Structure and Properties of Nanoparticles Formed by Ion Implantation

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Abstract. This chapter broadly describes the formation, basic microstructure, and fundamental optoelectronic properties of nanocomposites synthesized by ion implantation. It is not meant as a complete literature survey and by no means includes all references on a subject that has seen a considerable amount of research effort in the past 15 years. However, it should be a good starting point for those new to the field and in a concise way summarize the main lines of research by discussing the optical, magnetic, and “smart” properties of these nanoparticles and the dependence of these properties on the overall microstructure. The chapter concludes with an outlook for the future.

1 Introduction

The emphasis on nanotechnology-related research has now been sustained for several years. Strong research efforts focusing on nanotechnology are common and crosscut the disciplines of chemistry, physics, biochemistry, medicine and engineering. Much of the interest is stimulated by the fact that many properties emerge in nanophase systems that do not occur in bulk materials. The practical motivation for this intense research effort derives both from the fundamental characteristics of small particles as well as their numerous potential applications, particularly in the areas of optical devices, micromechanical devices, and information storage.

The unique properties of nanophase precipitates arise from two principle factors. First, the large surface-to-volume ratio can have profound physical and thermodynamic effects that lead to significant modifications of melting temperatures and other phase transitions. Second, the three-dimensional spatial confinement of electrons creates a variety of novel optical and electronic effects. Surface effects and electron confinement together combine to produce new 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 just a few.

As a result of the many interesting properties and potential applications of nanophase materials, many experimental techniques have been developed to produce and synthesize different types of nanocomposites. Depending on the application or property of interest, the synthesis technique must meet certain requirements. For example, since the critical properties are often directly dependent on particle size, it can be vital to obtain narrow size distributions. The ability to create core-shell structures or otherwise control the chemistry of the particles can greatly enhance certain optoelectronic effects. Solution chemistry has yielded some of the best results in these specific areas, although there has been some difficulty in producing materials that can be readily utilized in solid-state devices.

Here, we will review the experimental methods, formation, and properties associated with nanocrystalline materials produced by ion implantation. Nanocomposites produced by ion implantation have a number of attractive characteristics. The technique can produce a wide variety of single-element or compound nanocrystals embedded below the surface of virtually any solid host material with well-controlled depth and concentration. Because the particles are formed below the surface and are embedded within the host, the resulting composites are durable and the nanoparticles are protected from the environment. The physical properties of the nanocomposite can be optimized and tailored by controlling the concentration, crystal structure, orientation, and average size of the precipitates. By adjusting the experimental parameters, useful properties of two or more precipitated phases can be combined into a single integrated structure. Finally, ion implantation is widely employed in the semiconductor industry for doping silicon wafers, and therefore, it constitutes a mature materials technology that is established in the commercial synthesis and processing of materials with microscopic precision and control. The main disadvantages associated with the ion-implantation technique are the inability – so far – to produce suitably narrow size distributions and to control the lateral spacing of the precipitates. Additional difficulties can be caused by the effects of ion-beam damage, and high-temperature thermal processing may be necessary to remove matrix defects created in the implantation steps or control size distribution of the nanoparticles.

In this chapter, the main methods for using ion beams to produce nanocomposite materials will be discussed. The factors controlling the microstructure of the nanocomposites will be summarized. The microstructure has a major effect on the optoelectronic properties of the composite, and in this respect ion implantation offers a number of special advantages, as well as presenting some major difficulties. Next, some of the most attractive optical and electronic properties of nanocomposites produced by ion implantation will be briefly surveyed. Some aspects of the following will be based on a recent comprehensive review paper on nanocrystals produced by ion implantation, which we refer the reader to as the main citable reference [1]. The physics responsible for the optoelectronic properties of nanocrystals produced

by ion implantation will also be touched on in this chapter, and is derived in more detail in subsequent chapters. Since there are thousands of papers on nanoclusters produced by ion implantation, a complete literature survey is not the intent of this short work; an attempt was made to keep the number of citations to a nonoverwhelming level.

2 Nanoparticle Synthesis

Ion beams have been used in basically two different ways to create nanocomposite materials. Some of the early work used ion irradiation of doped glasses to produce various types of nanoclusters. In this technique, a glass containing selected impurities – usually metal oxides – is irradiated to high fluences with H, He or Ar ions (Fig. 1a). Electronic energy-loss mechanisms induce nucleation and growth through a complex radiolytic process involving interactions between the metal ions and irradiation-induced defects in the glass. More recently, heavy-ion irradiation (up to $Z = 35$) was used to nucleate metal clusters in a glass [2]. Precipitate nucleation was driven by electronic energy-loss processes, similar to the case for light ions, but there is clear evidence for a threshold electronic energy loss, below which nucleation does not occur.

One advantage of the irradiation-induced nucleation technique is that the nucleation and growth stages can be temporally separated. Seed nuclei can be formed during the irradiation procedure, which then ripen during subsequent thermal processing. This provides a means for controlling the volume density and narrowing the size distribution of the precipitates. Generally, however, the concentration of particles produced is low (typical of thermal nucleation in a glass), the range of possible particle–host combinations is small compared to ion-implantation techniques, and there are none of the advantages associated with the production of nanocrystals embedded in a crystalline matrix.

