarized in TABLE I.
TABLE I. Preliminary results

<table>
<thead>
<tr>
<th>Cell</th>
<th>Voltage (mV)-in open circuit</th>
<th>Initial current (mA)-in shortcut</th>
<th>Current final (mA)-after 30 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without mediator</td>
<td>115</td>
<td>0.010</td>
<td>0.150</td>
</tr>
<tr>
<td>With methylene blue</td>
<td>300</td>
<td>0.340</td>
<td>0</td>
</tr>
<tr>
<td>With WSQD</td>
<td>70</td>
<td>0.010</td>
<td>0.070</td>
</tr>
</tbody>
</table>

The results show that WSQD are not appropriate mediators in fuel cells, due to different concurrent inhibition factors, one them being that they can not form a genuine redox couple in combination with potassium ferricyanide. Nevertheless, WSQD proved to be a better indicator of bacterial activity.

4. Conclusions

WSQD not play a certain role as mediator, but can be sensors and indicators for bacterial activity. Further experiments to improve the novel biofuel cell design proposed in this work, under a variety of experimental conditions (concentrations, different mediators, varied amounts of microorganisms, and temperatures), are in progress.

References

ELECTRONIC PROPERTIES OF A PEANUT-SHAPED C$_{60}$ POLYMER

J. ONOE

Tokyo Institute of Technology and Japan Science and Technology Agency
2-12-1 Okayama, Meguro, 152-8550 Tokyo, JAPAN

1. Introduction

Since the first report on C$_{60}$ photopolymerization [1], there have been several reports of methods to produce C$_{60}$ polymers [2]. In particular, C$_{60}$ polymerization induced by light and electron-beam (EB) radiation is of great interest from a viewpoint of the nanofabrication of C$_{60}$-based carbon materials.

In our recent work [3-5], comparison of infrared spectra with theoretical IR calculations indicated that an electron-beam (EB) irradiated C$_{60}$ film is neither graphite nor carbon nanotube-like, but a peanut-shaped C$_{60}$ polymer as shown in Figure 1. Although many attempts to examine the electron-stimulated polymerization of solid C$_{60}$ have been made [6], there have been no previous reports of the formation of such a peanut-shaped polymer. Very recently, we demonstrated from four-probe measurements that the peanut-shaped polymer exhibits metallic properties in air at room temperature, with a drastic decrease in its resistivity to 1-10 $\Omega$cm compared to that of $10^8$-$10^{14}$ $\Omega$cm for pristine C$_{60}$ [6].

Here, we present in situ photoelectron spectra of the C$_{60}$ film before and after EB irradiation, in order to understand the metallic transport properties [7].

---

Figure 1. Schematic representation of a possible peanut-shaped C$_{60}$ polymer.
2. Experimental Details

After a C$_{60}$ film (100 nm thick) was formed on a stainless steel substrate, the pristine film was transferred to a UHV analysis chamber (base pressure: $10^{-7}$ Pa) and measured in situ by x-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS). The film thickness was sufficient to ignore the influence of the substrate on the valence electronic structure of solid C$_{60}$ [8]. Also, we had confirmed from in situ quadrupole mass spectra that no C$_{60}$ molecules were desorbed from the film under the same EB irradiation conditions [3]. After the measurements, the film was returned to the first chamber and irradiated with the EB-gun for 50 h, in 10 h increments. After every 10 h irradiation, the film was transferred to the analysis chamber for XPS and UPS measurements, with a step of 50 meV. After the measurements of the 50 h irradiated film, the sample was exposed to atmosphere for 5 days. Subsequently, the film was returned to the analysis chamber and studied by XPS and UPS spectroscopy.

3. Results and Discussion

Figure 2a shows UPS whole spectra of the EB-irradiated C$_{60}$ film along with that for highly oriented pyrolytic graphite HOPG. The narrow bands of the pristine C$_{60}$ film in the energy range 0–15 eV became broader after irradiation. Also, the whole spectrum of both EB-irradiated films (20 and 50 h) was quite different from that of HOPG, except for the binding energy around 15 eV. In accordance with this broadening, the density of states (DOS) for the EB-irradiated film increased near E$_F$ more than that for HOPG. Figure 2b shows the magnified spectra around E$_F$. A weak peak appears at around 1 eV in the binding energy for the pristine C$_{60}$ film. This is attributed to a satellite of the intense narrow HOMO excited by the He I$\beta$ (23.1 eV) emission line included in the present non-monochromatic He I light source, because a He I line with emission due to its satellites subtracted provided no such peak [9]. This peak is, therefore, neglected in the present discussion. For HOPG graphite as a semi-metal, the DOS should appear at E$_F$. As can be seen clearly in Fig. 2(b), the line arrowed by HOPG well expresses the semi-metallic feature of graphite. On the other hand, the DOS of the C$_{60}$ film became larger than that of HOPG with increasing EB irradiation time, and moved across E$_F$ to some extent. This suggests that the EB-irradiated C$_{60}$ film is more conducting than graphite. Accordingly, the EB-irradiated film changed from a semiconductor to a semi-metal or metal as a new $\pi$-electron-conjugated system. For low-dimensional materials in their metallic phase (for example, quasi-one-dimensional materials), no evidence of the Fermi step can be detected, though the Fermi discontinuity of the DOS was not clearly observed, as in bulk metals [10]. It is of further interest to clarify the dimension of the peanut-shaped C$_{60}$ polymer structure from the standpoint of the electronic properties.
To understand the metallic properties of the EB-irradiated C$_{60}$ film obtained in air at room temperature [6], we examined the valence structure of the 50 h EB-irradiated C$_{60}$ film after air-exposure. Figure 3(a) shows the UPS spectra of the film before and after 5 days of exposure, together with that of HOPG. Although the DOS of the film decreased after air-exposure, it was still similar to that of HOPG around $E_F$, indicating that the EB-irradiated C$_{60}$ film still had a metallic feature. This is the origin of the linear I-V curve obtained previously [6].

![Figure 2](image1)

**Figure 2.** (a) UPS whole spectra of the electron-beam-irradiated C$_{60}$ film and HOPG, and (b) its magnified spectra near the Fermi level.

![Figure 3](image2)

**Figure 3.** (a) UPS spectra of the 50 h EB-irradiated C$_{60}$ film before and after air-exposure near the Fermi level. (b) Valence XPS spectra of the 50 h EB-irradiated C$_{60}$ film before and after air-exposure.

To clarify how the EB-irradiated C$_{60}$ film maintained its metallic properties even after 5 days of air exposure, we measured the valence XPS spectrum of the 50 h irradiated film before and after air exposure, along with that of HOPG graphite. As in Fig. 3(b), a new broad intense peak appeared in the binding energy in the range 25–30 eV, after air-exposure. Since this peak is attributed to the O 2s orbital of an oxygen atom chemically bound to organic polymers [11], it is considered that molecular oxygen was chemisorbed onto reactive sites, such as in the region of negative curvature of the peanut-shaped structure (see Fig.1), and
dissolved to form C=O or C-O-C onto the peanut-shaped polymer. However, the atomic ratio of oxygen to carbon changed from 0.8 to 5.0 at% even after the air-exposure, which corresponds to 1.5 oxygen molecules per C_{60} molecule. This allows us to consider that molecular oxygen was adsorbed only on the surface layers of the EB-irradiated C_{60} film but did not diffuse into its bulk, so that the metallic feature of the film was not significantly affected by air-exposure.

This metallic property arises from the fact that no nodes are formed on the cross-linkage region between adjacent C_{60} molecules, and the HOMO spreads over the whole dimer structure [9].

4. Summary

In situ valence photoelectron spectroscopy demonstrated that the electronic structure of the EB-irradiated C_{60} film becomes closer to that of graphite as the EB-irradiation time increases, and that the DOS around E_F was eventually greater than for graphite. This indicates that the electronic structure of a C_{60} film was changed from a semiconductor to a semi-metal and/or metal after EB irradiation. It is interesting to note that the DOS at the Fermi edge for the peanut-shaped polymer is very similar to that for one-dimensional metals. Even after the film was exposed to air for 5 days, the electronic structure still remained metallic, which is the origin of the linear I-V curve of the EB-irradiated C_{60} film obtained in air at room temperature [6]. We explained qualitatively the origin of the electronic properties of the polymer, on the basis of DFT calculations.

References

THE GEL TRAPPING TECHNIQUE: A NOVEL METHOD FOR CHARACTERIZING THE WETTABILTY OF MICROPARTICLES AND THE REPLICATION OF PARTICLE MONOLAYERS

V.N. PAUNOV and O.J. CAYRE
Surfactant & Colloid Group, Department of Chemistry
University of Hull, Hull, HU6 7RX, U.K.
Email:V.N.Paunov@hull.ac.uk

1. Introduction

Determining the three-phase contact angle of small particles attached to liquid surfaces has been a long-standing challenge for surface and colloidal science over recent decades. Although several techniques have been developed for the determination of the wettability of powders [1,2] and microparticles [3], a simple method for measuring the three-phase contact angle of particles (θ) adsorbed at a liquid interface was not available until recently.

2. The Gel Trapping Technique (GTT): Measurement of Three-Phase Contact Angles (θ) and Preparation of Anisotropic Particles

![Figure 1: Schematic diagram of the “gel trapping technique” for determining three-phase contact angles of microparticles (θ) at an oil-water (A-F) and air-water (C-F) interface.](image)

For this purpose we have developed a new approach (see figure 1) based on replicating particle monolayers adsorbed at air-water or oil-water interfaces. The technique relies on the spreading of colloid particles at an air-water or oil-water interface by means of a spreading agent such as isopropanol (IPA), and subsequent gelling of the aqueous subphase with the non-adsorbing polysaccharide Gellan (which does not affect the interfacial tension of either the air-water or the oil-water interface [4]). The particle monolayer is then replicated on the gel surface with polydimethylsiloxane (PDMS or Sylgard 184, Dow Corning) and single particles partially embedded in the polymer matrix are imaged by SEM. Hence, the depth of embedding of the particles allows calculation of their three-phase contact angle $\theta$ at the original liquid interface.

**Figure 2**: Example of different colloid suspensions treated with the GTT. Particles, partially embedded on the PDMS surface: (a) 9.6 $\mu$m sulphate latex particles (Interfacial Dynamics Corporation) at the air-water interface ($\theta = 74^\circ \pm 4$), (b) 519 nm silica particles (microParticles GmbH) at the decane-water interface ($\theta = 99^\circ \pm 2$), (c) SU-8 microrods at the air-water interface and (d) soy protein powder (Supro 651m, DuPont) at the air-water interface.

Figure 2 presents SEM images of different types of colloid particle embedded at the air-water or decane-water interface. Note that the visible part of a particle's surface corresponds to what was immersed in the water phase when adsorbed at the original air-water or oil-water interface. Using the GTT, we have been able to determine the contact angle at both these interfaces, for particles of different materials and sizes: polystyrene microspheres [4], colloid silica (including particles in the submicron range) with different hydrophilic coatings and gold porous microparticles [5], non-spherical colloids such as polymeric microrods, and protein powders.
We also used this technique to fabricate two novel types of anisotropic particle, as shown in figure 3. By gold sputtering over colloid monolayers partially embedded within the protective PDMS matrix, “Janus-like” particles were prepared. By spreading a “cold” (20°C) particle suspension on the surface of the hot (50°C) gellan solution, it was possible to capture the gelled aqueous menisci around the particles and to replicate these supraparticles with PDMS.

