ELECTRON AND ION BEAMS IN NANOMATERIALS DEVELOPMENT

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Nanotechnology is a fast growing area in science, technology and engineering. For many years, radiation has been used to affect atoms with ion or electron beams. The ability to fabricate structures with nanometric precision is of great importance to any exploitation of nanotechnology. Nanofabrication involves various lithographic processes that create extremely small structures. Radiation based on X-rays, electron beams, ion beams and gamma sources is key to various approaches to nano-pattering. The radiation synthesis of copper, silver and many other metallic nanoparticles for use in polymers and zeolites is being studied. By exposing solutions of metal salts to gamma radiation, the reactive species generated reduces the metal ion to the zero-valence state yielding nano-particles. Metal sulphide semiconductors of nanometric size are prepared by using gamma irradiation of a suitable solution of monomer, sulphur and metals. A general overview of the use of radiation in nanotechnology is presented in the paper.

Electron beams ranging in energy from several keV to MeV's can be used. Nanolithography devices based on the principles of electron microscopes can also be used. Accelerators in the energy range of 100 to 300 keV are used for surface nanopatterning. High energy accelerators, as high as 10 MeV, can be used with materials fabricated with nano-particulates, such as nanocomposites. Ion beams have also been used in the fabrication of nano-structures. This review discusses the types of electron beam accelerators and of material engineering methods with nanoparticulates, using research conducted at the Polish Institute of Nuclear Chemistry and Technology (INCT) as examples.

I. INTRODUCTION

Nanotechnology is one of the fastest growing areas in science, technology and engineering. Radiation has been used for many years to affect atoms using ion or electron beam accelerators(1). Three types of accelerators are used for nanomaterials or nanostructures fabrication:

- low energy electron beams and ion beam accelerators for lithography
- high energy ion beam accelerators for implantation and for manufacturing ion track membranes
- medium and high energy electron beam accelerators and X-ray systems for surface curing and bulk nanocomposites synthesis.

In its entirety, nanotechnology is in the early development stage. However, lithography already plays a very important role in these developments. The term nanotechnology covers nanomaterials and nanomachines and related subjects. The synthesis of advanced materials and structures is an important field for nanotechnology applications. Nanorobots and nanomachines are being constructed. The first topical report on the application of ionizing radiation for nanomaterials and nanostructures was published by the International Atomic Energy Agency (IAEA) in 2005(2).

II. TECHNOLOGY AND ACCELERATORS

II.A. Lithography and nanostructures

II.A.1. Electron beams

Electron beam lithography (EBL) uses 10-50 keV electrons and offers higher patterning resolution than optical lithography even at its shortest wavelengths. Just like optical technique, electron lithography also uses positive and negative resists, which are electron beam sensitive materials that are applied to cover a wafer according to the defined pattern. Positive resists undergo bond breaking when exposed to electron bombardment, while negative resists form bonds or cross-links between polymer chains under the same situation. The classic radiation chemistry of polymers is used in this area(3).

Scanning electron microscopes can be converted into EBL systems. This involves the use of a scanning electron microscope (SEM) and a laser stage. The SEM is equipped with a hot field emitter and typically provides a beam diameter of less the 2 nm at 25 keV or about 3.5 nm at 5 keV. As a lithography unit, this allows the fabrication of nanostructures down to about 10 nm.

Single-walled carbon nanotubes (SWNT) possess remarkable electronic and mechanical properties. Various applications in nanoscale devices have been described. However, little progress has been reported on techniques for connecting such tubular structures. Although a connection between SWNTs would constitute a novel type of molecular junction, it is yet unknown whether such junctions exist at all and if they are stable. This is a key issue because both electronic devices and strong nano-mechanical systems need molecular connections between individual SWNTs. Recently, Terrones et al. have shown that crossing single-walled carbon nanotubes (SWNT) can be joined by electron beam irradiation to form molecular junctions(4). Stable junctions of various geometries are created *in situ* in a high voltage transmission electron microscope at specimen temperatures of 800°C. By irradiating two crossing tubes, their merging was observed at the point of contact, resulting in the formation of a junction with an X shape. The ready-formed X junctions can be manipulated in order to create Y- and T-like molecular connections. Electron beam exposure at high temperatures induces structural defects, which promote the joining of tubes via cross-linking of pendant bonds. The junctions described here are created via vacancies and interstitials, induced by the focused electron beam, which promotes the formation of inter-nanotube links. The results suggest that it may now be possible to construct nanotube networks by growing cross-link SWNTs followed by controlled electron beam irradiation at high temperature.

II.A.2. Ion beams

A focused ion beam (FIB) is a device that uses ions to expose a resist. The FIB system consists of an ion source, a beam defining aperture, and an electrostatic lens for focusing the beam. Higher resolution limits should be obtainable because resists are more sensitive to the higher mass of ions than to electrons, and the higher mass of ions are less prone to backscattering, which is one of the limitations in electron beam lithography. Usage of 75 keV He ions is one technique.

