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Submitted at the *Fall 2000 Materials Research Society Meeting*
Symposium Proceedings, "Ion Beam Synthesis and Processing of Advanced Materials"

Nanophase Composites Produced by Ion Implantation: Properties, Problems, and Potential

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Prepared by the
SOLID STATE DIVISION
OAK RIDGE NATIONAL LABORATORY
Managed by
UT-BATTELLE, LLC, for the
U.S. DEPARTMENT OF ENERGY
Under Contract No. DE-AC05-00OR22725

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Abstract

Ion implantation has become a versatile and powerful technique for synthesizing nanometer-scale clusters and crystals embedded in the near-surface region of a variety of hosts. The resulting nanocomposite materials often show unique optical, magnetic, and electronic properties. Here we review some of the principal features of this nanophase materials synthesis technique and discuss the outstanding experimental difficulties that currently hamper the development of devices based on the many unique properties of these nanocomposite materials. Possible solutions to these problems and future research directions are discussed. The following is a summary paper that is partially based on a recent invited article by the above authors to appear Advanced Materials.[1]

1. Overview

Nanophase materials are frequently characterized by novel properties that can be significantly different from those of the corresponding bulk phase. As precipitated nanocrystals (NCs) are formed on ever decreasing length scales, the differences between the bulk and small-particle properties become increasingly pronounced. These differences have stimulated a growing worldwide effort that cuts across many disciplines and research areas that emphasizes the synthesis and characterization of an increasingly wide variety of nanocomposite materials. The practical motivation for this intense research effort derives both from the fundamental characteristics of small particles as well as the numerous potential applications of these materials, particularly in the areas of optical devices, micromechanical devices, and information storage. The novel properties of nanophase particles are dominated by two major effects. These are, first, the increasing relative significance of the surface-energy contributions associated with the larger surface-to-volume ratio of small particles and, second, the unique characteristics of electrons in confined systems. The first effect largely determines the physical properties of the particles or the nanocomposite (*e.g.*, melting points, solid phase transitions, bulk modulus). Both the surface properties and electron confinement combine to produce novel electronic properties that can be manifested in a wide range of effects, such as a large nonlinear optical susceptibility, intense photoluminescence, altered band structures, and superparamagnetism, to name but a few.

Many experimental techniques have been developed for synthesizing various types of nanocomposite materials. Ion implantation was first used for this purpose in the 1970s to form

Ag and Au nanocrystals embedded in silica glass.[2] At that time, however, there were no obvious applications for such nanocomposites, so it was not until the 1990s that ion implantation became an important and widely used research technique for synthesizing nanocomposite materials. Today, over two dozen research groups on five continents are actively involved in the synthesis and characterization of nanocomposites formed by ion implantation, and entire sessions or symposia at major conferences are now devoted to this topic.

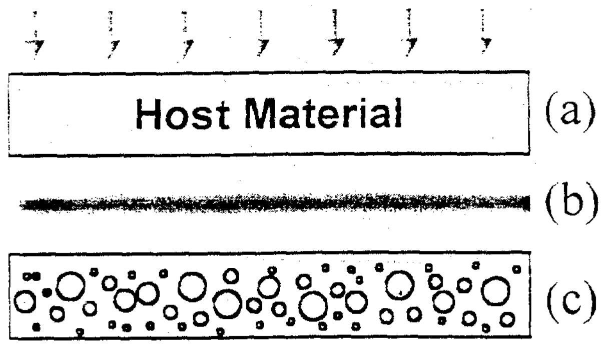

Fig. 1. Schematic of the ion implantation technique. In (a), a chosen host material is implanted with energetic ions (arrows), producing a supersaturated solid solution in the near-surface region (b). In (c), subsequent thermal processing has caused the implanted material to precipitate as discrete particles.