Fig. 1. Schematics of the ion-beam-induced nucleation and ion-implantation processes

The second main technique, now more commonly employed, uses ion implantation to inject impurities that subsequently nucleate as nanoparticles (Fig. 1b). In a method borrowed directly from the semiconductor industry, a high concentration of impurity ions is implanted into the near-surface region of a selected host material. This produces an impurity supersaturation within a few hundred nanometers of the surface, depending on the implantation energy and ion mass. Particularly for glass substrates it provides a method of achieving nonequilibrium concentrations of dopant ions without the need for glass modifiers to avoid phase separation in the glass. These glass modifiers can lead to increased absorption and degradation of the linear and nonlinear optical properties. Ion implantation can yield high-purity materials with large nanoparticle volume fractions and with accurately determined dopant concentration. In practice this permits the use of very high purity silica and other important optoelectronic materials without unwanted dopants that can degrade performance. Fluences can range up to 10^{17} ions cm^{-2} or higher, depending on the average size and particle concentration desired. One or more elements can be sequentially implanted in order to produce compound or chemically doped nanocrystals. The freeware computer program SRIM [3] is generally used with good results to ascertain the range and straggling in order to ensure overlapping concentration profiles. If the implants are done “hot” (i.e., above room temperature), particles may nucleate and grow during the implantation stage. On the other hand, if the specimen is cooled to liquid nitrogen temperatures, the implantation process can generally be completed without the nucleation of nanoparticles in the implanted layer, depending on the interactions of the implanted ions with the host material (e.g., diffusion rates). Care must be taken, however, because many crystalline host materials can become amorphous during implantation at low temperature, potentially leading to zone refining and other issues discussed below. The total current on the sample is a delicate balance between implantation time and the potentially negative consequences of specimen heating and adverse dose-rate effects. In general, beam current densities less than $\sim 20 \mu\text{A cm}^{-2}$ are recommended.

Once the implantation process is completed, subsequent steps can be taken to nucleate and ripen the precipitates. This is usually done by high-temperature thermal processing in a controlled-atmosphere furnace (note that the term “annealing” is widely used in metallurgy to refer to heat treatment of metals). During thermal processing, a variety of nucleation and growth mechanisms occur, leading to the potential for many different microstructures and particle sizes. Diffusion-driven nucleation and ripening will depend on processing time and temperature, and on the interactions between the implanted ions and the host material. The selection of thermal processing atmosphere can also affect the particle size and microstructure and can have a major effect on the optoelectronic properties, due to surface passivation. Most anneals are done in reducing (ArH_2 , N_2H_2) or neutral (Ar or N_2) at-

mospheres in order to prevent unwanted oxidation of the particles or the host. However, in the case of oxide substrates, annealing in oxygen can promote diffusion of the implanted ions and reduce unwanted defects introduced by the implantation process, in particular for some of the noble metals, or it can create oxide nanoparticles instead of metals. In either case the annealing atmosphere is an important parameter in determining the final size distribution. The cooling rate can also be a critical parameter – if the specimen is quenched, high-temperature metastable phases may be formed. So-called “zone refining” can be a problem if the specimen becomes amorphous during implantation. During the thermal processing step, a crystalline–amorphous boundary can progress toward the surface as the host material recrystallizes epitaxially, thereby “refining”, or concentrating the implanted material nearer to the specimen surface. The affects of atmosphere, temperature, time, cooling rate, zone refining, etc. must be considered at the thermal processing stage.

The application of lasers for nucleating metal nanoclusters using frequencies on either side of the surface plasmon resonance (SPR) represents a powerful new tool for controlling the size and size distribution of the nanocrystals [4]. Various groups began investigating the use of laser annealing for creating metal nanocrystals with and without additional thermal treatments in attempts to narrow the size distribution of the metal nanocrystals. The effects on the metal nanocrystals were shown to depend upon the wavelength, power and pulse duration of the laser. Until very recently there were two processes used. In the first case, the substrate is transparent to the laser wavelengths and the radiation is absorbed by the metal nanocrystals. In the second case, the laser radiation is absorbed by the substrate in the UV region. At present, the fundamental understanding of the physics of either process on the changes of the metal nanoclusters is still an open question and the subject of continuing research.

More recently, the modification of the size of metal nanoclusters using a free-electron laser (FEL) with wavelengths in the range of 2–10 micrometers has been investigated [5]. In this scenario, the wavelengths corresponding to the vibration modes of the substrate are targeted. The excitation of the vibration modes can result in rapid heating and cooling of the composite with changes effectively occurring during the duration of the pulse. This technique was used in an effort to avoid difficulties produced with a high-temperature thermal processing discussed above. Initial efforts involving Au and Ag nanocrystals formed by ion implantation in type-III silica produced pronounced effects on the linear optical properties of the composite as well as on nanocrystal size. While conventional thermal treatments have been demonstrated to be sensitive to the annealing atmosphere, the FEL process showed no dependence on atmosphere.

Ion implantation will often produce a near-Gaussian concentration gradient of the implanted material, which can lead to wide size distributions

if the larger clusters form at the peak of the implanted ion concentration. A commonly employed method to narrow this size distribution uses multiple implantation energies to obtain a more uniform concentration gradient in the sample. In order to narrow the size distribution, some workers avoid the thermal processing steps altogether – instead preferring to use a subsequent high-energy ion irradiation to nucleate precipitates in the implanted layer in a process similar to that for doped glasses, with some of the same advantages. In theory, at least, it should be possible to obtain narrower size distributions – although, unlike for doped glass, the concentration variation across the implant profile can remain problematic. At this point, irradiation of preimplanted layers has not yet produced any striking benefits over thermal processing.