3. Fabrication of Microlens Arrays Using the GTT

We also used the GTT to replicate self-assembled monolayers of charged monodisperse PS latex microparticles adsorbed at the oil-water interface [6]. By removing partially embedded particles from the PDMS matrix, elastomer surfaces of controlled microporosity were produced. By further casting this surface with a photopolymer, microlens arrays with well-defined properties were prepared. The porous template was first obtained by dissolving the latex particle monolayer in toluene, then drying under vacuum and coating with a layer of Norland optical adhesive 61 on a glass slide. After UV curing of the optical adhesive, the PDMS template was peeled off to produce a microlens array on the glass support. The properties of the arrays prepared by this method are defined by the size and the contact angle of the templated particles, and by the interparticle distance within the original monolayer formed at the oil-water interface.

Figure 4 shows observations made at different stages of the replication of a monolayer of 3.9 μm sulphate latex particles (from IDC) from the decane-water interface, and the formation of a microlens array on the cured photopolymer surface. By changing the concentration of latex particles within such a monolayer, microlens arrays of varying inter-lens distance have been obtained, as shown in figures 4c and 4d for two distinct particle concentrations.
Figure 4: (a) An optical microscopy image of an array of 3.9 µm sulphate PS particles at the decane-water interface; (b) SEM pictures of the microporous surface after removing the particles trapped in the polymer matrix; (c and d) replication of the microporous surface with a photopolymer on a glass slide.

4. Conclusions

We have developed a new technique for measuring the three phase contact angle of colloid particles adsorbed at both air-water and oil-water interfaces. The method is applicable to a large range of colloids, from standard spherical shape particles to proteins including submicron size colloid silica. Anisotropic particles and ordered microlens arrays were also produced by modifying the apparent surface of the particles and by replicating self-assembled monolayers.

References

1. Introduction

Unique applications of high-T$_c$ and room-T$_c$ superconductivity (HTSC) in two-dimensional (2D) bundles and ropes of carbon and non-carbon nanotubes (NTs), and nanotubular crystals (NTCs) are presented. Unique properties of NTs stem from the phase transition connected with the change in the aspect ratio i.e. by reducing the tube diameter to nanoscale dimensions. A nanotube becomes a quantum quasi-1D cylinder, nanoscopic in diameter while macroscopic in length. Lattices of 2D ordered bundles or ropes of NTs are expected to be more unique. A 2D lattice of superconducting non-carbon NTs was first proposed by combining the theory suggested by Little and Ginzburg with the recent progress in NT research to produce an ideal superconductor with a record room T$_c$ [1,2]. The mechanism of superconductivity was proposed on the basis of a whispering mode of phonon vibration, which is shown to be responsible for a strong enhancement of the electron-phonon interaction and for an increase of T$_c$ and J$_c$. Coherent and low attenuated vibrations of all atom pairs on diametrically-opposite walls of NTs induce coherent states of their nearest electron pairs with opposite impulses (-k,k), providing ideal conditions for Cooper pair formation and peculiar Bose-Einstein condensation [1,2]. The unique resonant Bose-Einstein condensate appearing in such crystals is suggested to be recognized as a novel universal peculiar structural state of matter [3], that can manifest itself not only in the enhancement of superconductivity by the resonant electron-phonon coupling [4], but also in the photogalvanic [5], acoustoelectronic [6] and other effects.

Peculiar features arise in cylindrical quasi-1D NTs, distinguishing them from conventional 2D planar sheets, namely: 1) Peaks of the density of electronic states with energies E$_E^l$, caused by circular l-bands or orbital plasmons degenerated in planar sheets; 2) A gallery of whispering ring phonon modes v$_A^j$ as non-vanishing zero-point vibrations. Coherent electron-phonon coupling occurs in resonant conditions when the phonon energy matches that of the electron interband transitions, $h\nu_A^j = E_{E_1}^E - E_{E_1}^{E_2}$. Superconductivity arises in such a resonant electron-phonon state. Room T$_c$ superconductors have been proposed [3] to be fabricated on basis of special NTCs of MgB$_2$-type (see Figure 1).
Two kinds of ideal high-$T_c$-superconductors based on membrane 2D crystals (the lattice parameter of which is about the double the penetration depth of a magnetic field $a \sim 2\lambda$), built from nanotubes (diameter $\sim$ the correlation length $d \sim \xi$), wrapped from layered superconducting materials [3]: a – square lattice of nanotubes deposited on the inner walls of nanocylinders of a 2D-membrane; b – triangular lattice of nanotubes deposited on the outer walls of nanofibers of a 2D brush-like lattice; c – cross-section of the single-walled LuNiBC nanotube; d – cross-section of the two-walled MgB$_2$ nanotube.

2. **Resonance Effects in Nanotubes**

Here we propose the further applications of such HTSC NTCs that are possible when interacting with optical frequency photons. In complicated photon-electron-phonon systems, double and triple resonances can occur, resulting in novel phenomena, applications and devices, in which the NTC plays the role of a lossless barrierless electron-phonon transducer. Such resonances have become possible exceptionally in NTs and NTCs, due to their very low diameter $d$.

A photogalvanic effect in non-centrosymmetric non-carbon B$_x$N$_y$C$_z$ chiral nanotubes was shown to arise when a quantum polarized along the axis causes interband excitations [5]:

$$h\nu^L_j = E^E_{1} - E^E_{1+i}. \quad (1)$$

Thus, such a NT can act as a photovoltic nanodevice.

In HTSC 2D NT crystals, such electronic excitations may be suggested to transform into phonon vibrations in the case of double resonance:

$$h\nu^L_j = E^E_{1} - E^E_{1+i} = h\nu^A_j. \quad (2)$$
Hence, such a photoacoustic transducer would be able to transform the energy of external electromagnetic waves without losses into the vibrational energy of natural acoustic hyper-sound phonons, acting as an ideal nano-antenna vibrator. The frequencies depend on the NT's diameter, and lie in the range 1 GHz - several THz, where no effective acoustic generators exist. Such a photoacoustic (acoustoelectric) effect in NTCs has been observed experimentally at a relatively low frequency, 0.33 GHz [6]. When the carbon NT bundles were placed in a microwave electromagnetic field at a temperature 1K lower than the superconducting \( T_c \), a series of stress peaks was excited at the ends of the nanotubes. Such a photoacoustic transducer can be utilized in a generator (phaser) and detector of extremely high-frequency hypersound phonons. Such HTSC NTCs also appear to act as 2D photonic crystals in the range from visible up to X-ray, due to the size effect, \( \lambda \sim d \).

One can possibly suggest another double resonance reversible to the previous one, namely

\[
\hbar v^A_j = E_{E+1}^E - E_{E+i}^E = \hbar v^L_j. \tag{3}
\]

If phonons are excited in any way, then they may be transformed through electronic excitations into a quantum of light. Hence, on the basis of HTSC NTCs it may be possible to develop a number of quantum generators of electromagnetic waves (nanoantenna) in the visible, ultraviolet and soft X-ray ranges, depending on the nanotube diameters.

Carbon NTCs are now being studied to develop high resolution electron nanoemitters. Direct and phonon mediated field and photo emission:

\[
\hbar v^L = E_{E+1}^E - E_{E+i}^E = \varphi_a \tag{4}
\]

\[
\hbar v^L_j = \hbar v^A_j = E_{E+1}^E - E_{E+i}^E = \varphi_a \tag{5}
\]

is suggested to be enhanced in many orders of magnitude, due to a drop in the electronic work function \( \varphi_a \) in a nanotube in the high-\( T_c \) superconducting state. Lossless resonant transformation of photons into electron excitation is responsible for this drop. Hence, such HTSC NTCs are expected to be ideal nanoemitters of electrons, that can be utilized in the development of a panel nanodisplay with a record pixel density \( \sim 10^{10} \) emitters/sm\(^2\).

3. Routes for the Fabrication of NTCs

Four routes have been proposed to fabricate such record nanotubularcomposites [7,8]. The first route includes the fabrication of a membrane template comprising a lattice of cylindrical nanopores \( \sim \xi \) in diameter separated by a \( \sim 2\lambda \) lattice parameter, where \( \xi \) is a correlation length and \( \lambda \) is the penetration length of the NT material (Figure 1). On the inner walls of the nanochannel
template, both a catalyst and then a high-\(T_c\) superconducting covering layered material should be deposited, which must be grown epitaxially in the form of nanotubes. The reality of this approach was demonstrated recently [9,10], when single-walled C-NTs within the channels of a membrane were produced.

In the second route, an ordered metallic nanofiber brush with the same \(\zeta\) and \(2\lambda\) parameters are used as the template. Then the superconducting multilayers are grown on the outer surface of the nanofibers. The third route is based on a nanolithography technique, and the fourth on the sol-gel method.

There is no doubt that the realization of the proposed routes will result in the fabrication of a RTSC based on 2D NTCs, in the near future. In such a manner, it is believed that superconductors based on MgB\(_2\), C, NbSe\(_2\) and other simple compounds will be produced.

4. Promising Applications

Following are the possible applications of NTCs: a superconductor with a record room \(T_c\); a phonon quantum generator (phaser) of hypersound with extremely high frequency; a noiseless lossless nanoantenna for the super-frequency range; a low-barrier emitter for flat displays; and a solar cell with a record efficiency.

Such NTCs, if fabricated, also appear to act as 2D photonic crystals, as left-handed materials, etc. Thus, we must recognize them as miracle crystals or even a novel unique structural state of matter.

Acknowledgements

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References

PHOTOLUMINESCENCE AND XPS STUDY OF SELENIUM TREATED POROUS SILICON

R. JARIMAVIČIŪTĖ-ŽVALIONIENĖ, S. TAMULEVIČIUS, M. ANDRULEVIČIUS, R. TOMAŠIŪNAS, V. GRIGALIŪNAS and Š. MEŠKINIS

a Department of Physics, Kaunas University of Technology, Studentų 50, LT-51368 Kaunas, Lithuania
b Institute of Physical Electronics, Kaunas University of Technology, Savanorių 271, 50131 Kaunas, Lithuania
c Institute of Materials Science and Applied Research, Vilnius University, Saulėtekio 10, 2040 Vilnius, Lithuania

1. Introduction

Porous silicon (PS), as a promising material for visible light emission by photoluminescence (PL), attracted attention due to possible photonic applications in different devices like LEDs, wave guides, field emitters, optical memories or gas (NO₂, CO, etc.) sensors etc. [1-5]. The theoretical assumption of the visible light luminescence is based on a quantum explanation, but the details of the mechanism are still not completely understood [6, 7]. The stability and lifetime of PS photoluminescence are very important factors, and can be significantly improved by use of an efficient surface passivation method. Recently, different chalcogenide (selenium or sulphur) treatments received attention as an alternative method, heteroepitaxy-compatible with Si surface passivation [8, 9]. In the present study, porous silicon was produced by ultrasound enhanced DC etching and PS surface selenious acid treatment was performed to improve the stability and lifetime of the PS photoluminescence. The surface chemical composition was investigated by X-ray Photoelectron Spectroscopy (XPS), to contribute to the understanding of the enhancement of the PL.

2. Experimental Details

PS layers were prepared at room temperature, using ultrasonically enhanced DC electrochemical etching of Si in HF:H₂O:C₂H₅OH solutions. The backside of
the sample was illuminated with a 50 W halogen lamp. More details of the experimental equipment are presented in [10].

Selenium treatments of the PS samples were performed by exposing in 10% H₂SeO₃ acid for 30-150 seconds. The resulting porous silicon microstructures were investigated using a scanning electron microscope (SEM) JEOL JSM-IC25S. The depth and width of the pores was measured from the SEM images, using a standard programme ImageJ.

XPS spectra were recorded with a KRATOS ANALYTICAL XSAM800 XPS analyser. Al Kα radiation (hv=1486.6 eV) was used. The energy scale of the system was calibrated according to the positions of the Au4f7/2, Cu2p3/2 and Ag3d5/2 peaks. The C1s, Si2p, Se3d and O1s spectra were determined at a 20 eV pass energy (0.1 eV energy increment), with the analyser in the constant transition mode.

The PL properties of the initial and selenium treated PS structures were investigated in the visible spectral region, illuminating with a 1000 W halogen lamp. An excitation wavelength of 400 nm was used.