A new method to grow carbon nanotubes was reported in 1996 by Yamamoto et al. where they grew carbon nanotubes using argon ion beam irradiation of an amorphous carbon target under high vacuum condition ($4 \cdot 10^{-5}$ Torr)(5). The incident angle of the ion beam was normal to the target surface; and the acceleration ion energy was 3 keV. Nanotubes were produced outside the sputtering region on the target surface. The tubes have multilayered walls, the distance between carbon layers is 0.34 nm, and the wall thickness of the tubes ranges from 10 to 15 layers.

II.B. Track membranes

The formation of microporous and nanoporous membranes having highly uniform geometry and precisely determined structures is an exciting example of an industrial application of ionizing radiation. The manufacturing method makes use of heavy ion beams, usually of energy on the order of several MeV, from accelerators. [A heavy ion beam with acceleration energy of >1 MeV/u deposits its energy into a substrate in the order of <10 nm in diameter (an ion track); the depth of the affected region can be regulated by changing the energy or replacing species of ion particles.] Ion track membranes commonly use polyethylene terephthalate (PET) and polycarbonate (PC) films. By bombarding PET or PC films with accelerated heavy ions (e.g. Ar^+, N^+ or Xe^+), linear tracks of latent radiation damage is created within the samples. Following sensitization and etching with an alkali solution (NaOH for instance), uniform cylindrical, conical, tunnel-like, or cigar-like pores have been obtained. Pore sizes or dimensions depend upon various factors, that is the ion and energy of incident particles, the target material, etch conditions, such as temperature, the type of etchant, pre-etch storage conditions, etc., all of which are controllable.

Cylindrical channels 0.02–5.0 μm in diameter with lengths of 10–50 μm have been produced in membranes containing anywhere from a single pore up to 10^9 pores/cm^{-2}. These thin film polymer membranes have highly uniform pore size. A wide variety of porosities in well-distributed areas of the template (patterning) are already commercially available(6). A number of modification methods have been devised for creating track membranes with special properties and functions.

These isoporous membranes are used as template materials for the synthesis of micro- and nanostructures. The template-base method consists of filling a host porous medium with one or more desired materials. Three main processes are used for the synthesis of various combinations of polymers and/or metals:

(a) electrodeposition;
(b) chemical polymerization;
(c) electrodeless plating.

The micro- or nanomaterials, which are produced in this way, take the form of wires or tubules.

Ion tracks can be used as a tool for building nano-devices. The small diameter of the track, which is around 10 nm, defines the lateral dimension; the length of the structure is given by the film thickness and can vary from less than a nanometer to several micrometers. Other structures are the recently developed conducting ion tracks in diamond-like carbon films and metal membranes that can be produced by direct duplication of etched ion-track templates.

II.C. Implementation

The modification of surfaces of solids using ion beams can be divided into two groups:

The first one is classic ion implantation employing low energy ion implanting accelerators. These low energy accelerators are specially designed to produce high intensity ion beams that can be easily distributed over large surface areas. They are usually equipped with different types of ion sources in order to be able to deliver a great variety of ion species. The typical acceleration voltage for these ion implanting accelerators ranges from 50 kV to 300 kV. The delivered beam power can be as high as 25 kW.

With the development of a new type of tandem accelerator, another class of high current accelerators emerged in the second half of 1980's . These are typically equipped with the sputter type ion sources that make it possible to produce virtually any kind of ion. With the terminal voltage up to 6 MV, tandem accelerators are capable of delivering multiple charged heavy ions of energies well above 100 MeV(7).

Accelerated heavy ions are a powerful tool which can tailor surfaces under controlled conditions at a nanometric scale. The growing importance of nanostructured surfaces for a wide variety of applications and fundamental investigations is now well established. The solid–liquid interfaces for such systems have been studied. The role played by topographical defects on the wetting of solid surfaces as well as both the dissipative and the confinement effects on the interface have been demonstrated (8).

II.D. Surface curing

Material surface structures are important in many applications, e.g. mechanical scratch resistance, chemical or physical corrosion resistance, surface wettability, chemical activity (adsorption, catalytic behavior) etc.

A novel method for preparing micro- and nanoscale patterns of polymer chains grafted onto flexible polymer substrates based on the combination of the two techniques of radiation grafting and "grafting-from" has been developed. This combination makes it possible to prepare grafted structures having micro- or nanoscale lateral dimensions that are determined by the electron beam or X-ray irradiation patterns. The height of the grafted features can be controlled by the irradiation dose or by such grafting reaction conditions as time, temperature, or monomer concentration. In this method, the resolution of nanopatterned materials is comparable to that of other polymer-based lithography processes. This new method based on radiation grafting creates polymer structures with lateral dimensions as small as 100 nm on the surface of polymer films. In radiation grafting, reactive radical species are first generated within a polymer substrate through electromagnetic or particle (e.g., electron beam) irradiation, and then the grafting is carried out in a separate subsequent step. Lateral definition of the structures can be achieved by localized creation of radicals using a focused electron beams or synchrotron radiation in an X-ray interference setup(9).