Other methods for narrowing the size distributions have produced some success. One is the use of low-energy implants (e.g., <20 keV), which limits the implanted-ion distribution to very shallow depths. A second is the use of a sequential ion-implantation process to modify the substrate with dopants that are incorporated into the substrate and do not precipitate out as nanoparticles. These modifications of the substrate before the nanocrystals are formed can result in changes in the defect zone around the inclusion due to the distortion of the local matrix and yield greater control over nanocrystal microstructure by providing more nucleation sites in the implanted zone [6]. Both of these techniques have been shown to help narrow size distribution, but have not provided significant advancement to solving the lateral-spacing control issues.

3 Microstructures

Particle-size distributions are generally wide, as compared to those obtained by solution chemistry and thin-film methods (chemical and physical vapor deposition), and bimodal size distributions are not uncommon. Figure 2 is a

Fig. 2. Cross-sectional TEM images of InP, PbS, or ZnS nanocrystals in SiO₂. See [7] for implantation and thermal-processing conditions. Note the location of the band of larger particles in each of the specimens

Fig. 3. Cross-sectional images showing Fe nanoparticles in a [110]-oriented YSZ wafer (*left*) and in a fused silica substrate (*right*). In YSZ the particles are well-faceted cubes, whereas in fused silica they show only a hint of faceting

set of cross-sectional TEM micrographs showing bimodal size distributions in compound semiconductor nanocrystals. Particularly interesting is the location of the layer of large particles. Pure Ostwald ripening would imply that the largest particles should form in the region of highest implanted-ion concentration (i.e., at the center of the implant profile), as is the case of PbS nanocrystals in SiO₂. However, in practice, a layer of larger precipitates can form near the surface (e.g., InP nanocrystals) or at the back of the implanted layer (ZnS nanocrystals) [7]. In the case of ZnS, the layer of large particles corresponds to the boundary between SiO₂ that was damaged by the implantation process and the pristine SiO₂ at greater depths. A similar effect occurs for metallic Zn nanocrystals in SiO₂. Zn rapidly diffuses into the substrate during thermal processing, probably at a faster rate in the ion-beam damaged surface layer. This leads to a “piling up” of implanted material at the boundary, creating the layer of larger nanocrystals. Other materials have a preference to migrate toward the surface during annealing – potentially leading to the type of microstructure characteristic of InP nanocrystals in fused silica. Attempts to narrow the size distributions by using lower-temperature thermal processing or irradiation-induced nucleation and growth have met with some success. Laser annealing has added to this success in controlling the size of the nanoparticles and may be more compatible with device-fabrication processes.

Precipitate faceting and crystallographic orientation can be controlled by the selection of host material and by the thermal processing conditions. Nanocrystals that form in a crystalline matrix have a strong tendency to be crystallographically aligned with the host. Figure 3 shows cross-sectional TEM micrographs of Fe nanocrystals in yttrium-stabilized zirconia (YSZ)

Fig. 4. Cross-sectional TEM micrograph showing Zn precipitates in silicon. The particles have an octahedral form in the silicon, despite the fact that zinc has a hexagonal crystal structure. After [9]

and fused silica hosts. In the glass, the Fe nanocrystals are spherical and randomly oriented; whereas in the YSZ, they have a well-faceted cubic shape and are crystallographically aligned [8]. The actual orientation relationship appears to be similar to the stress minimization that occurs in thin films – crystallographic directions that have similar spacings or multiples of spacings tend to align parallel to one another. In many cases, more than one specific orientation is possible due to the equivalence of crystallographic directions.

On the other hand, particle faceting is strongly controlled by surface-energy considerations. This is because the host material must “open up” to accommodate the particle. For example, nanocrystals embedded in pure silicon tend to form octahedra with apices pointing in the three equivalent $[100]$ directions of the host. Figure 4 shows nanoscale octahedra of Zn embedded in crystalline Si [9]. The faces of the octahedra are parallel to silicon $[111]$ planes – which have the lowest surface energy. The fact that zinc is not cubic and does not normally form octahedral crystals is clear evidence of the importance of the host material in governing precipitate morphology. For similar reasons, nanocrystals formed in YSZ have a cubic form, while those in sapphire frequently appear triangular or hexagonal when viewed down the $[0001]$ axis of the Al_2O_3 .

Thermal processing also affects the particle size and size distribution, and the defect concentration in the host material. Obviously, a higher processing temperature or a longer time tends to produce larger particles and/or fewer defects. This can be very important, for example in the case of silicon nanocrystals in which both the size and interface defects (dangling bonds) play major roles in the resulting luminescence properties [10]. Recently, a

detailed investigation explained the physical origin of the lognormal size distributions characteristic of nanocrystals formed by ion-implantation and thermal-processing methods [11].