3. Results and Discussion

![Figure 1](image.png)

The porous layer of silicon was fabricated by means of electrochemical etching in a HF solution, using ultrasound excitation. At different current densities and levels of ultrasound excitation, pores in the silicon with coefficients of anisotropy from 7.31 to 158.4 were produced. The average depth of the pores varied from 25 to 122 µm, and the average width was 3.42 to 0.77 µm.

Figure 1 presents the photoluminescence of PS exposed to selenious acid for 30 s – 1, 150 s – 2, 90 s – 3.
acid treatment, the PL increases by approximately 20% if exposure time does not exceed 90 s. According to these results, the intensity of the PL is a non-monotonic function of exposure to selenious acid. The only reason for this can be the changes in the chemical composition of the PS surface layer if the PL is measured in similar surface regions. The XPS analysis was performed to determine the surface composition of the PS after selenious acid treatment. The Si2p spectra of PS treated with selenious acid for 30 s are shown in Figure 2, and the insert represents the Se3d spectrum. The Si2p spectrum is fitted with four lines. Line ”1” we attribute to Si-Si bonds line ”2” to silicon bound to selenium through oxygen atoms. Lines ”3” and ”4” can be attributed to Si-O\textsubscript{x} and SiO\textsubscript{2} bonds respectively. The SiO bond, if it exists, is overlapped by the stronger Si-Se\textsubscript{x}-O\textsubscript{y} signal (line”2”).

![Figure 2. The Si2p spectrum of PS treated with selenious acid for 30 s. The insert in the upper left corner represents the Se3d spectrum.](image)

The difference between peak “1” and “4” energy values (4.5 eV) is close to the theoretical value for pure SiO\textsubscript{2} - 4.2 eV. From Figure 2 it is clear that after treatment, about 58% of silicon atoms are bound to oxygen, forming oxides of varying stoichiometry – from SiO to SiO\textsubscript{2}. In the case of the untreated PS Si2p spectrum (not shown here) almost 90% of silicon is bonded to oxygen. In the F1 spectra (not shown here) of treated PS, no fluorine peak was found. The selenious acid treated PS Se3d spectrum (insert in Figure 2.) is fitted with two lines. Line “5” (at 54.7 eV) with low intensity we attribute to non-stoichiometric Si-Se\textsubscript{x} bonds, the position of which is lower than that of the Se-Se bond (55.3 eV) [11]. The position of the high intensity line “6” (at 56.7 eV) is significantly lower than those of SeO\textsubscript{2} (59.4 eV) or H\textsubscript{2}SeO\textsubscript{3} (61 eV), but it is above those for Se-Se bonds [11]. Therefore we attribute it to Si-Se\textsubscript{x}-O\textsubscript{y} bonds. No peaks
for selenium oxide, free selenium or selenious acid were found in the Se3d spectra, indicating that selenium is bound to the silicon through oxygen bonds.

4. Conclusions

The PL is a non-monotonic function of time exposure of PS in Se acid. After initial growth, the PL starts to decrease after exposures of 90 s and more. The XPS analysis shows that the process of redistribution between the silicon-oxygen and silicon-selenium-oxygen bonds takes place after PS surface treatment with selenious acid. No peaks for selenium oxide, free selenium or selenious acid were found in the Se3d spectra, indicating that selenium is bound to the silicon through oxygen.

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SYNTHESIS AND CHARACTERIZATION OF PbS NANOCRYSTAL ASSEMBLIES

T. SARAIDAROV and R. REISFELD
Department of Inorganic and Analytical Chemistry,
Hebrew University of Jerusalem, 91904 Israel

1. Introduction

Semiconductor nanocrystals (NCs) are the subject of great interest for both fundamental research and technological applications, due to their strong size and shape dependence properties, and excellent chemical processibility. Because of their unique optical and electrical properties, semiconductor NCs are likely to play a key role in the emerging new field of nanotechnology in applications from optoelectronic to chemical sensing devices and solar cells [1-3]. A number of methods for the preparation of PbS NCs have already been reported, such as employing sonochemical and solvothermal interface reactions, microemulsion systems, different surface capping agent and strong organic or inorganic matrices [4-10]. It is known that the presence of a surfactant during the formation of NCs has a great influence on the shape and size of the final products. CTAB is a widely applied surfactant used to control the morphology of NCs [11].

In this work, we present a relatively simple and effective procedure for the synthesis and evolution of PbS NCs from spherical to rod-like morphological assemblies, via a solvothermal reaction at 200°C using a lead thiocyanate colloidal solution, surfactant CTAB, and benzyl alcohol as solvent. The important feature is that rod-like PbS NCs can be obtained by controlling the surfactant concentration and reaction temperature.

2. Experimental Details

Differently shaped PbS nanoparticles were synthesized using a colloidal solution (1) of lead thiocyanate in methylethanol, which can be obtained separately as described previously [10]. 0.4 to 4 mM of CTAB was dissolved in deionized water at the boiling temperature and added to 3 ml of solution (1) to obtain a stock solution (2). The synthesis of PbS NCs was carried out in benzyl
alcohol (BA). 100 ml of BA was briefly heated to boiling temperature in a three necked flask, with constant stirring under reflux. The stock solution (2) was quickly injected into the boiling BA. Continuous stirring was applied during heating for 10 min, 1 hour and 6 hours. The reaction includes the solvothermal decomposition of Pb(CNS)$_2$ in a boiling solvent at 200°C and results in the formation of a suspension of PbS in BA. The first sample (10 min. reaction time) was cooled and allowed to sediment for two hours at room temperature. Supernatant liquid was removed and allowed to precipitate again. Each fraction contained different sizes of PbS NCs. The second (1 hour) and third (6 hour) samples were also precipitated. The fourth sample was synthesized with the CTAB concentration increased from 0.4 to 4 mM. The resulting brown or black solid fractions were washed three times with absolute ethanol. Finally, the prepared products were dried at 40°C and then heated at 220°C/1 hour.

HR-TEM observations were made using a TECNAI F20 G$^2$ electron microscope (FEI Company) operating at 200 kV and equipped with an EDAX EDS detector.

3. Results and Discussion

![Figure 1. TEM images of PbS NCs obtained (a,b,c) after 10 min solvothermal reaction of Pb(CNS)$_2$ in BA with the presence of 0.4 mM of CTAB and using two-step fractional precipitation: (a): (bar = 200 nm), NCs obtained from first precipitate; (b): (bar = 200 nm) NCs obtained from supernatants; (c): (bar = 50 nm) sample (b) at increased magnification; (d): (bar = 500 nm) HR-TEM images of PbS NCs obtained after 1 hour reaction in the presence of 0.4 mM CTAB; (e): bar = 200 nm) after 6 hours reaction in the same conditions; and (f): (bar = 200 nm) after 6 hour reaction in the presence of 4 mM CTAB.](image-url)
Figs. 1a,b,c present TEM pictures of the PbS NCs obtained at 200°C with a reaction duration of 10 minutes and after two-step fractional separation and thermal treatment at 220°C. Fig. 1a shows the TEM images of the first fraction of particles (8-14 nm) sedimented from a suspension of PbS in BA. Figs. 1b,c show the second fraction (3-7 nm) sedimented from supernatants. TEM analysis reveals a narrow size distribution of the particles, as has been confirmed recently [10]. HR-TEM images (1d,e,f) show the evolution process of assemblies of rod-shaped NCs with about 50-80 nm width and 500-800 nm length, using 0.4mM of CTAB with reaction durations of 1 and 6 hours. Sample (1f) shows uniform nanorods, with a size of about 30 x 200 nm, obtained after increasing the CTAB concentration from 0.4 to 4mM. A SAED (Selected Area Electron Diffraction) pattern (Fig.2) of a rod-shape (1e) assembly shows a “single crystal” diffraction with an ordered rock salt cubic structure. In the first step of reaction (1a,b,c), adsorption of CTAB molecules on the surface of NCs can tend to shrink and bind the growing particles, reducing the surface energy as can be seen. Increase of the reaction time to 1-6 hours led to the formation of rod-shape structures(1d,e,f). This phenomenon can be related to the interaction of oriented surfactant chains and NCs. From the evolution process of the images 1a-1f, it can be assumed that the presence of CTAB micelle forming surfactant is necessary for the formation of nanorods. The exact formation mechanism of PbS rod-shape structures in our case is still not clear. It follows that more detailed studies are required.

Figure 2. The SAED pattern of the rods (1e) recorded with an electron beam, presents the 111 and 200 reflections of the cubic PbS phase.

4. Conclusions

PbS semiconductor NCs of various shapes and sizes can easily be synthesized using CTAB surfactant in the solvothermal decomposition process of pb(CNS)₂. Various reaction durations led to the formation of spherical or rod-like PbS NC assemblies. Two-step fractional separation-precipitation can be used to obtain narrow size PbS NCs in the range of 3-7 nm and 8-14 nm (reaction time
10 min.). Solvothermal reaction durations between 1 and 6 hours enabled the formation of assemblies of rods with widths of 50-80 nm and lengths of 500-800 nm. Increasing the concentration of the CTAB micelle forming surfactant led to the formation of uniform nanorods of size about 30x200 nm. The SAED pattern, recorded with an electron beam, confirmed the existence of the rock salt cubic structure of the PbS NCs. The particles were usually highly crystalline and most of the rods were even single crystals.

References

LASER ASSISTED FRAGMENTATION OF SILVER AND COPPER NANOCLUSTERS IN SiO$_2$ THIN FILMS

M. SENDOVA, M. SENDOVA-VASSILEVA* and J.C. PIVIN**
New College of Florida, Division of Natural Sciences, 5700 North Tamiami Trail, Sarasota, Florida 34243-2197, USA
*CL SENES, Bulgarian Academy of Sciences, 72 Tzarigradsko Chausee, 1784 Sofia, Bulgaria
**Centre de Spectrométrie Nucléaire et de Spectrométrie de Masse, CNRS, Bâtiment 108, 91405 Orsay Campus, France

1. Introduction

Dielectrics containing metal nanoclusters have been much studied recently, in view of their potential applications in all-optical switching technology. Such materials can be prepared in various ways, among which are ion implantation of metal ions [1,2,3] and ion exchange in glasses [4]. In addition, the cluster size can be modified by thermal annealing [3], ion irradiation [1,4] and laser treatment [3]. The first two techniques lead to an increase in the cluster size, while laser irradiation results in smaller clusters. In order to be able to control the cluster size distribution and achieve a predetermined mean cluster size necessary for applications, one would need to apply two post-deposition treatments which act in opposite directions. On the other hand the mechanism of interaction of metal clusters embedded in a matrix with laser radiation is not yet fully understood. Therefore, further investigation in this area is of primary importance. This study is the first attempt to use laser radiation to modify the size distribution of silver and copper clusters in thin SiO$_2$ films obtained by co-sputtering. Co-sputtering has an advantage over the widely used technique of ion implantation in that the thin films can have a uniform metal concentration across their thickness.

2. Experimental Details and Fitting Procedure

Thin films of SiO$_2$ containing silver or copper were deposited on glass substrates by magnetron co-sputtering of a herasil target with silver or copper
chips placed on it. The metal concentration in the as-deposited films was determined by RBS, and was between 1 and 10 at % (see Figure 1).

The optical transmission spectra of the films in the visible range were measured at normal incidence, using an Ocean Optics single beam fiberoptic spectrophotometer. Laser modification was performed with the 4th harmonic of a New Wave Research Co. Nd:YAG laser (266 nm) with a pulse width of 5 ns at a repetition rate of 10 Hz. Laser energies of 35 to 125 mJ/cm² per pulse were employed. Thermal annealing of the Ag:SiO₂ films was performed in air at a temperature of 550°C for 2.5 hours. Thermal annealing of the Cu:SiO₂ films was performed in an Ar atmosphere, with the same temperature and time duration.