The increasing popularity of the ion implantation technique is due in part to its versatility and flexibility. In this technique, a selected host material (frequently an insulating ceramic) is injected with energetic ions that are accelerated from a few tens to a few thousand kilovolts. High-dose implantation can create a solid state supersaturation of the implanted ions in a layer extending from the specimen surface to a depth of several tens to hundreds of nanometers. Subsequent thermal processing or further irradiation can, depending on the specific host/nanoparticle solid state chemistry, induce the implanted material to precipitate as discrete nanoparticles (Fig. 1). The versatility of the implantation technique arises from the fact that essentially any element in the periodic table can be implanted into virtually any selected host material. This versatility and the various possible combinations of implanted ions allow for an extremely large range of potential nanoparticle-host combinations. Useful properties of two or more precipitated phases can be combined into one well-defined, integrated structure; and the important physical properties of the nanocomposite can be optimized for a particular application by controlling the concentration and average size of the precipitates. Depending on the physical and chemical properties of the host material, nanocomposites formed by ion implantation can be durable since they are formed below the host surface and are thus protected from the surrounding environment. The average precipitate size can be controlled by varying the concentration of implanted ions (*e.g.*, by selecting the appropriate dose, dose rate, and energy). Finally, ion implantation is now widely employed in the semiconductor industry for doping silicon wafers, and therefore, it constitutes a materials technology that is already established in the commercial synthesis and processing of materials with microscopic precision and control.

Types of Composites

Metallic clusters embedded in an insulating host were among the first nanocomposite systems to be formed by ion implantation.[2] In the early work, it was noted that an extremely high local concentration of precipitates was obtained in a thin layer near the specimen surface. This physical configuration is quite different from conventional nanocluster composite glasses made from melt processes, where the particles are relatively uniformly dispersed throughout the bulk. Metal-nanocluster composites formed by ion implantation exhibit pronounced optical effects including: 1) absorption due to surface-plasmon resonance, and 2) strong third-order nonlinear optical susceptibility. Both classical and quantum-mechanical effects are at work in these phenomena. The spatial confinement of the metallic electrons by the insulating host produces an enhanced electromagnetic field due to the large dipole moment induced by the optical field. In addition, for very small nanocrystals (with diameters less than approximately 10 nm) the confinement of the electron wave functions in either the initial or final states to a volume much smaller than their bulk mean free path produces an additional contribution to the electric susceptibility.

Metal-cluster nanocomposites formed by ion implantation have excellent nonlinear optical properties. The experimentally determined value of the effective nonlinear optical susceptibility ($\chi^{(3)}_{eff}$) is generally higher by a factor of 10^3 over conventional quenched nanocomposite glasses, and the response times are on the order of picoseconds. Several authors have suggested that these materials may have potential applications in all-optical memory or optical switching devices [3,4]. However, certain difficulties remain to be addressed before these types of device applications can be realized. A major problem is that the linear absorption and the nonlinear optical susceptibility both peak at the surface plasmon resonance (SPR) frequency. In addition to decreasing optical transmission, the high SPR absorption coefficient can produce an associated long-lived thermal component in the nonlinear response, although the thermal relaxation problem may be decreased if sufficiently short optical pulses are used [5]. One way to solve some of these problems is to have a extremely narrow size distribution of the smallest particles – enhancing $\chi^{(3)}_{eff}$ and decreasing the SPR absorption.

Table 1. Catalogue of semiconductor nanocrystals produced by ion implantation.

Nanocrystal	Host Material		
	Al_2O_3	Si	SiO_2
CdS	⚑	⚑	⚑
CdSe	⚑	⚑	⚑
CdTe		⚑	⚑
GaAs	⚑	⚑	⚑
GaN	⚑		
GaP	⚑	⚑	⚑
Ge	⚑		⚑
InAs		⚑	⚑
InP		⚑	⚑
PbS	⚑		⚑
PbTe	⚑		
Si	⚑		⚑
ZnS	⚑	⚑	⚑
ZnSe			⚑
ZnTe			⚑
VO_2	⚑		⚑

Semiconductor nanocomposites formed by ion implantation have also been widely investigated, due to their potential applications in as light-emitting diodes [6] and single-electron transistors [7]. They have potential applications in nonvolatile memory [8], nanocrystal gate oxide [9], and "smart" temperature- and light-sensing devices [10]. A large number of single-element and compound nanoclusters have been formed in a variety of insulating host materials (Table 1), and prototype devices have been built [11]. These materials have many unique properties, for example, Si NCs in SiO_2 are strongly luminescent (although the origin of the light emission is still debated), CdS nanocrystals show clear evidence for quantum-confinement-induced bandgap shifts, and VO_2 precipitates switch from the semiconducting state to the metallic state over the temperature range 340-360 K, suggesting applications as optical switches or "smart" temperature sensors [12].