Clearly, the main factors controlling size distributions and precipitate microstructures are: ion species, implant fluence, implant temperature, thermal-processing time, temperature, atmosphere and cooling rate, and the selection of host material. Variation of one or more of these parameters provides experimental control over the average size, orientation, faceting, and composition of the resulting nanocrystals. The relatively wide size distributions and lack of lateral spatial control obtained by these methods remain some of the most significant problems associated with the ion-implantation technique. New methods, such as lithographic masking and focused ion beams offer hope for obtaining better size distributions in the near future, as discussed in Sect. 5.

4 Optoelectronic Properties

The versatility of the ion-implantation method has permitted the synthesis of a wide variety of nanoparticle-host combinations. The main goal of this research is in the creation of new materials with well-controlled optical, electronic, or magnetic properties. The following sections discuss the main physical effects and outline the optoelectronic properties of nanocomposites produced by ion implantation. A considerable portion of the work has concentrated on nonlinear optical effects, light-emitting applications, and magnetic properties of implanted nanocomposites, so these three topics will be given separate headings.

4.1 Nonlinear Optical Materials

Nanocomposites produced by ion implantation have many attractive characteristics with respect to nonlinear optics [1, 12, 13]. Both metal and semiconductor nanocrystals can exhibit pronounced third-order optical susceptibility, although for somewhat different reasons. Most of the work on ion-implanted materials has been done on metallic nanoclusters, due to the large local-field enhancement produced by the real part of the metal dielectric constant. Metal–nanocluster composites formed by ion implantation exhibit distinct optical effects including: (1) absorption due to surface-plasmon resonance, and (2) strong third-order nonlinear optical susceptibility.

Both classical electronic and quantum processes are responsible for these effects. The contribution of each process to the total optical response is a strong function of size, shape and ion species. 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 effect, the conduction electrons oscillate as a group with a characteristic

frequency that depends on the electronic properties of the particles and of the host. In addition, the confinement of the electronic wavefunctions to a volume much smaller than the bulk mean free path produces an additional contribution to the electric susceptibility.

Assuming noninteracting particles, size effects can be divided into three regions for small spherical nanoparticles [14]. The first is for diameters < 5 nm where quantum-size effects can become important and dominate the nonlinear optical properties. The second region extends from approximately 5 nm to 50 nm in diameter. For such particles the dielectric functions of the metal are expected to approach that of the bulk metal. In this region the extinction is dominated by the dipole absorption term for particles less than ~ 25 nm in diameter with scattering becoming more important as the diameter increases. The absorption and scattering cross section contributions as a function of particle size are also a function of ion species. The third region is for nanoparticles > 50 nm in diameter. In this third region higher-order multipole terms are needed to describe the extinction both in absorption and scattering, again with higher-order scattering terms becoming more important with increasing diameter. The additional higher-order multipole terms lead to additional absorption peaks due to the higher-order multipole resonances. It is noteworthy that additional important effects can arise for the linear and nonlinear optical properties for nonspherical nanoparticles as discussed in [14, 15]. Other effects can also modify the optical absorption for nanocrystals. Particle-particle interactions can occur resulting in the appearance of a second peak in the absorption spectra that splits from the electric dipole SPR peak and redshifts away from the dipole peak with increasing degree of interaction.

For clusters of size in region 2, the optical field is nearly constant across the particles and the absorption is described by the electric dipole approximation derived by Mie and Maxwell-Garnett, and refined by Fröhlich in the first half of the twentieth century:

$$\alpha = p \frac{18\pi n_d^3}{\lambda} \frac{\varepsilon_2}{(\varepsilon_1 + 2n_d^2)^2 + \varepsilon_2^2}, \quad (1)$$

where α is the absorption coefficient, p is the volume fraction of the precipitates, n_d is the refractive index of the host, and ε_1 and ε_2 are the real and imaginary parts of the wavelength-dependent metal dielectric constant. The peak absorption occurs when $\varepsilon_1 + 2n_d^2 = 0$, at the surface-plasmon resonance frequency. Further effects occur as particle sizes become smaller than the electron mean-free path, when free-electron contributions to the metal dielectric function are strongly affected by the particle surface. The surface-plasmon resonance absorption both weakens and broadens due to a resulting linear increase in the imaginary part of the dielectric constant (ε_2) with decreasing particle size, and there is also a weak blueshift of the resonant energy. One of the problems with the size distribution observed in nanoclusters formed by ion implantation is that surface-plasmon resonance peak position, magnitude,

and full width at half-maximum are due to the distributions of particle sizes in most samples. The broader size distribution leads to greater absorption for all wavelengths, because larger nanocrystals have larger absorption cross sections than the smaller nanocrystals, as well as increasing the possibility of scattering. Larger particles can dominate the optical properties of the composite provided that the numbers of large and small particles is comparable. This increase in absorption can lead to some degradation of the figure of merit, as discussed below for these materials.