The size of the silver clusters was estimated using numerical modeling based on the Mie theory in the static approximation. From previous investigations on similar samples [1], it was established that the silver clusters in these films satisfy the assumptions of the theory – they are much smaller than the wavelength of light, have a spherical shape and are situated at distances from each other precluding any interaction. The dependence of the metal dielectric function on the size of the clusters was taken into account using the model presented in [5]. The parameters deduced from the fits were the volume fraction of the clusters, the refractive index of the matrix and the radius of the nanoclusters. As shown in [1], the cluster size obtained by the fit is in good agreement with the mean cluster size obtained by TEM.

2. Results and Discussion

The experimental optical transmission spectra are shown in Fig. 2a for Ag:SiO₂ and in Fig. 2b for Cu:SiO₂ films. The fitted curves in the case of silver clusters

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**Figure 1.** RBS spectra of 2.4 MeV He²⁺ recorded at normal incidence; and at a scattering angle of 165°. They were fitted with following concentrations and thicknesses using the RUMP code: a) Ag:SiO₂ film with 3 at.% Ag and thickness of 326 nm; b) Cu:SiO₂ film with 8 at.% Cu and thickness of 145 nm.
Figure 2. Plasmon resonance of (a) a Ag: SiO₂ film after thermal annealing (1) followed by laser treatment at 35 mJ/cm² (2), 75 mJ/cm² (3) and 125 mJ/cm² (4). The experimental spectra are drawn in full lines, the fits with dashed lines; (b) Cu:SiO₂ as deposited (1), followed by thermal annealing (2) and followed by laser treatment at 35 mJ/cm² (3).

<table>
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<th>Ag [at. %]</th>
<th>Film Thickness [nm]</th>
<th>Consecutive laser treatment</th>
<th>Cluster radius, R [nm]</th>
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are given in Fig. 2a. The estimated silver cluster sizes from three different samples are summarized in Table 1.

We have demonstrated [6] the possibility to alter reproducibly the size of silver nanoclusters embedded in sputtered silica thin films by laser irradiation, and to restore the initial mean cluster size by thermal annealing. It was found that using different laser fluences above a certain lower threshold, the extent of the size reduction could be controlled. After long enough treatment with the same laser fluence, the effect saturated. The mean cluster size after long treatment with the same fluence depended on the fluence but not on the starting mean cluster size. There was a lower threshold fluence for observing an effect for each mean cluster size. The process of laser size reduction was attributed to photofragmentation or ablation of single atoms, dimers or larger groups of
The change of the plasmon resonance of copper clusters after thermal annealing and following the laser treatment at a fluence of 35 mJ/cm² are shown in Fig. 2b. The theoretical calculations using the model described above show a well defined tendency of the low energy slope of the plasmon resonance peak to increase with increasing copper cluster size. This allows us to conclude that the thermal annealing of Cu:SiO₂ films leads to an increase of the cluster size, and that the laser treatment diminishes the size of the clusters in a similar fashion to the reaction of silver clusters in the same matrix subjected to the same treatment.

3. Conclusions

Laser assisted photofragmentation, in combination with heat treatment, can be used for tailoring both the silver and copper cluster size. Numerical modeling based on the Mie theory in the static approximation was successfully applied for estimating silver cluster size and the trend in the copper cluster size evolution. We demonstrated that a similar process of fragmentation takes place for both types of cluster subjected to laser irradiation with a fixed wavelength.

Acknowledgement

We are grateful to M.A. Garcia for the program code.

References

Nd³⁺ PHOTOLUMINESCENCE IN SILICA THIN FILMS

M. SENDOVA-VASSILEVA, J.C. PIVIN*,
A. PODHORODECKI**, O. ANGELOV and
D. DIMOVA-MALINOVSKA

Central Laboratory for Solar Energy and New Energy Sources,
Bulgarian Academy of Sciences, Tzarigradsko Chaussee 72, 1784
Sofia, Bulgaria,
*Centre de Spectrométrie Nucléaire et de Spectrométrie de Masse,
Bâtiment 108, 91405 Orsay Campus, France,
** Institute of Physics, Wroclaw Institute of Technology, Wybrzeze
Wyspianskiego 27, 50-370 Wroclaw, Poland

1. Introduction

SiO₂:Nd is a prospective material for light sources in planar waveguides, as it
emits strongly in the near infrared (IR) part of the optical spectrum. This work
compares the photoluminescence (PL) of sputtered SiO₂:Nd films with that of
Nd doped silica films obtained in other ways.

2. Experimental Details

Three methods of sample preparation were used. The first was rf magnetron co-
sputtering of a SiO₂ target with Nd chips placed on it. The second was ion
implantation with 300 keV Nd ions at fluences of 10¹⁵ to 5×10¹⁵ cm⁻² of thermally
grown films of stoichiometric silica. These conditions give a Gaussian depth
distribution at 100 nm from the surface with a FWHM of 30 nm and a
concentration maximum of 0.2 to 1 at.%, as checked by RBS. The third group of
samples was prepared by the sol-gel method. Hydrolysis of tetraethoxysilane
(TEOS) was performed. NdNO₃.xH₂O diluted in ethanol was added to the TEOS
sol in proportions from 0.1 to 1 mole%. The films were deposited by spinning at
3000 rpm. The thickness of all types of films was between 100 and 500 nm. The
Nd concentration, as measured by RBS, was between 0.03 and 2.0 at.%. The
samples were annealed at temperatures between 500 and 1000°C, in vacuum or
air. The visible PL was excited with a Nd:YAG laser fitted with a Panther OPO, which allows a wavelength between 410 and 2250 nm to be chosen, and detected with a CCD camera. The near IR PL spectra were excited with the 488 nm line of an Ar⁺ laser, and detected using a Ge detector.

3. Results

Figure 2. PL spectra of implanted samples in the (a) visible and (b) IR.

Figure 1a exhibits the energy level diagram of Nd³⁺ [1] and Figure 1b the excitation spectrum of the ⁴F₃/₂→⁴I₉/₂ transition of Nd³⁺, measured for an implanted sample. Based on this PL excitation spectrum, the 587 nm
Nd$^{3+}$ PHOTOLUMINESCENCE IN SILICA THIN FILMS

Figure 3. PL spectra of co-sputtered samples in the (a) visible and (b) IR.

Figure 4. PL spectra of TEOS samples in the (a) visible and (b) IR.

wavelength was chosen for the excitation of the visible PL spectra. The PL transitions are assigned letters for easier identification in the figures (see Figure 1a): A - $^4F_{7/2}$$^4S_{3/2} \rightarrow ^4I_{9/2}$, B - $^4F_{5/2}$$^4I_{9/2}$, C - $^4F_{3/2}$$^4I_{9/2}$ and D - $^4F_{3/2}$$^4I_{11/2}$. This notation will be used in the rest of the paper.

In all three matrices, the visible PL spectrum consists of the A, B and C transitions and the IR PL involves the C and D transitions. Figure 2 shows the PL spectra of implanted samples. Figure 3 shows those of sputtered samples and Figure 4 those of sol-gel samples. The Nd concentrations measured by RBS are indicated in all figures. The intensity passes through a maximum at a comparatively low concentration for all samples, as can be seen.

4. Discussion and Conclusions

The intensities of the Nd$^{3+}$ PL spectra in the three differently prepared silica matrices are very similar. There are some differences in the relative intensities.
of the different components of the multiplets and the number and positions of these components, which may be due to differing local symmetries.

In the literature [2], it has been shown that the Nd$^{3+}$ PL spectrum in silicate glasses consists of a fast decay component (FDC) and a slow decay component (SDC). The SDC is emitted by Nd$^{3+}$ ions uniformly dispersed in the matrix, while the FDC is emitted by clustered Nd$^{3+}$ competing with non-radiative decay because of concentration quenching. In transition C, the SDC is at about 900 nm and the FDC at 880 nm. In transition D, the SDC is at 1090 nm and the FDC at 1060 nm. Also, for SDC it is characteristic that the D transition is much less intense than the C transition. Assignment of the bands to SDC and FDC has been done in Figures 2 to 4. The 880 nm (FDC) line appears in all measured visible PL spectra in the three kinds of matrix. This shows that a major part of the luminescence signal comes from clustered ions. In the IR spectra of the samples annealed in air, the D transition predominates, which is again a sign of clustered ions. In Figure 3b, it is evident how the SDC contribution falls with concentration. Clustering leads to concentration quenching, and this is confirmed by the low values of the Nd concentration at which the PL starts to fall as a function of the Nd content.

Our results on the PL intensity of sputtered samples after annealing in air and in vacuum let us conclude that clustering and concentration quenching take place at a lower temperature, and are more pronounced after annealing in air. When annealing is done in air at 620°C and 800°C, the PL intensity is higher for the 620°C annealing while after treatment in vacuum at 510°C and 800°C a higher PL intensity is observed for the 800°C annealing. Concentration quenching for annealing in air begins at 0.06 at.% Nd, while for annealing in vacuum it begins at 0.8 at. % Nd in the film.

In all studied matrices, co-doping with Al or another dopant, which can reduce the clustering of Nd$^{3+}$ ions, is needed for increased efficiency at higher concentrations.

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References

CHARACTERIZATION OF THE METAL-SEMICONDUCTOR INTERFACE FOR SILICON CARBIDE BASED SENSORS

A.A. WOODWORTH, C.Y. PENG, C.D. STINESPRING and K. MEEHAN*
Chemical Engineering, West Virginia University, Morgantown, WV 26506-6102 and
*Electrical Engineering, Virginia Tech, Blacksburg, VA 24062. USA

1. Introduction

Silicon carbide (SiC) is a robust, wide band gap semiconductor suitable for fabricating gas sensors [1]. The simplest sensors are Schottky diodes that change their electrical characteristics when gases such as H₂, O₂, CO, NO, and hydrocarbons are adsorbed on the metal contact [2].

Lifetime studies indicate that thermally induced compositional and structural changes at the metal-SiC interface adversely impact the performance of these sensors [3]. One factor that may contribute to the observed thermal instability is the quality of the SiC substrate surfaces on which the devices are fabricated. Vendor-supplied 6H-SiC substrates contain a large number of surface and sub-surface defects associated with the polishing process, as well as native defects associated with SiC growth.

High temperature hydrogen etching of SiC is known to remove surface and sub-surface polishing damage, and to leave behind a periodically stepped surface [4]. In this paper, we report studies comparing the thermal stability of Pd-SiC interfaces formed on these stepped surfaces with those formed on the standard surfaces commonly used in SiC sensor device fabrication.

2. Experimental Procedure

The samples used for these studies were 1 cm x 1 cm, 6H-SiC squares cut from n-type wafers purchased from CREE Research Inc. and Sterling Semiconductor. All wafers had vendor polished (0001)-Si faces. The CREE wafers were cut 3.5° off axis, while the Sterling samples were on axis. The nominal resistance of all the wafers was 0.03 ohm-cm.
Standard SiC surfaces were prepared by wet chemical (HF based) cleaning to remove the oxide layer. Stepped surfaces were prepared using an additional H$_2$ etching step. The details of the preparation procedure are discussed elsewhere [5]. The pre-treated samples were mounted on a molybdenum puck and load-locked into the ultrahigh vacuum growth system. The growth system [5] was equipped with an effusion cell for Pd deposition, a resistance heater, an optical pyrometer, and an Auger electron spectrometer (AES). Deposition rates for Pd were determined by weight gain.

AES peak intensities and known elemental sensitivity factors were used in a standard manner to determine the amount of each element present in the AES sampling volume [6]. In addition, the lineshape of AES transitions involving a valence band state are sensitive to the chemical bonding of the atoms in the solid. In fact, Bermudez [7] demonstrated that the stoichiometry of Pd$_x$Si can be determined from the lineshape of the Si-LMM AES peak.