Despite these recent successes, several problems currently hinder the development of functional semiconductor-NC-based devices. Particle size distributions are too broad and the microstructural relationships between the precipitates and the host material are often complex. These problems are more severe for compound nanoparticles. The broad size distribution is a particular problem for semiconductor nanocomposites, since the electronic properties of the precipitates are so strongly dependent on particle size. The band structure of the composite is thus "blurred" over a range of precipitate sizes. Complex microstructures, too, are a problem since it becomes difficult to determine the origin of certain types of optical signals. For example, particles may form as hollow shells, thus increasing the internal surface area and possibly enhancing surface effects [13], they may be blanketed by reaction rims [13], or they may have non-uniform compositions [14,15].

Ferromagnetic nanoparticles formed by ion implantation also show several unique properties. Ion implantation has the advantage that the precipitates can be made to crystallographically align with the host material, so that the magnetic "easy" axes of the precipitates are parallel. This type of alignment has been demonstrated for Fe and Co particles emedded in transparent crystalline hosts [16,17]. As a result of precipitate alignment and the near two-dimensional specimen geometry, the magnetic hysteresis is strongly dependent on the orientation of the magnetic field with respect to the specimen. The hysteresis and coercivity can, in fact, be controlled by subsequent implantation of Pt or Xe into the layer containing the nanoparticles [17]. These initial results are encouraging; however, for single-particle-per-bit magnetic recording, the precipitates must also be magnetically isolated, similar in size, and their position and spacing must be controlled [18]. Control over the size, position, and spacing of the particles is a problem that is yet to be solved.

Outstanding Difficulties

Ion implantation has been used to form a wide range of nanoparticle-host combinations (e.g., see Table 1). Clearly, the versatility and flexibility of ion implantation for producing many types of nanocomposites has been conclusively demonstrated by many research groups. Control over average size, orientation, morphology, crystal structure, and composition has been demonstrated in various experiments. That these nanocomposites have interesting and often unique properties is clear; however, development of actual devices has been hampered by several outstanding experimental difficulties associated with the implantation technique.

First and foremost of these difficulties is the control over the size distribution of the precipitates. Since the properties of nanoparticles are dependent on their size, for many types of applications it is essential to obtain an extremely narrow size distribution. By the nature of ion beam-solid interactions, injecting mono-energetic ions into a solid material produces a roughly Gaussian distribution of implanted ions. This is due principally to ion straggling (the statistical nature of ion-target collisions); however, irradiation-induced modifications to the host material (e.g., changes in density, crystal structure, etc.) and energy variations within the ion beam may also affect the distribution of implanted material. Due to the non-uniform implant profile, larger particles often form where the injected ion concentration is the highest (as depicted in Fig. 1). Nucleation and growth of precipitates during a thermal processing step frequently compounds the problem. Conventional Ostwald ripening processes generally do not occur due to the complex nature of the composite: Radiation damage, the presence of a specimen surface, and interactions and reactions involving the implanted material and the host all serve to complicate the microstructures and size distributions. In short, ion implantation combined with thermal processing has not - thus far - produced suitably narrow size distributions for many types of device applications.

A second requirement for applications such as magnetic data recording is control over the spatial location of the precipitates. Ion implantation has the advantage over conventional quenched nanocomposite glasses in that the depth and depth distribution of particles can be controlled, and additionally, nanocomposites consisting of several types of clusters located at different layer depths can be produced. However, ion implantation is currently unable to control the location of the precipitates within the implanted layer. In many types of applications (e.g., magnetic recording, optical memory, *etc.*), regular spacing of the precipitates is of critical importance.

A third difficulty is related to compositional uniformity and nanocrystal-host interface states. Although compositional uniformity generally is not a problem in single-element NCs, compound multi-element nanoparticles can have significant non-uniformities in terms of their composition and structure [13]. Nanocrystals prepared by chemical techniques are passivated with selected organic ligands and the nature of the interface is fairly well understood; however, the effects of the particle-host interface, particularly on the optical properties of embedded nanocrystals formed by ion implantation, is thought to be important but is poorly understood. In some cases (e.g., Si NCs in SiO_2), the interface is probably controls the strong light emission [19,20], but the exact mechanism is still under investigation.