The effective third-order optical susceptibility ($\chi_{\text{eff}}^{(3)}$) is strongly enhanced by local electric fields near the surface-plasmon resonance frequency. This enhancement is considerably larger for metals than for semiconductors. In the dielectric approximation, the intensity of the nonlinear susceptibility depends on several of the same parameters as the surface plasmon absorption [16]:

$$\chi_{\text{eff}}^{(3)} = p \left[\frac{3n_d}{\varepsilon_1 + \varepsilon_2 + 2n_d^2} \right]^2 \cdot \chi_{\text{met}}^{(3)}, \quad (2)$$

where $\chi_{\text{met}}^{(3)}$ is the third-order susceptibility of “bare” metal clusters. The $\chi_{\text{met}}^{(3)}$ term varies with frequency due to variations of the energy and coherence relaxation times that are themselves dependent on the electronic properties of the specific metal. For cluster sizes smaller than the mean-free path of the conduction electrons, $\chi_{\text{met}}^{(3)}$ is proportional to $1/r^3$, where r is the radius of the nanoparticle [17]. Therefore, decreasing the particle size has the double benefit of enhancing the third-order susceptibility due to confined conduction-band transitions, and simultaneously decreasing the optical density due to an increase in ε_2 . Note that the increase in ε_2 also decreases $\chi_{\text{eff}}^{(3)}$; however, this decrease is overwhelmed by the larger increase in $\chi_{\text{met}}^{(3)}$. Thermal effects can also enhance $\chi_{\text{eff}}^{(3)}$ through the thermo-optic coefficient of the composite, although the thermal relaxation lifetimes must be short for device applications. The effective medium theory used to model the nonlinear optical properties has recently been extended to include nanoparticles in a nonlinear medium and core-shell effects. In the latter case the core and shell can both be metallic, or one metallic and the other a semiconductor. This additional work has indicated that even greater enhancements of $\chi_{\text{eff}}^{(3)}$ of the nanoparticles is possible as the nonlinearity of the host matrix increases or for core-shell nanoparticles leading to the possibility of several orders of magnitude increase in the nonlinearity of the composite [18].

Experimental techniques can readily be used to measure the nonlinear refractive index, nonlinear absorption, obtain the decay rates, and deconvolute the thermal and electronic contributions to the optical susceptibility. Both four-wave mixing and Z-scan techniques have been used to measure the nonlinear properties of ion-implanted specimens, and each technique has its own specific advantages and limitations. In cases where absolute values of $\chi_{\text{eff}}^{(3)}$ in ion-implanted nanocomposites have been measured (e.g., Au nanocrystals in SiO_2 and Al_2O_3 , and Cu clusters in SiO_2), the nonlinear refractive

index exceeded by as much as several thousand times that of quenched nanocluster glass composites, with picosecond response times for the electronic component of the nonlinear index. Particle-size-induced enhancement in the third-order susceptibility was clearly observed. Short switching times and the large values of n_2 and $\chi_{\text{eff}}^{(3)}$ have led many authors to suggest potential applications for these materials in optoelectronics.

Despite these attractive characteristics of ion-implanted nanocomposites, difficulties remain to be addressed. A figure of merit for absorbing nonlinear optical materials is $\chi^{(3)}/\alpha\tau$ [19], where τ is a relaxation time. Metal nanocluster composites produced by ion implantation have high values of $\chi^{(3)}$; however, both $\chi^{(3)}$ and α have a peak near the same wavelength (when $\varepsilon_1 + 2n_d = 0$). The high value of α and the corresponding long thermal relaxation time decrease the figure of merit for these materials, particularly for laser excitation lasting longer than a few ps. For high-pulse-repetition-rate applications, reducing the overall thermal relaxation time is also critical.

Recent work has aimed at finding methods for reducing the optical density due to the surface-plasmon resonance, while maximizing $\chi_{\text{eff}}^{(3)}$. This can, in theory, be accomplished if one can synthesize a uniform size distribution of nanoparticles whose radius is smaller than the electron mean-free path. In the quantum-confinement regime, $\chi_{\text{eff}}^{(3)}$ varies as $1/r^3$, and α is decreased due to the weakening of the plasmon resonance. So far, however, it has not been possible to produce suitably narrow size distributions by ion implantation, so research has been instead focusing on other means to minimize α and maximize $\chi_{\text{eff}}^{(3)}$. For example, in one experiment both Au and Ti were implanted into silica glass [20]. The implanted Au precipitated as metallic colloids but the Ti remained dissolved in the glass. The polarizable Ti ions increased $\chi_{\text{eff}}^{(3)}$ by a factor of approximately 2. This type of multi-implantation protocol can also be used to increase or decrease the refractive index, depending on the metal dielectric function and the optical frequency. In another multi-implantation experiment, surface plasmon absorption from Ag nanocrystals in SiO_2 was found to become weaker with an increasing concentration of implanted Sb [21]; whereas, Ag + Cd-implanted SiO_2 exhibits absorption that is consistent with a superposition of the surface plasmon peaks from both Ag and Cd phases [22]. Similar effects have been observed in a variety of other metallic alloy nanocrystals. By implanting various concentrations of Ag + Cu into SiO_2 , a transition can be induced from the nonlinear absorption to nonlinear saturation regime [23]. Other experiments have aimed at forming bimetallic “core-shell” nanoparticles, where changes in the electronic properties across the core-shell boundary add an additional degree of freedom for the experimental reduction of α and for increasing $\chi_{\text{eff}}^{(3)}$.