The surface morphology was determined by ex-situ atomic force microscopy (AFM). As with the AES analyses, AFM was performed before and after each surface preparation step, before and after Pd deposition, and after annealing the Pd films.

3. Results and Discussion

AFM images of the standard surface reveal a random scratch pattern. These scratches may be as deep as 20 nm and as wide as 250 nm. These surfaces typically have overall rms roughness values of the order of 1.5 nm. Hydrogen etching of the standard surface produces a periodically stepped surface. Depending upon the angle at which they are cut, the stepped surfaces have terraces that are 50 – 100 nm wide and have step heights of ~ 1.5 nm. The overall rms roughness values for these surfaces are typically 1.0 nm and half that for the terraces.

After the deposition of 46 nm of Pd, AFM analyses revealed that the coatings were conformal, with little if any change in the rms roughness. Given the thickness of these films and the limited AES sampling depth [6] (e.g., ~ 3 nm), AES analyses revealed only features associated with elemental Pd.

When the 46nm Pd films were annealed at 670°C, distinctly different cluster formation modes were observed for the standard and stepped surfaces. The clusters formed on the standard surfaces were hillock-like, while the clusters formed on the stepped surfaces were columnar. The AES line shapes for the Si-LMM peaks (Figure 1) reveal that for both surfaces, Si has reacted with Pd to form a Pd-rich silicide with approximately the same stoichiometry (Pd$_3$Si) [7]. This level of reaction clearly indicates significant interdiffusion of Si and/or Pd. Moreover, both surfaces exhibit graphite-like C-KLL peaks [8].
The major differences in these spectra are in the relative intensities. The stepped surface has silicide peaks that are more than twice the intensity of those observed on the standard surface, while the corresponding carbon (graphite) peak for the stepped surface is less than one half of that for the standard surface.

These AES and AFM results reflect differences in the reaction product microstructure, that may be due to differences in the transport processes for the two surfaces. For the standard surfaces, Pd diffuses into the substrate to react with Si leaving a graphitic overlayer with hillock-like morphology. This overlayer produces a large C-KLL peak (since it is at the surface), and it attenuates the Si-LMM peak from the underlying silicide. For the stepped surfaces, Si diffuses out to react with the Pd and produces a silicide overlayer with a columnar morphology. This leaves a C-rich (graphite-like) underlayer. The silicide overlayer produces a large Si-LMM peak (since it is at the surface), and it attenuates the C-KLL peak from the underlying graphitic layer.

To investigate the basis for the observed behaviour of the 46 nm films, a series of annealing studies was performed for very thin films (0.3, 0.4, 0.5, 0.6 and 2.4 nm). For both types of initial surface, AFM revealed that the as-deposited films were conformal, and AES revealed no evidence of a reaction between Pd and Si.

After annealing, AES analyses showed that silicides always form on the standard surfaces, regardless of the initial film thickness. AFM analyses indicate that 0.3 nm and 0.4 nm thick films remain conformal. For thicker films, the formation of hillock-like clusters was observed, along with the reaction to form silicides and a strong graphite component. These observations are consistent with those for the annealed 46 nm films deposited on the standard surfaces.

AES analyses of annealed films deposited on the stepped surfaces reveal little, if any, reaction of Pd with Si, for films of thickness 0.3 and 0.4 nm. For
films of this thickness, stepped surfaces appear to be more thermally stable than the standard surfaces. As with the latter, there was no change in the surface morphology. For 0.5 nm and thicker films, annealing led to the formation of silicides in the form of triangular crystallites on the terraces. These crystallites appear to be the precursors to the columnar features observed on the annealed 46 nm films.

4. Conclusions

These data illustrate the dependence of the Pd-SiC interaction (reaction and transport) on the initial surface preparation. For the standard surfaces with thick (46 nm) annealed (670°C) Pd films, the Pd appears to diffuse into the substrate to form PdxSi, leaving a graphitic overlayer with a hillock-like morphology. For the stepped surfaces, Si diffuses out of the SiC substrate to form Pd_xSi columns on the surface, leaving a graphitic underlayer. Differences in the reactivity can be seen for films of several monolayers and less, while differences in the morphology (i.e., transport) can be seen for films with thicknesses of several monolayers and greater.

5. Acknowledgments

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6. References

1. Introduction

Recent awareness of the potential for the inadvertent or deliberate introduction of virus, bacteria, or pathogens has made stand-alone sensing an important issue in national security. While analytical instruments and laboratory procedures are available for collecting the required data, such approaches are expensive and time consuming. Progress in the synthesis and characterization of nanostructured materials and continuously emerging nanotechnologies promise dramatic changes in sensor design and capabilities. The versatility of the carbon-carbon bond, attaching with different functional groups to the end of the carbon nanotube (CNT), offers the potential for it to be used as a new material for sensors in (bio) chemical applications [1,2]. Nanowires modified with specific receptors can be assembled into integrated nano-biosensors for the parallel detection and diagnosis of trace amounts of dangerous viruses and bacteria [3]. Porous silicon (PS) offers a controllable surface topography at a nanometer resolution in three dimensions, and allows chemical surface modification [4]. The basic concept involves linking the antigen to the nanotube while retaining its conformation, which in turn induces an antibody response without triggering the immune system. Similarly, using sensitised and patterned porous material surfaces; detection is possible in both the liquid and gas phase, thus allowing the parallel detection of multiple agents, as the process is highly multiplexable. A unique and important aspect of PS relates to its use as a sensitive biosensor for monitoring bio-interactions related to antigen-antibody of specific pathogens and DNA hybridization. Hence, a nanotechnology based sensor platform will enable the direct electrical detection of biological and chemical agents in a highly multiplexed format over a broad dynamic range. The platform utilizes functionalized nano-PS, nanowires or nanotubes to detect molecular binding events with exquisite sensitivity and selectivity. The objectives of our investigations are as follows: to develop nanostructure based
sensors for the real-time monitoring of multiple biological variables, to develop novel protocols for the surface modification and patterning of these structures, and to functionalize the surface with suitable chemistry to monitor binding events related to antigens and antibodies of pathogens and toxins. The results presented here are from our initial investigation on nano-material based biomolecular detection devices.

2. Materials and Methods

The experimental methods and data for electrochemical biosensors using different indicators or a label-free system, and surface plasmon resonance (SPR) are reported here. Detailed results employing CNTs and nanoporous materials are presented elsewhere [5]. The first category of sensors presented here is electrochemical biosensors (genosensors). In these, a probe sequence is immobilized within the recognition layer, where a base-pairing interaction recruits a target molecule to the sensor. It is vital to develop sensing strategies to maintain critical dynamics of target capture, to generate a sufficient recognition signal. Standard electrochemical techniques, such as differential pulse voltammetry (DPV), potentiometric stripping analysis (PSA), square-wave voltammetry (SWV), etc. are used as genosensors. These devices can be used for monitoring sequence-specific hybridization events directly [6], based on the oxidation signal of guanine, DNA intercalators (metal coordination complexes, antibiotics etc.) [7], or using some metal tags viz. gold or silver nanoparticles or magnetic particles, for detecting the oxidation signal of gold or silver, or electro active DNA bases in the presence of DNA hybridisation [8].

The second type of biosensor is developed by using SPR to detect *E. coli* O157:H7 bacteria. Self assembled monolayers (SAM) layer of thiols were activated by passing an equal mixture of freshly prepared 0.4 M *N*-ethyl-*N*'- (dimethylamino dimethyl-aminopropyl) carbodiimide hydrochloride (EDC) and 0.1 *N*-hydroxy-succinimide (NHS), to produce receptors (NHS esters) capable of binding to the amino group of antibodies to form an amide bond. An antiserum against *E. coli* O157:H7 was suspended in sodium acetate (NaOAc) (pH 5.5) or Phosphate Buffered Saline/Tween (PBST) (pH 7.4), and transferred over the activated surface. Reversibly bound antibodies were cleaned from the surface by flowing ethanolamine (pH 8.5). The sample was returned to PBST (pH 7.4) to remove unbound antibodies from the surface, thus establishing a baseline for the sensorgram.

The PS biosensors were developed using bulk silicon crystal, by partial electrochemical dissolution in hydrofluoric acid solutions. Depending upon the etching conditions, PS has a very complex, anisotropic, and nanocrystalline architecture of high surface area. The PS surface is hydrophobic, and functionalization of the surface renders it as a biomaterial.
The PS biocompatibility can be improved by a suitable change of the surface parameters. It is determined by two main properties: the normal electrochemical potential and the surface energy with respect to the living body. Studies of the electrochemical potential of a number of materials used in medicine have shown that only carbon, gold, and platinum have values close to those of living tissue: +0.330, +0.332, and +0.334 mV respectively. The surface energy of these elements ranges from 20 to 30 erg/cm², which likewise corresponds to the values for living tissue. Generally, the carbon layer structure is formed by mixing sp² and sp³ bonding. A high fraction of sp³ bonds gives a highly hydrophobic surface, which is responsible for the cell attachment. For biological applications, we have developed technology to obtain different PS layers with 35-50% porosity on Si-p+ (100) and (111), followed by different treatments for surface structure modification/stabilization, by which the modified surface acquires biomaterial properties. Finally, the CNTs and nanowires for the proposed work were grown by thermal CVD using C₂H₆ in different ambient environments on Ni and Fe coated Si substrates. Vertically aligned CNTs were grown using MPECVD using hydrogen-methane-nitrogen gas reactants on a few nanometers thick metal catalyst layer on silicon substrates, and were characterized by Raman spectroscopy, scanning and transmission electron microscopy. CNTs are particularly biocompatible and have an excellent ability to conduct current. These characteristics, in conjunction with their ability to respond reliably and reversibly to bio-chemical agents have become indispensable for bio-probing and detection applications on the nanoscale. Furthermore, a possible interfacing of CNTs with electro active proteins, by establishing molecular links, is likely to become a convenient vehicle for studying cell organization and functioning. Recently obtained readings from oocYTE cells using single CNT, albeit preliminary, strongly suggest a bio-probing feasibility through such a nano-approach.

3. Results and Interpretation

For electrochemical sensors, the hybridization detection of samples was transduced by means of different electrochemical techniques performed using a potentiostat such as the Autolab PGSTAT 30 electrochemical analysis system. The oxidation or reduction signal of the electro active DNA bases or metal indicators was measured and used as an analytical signal. The procedure of hybridization detection of the PCR amplified real samples consisted of the following steps: The first was the immobilization of the capture probe in a phosphate buffer solution (PBS) (pH 7.40). The probe was subsequently immobilized onto the pretreated electrode in an acetate buffer solution (ABS) (pH 4.8). After immobilization, the probe-modified electrode was washed with blank ABS. This step was followed by a hybridization event onto the surface of the probe-modified electrode. The hybridization was allowed to proceed for 5-15 minutes. Non-specific adsorption effects were eliminated, followed by various
washing steps such as using a 1% sodium dodecylsulphate (SDS) solution dissolved in buffer solution for 3 seconds. A small amount (10-20 µL) of the denatured PCR sample was pipetted directly onto the surface of the probe-modified electrode. After the washing step, the hybridisation signal was checked by voltammetric transduction. The oxidation or reduction signal of the electroactive DNA bases or metal indicators was measured in a buffer as ABS by the voltammetric technique. The detection limit for the different PCR amplicons was generally found to be between 1-100 femtomoles of DNA.