Another difficulty relates to the means by which the nanocomposites are synthesized and studied. Currently, specimens must removed from the implanter for thermal processing and characterization – *i.e.*, a serial technique. For example, as discussed above, recent work has shown that the magnetic properties of Co precipitates in a sapphire host can be controlled by subsequent implantation of Pt or Xe. However, to perform these experiments requires specimens to be re-implanted many times, sometimes re-annealed, and the specimens are exposed to atmosphere on many occasions. Thus, the experiments are laborious and time consuming, may be non-reproducible, and possibly, interesting physics could be missed - for example at intermediate ion doses. The possibility of combining ion implantation with *in-situ* specimen characterization will be explored below.

New studies are clearly needed that focus on innovative ideas and solutions relating to some of these outstanding problems. Much work has been done in the last decade to clearly demonstrate the novel properties of these composites, and to show that an extremely large number of nanoparticle compositions can be formed in an almost unlimited number of host materials. The direction is now towards optimization of these materials and finding solutions to the outstanding difficulties that hamper the development of these nanocomposites in various types of devices. This will involve several factors, including the development of newer implantation techniques (e.g., focused ion beams), the combination of ion implantation with other techniques such as pulsed laser deposition (e.g., the new Vanderbilt system) or thin film growth (either by implanting thin films or by using lithographic films as masks), and the development of *in-situ* ion implantation facilities such as that recently funded at the University of Alberta. These kinds of new research directions and their potential benefits will be discussed in the following section.

Potential solutions and Future Research Directions

Focused ion beams

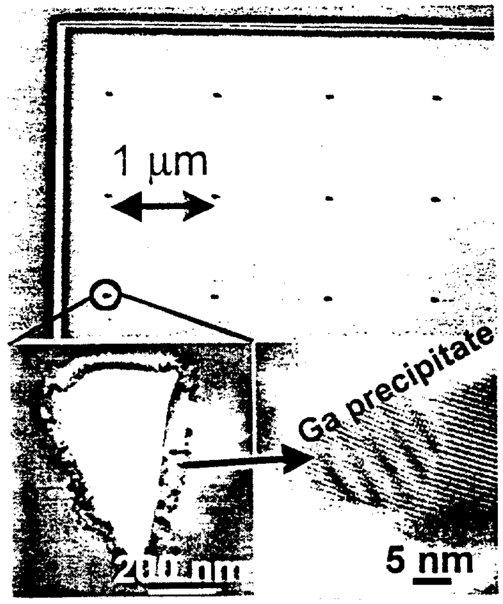

Fig. 2. Top: backscattered SEM image showing an array of holes "drilled" in single-crystal silicon with a focused 35kV Ga ion beam. Bottom left: TEM image showing a layer of precipitates around the edges of one of the holes. One of the precipitates is magnified in the bottom right image.

One idea to overcome particle size and spacing difficulties is to selectively implant specific areas of a specimen using a focused ion beam (FIB). This is an emerging technology in which a set of electromagnetic lenses is used to collimate and focus an ion beam into a narrow spot (somewhat akin to electron lenses in electron microscopy). The most modern instruments claim minimum spot sizes as small as about ten nanometers. Commercial FIBs are primarily restricted to 35 kV Ga sources, which is currently a major limitation to their use as implanters. At this low energy, sputtering is the major difficulty since the implanted ions cannot be injected sufficiently deep into the host, and the beam acts more like an "ion drill" (e.g., Fig. 2). Ga may have some applications (e.g., it may be possible to make GaAs particles in specimens pre-implanted with As); however, the applications of a Ga ion beam for implantation are limited.