The nonlinear optical properties of ion-implanted nanoclusters composites are attractive for a variety of reasons, including high values of $\chi_{\text{eff}}^{(3)}$, short response times, relative ease and flexibility of synthesis, and compatibility with materials processing technology widely employed in industry. Research

is focusing on multi-implantation means to enhance the figure of merit and on narrowing the size distributions (thereby providing the double benefit discussed above). Both aspects of metal-quantum-dot nanocomposite research will be critical with respect to future device applications. Surface-plasmon effects may find applications as optical filters or in future devices based on the “plasmon waveguide” concept [24]. Surface-plasmon oscillations of closely spaced nanoparticles are coupled in the near field, giving rise to a coherent energy propagation that can be guided along chains or arrays of nanoparticles. This could represent a new way to transmit and guide optical signals on dimensions smaller than the diffraction limit. Surface-plasmon resonance may also find applications in submicrometer “plasmon printing” lithography, where a broad optical stimulus excites the surface-plasmon resonance of strategically placed nanoparticles, which in turn emit light at a wavelength that develops a photoresist in their immediate vicinity [25]. Other potential areas of use that may not depend as strongly on the control of the size distribution are optical recording [26], sensitizers in erbium-doped fibers [27] and enhanced photoconductors [28]. However, for broad acceptance of ion implantation to applications in many of these areas, it will be necessary to control the size, size distribution and lateral spacing of the metal nanoparticles.

4.2 Light-Emitting Materials

The effects of particle size on optical properties are also pronounced in semiconductor nanoparticles. Many review articles [29, 30] and books [31, 32] deriving in detail the basic physics of nanoscale semiconductors have been published. In semiconductor nanocrystals, the energy bands become quantized at energies that are a function of the radius, r , of the crystal [33]:

$$E = \frac{\chi^2 \hbar^2}{4r^2} \cdot \left[\frac{1}{m_e^*} + \frac{1}{m_h^*} \right] - \frac{1.8e^2}{\varepsilon_2 r} + \frac{e^2}{r} \cdot \sum_{n=1}^{\infty} a_n \left(\frac{S}{r} \right)^{2n}, \quad (3)$$

where χ is the root of the spherical Bessel function, m_e^* and m_h^* are the effective masses of electrons and holes, a_n is a term that depends on the dielectric properties of the particle and the host, and S is a position variable. The first term on the right-hand side of (3) is the electron-hole quantum localization term, the second is the Coulomb attraction term, and the third is due to polarization. The polarization term is small compared to the first two terms and can often be ignored.

The exciton radius, r_e , can be estimated with the following equation:

$$r_e = r_B \frac{\varepsilon \cdot m_e}{\left[\frac{1}{m_e^*} + \frac{1}{m_h^*} \right]}, \quad (4)$$

where r_B is the Bohr radius (0.053 nm), ε is the dielectric constant of the nanocrystal, and m_e is the electron rest mass. Materials that have a large exciton radius (e.g., PbS: 20 nm; CdSe: 9 nm) should show pronounced quantum-confinement effects; whereas, if the exciton radius is small (e.g., Si: 4.3 nm;

Fig. 5. Photoluminescence spectra from Si nanoclusters in SiO_2 , after [59]

CdS: 3.5 nm; ZnS: 2.5 nm), the precipitates must be correspondingly smaller in order for strong confinement effects to be observed. Other effects controlling the optical properties of semiconductor nanocrystals involve the spatial isolation of nonradiative traps and the electronic states at the cluster/matrix interface.

Many types of single-element and compound semiconductor nanocrystals have been formed by ion implantation of either fused silica glass or sapphire wafers. Figure 2 shows that the microstructure of these composites can be complicated, and the size distributions are wide compared to semiconductor nanocrystals synthesized in solution, and compared to nanocrystals in films formed by physical or chemical vapor deposition. Nevertheless, these composites show clear evidence of quantum confinement and can demonstrate relatively intense light emission.

Silicon nanocrystals embedded in fused silica have been the most extensively investigated semiconductor nanocomposite formed by ion implantation. Although in a short chapter it is impossible to summarize the hundreds of papers published on this topic, some of the basic observations can be summarized. Shortly after the report of strong visible PL in porous silicon [34], Si nanocrystals formed by ion implantation of Si into SiO_2 glass were found to exhibit a strong and broad PL peak at wavelengths centered at ~ 750 nm [35]. Since the initial observation, many workers have reported and confirmed intense PL at 750–950 nm from Si nanocrystals embedded in silica glass (e.g., Fig. 5). The emission dynamics follow the stretched exponential function with characteristic decay times of several tens to hundreds of microseconds and an exponent, β , of ~ 0.7 . Si nanocrystals produced by implantation of silicon into SiO_2 have potentially attractive properties with respect to possible silicon-based lasers [36, 37], light-emitting diodes [38, 39], and nonvolatile memory [40, 41]. Optical gain has been reported in ion-implanted silicon nanocrystal composites [42, 43]. The waveguiding properties of silicon nanocrystal layers have been extensively investigated [44] and the relevant optical cross sections are well known (e.g., [45]).

The ion doses and energies (and postimplantation annealing) required for forming highly luminescent silicon nanocrystals are interdependent parameters. The most intense PL appears to occur for film compositions close to $\text{SiO}_{1.5}$ [46]; at higher silicon concentrations the nanocrystals can become large and interconnected, while at lower silicon concentrations the number density of luminescent nanoclusters is low. For ion energies ranging from tens to hundreds of kV, implant fluences are typically in the range of 10^{16} to 10^{17} ions cm^{-2} . Generally, SRIM simulations are run in order to obtain the desired concentration gradient in the specimen. A major difficulty for the ion-implantation technique is the near-Gaussian concentration gradient of implanted silicon that causes a much wider size distribution than can be obtained, for example, by physical vapor deposition.