In order to investigate the capability of a SAM based SPR biosensor for pathogen detection, various experiments were conducted. Immobilization using *Escherichia coli* O157:H7 polyclonal antibodies suspended in NaOAc (pH 5.5) produced a pixel change of 12, while *Escherichia coli* O157:H7 (pH 7.4) polyclonal antibodies suspended in PBST produced a pixel change of 7. Increasing the concentration of antigen in direct assay resulted in an increased response. Upon passing the antigen sample at a concentration of 4 x 10⁸ CFU/ml for 10 min, a change in the pixel value of 0.1 was noted, while a concentration of 7 x 10⁹ CFU/ml produced an average change in the pixel value of 0.1667. One pixel change is equivalent to a 0.006º change in angle. For the same concentrations of antigens and different concentrations of secondary antibodies in the sandwich assay, the response obtained was almost 30 times higher than for the direct assay. Preliminary studies clearly showed that the SAM based LEICA SR 7000 SPR biosensor can be used to monitor biomolecular interactions, and to rapidly detect pathogens. With improvements in the detection protocol and sensor chips, the sensitivity and specificity can be enhanced considerably.

4. References

1. Introduction

There are many studies of glass-ceramics for application as biomaterials [1]. Glass-ceramics forming apatite as a crystallisation product are promising for restoring and replacing hard tissues in orthopaedics and dentistry, because of the good biocompatibility conferred by the apatite crystal. Recently, apatite-mullite glass-ceramics have been developed based on SiO$_2$-Al$_2$O$_3$-P$_2$O$_5$-CaO-CaF$_2$ [2-4]. The glasses crystallise to form fluorapatite (FAP) and mullite on appropriate heat treatment. Both the apatite and mullite crystals are needle-like, and interlock to give a high fracture toughness. Magic angle spinning nuclear magnetic resonance spectroscopy (MAS-NMR) has been used to investigate the structures of various P-containing silicate or aluminosilicate glasses [4, 5-9]. There are also MAS-NMR studies of the crystallisation process [4, 10-11]. In this study, $^{27}$Al, $^{29}$Si, $^{31}$P and $^{19}$F MAS-NMR analyses are used to characterise the crystallisation of glass-ceramics.

2. Materials and Methods

<table>
<thead>
<tr>
<th>Glass Code</th>
<th>$z$</th>
<th>$T_g$(°C)</th>
<th>$T_{p1}$(°C)</th>
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<tr>
<td>LG99</td>
<td>3</td>
<td>606</td>
<td>742</td>
<td>888</td>
</tr>
</tbody>
</table>

The glass compositions were based on 4.5SiO$_2$3Al$_2$O$_3$1.5P$_2$O$_5$(5-z)CaO$_z$CaF$_2$ (Table I). Fluorine was progressively substituted for oxygen, and the Ca:P ratio was fixed at 1.67, corresponding to FAP. The glasses were prepared at melting...
temperatures in the range 1380-1475°C, depending on the composition. X-ray powder diffraction analysis was performed on the heat-treated glass samples, for qualitative purposes. The samples were heat-treated in a DSC at 10°C min⁻¹ to the crystallization temperatures (Tp1 and Tp2) and to (Tp1+Tp2)/2. MAS-NMR analysis was conducted, using suitable FT-NMR spectrometers, for ²⁹Si and ³¹P nuclei at resonance frequencies of 79.50 and 161.98 MHz, respectively, and for ²⁷Al and ¹⁹F measurements at 156.3 and 188.20 MHz, respectively.

3. Results and Discussion

After heat treatment to Tp1, the crystallization product was only FAP in the glasses containing fluorine and β-Ca₅(PO₄)₂ (whitlockite) in the z = 0 glass. In contrast, after heating to Tp2, anorthite and β-Ca₅(PO₄)₂ were formed in the glass containing no fluorine. FAP was exclusively formed in the glass with z = 1, whereas in the glasses containing more fluorine (z = 2 and 3), FAP crystallized at Tp1 and mullite crystallized at Tp2.

The ²⁷Al MAS-NMR spectrum of the z = 0 glass showed a broad peak around 49 ppm assigned to a tetrahedrally coordinated Al (IV). A large broad peak at around 55 ppm after heating to Tp2 was assigned to anorthite. The strong sharp peak around -10 ppm suggested the presence of octahedrally coordinated Al (VI). The ²⁷Al spectrum of the z = 1 glass showed similar peaks. These did not change after crystallization of FAP on heating to Tp1 and (Tp1+Tp2)/2, so the chemical environment of Al in the glass seemed unaffected by the crystallization. The spectrum of the glass heated to Tp2 however, showed a small shoulder peak at 39 ppm assigned to crystalline AlPO₄ and a sharp large peak at 11.4 ppm corresponding to Al (V). The crystallites in the AlPO₄ were too small (< 50 nm) to be detected by X-ray diffraction. Aluminium in higher coordination states may be promoted in these glasses on crystallization of FAP. The ²⁷Al spectrum of the z = 2 and 3 original glasses showed similar peaks. The two peaks at 20 and -10 ppm were assigned to Al(V) and Al(VI) existing as aluminum-fluoride [AlFx] or fluoride/oxygen [AlFxOy] complex species in the original glass. Thus, fluorine additions to the glass resulted in the formation of Al (V) or Al (VI) species. It is tempting to associate the reduced intensity of the signal corresponding to Al(V) or Al(VI) to a reduction in the amounts of fluorine complexed by Al. However, it appears to be the fluorine complexed to Ca that is used for the formation of FAP, rather than that complexed to Al. The spectrum of the glasses heated to Tp2 was quite different from those heated to lower temperatures. A shoulder peak around 20 ppm corresponding to Al(V) disappeared as mullite crystallization occurred.

In the ²⁹Si MAS-NMR spectrum of the fluorine free glass, the peak around -86 ppm after crystallization was assigned to anorthite. No further changes in the chemical shift were observed. Similarly, the ²⁹Si MAS NMR spectra of z = 1 glass showed a large broad peak around -87 ppm, which was unchanged on heating to Tp2. X-ray diffraction of the heat treated glass at Tp2 confirmed the formation of
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anorthite. The broad peak in the $^{29}$Si MAS-NMR spectra of the $z = 2$ glass heated to Tp1 and (Tp1+Tp2)/2 shifted slightly in a negative direction compared to that of the original glass. The spectral pattern of the glass heated to Tp2 was similar to that of mullite, though the peaks were poorly separated.

The $^{31}$P MAS-NMR spectrum of the $z = 0$ glass heated to Tp1 showed peaks at 0 and -2 ppm assigned to $\beta$-Ca$_3$(PO$_4$)$_2$ (whitlockite) and at -20 ppm, probably due to an orthophosphate ion coordinated by one or more Al ions. The spectrum of the $z = 1$ glass heat-treated to Tp1 showed a strong sharp peak at 3 ppm, assigned to PO$_4$$^{3-}$ in FAP, and a peak at -29 ppm assigned to PO$_4$ in crystalline AlPO$_4$. A weak broad peak around -8 ppm indicated that the P atoms in the remaining glass phase had an environment different from that of FAP. The peak shifted in a negative direction for heating above Tp2, suggesting an increased number of Al atoms coordinating around a PO$_4$$^{3-}$ tetrahedron. Similar peaks were observed for the $z = 2$ and 3 glasses heated to Tp1.

The $^{19}$F spectra of the $z = 1$ glass heated to Tp1, (Tp1+Tp2)/2 and Tp2 showed a sharp peak at ~ -103 ppm corresponding to crystalline FAP. The initial glass showed $^{19}$F peaks at -90 and -150 ppm, assigned to F-Ca(n) and Al-F-Ca(n). The peak corresponding to F-Ca(n) in the initial glass decreased in magnitude and disappeared on formation of FAP. It appeared that the F present as F-Ca(n) species was again preferentially used in forming FAP. This might indicate that F-Ca(n) type species preferentially charge balance the non-bridging oxygens attached to the P. The $^{19}$F MAS NMR spectra of the initial glasses $z = 2$ and 3 (Figure I) showed also the presence of F-Ca(n) and Al-F-Ca(n) species.

Both glasses had a small peak at -103 ppm corresponding to FAP. The amount of F in a FAP environment was very small (<1%), since the peak at -103 ppm was a very small fraction of the total $^{19}$F MAS-NMR signal. No FAP was detected by XRD, due to the amount and probably the size of the FAP crystals being too small. On heating to Tp1, as well as the sharp peak at -103 ppm there was a broad one with a maximum at -150 ppm corresponding to F in the residual glass phase as Al-F-Ca(n) species. This peak was much stronger than in the $z = 1$ glass heated to Tp1, indicating a much higher F content in the residual glass phase.

Figure 1. $^{19}$F spectra for the $z = 3.0$ glass heat-treated to Tp1, Tp1+Tp2/2 and Tp2.
On heating to \((T_p1 + T_p2)/2\), the proportion of F in the residual glass phase decreased slightly, indicating that more F was being lost from the glass phase in forming more FAP. A shoulder appeared at \(\sim -130 \) ppm on heating to \(T_p2\), for both the \(z = 2\) and the \(z = 3\) glass. This may reflect F changing its structural role in the residual glass network following the crystallization of mullite. This crystallization and a reduction of the Al concentration in the residual glass phase may force fluorine to form Si-F bonds. Quantification of the \(^{19}\text{F} \) NMR data by integrating peak areas showed in all cases that the amount of FAP formed was significantly less than the theoretical maximum. Thus, additional Ca and P must remain in the glass composition, or form alternative crystalline phases such as \(\text{AlPO}_4\).

4. Conclusions

Substitution of fluorine for oxygen strongly influences the crystallization of \(4.5\text{SiO}_2-3\text{Al}_2\text{O}_3-1.5\text{P}_2\text{O}_5-(5-z)\text{CaO}-z\text{CaF}_2\) glasses. A glass with \(z = 0\) crystallized to whitlockite and anorthite. Introduction of F caused the formation of FAP instead of whitlockite, and inhibited anorthite formation. For \(z = 1\), only FAP was formed. For \(z > 2\), mullite also crystallized. The inhibition of anorthite favors mullite formation, probably due to the high Al:Si ratio of the glasses and, following FAP crystallization, the lack of charge balancing cations for maintaining the Al(IV) state. Al is mainly Al(IV) for \(z = 0\), while F causes the formation of Al(V) and Al(VI). These seem to disappear on heat treatment at \(T_p1\) and \((T_p1 + T_p2)/2\), but new Al(V) and Al(VI) species often appear on heating to \(T_p2\). The F is present initially as F-Ca(n) and Al-F-Ca(n) species. The former appear to be used preferentially in forming FAP. The P in the glass is present initially as Al-O-PO\(_4^3-\) type species, but forms FAP and a small amount of AlPO\(_4\). A small amount of P remains in the residual glass as PO\(_4\) tetrahedra, coordinated primarily by Al.

5. References

GROWTH AND CHARACTERIZATION OF NANOCRYSTALLINE DIAMOND AND CARBON NANOTUBES BY MICROWAVE PLASMA CHEMICAL VAPOR DEPOSITION

T. SHRADA and A. VASEASHTA*
Seki Technotron Corporation, Tokyo, Japan
* Marshall University, Huntington, WV-25755-2570, USA

1. Introduction

The microwave plasma technique has been at the forefront of chemical vapour deposition (CVD) techniques for the growth of diamond and carbon nanotubes (CNTs) for various applications. It is a preferred one because it offers optimal quality and purity of the material, availability of high power over large areas, high growth rates and greater flexibility in selecting reactants. The microwave plasma enhanced CVD (MPECVD) technique has produced the highest quality CVD-diamond for electronic, optical and thermal applications [1]. Recent literature points to the usefulness of the same technique in the rapidly growing fields of nanoscience and nanotechnology, such as excellent growth of nano-crystalline diamond (NCD) films having a grain size from two to a few hundred nm (with varying phase purity from phase-pure NCD to NCD embedded in ta-C or a-C films) [2,3] and highly aligned CNTs [4]. The objective of this investigation is to study the structural and field emission properties using several characterization methods of NCD and aligned CNTs grown by MPECVD using varying hydrogen-methane-nitrogen gas reactants.