In recent experiments [21], a focused ion beam was used to implant an array of spots in a silicon host. The FIB was programmed to inject a 1 mm^2 area with 2 x 10^{10} ions/spot at a spot spacing of 10µm. The regions around the edges of the drilled holes do contain fine Ga precipitates (Fig. 2). This proof-of-principle experiment conclusively demonstrated that the FIB can produce ordered spots on a substrate, and that it is even possible to produce precipitates around the edges of the ion-drilled regions. The results suggested that commercial FIB technology is promising technique, but it has not yet reached the level of sophistication required to provide the higher energies and a wider range of ions necessary for its use in implantation. Additionally, FIB implantation is a serial technique, so even if ion source difficulties are overcome, implantation of relatively large areas will still be a slow and costly procedure. For example, the specimen described above contained one 10,000 individual implanted spots, requiring many hours of implantation time. To synthesize a larger specimen with a higher concentration of particles would, at the current level of technology, require a prohibitively long implantation times.

Combination techniques

One particularly interesting area is the combination of thin film growth with ion implantation. The ability to create high quality waveguide films, for example, leads to the possibility of implanting such materials to create an enhanced optical response. In one idea, it may be possible to create buried layers of particles within a thin waveguide film. The formation of nanoparticles within a waveguide film has been, in recent years, the focus of intense research efforts (e.g., see Ref. 22). The optical response of the nanoparticles, when measured "edge-on", should be orders of magnitude stronger than conventional plane perpendicular measurements. Obviously, many difficulties may be encountered, such as the effects of implantation on the optical properties of the film, the effects of the interface (e.g., the interface may be a favorable nucleation site for the precipitates), and chemical reactions between the film and the implanted material. A new state-of-the-art UHV thin film deposition system is being built at the University of Alberta that will find considerable use this research area.

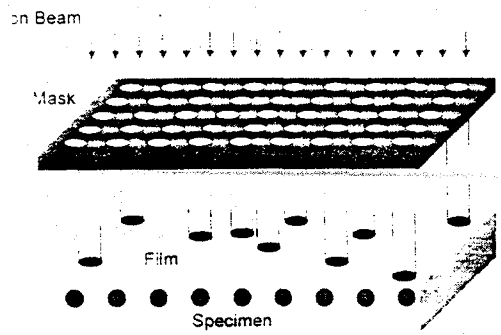

Fig. 3. Schematic of experiment using a lithographically patterned mask to create arrays of precipitates. The mask may be a separate membrane, as shown here, or may directly contact the substrate.

In another application combining thin films and ion implantation, it may be possible to use conventional lithographic techniques to synthesize films or membranes with regularly spaced holes. A selected substrate could then be implanted through the holes to create an ordered array of nanoparticles (Fig. 3). This technique has been highly successful in producing ion-beam-patterned magnetic films. For example, the Orsay group synthesized ~400-nm-thick silica films using a conventional lithographic technique [23]. These masks were located directly on the a specimen for ion implantation (Fig. 4). After implantation of He ions, the mask was removed and the magnetic properties of the resulting film we patterned according to the mask shape.

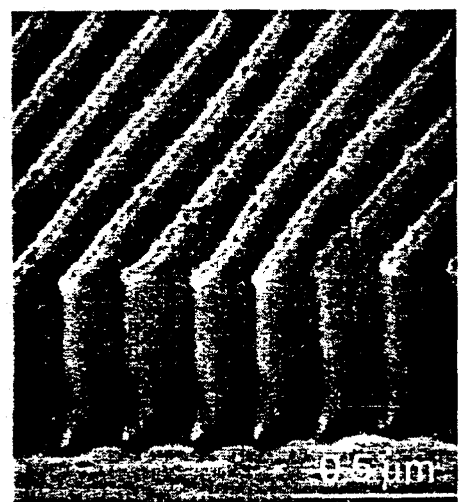

Fig. 4. SEM image showing a 450-nm-high SiO_x line mask deposited on a magnetic substrate (from Ref. 23).

Here, we envision the possibility of using a similar technique to create ordered arrays of nanoparticles. The mask requirements will be fairly severe. The film would have to be thick enough to stop the ions, and durable enough to withstand high-dose implantation without breaking, disintegrating, or swelling. The size of the holes and the thermal processing conditions will probably determine whether a single particle would form at each location, or a group of particles. If, for example, this technique could be used to synthesize a regular array of embedded nanoparticles, this would overcome a major obstacle currently limiting the potential application of such materials in magnetic recording and optical memory. This is a research idea that is one objective of the nanoparticle research being conducted through collaborations between ORNL, Vanderbilt, and the University of Alberta.