The microstructure of silicon nanocrystals produced by ion implantation has been extensively investigated by several groups [47–51]. There is evidence for the generation of amorphous silicon-rich regions when specimens are annealed at temperatures lower than 900°C , as confirmed by a detailed study of films grown by electron-beam evaporation [52]. At higher annealing temperatures, the silicon nanocrystals are well crystallized, demonstrating few lattice defects and good crystal faceting. For higher implanted-ion concentrations, larger nanocrystals have been reported to contain twin planes and stacking faults, with a critical diameter for the presence of these volume defects of $\sim 5\text{--}6\text{ nm}$ [49]. These crystal shapes have also been investigated by Monte Carlo simulations [53]. Size distributions are narrower than for compound nanocrystals formed by ion implantation, and can be further narrowed (or involve the formation of platelet structures) by using low-energy implants, as has been done for silicon-nanocrystal-based nonvolatile memory devices [54, 55].

The sensitizing action of silicon nanocrystals for 4f-shell transitions in Er^{3+} is of particular technological interest (e.g., see [56, 57] and references therein). Ion implantation offers a versatile and flexible method to control the concentration of erbium within the layer of silicon nanocrystals, subject to the limitations of the concentration gradient discussed earlier. The erbium site has been determined to be outside the nanocrystals [58]. In order to form silicon-nanocrystal-sensitized erbium-luminescent films, one may coimplant silicon and erbium (the latter to a much lower implanted concentration in order to avoid undesirable erbium–erbium interactions) followed by thermal processing to precipitate the clusters and activate the erbium. Alternatively, one can first implant the silicon and treat at high temperature, followed by erbium implantation and a second postimplantation thermal processing to recover the crystallinity of the nanoclusters. The latter method has the advantage that the optimum temperature for activating the erbium ions can be selected independently of the initial high-temperature treatment required to nucleate and grow the nanocrystals.

The origin of the intense red and infrared luminescence characteristic of Si nanocrystals in fused silica has been a matter of considerable debate. Although not the main object of this short chapter, a very brief discussion of this contentious topic is given. Several effects probably play important roles, including quantum confinement, the effects of radiative centers and nonradiative traps at the nanocrystal/matrix interface, and transfer of carriers between closely spaced nanocrystals. Hydrogen annealing enhances the PL intensity from Si nanoparticles in SiO₂ [59, 60], probably due to effective passivation of nonradiative traps. The critical role of the interface was recently confirmed in a study using electron spin resonance to identify dangling Si bonds at the SiO₂/Si interface as the main nonradiative recombination site [61]. One model consistent with these observations is that light emission from SiO₂-Si composites is controlled by two types of surface “defects”: the Si=O double bond, if present, may be the effective radiative recombination site, and the dangling Si bond, if present, is the preferred nonradiative site. A slightly more detailed model consistent with some of the existing observations has recently been proposed [62]. In this “reactive nanocluster” model, interactions between nearby particles separated by a thin oxide layer decreases the effective energy levels of the radiative interface defects. Others have shown the critical importance of migration of carriers from smaller clusters to larger ones [63]. The physical mechanisms responsible for the PL of silicon nanoclusters appear to be very complicated and continue to lead to much constructive debate in the literature.

Since germanium has a larger exciton radius than Si, quantum-confinement effects should, in theory, be even more pronounced for Ge nanocrystals. Like with Si nanocrystals, Ge clusters may also find nonvolatile memory applications [64]. Many experiments, of which only a small sampling can be provided here, have shown that Ge-implanted and annealed SiO₂ has a fairly pronounced and quite broad emission line peaking in the red or infrared, possibly with a defect-related emission in the blue. The red band has been ascribed to radiative recombination of quantum-confined excitons, but most studies have suggested oxide-related luminescent defects [65–67]. The interface defect hypothesis clearly illustrates the importance of detailed studies in order to determine the origin of the luminescence from Group IV nanocluster composites formed by ion implantation. The microstructure of Ge nanocrystals formed by ion implantation seems to be generally similar to that for silicon – i.e., narrower than for compound nanocrystals but still limited by the implanted-ion concentration profile. Recent work has demonstrated narrower distributions by using a low-energy Ge implantation protocol [68].

Direct-gap compound semiconductor nanocrystals formed by ion implantation can also be strongly luminescent. For example, GaAs nanocrystals formed by sequential implantation of Ga and As in fused silica luminesce in the red and near-IR portions of the spectrum [69]. The emission mecha-

nism is not fully understood, although quantum confinement probably plays a role, since the emission energy is slightly higher than the bandgap of bulk GaAs. ZnS nanocrystals in fused silica are usually not luminescent (probably due to nonradiative defects and the small exciton radius); however, implantation of a manganese impurity into the ZnS nanocrystals creates a weak yellow luminescence band [70]. Excited carriers in the ZnS nanocrystals are probably trapped at levels associated with the incorporated Mn ions. The emission is at shorter wavelengths than for bulk Mn-doped ZnS and has been observed only for the smallest ZnS nanoclusters. Both observations suggest that quantum confinement is a likely origin for the yellow luminescence.