II.E. Bulk materials

Electron accelerators of 10 MeV energy or X-ray systems are applied to treat bulk materials(10,11,12). The technology is a material processing technique(13, 14).

II.E.1.Nanocomposites

The modification of semiconductors by radiation is a well established technology(15). A good amount of research has been devoted to hybrid inorganic semiconductor-polymer nanocomposites because they frequently exhibit special properties that are combinations of the original semiconductor and polymeric materials. Thus, the addition of inorganic nanoparticles to polymers can enhance conductivity and mechanical toughness for applications as organic batteries, microelectronics, non-linear optics and sensors. Only few methods have been used to prepare the composites. In general, two basic steps are needed: (a) metal ions are introduced into the polymer by copolymerization of an organic monomer and the metal ions, or by an ion-exchange process; (b) a chalcogen source is introduced for the preparation of nanocrystalline chalcogenide. In these methods, the polymerization of an organic monomer and the formation of nanocrystalline metal chalcogenide particles are performed separately. It is very difficult to control the dispersion of metal chalcogenide in the polymer matrix. Moreover most of the products prepared by these routes at room temperature are amorphous and post-treatment under high temperature or pressure is often necessary. Synthesis of semiconductor-polymer nanocomposites at room temperature and in a single step would be an ideal method for material chemists. As described earlier, "wet" routes have been investigated in various laboratories(16). These methods can be used for the incorporation of microstructures in polymer matrices as well(17).

II.E.2. Nanogels

There are at least two ways of defining polymeric nanogels and microgels. One originates from the definition of polymer gels. A polymer gel is a twocomponent system consisting of a permanent three-dimensional network of linked polymer chains, and molecules of a solvent filing the pores of this network. Nanogels and microgels are particles of polymer gels having the dimensions in the order of nano- and micrometers, respectively. The other definition of a nanogel or a microgel is an internally crosslinked macromolecule. This approach is based on the fact that, in principle, all the chain segments of a nanogel or microgel are linked together, thus being a part of one macromolecule. It also reflects the fact that such entities can be synthesized either by intramolecular crosslinking of single linear macromolecules or in a single polymerization event (e.g. initiated by one radical) that in the absence of crosslinking would lead to the formation of a single linear polymer chain(18).

The latter definition allows one to consider nano- and microgels as a specific form of macromolecules, along with linear, branched, comb-like, circular, star-shaped, dendrimer, and others macromolecule structures. Since the shape of a nano- or microgel usually resembles a linear macromolecule in a coiled conformation, these structures are often seen as permanently "frozen" polymer coils.

Depending on the irradiation parameters (radiation dose, dose-rate, polymer concentration, irradiation temperature) molecules with different structures can be obtained (long-chain branches, nanogels, microgel or microgel particles).

II.E.3. Nanoclusters

The use of radiation to synthesize nanoparticles in aqueous dispersions began in the late 1970's. To obtain metallic particles from their parent ions, one only needs to ensure reductive conditions during the irradiation. The oxidizing equivalents, OH radicals, can conveniently be converted to reducing radicals by the addition of organic scavengers (e.g., alcohols, formate ions). The latter will produce reducing radicals following hydrogen abstraction by the OH radical(19).

(1) H_2O /\/\/—> e-aq, H, OH, H_2, H_2O_2
(2) OH + RCH_2OH —> RC•HOH + H_2O
(3) nC•HOH + M(I) —> (M)n + RCH_2OH (M = a metal)
(4) ne-aq + M(I) —> $(M)_n$

The radiolytic approach may offer some advantages because of the control over the rate of generation of the growing species afforded by the control over the dose-rate delivered to a sample(20). Radiation is used to obtain metal structures in molecular sieves and other metalo-organic structures(21, 22)

Another method to obtain nanoclusters is that of ion implantation. There is a threshold implantation dose, after which some of the implanted species will tend to spontaneously form nanoclusters, due to over-dose implantation. Similarly, there is a threshold implantation dose for the implanted species in a layer of the host material, such that after high temperature annealing the nanoclusters can nucleate before the implanted material can dissolve in the host material during such heat treatment or annealing process. There is work on producing nanoclusters of gold in silica at fluences of two orders of magnitude less than what is traditionally used. This is accomplished by implanting 2.0 MeV Au^+ into silica followed by MeV bombardment with Si^+ ions. This process reduces the threshold implantation dose by at least two orders of magnitude. The size of the nanoclusters, ranging from 1 to 10 nm, is controlled by the implantation dose and by the total electronic energy deposited by each post-bombarding ion in the implanted layer. Active species such as gold nucleates form nanoclusters, either by induced strain or by radiation enhanced nucleation at a dose below that needed for spontaneous nanocluster formation(23).

III. CONCLUSIONS

Radiation methods based on ion and electron accelerators play an important role in nanomaterial fabrication. Electron beams ranging in energy from several keV to MeV's, that are being used in different technologies, can be used in this innovative nano-technology areas. Ion beams can also be used in the fabrication of nano-structures.

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