In-situ techniques

In-situ experimental techniques can be useful for optimizing specific microstructural or electronic properties of ion-implanted nanocomposites. In one idea, we have attempted to use in-situ TEM techniques to monitor specimens *during* implantation and thermal processing. The

IVEM-Tandem Facility at Argonne National Laboratory consists of a 650 keV NEC accelerator interfaced to a Hitachi H9000NAR transmission electron microscope [24]. This facility has traditionally been used for *in-situ* radiation-damage experiments; however, by decreasing the ion energy it is readily possible to *implant* a TEM specimen. In one example illustrating the flexibility of the ion implantation technique, both ferromagnetic and Type I superconducting particles were produced in the same sample. A sample containing pre-existing Ni nanocrystals was implanted with Pb ions *in-situ* directly in the TEM. Two distinct and separate types of nanoparticles were formed: i.e., relatively large Pb precipitates and small magnetic Ni particles (Fig. 5). The implanted Pb concentration was increased until radius of the Pb precipitates was larger than the coherence length for bulk Pb. This represents one example where *in-situ* ion implantation can be used to directly monitor the specimen evolution during the implantation and thermal processing steps. The experiment also illustrates that ion implantation can be used to create two distinct types of particles with different properties at the same layer depth within a single specimen. In this specimen, the ferromagnetic Ni precipitates might be expected to modify the correlated-electron properties of the Pb precipitates at cryogenic temperatures. Magnetic measurements of this specimen are ongoing.

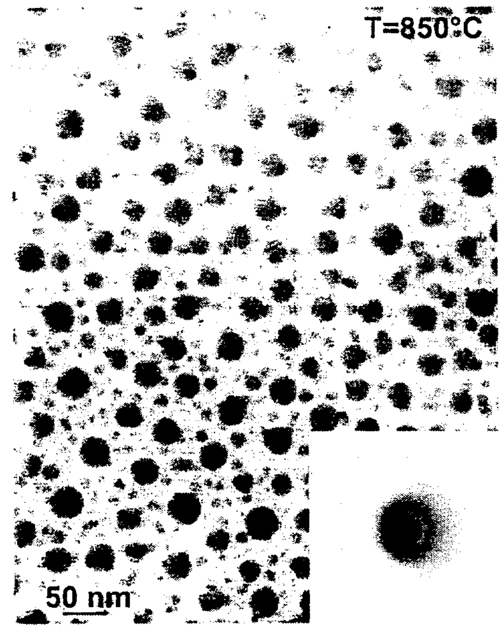

Fig. 5. TEM micrograph showing molten Pb spheres (large dark circles) co-existing with crystalline Ni precipitates (smaller light-contrast circles). Image taken at 850°C.

In-situ specimen characterization is also important. At the University of Alberta we have recently obtained funding to build a modified endstation on our Varian CF3000 ion implanter. This endstation will be interfaced to an independent photoluminescence system consisting of a deuterium lamp and associated lenses, CCD camera, and computer hardware. A second port will interface to a picosecond pulsed Ti:sapphire laser for pump-probe reflectivity measurements. We hope to be able to measure various opto-electronic properties as the specimen is implanted (by stopping the ion beam) or during subsequent *in-situ* thermal or irradiation-induced nucleation and growth. The ability to directly measure the optical properties *in-situ* should greatly assist in optimizing the desired properties of the nanocomposite, and we also anticipate numerous other applications in non-nanocrystal-related research.

New nucleation techniques and low-energy implantation

Non-thermal nucleation and growth techniques may be able to produce narrower size distributions than more conventional thermal tech-niques. In one example, a specimen of SiO_2 glass was implanted with Zn + S at cryogenic temperatures, to prevent nucleation during the implantation step. Subsequent room-temperature electron irradiation produced a narrow size distribution (by ion implantation standards) of ZnS nanocrystals embedded in the SiO_2 (Fig. 6). Thermal nucleation, in contrast, produces an extremely wide – almost bimodal – size distribution of precipitates. Electronic energy loss processes were dominantly responsible for particle nucleation [15]. More recently, the Orsay group has demonstrated means by which the nucleation and growth stages can be temporally separated, so that both processes are independent [25]. These workers used MeV ion irradiation of metal-doped glasses to produced embedded metallic precipitates. Similar to the results in Fig. 6, an electronic energy loss mechanism was found to control the nucleation stage. Other groups are also actively involved in non-thermal nucleation techniques, for example, the Alabama A&M and ORNL groups have investigated the properties of specimens in which high-energy ion irradiation induced nanoparticle formation in pre-implanted specimens [26]. Overall, these techniques do seem to offer hope for considerably narrowing the size distributions, although it is very doubtful that the type of monolayer control demonstrated in chemical techniques will be achieved using irradiation-induced nucleation and growth protocols.