2. Materials and Methods

The common system used to grow aligned CNT and uniform NCD films is a 2.45 GHz MPECVD, model #AX5200 system (Seki Technotron Corp.), as shown in figure 1. A 4" diameter sophisticated RF auto-matching substrate heater is used to uniformly heat substrates to 900°C without the use of plasma. Substrates are kept on a Mo holder that rests on a graphite susceptor, which is fixed on top of a Z-motion motorized position control stage. Substrates can be biased up to a high DC voltage, as needed. The reactor is a water-cooled double walled steel chamber with walls remaining at room temperature during the high
power deposition processes. With all these capabilities, various materials can be grown, such as highly aligned CNT over 4" area by microwave plasma in combination with the heater, thermal CNT by thermal CVD, nano- and micro-crystalline diamond, etc.

Three series of CNT were grown by varying the temperature, the gas (methane and nitrogen in partial pressure of hydrogen) composition, and the microwave power. Only one parameter was varied during a growth run. In the first series, the temperature was varied from 700 to 900°C while the power and CH₄/H₂/N₂ ratio (1:1:0) were kept constant. In the second series, the CH₄/H₂/N₂ ratio was varied while the power and temperature (850°C) were kept constant. The CH₄/H₂/N₂ ratio of (1:1:0) was changed to (1:2:0) and to (3:4:1). For the third series, the microwave power was varied in the range 200 to 400 W, while keeping the temperature (850°C) and the CH₄/H₂/N₂ ratio (3:4:1) constant.

The same MPECVD system was used to grow uniform NCD thin films on mirror polished Si substrates using the BEG process described elsewhere [2]. In this process, a negative bias (-200 V) was applied to the substrate and the bias current density to the substrate was controlled while using 5% CH₄/H₂, 600°C substrate temperature and 30 Torr. chamber pressure at 1 kW microwave power.

3. Results and Interpretation

3.1 SEM INVESTIGATION

SEM pictures of samples grown under typical conditions on 2 and 5 nm Co-coated Si substrates are shown in figure 2 at two different magnifications. The micrographs suggest that the nanotubes on 2 nm thick Co (Figure 2a and 2b) for the samples are thinner (15-25 nm diameter) compared to the one grown on 5 nm Co (25-40 nm diameter), with both aligned perpendicular to the substrates. Although these results are preliminary, work is in progress to study the effect of electric field during growth on vertical CNT alignment.

Figure 3 shows a FESEM micrograph of a 4 µm NCD film, grown using the BEG process. As is evident, the diamond grain size is in the range 5-20 nm. The advantage of the BEG process over other methods is its ability to maintain the nano-crystallinity irrespective of the thickness of the film.
3.2 FIELD EMISSION INVESTIGATION

We investigated electron emission from carbon nanotubes in a vacuum. The onset of emission occurred at an electric field of 2.15 V/μm, which is similar to the values reported in literature. An emission current of 0.35 mA was observed at an electric field of 4.0 V/μm, and the experimental data fit well into a Fowler-Nordheim (F-N) plot. The values of the turn-on field, $E_{\text{to}}$, and the threshold field, $E_{\text{thrs}}$, i.e., the electric fields to produce current densities of 10 μA/cm² and 10 mA/cm², respectively, were compared with the values reported in the literature [5]. The field amplification factor $\beta$ was estimated to be around 850 from the I-V and F-N plots. A detailed investigation relating growth parameters, and CNT spacing with field emission is in progress.
3.3 RAMAN INVESTIGATION

Structural characteristics such as the crystallinity and alignment of CNTs were measured using a STR250 (Seki Technotron Corp.) micro-Raman spectrometer at 2.54 eV (488 nm), with a X50 objective producing a spot size of 2 μm. Spectra of three samples (one from each set having the highest G/D ratio in that set) are shown in Figure 4. The structure of a CNT is specified by its diameter and chiral indices. Due to the unique relation between the electronic structure and chirality, Raman spectra allow the observation of spectral features that are dispersive and non-dispersive. Observation of first and second order D and G bands and their ratios study these features. The Raman data indicate that the samples grown under the selected conditions have highly crystalline multiwall CNTs. No effect of N₂ addition was seen in the Raman studies, but its addition reduced the growth rate. However, the emission properties of the samples will suggest if the addition of N₂ is necessary. A detailed investigation is in progress.

![Figure 4. Raman spectra of three samples (one from each set with the highest D/G ratio in that set)](image)

4. References

ASI GROUP PHOTOGRAPH
Participants and Administrative Staff

LIST OF PARTICIPANTS

ANGELESCU, Anca Smaranda
National Institute For Research and Development in Microtechnologies
Center of Nanotechnology
32B Erou Iancu Nicolae St
72296, Bucharest
ROMANIA
ancaa@imt.ro

Dr. ANGELOV, Christo
Institute for Nuclear Research and Nuclear Energy
Bulgarian Academy of Sciences
72 Tzarigradsko Chaussee
1784 Sofia
BULGARIA
hangelov@inrne.bas.bg

Dr. BERGER, Andreas
Max Planck Institute of Microstructure Physics
Weinberg 2
D-06120 Halle
GERMANY
berger@mpi-halle.mpg.de

Dr. BOVIN, Nicolai
Shemyakin & Ovchinnikov Institute of Bioorganic Chemistry
Russian Academy of Sciences
16/10 Miklukho-Maklaya St
117997 Moscow
RUSSIA
bovin@carbohydrate.ru

Akad. BUDEVSKI, Evgeni
Institute of Electrochemistry and Energy Systems
Bulgarian Academy of Sciences
Acad. G. Bonchev St., Bl. 10
1113 Sofia
BULGARIA
budevski@mail.orbitel.bg

DEMYDOV, Dmytro
Kansas State University
Chemistry Department
111 Willard Hall, KSU
Manhattan, KS 66506
USA
demydov@ksu.edu

DIKOV, Christosko
Central Laboratory of Solar Energy and New energy Sources
Bulgarian Academy of Sciences
72 Tzarigradsko Chaussee
1784 Sofia
BULGARIA

DIMITROV, Krassimir
Institute of Solid State Physics
Bulgarian Academy of Sciences
72 Tzarigradsko Chaussee
1784 Sofia
BULGARIA
krasimir@issp.bas.bg

Prof. DIMOVA-MALINOVSKA, Doriana
Central Laboratory of Solar Energy and New Energy Sources
Bulgarian Academy of Sciences
72 Tzarigradsko Chaussee
1784 Sofia
BULGARIA
doriana@phys.bas.bg

DOW, Peter
New College of Florida
5700 N. Tamiami Trail
Sarasota, Fl 34243
USA
pndow@ncf.edu
Dr. DÓZSA, László Jenő
Research Institute for Technical Physics and Materials Sciences
Hungarian Academy of Sciences
29-33 Konkoly Thzege St
1121 Budapest
HUNGARY
dozsa@mfa.kfki.hu

Dr. DUTTA, Joydeep
Microelectronics, School Of Advanced Technology
Asian Institute of Technology
P.O.Box 4, Klong luang
12120 Pathumthani
THAILAND
joy@ait.ac.th

Dr. EICKHOFF, Martin
Walter Schottky Institute
Technical University Munich
Am Coulombwall
D-85748 Garching, Munich
GERMANY
martin.eickhoff@wsi.tu-muenchen.de

Dr. ERAY, Aynur
Hacettepe University
Faculty of Engineering
Dept. of Physics Engineering
06800- Beytepe, Ankara
TURKEY
feray@hacettepe.edu.tr

Dr. ERDEM, Arzum
Analytical Chemistry Department
Faculty of Pharmacy
Ege University
35100 Bornova
Izmir
TURKEY
erdema@pharm.ege.edu.tr

Dr. FLAHAUT, Emmanuel
Centre Interuniversitaire de Recherche et d'Ingénierie des Matériaux
UMR CNRS 5085
Université Paul Sabatier
31062 Toulouse
FRANCE
flahaut@chimie.ups-tlse.fr

Dr. FLEWITT, Andrew
Engineering Department
Cambridge University
Trumpington Street
Cambridge CB2 1PZ
UK
ajf@eng.cam.ac.uk

Prof. FUHS, Walther
Hahn-Meitner-Institut
Abt. Silizium Photovoltaik
Kekulestr. 5
D-12489 Berlin
GERMANY
fuhs@hmi.de

Dr. GACOIN, Thierry
Laboratoire de physique de la matiere Condensee
Ecole Polytechnique
91128 Palaiseau
FRANCE
thierry.gacoin@polytechnique.fr

Dr. GAO, Nora
Department of Physics and Physical Sciences
Marshall University
One John Marshall Drive
Huntington, WV 25575-2571
USA
gao2@marshall.edu
LIST OF PARTICIPANTS

Dr. GESHEVA, Kostadinka
Central Laboratory of Solar Energy and New Energy Sources
Bulgarian Academy of Sciences
72 Tzarigradsko Chaussee
1784 Sofia
BULGARIA
kagesh@phys.bas.bg

Prof. GOGOTSI, Yury
Professor of Materials Engineering
Drexel University
Department of Materials Engineering
LeBow Bldg., Room 431
3141 Chestnut St.
Philadelphia, PA 19104
USA
gogotsi@drexel.edu

GÖKTAŞ, Oktay
Izmir Institute of technology
Department of Physics
Gulbahce, Urla Izmir
TURKEY
oktaygokas@iyte.edu.tr

Dr. HOFMEISTER, Herbert
Max Planck Institute of Microstructure Physics
Weinberg 2
D-06120 Halle
GERMANY
hof@mpi-halle.mpg.de

Dr. HORVÁTH, Zsolt József
Research Institute for Technical Physics and Materials Science
Hungarian Academy of Sciences
Budapest 114, P.O.Box 49
H-1525 HUNGARY
horvzsj@mfa.kfki.hu

Prof. HURLEY, Richard
Northern Ireland Semiconductor Research Centre, School of Electrical & Electronic Engineering
The Queen’s University of Belfast
Belfast, BT9 5AH
Northern Ireland, UK
r.hurley@ee.qub.ac.uk

IVANOV, Plamen
Central Laboratory of Solar Energy and New Energy Sources
Bulgarian Academy of Sciences
72 Tzarigradsko Chaussee
1784 Sofia
BULGARIA
Phone: +359 2 7144 770
plivanov@phys.bas.bg

IVANOVA, Katya
Central Laboratory of Solar Energy and New Energy Sources
72 Tzarigradsko Chaussee
1784 Sofia
BULGARIA
kivanova@phys.bas.bg

Dr. IVANOVA, Tatyana
Central Laboratory of Solar Energy and New Energy Sources
72 Tzarigradsko Chaussee
1784 Sofia
BULGARIA
tativan@phys.bas.bg

JARIMAVIČIŪTĖ-ŽVALIONIENĖ, Renata
Physics Department
Kaunas University of Technology
50 Studentu St
Kaunas 51368
LITHUANIA
renata@kauko.lt
JÓZWIK, Iwona
Institute of Physics
Lublin University of Technology
Nadbystrzycka 38
20-618 Lublin
POLAND
i.jozwik@pollub.pl

KAMENOVA, Mariyka
Central Laboratory of Solar Energy and New energy Sources
Bulgarian Academy of Sciences
72 Tzarigradsko Chaussee
1784 Sofia
BULGARIA
photomat@phys.bas.bg

KAVALAKOVA, Slavyanka
Central Laboratory of Solar Energy and New energy Sources
Bulgarian Academy of Sciences
72 Tzarigradsko Chaussee
1784 Sofia
BULGARIA
s.kavlakova@mbox.bol.bg

Prof. KLABUNDE, Kenneth
Dept. of Chemistry
Kansas State University
Manhattan, Kansas 66506
USA
kenjk@ksu.edu

Dr. KOČHEV, Konstantin
Central Laboratory of Solar Energy and New Energy Sources
Bulgarian Academy of Sciences
72 Tzarigradsko Chaussee
1784 Sofia
BULGARIA
kochev@phys.bas.bg

Dr. KOŁODZIEJ, Andrzej
AGH University of Science and Technology
30 Mickiewicz Avenue
30-059 Krakow
POLAND
kolodzie@agh.edu.pl

KONSTANTINOVA, Mariana
Central Laboratory of Solar Energy & New Energy Sources
Bulgarian Academy of Sciences
72 Tzarigradsko Chaussee
1784 Sofia,
BULGARIA
koprin@pronto.phys.bas.bg

Prof. KOPAĆ, Türkan
Zonguldak Karaelmas University
Department of Chemistry
67100 Zonguldak
TURKEY
turkan_kopac@hotmail.com

Dr. KOPRINAROV, Nikola
Central Laboratory of Solar Energy & New Energy Sources
Bulgarian Academy of Sciences
72 Tzarigradsko Chaussee
1784 Sofia
BULGARIA
koprin@pronto.phys.bas.bg

Dr. KUDOYAROVA, Vera
A. F. Ioffe Physico-Technical Institute of the Russian Academy of Sciences
Politechniheskaya 26
194021 St.-Petersburg
RUSSIA
kudoyarova@mail.ioffe.ru
Dr. KUKHTA, Alexander  
Institute of Molecular and Atomic Physics  
National Academy of Sciences of Belarus  
70F.Skaryna Ave.  
220072 Minsk,  
BELARUS  
kukhta@imaph.bas-net.by

Dr. MADJAROVA, Galia  
Faculty of Chemistry  
University of Sofia  
1 J. Bourchier Blvd.  
1126-Sofia  
BULGARIA  
gmadjarova@chem.uni-sofia.bg

Prof. MARSHALL, Joe  
Professor Emeritus, Univ. Wales Swansea  
Address for correspondence:  
64 Ridgeway, Killay,  
Swansea SA2 7AP  
UK  
joe.marshall@killay9.freeserve.co.uk

Dr. MATHUR, Sanjay  
Institute of New Materials  
Saarland University Campus  
D-66041 Saarbrücken  
GERMANY  
smathur@inm-gmbh.de

Dr. MAUD, John Michael  
Department of Chemistry  
University of Wales Swansea  
Singleton Park  
Swansea SA2 8PP  
UK  
j.m.maud@swansea.ac.uk

Dr. MIKLI, Valdek  
Centre for Materials Research  
Tallinn Technical University  
Ehitajate tee 5  
19086 Tallinn  
ESTONIA  
miku@staff.ttu.ee

MOROZAN, Adina  
University of Bucharest  
Faculty of Physics, Polymer. Dept.  
Research Centre, "3Nano - SAE",  
Bucharest- Magurele, MG-11  
ROMANIA  
adina@polymer.fizica.unibuc.ro

MURPHY, Hayley  
School of Electrical and Mechanical Engineering  
Northern Ireland Bioengineering Research Centre  
University of Ulster at Jordonstown  
Newtownabbey Co. Antrim, BT37 OQB  
Northern Ireland, UK  
hayley@nibec-s1.nibec.ac.uk

Prof. NASSIOPOULOU, Androula  
Director of IMEL  
Vice President of NCSR Demokritos  
P.O. Box 60 228  
153 10 Aghia Paraskevi  
Athens  
GREECE  
A.Nassiopoulou@imel.demokritos.gr

NÉMETH, Ágoston  
Research Institute for Technical Physics and Materials Sciences  
P.O. Box 49, H-1525 Budapest  
HUNGARY  
nemeth@mfa.kfki.hu

Dr. NESHEVA-SLAVOVA, Diana  
Institute of Solid State Physics  
Bulgarian Academy of Sciences  
72 Tzarigradsko Chaussee  
1784 Sofia  
BULGARIA  
nesheva@issp.bas.bg

NGUYEN, Thuat Tran  
Laboratoire de Physique des Interfaces et des couches Mince (LPICM)  
Ecole Polytechnique  
91128 Palaiseau Cedex  
FRANCE  
tran-thuat.nguyen@polytechnique.org
Dr. NIKOLAЕVA-DIMITROVA, Miglena
Central Laboratory of Solar Energy and New Energy Sources
Bulgarian academy of Sciences
72 Tzarigradsko Chaussee
Sofia 1784
BULGARIA
miglena@phys.bas.bg

Dr. ONOE, Jun
Research Laboratory for Nuclear Reactors
Tokyo Institute of Technology
2-12-1 O-okayama, Meguro
152-8550 Tokyo
JAPAN
jonoe@nr.titech.ac.jp

Dr. PACKA, Juraj
Slovak University of Technology
Faculty of Electrical Engineering and Information Technology
llkovičova 3
Sk-812 19 Bratislava
SLOVAK REPUBLIC
packa@elf.stuba.sk

Dr. PAUNOV, Vesselin
The University of Hull Surfactant & Colloid Group
Department of Chemistry
University of Hull
Hull, HU6 7RX
UK
N.Paunov@hull.ac.uk

Dr. PERNIU, Dana
Transilvania University of Brasov
Chemistry Department
50 Iuliu Maniu St.
500091 Brasov
ROMANIA
d.perniu@unitbv.ro

Prof. PIETRUSZKO, Stanislaw
Warsaw University of Technology
Department of Electronics and Information Technology
Institute of Microelectronics and Optoelectronics
IMIO PW, Koszykowa 75,
00-662 Warszawa
POLAND
pietruszko@imio.pw.edu.pl

Dr. PIVIN, Jean-Claude
Centre de Spectrometrie Nucleaire et de Spectrometrie de Masse
IN2P3, Bat. 108, 91405
Orsay Campus
FRANCE
pivin@csnsm.in2p3.fr

Dr. PRAMATAROVA, Lilyana
Institute of Solid State Physics
Bulgarian Academy of Sciences
72 Tzarigradsko Chaussee
Sofia 1784
BULGARIA
lpramat@issp.bas.bg

Dr. PRESKER, Radina
TU-Muenchen
Walter Schottky Institute
Am Coulombwall 3
D-85748 Garching, Munich
GERMANY
radina.presker@wsi.tum.de

RACHKOVA, Avgustina
Institute of Solid State Physics
Bulgarian Academy of Sciences
72 Tzarigradsko Chaussee
1784 Sofia
BULGARIA
Gusty@issp.bas.bg
Prof. RANGELOW, Ivo
Institut für Mikrostrukturtechnologie und Analytik (IMA)
Universität Kassel
Heinrich-Plett Straße 40
34132 Kassel
GERMANY
rangelow@uni-kassel.de

Prof. REISFELD, Renata
Enrique Berman Professor of Solar Energy
Department of Inorganic Chemistry
The Hebrew University
91904 Jerusalem
ISRAEL
renata@vms.huji.ac.il

Dr. ŠALY, Vladimír
Slovak University of Technology
Faculty of Electrical Engineering and Information Technology
Ilkovičova 3
SK-812 19 Bratislava
SLOVAK REPUBLIC
vsaly@elf.stuba.sk

Dr. SARAI DAROV, Tsiala
The Hebrew University of Jerusalem
Department of Inorganic and Analytical Chemistry
Givat-Ram
91904 Jerusalem
ISRAEL
tsiala@cc.huji.ac.il

Dr. SCAGLIONE, Salvatore
ENEA – National Agency for Energy
New Technology and The Environment
CR Casaccia, Via Anguillarese 301
00060 Rome
ITALY
salvatore.scaglione@casaccia.enea.it

Dr. SCHIFFBAUER, Jarrod
Department of Physics
West Virginia University
Morgantown, WV 26506-6315
USA
jschiff1@mix.wvu.edu

Prof. SCHOONMAN, Joop
Laboratory for Inorganic Chemistry
Delft Institute for Sustainable Energy
Delft University of Technology
Julianalaan 136
2628 BL Delft
THE NETHERLANDS
j.schoonman@tnw.tudelft.nl

Dr. SENDOVA, Mariana
New College of Florida
5700 N. Tamiami Trail
Sarasota, Fl 34243
USA
sendova@ncf.edu

Dr. SENDOVA-VASSILEVA, Marushka
Central Laboratory of Solar Energy and New Energy Sources
Bulgarian Academy of Sciences
72 Tzarigradsko Chaussee
1784 Sofia
BULGARIA
marushka@phys.bas.bg

Dr. SHARDA, Tarun
Research and Development
Seki Technotron Corporation
5-6-30, Kiba, Koto-ku
1350042 Tokyo
JAPAN
tsharda@stc.sekitech.co.jp

Dr. SILVA, Carlos J. R.
University of Minho
Department of Chemistry
Campus de Gualtar
4710-057 Braga
PORTUGAL
csilva@quimica.uminho.pt

Dr. STAMBOULIS, Artemis
University of Ulster
School of Electrical and Mechanical Engineering, Jordanstown Campus
Newtownabbey Co Antrim, BT37 0QB
Northern Ireland, UK
a.stamboulis@ulster.ac.uk
STANIMIROV, Stanislav  
Sofia University, Faculty of Chemistry  
Organic Photochemistry Group  
1 J. Bouchier Blvd.  
1126 Sofia  
BULGARIA  
sstanimirov@chem.uni-sofia.bg

STAVROV, Vladimir  
Institute of Solid State Physics  
Bulgarian Academy Sciences  
72 Tzarigradsko Chaussee  
1784 Sofia  
BULGARIA  
conel@ttm.bg

Dr. THANACHAYANONT, Chanchana  
The National Metal and Materials Technology Center  
114 Thailand Science Park  
Paholyothin Rd, Klong 1  
Klong Luang  
12120 Pathumthani  
THAILAND  
chanchm@mtec.or.th

Prof. VASEASHTA, Ashok  
Dept. of Physics and Physical Sciences  
Materials Processing and Characterization Laboratory  
One John Marshall Drive  
Huntington, WV 25755  
USA  
vaseashta@marshall.edu

Dr. VOMVAS, Athanassios  
University of Patras  
Dept. of Physics  
26100 Patras  
GREECE  
avomvas@physics.upatras.gr

WOODWORTH, Andrew  
Department of Physics  
West Virginia University  
403 Engineering Sciences Bldg  
P.O. Box 26506  
Morgantown, WV 26506-6102  
USA  
awoodwor@mix.wvu.edu

Dr. YEROKHOV, Valery  
National university “Lviv Polytechnic”  
P.O. Box 1050  
79045 Lviv-45  
UKRAINE  
yerokhov@polynet.lviv.ua

YORDANOV, Georgi  
Group of Nanoparticle Science and Technology  
Department of General and Inorganic Chemistry  
Faculty of Chemistry, University of Sofia  
1 James Bourchier Blvd.  
1126 Sofia  
BULGARIA  
chem_gbg@yahoo.com

Dr. ZHIVKOV, Ivaylo  
Central Laboratory of Photoprocesses  
Bulgarian Academy of Sciences  
G. Bonchev St, bl. 109  
1113 Sofia  
BULGARIA  
izhiv@clf.bas.bg
Poem for the ASI - Professor Herbert Hofmeister

Sozopol NATO-ASI,
Just in 2004,
Has got to get its finish,
At fairly high-rank score.

We did have lots of lectures,
And also seminars,
And topical discussions,
That’s what the meeting was.

There was, still in addition,
A very special fun,
The poster exhibition,
Quite well prepared and done.

And those who missed to get in,
Could do it with some beer,
Each complicated issue,
Was solved then without fear.

Bulgarian gipsy summer,
Did draw us to the beach,
With water, sand and sunburn,
Available for each.

We did have lots of coffee,
And sweetened cakes as well,
And fried Bulgarian yogurt,
Just as a counter – spell.

The Windmill-farewell-party,
With music, meals and dance,
Was quite a great experience,
We did enjoy at once.

Now, if it’s time for leaving,
We should not hesitate,
To thank Bulgarian people,
For hospitality.
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