Low-energy (E_{beam} ≤50 keV) ion implantation also offers significant potential for control of nanocrystal size in layered structures. At low energy and high beam current density, deposition time and range straggling are minimized, while depth uniformity is simultaneously maximized. Post-deposition laser or thermal annealing treatments can be carried out with higher efficiency and at lower temperature, because implantation-induced end-of-range damage is also reduced. Enhanced control of nanocrystal size was recently demonstrated for a single-layer array of Sn nanocrystals (diameter 4.8±1.0 nm) in SiO_2 film by implanting at 10 keV, to doses of order $5 \cdot 10^{15}$ ions·cm^{-2} [27]. This approach solves many problems in present blanket implantation experiments, but still exhibits one major weakness – the random lateral spacing of the nanocrystals.

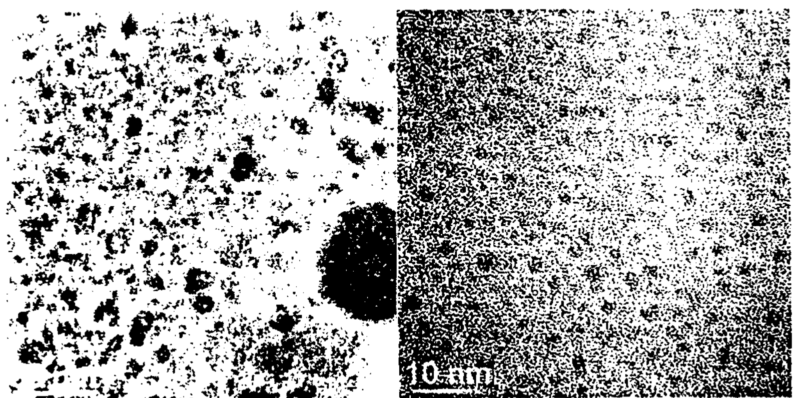

Fig. 6. ZnS nanocrystals grown by ion implantation of Zn+S followed by thermal processing (left) or electron-irradiation-induced nucleation and growth (right). Both specimens were implanted under similar conditions and to similar doses (a complete description of implantation and annealing conditions is given in Ref. 15). Irradiation-induced nucleation and growth produces a considerably narrower size distribution.

Conclusions

Ion implantation is a versatile and flexible technique for creating a wide range of nanocomposite materials with many promising applications. Prototype devices have been built and the results are encouraging. Recent developments in the areas of noble metal, semiconductor, and ferromagnetic nanoparticles were discussed. Despite the many advantages and unique properties of these nanocomposites, several problems may hamper the future development of actual devices. The most critical of these are control over the size distribution and spacing of the precipitates. Future research directions and possible means to solve these problems were discussed. The combination of ion implantation with thin film technology (implantation of thin films, development of durable lithographic masks) appears to be one of the most promising research directions. The versatility of ion implantation for producing many types of nanocomposites has been clearly established at this juncture: the critical research direction is now towards finding solutions for the outstanding problems and the optimization of the unique properties of these materials.

Acknowledgments

The *in-situ* ion implantation experiment was carried out at the IVEM Facility, Argonne National Laboratory. Research at the University of Alberta is supported by the NSERC, Canada. Work at ORNL is sponsored by the U.S. Department of Energy under contract DE-AC05-00OR22725 with Oak Ridge National Laboratory (ORNL), managed by UT-Battelle, LLC. C. W. White and L. A. Boatner also received support from the Laboratory Directed Research & Development Program of ORNL. Nanostructure research at Vanderbilt is supported by a Major Research Instrumentation grant from the National Science Foundation (DMR-9871234), the Southeastern Universities Research Association and the Vanderbilt University College of Arts and Science.

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