Al₂O₃-CdS composites seem to be more strongly luminescent and have been investigated using single-particle spectroscopy techniques. Composites annealed at 1000°C in a reducing atmosphere show a broad, relatively intense luminescence band centered at ~500 nm, near the bandgap of bulk CdS. This PL is nearly independent of particle size, suggesting the influence of defects. Using scanning near-field optical microscopy (SNOM), two-dimensional luminescence images of CdS nanoclusters in Al₂O₃ have been obtained [71]. These images show randomly distributed bright regions attributed to the presence of CdS nanocrystals. Individual spectra were obtained from each of these regions, which permitted the broad emission band from the entire composite to be resolved into separate sharper components from each bright region. The narrower lines in each single-particle spectrum were consistent with a variety of oxygen and aluminum defects and impurities within the CdS nanoparticles. Different particles contained different defects, so the broad luminescence of the entire composite is actually a sum of several sharper peaks. If this interpretation is correct, sharp emission bands will be difficult to obtain from ion-implanted samples even if the size distributions are narrowed, since impurities from the host material may always be present.

Recently, PbS nanocrystals formed by ion implantation have been found to have many interesting properties, including strong luminescence in the technologically relevant infrared wavelength range around 1.5 micrometers [72–74]. These investigations explained the complex microstructures that had been observed in previous reports (see Fig. 2), and greatly enhanced the luminescent properties of the PbS nanocrystals via better-controlled nucleation and growth techniques. This work even demonstrated the luminescence blinking properties and energy splitting of the ground-state exciton that had previously been observed almost exclusively in solution-based nanocrystals. Due to the high degree of control over the particle-size distribution (at least, for ion-implantation studies), this work appears to represent one of the most promising routes toward feasible luminescent devices based on nanocrystals formed by ion implantation.

Several other potential applications for ion-implantation-produced semiconductor nanocomposites are being investigated. For example, semiconductor nanocrystals embedded in a gate oxide have charge-storage capabilities that may be useful in future high-performance nanocrystal-based floating-gate memory devices [75]. Continuous layers of superconducting nanoparticles can be formed in thin films on silicon, suggesting possible integration of superconducting materials compatible with silicon technology [76]. Ion implantation can also be used to create lightweight engineered nanocomposites with remarkable durability, where the embedded nanocrystals harden the surface and reduce crack formation. Photovoltaic devices based on the ion-implantation concept are being explored. If size-graded particles can be embedded in an appropriate matrix, the effective bandgap could be tailored to extend across the solar spectrum.

4.3 Magnetic Materials

Ion implantation can be used to create ferromagnetic nanocomposites consisting of transition-metal nanocrystals embedded in an insulating host. By injecting varying concentrations of Fe, Co, or Ni into dielectric host materials such as SiO_2 , soft magnetic composites are created, with low coercivities and a magnetic moment per atom similar to that of bulk magnetic material. Superparamagnetism is often observed due to particle sizes well below that needed to prevent random thermal reorientation of the particle magnetization. Blocking temperatures have been calculated from the precipitate sizes and anisotropy constants, and seem to agree reasonably well with experimentally observed blocking temperatures obtained from field-cooled and zero-field-cooled measurements of the magnetization. Nevertheless, the size distributions are relatively wide and the thermal blocking temperature is accordingly smeared over a range of temperatures.

One motivation for research on ferromagnetic nanocomposites produced by ion implantation has been the potential for creating materials with applications in magnetic recording (see chapter “Magnetic Properties and Ion Beams: Why and How” by Devolder and Bernas). Single-nanocrystal-per-bit data recording could represent an important step forward for the information storage capacity of such media [77]. Nevertheless, several stringent requirements must be satisfied in order to achieve device-quality performance. For single-particle bits to be written individually, the precipitates must be discrete, magnetically isolated, single-domain ferromagnetic nanoparticles that are larger than the superparamagnetic limit and whose coercivity, size, orientation, and position can be controlled. Ferromagnetic nanoclusters produced by ion implantation are single domains, they can be made larger than the superparamagnetic limit, the coercivity can be controlled by postimplantation treatment or by creating magnetically hard alloy particles, and the crystallographic orientation (and, therefore, magnetic anisotropy directions) can be

selected. However, the question of magnetic isolation is debatable, particle-size distributions are wide, and there has been, until recently, no inplane spatial control over the distribution of nanoclusters.

In ferromagnetic nanocrystalline composites, experimental data is usually explained by assuming an ensemble of particles that do not interact magnetostatically and whose anisotropy axes are randomly oriented. Ion implantation offers an excellent opportunity to test these assumptions, because nanoparticles can be formed that are *not* randomly oriented, and that have symmetrical crystal shapes including cubes (e.g., Fig. 3) or hexagonal prisms. Since the nanoparticles are single domains that show coherent magnetization reversal, only three main energy contributions control the magnetic properties of the composite [8]: (i) the Zeeman energy that couples the particle magnetization to the applied field, (ii) the net anisotropy energy of the particles, and (iii) the interparticle interaction energy. The second term is often the most difficult to estimate, because there are several contributions to the effective anisotropy, including crystalline anisotropy, shape anisotropy, surface anisotropy, and magnetostriction.

Strong arguments have been put forth that support interparticle interactions in ion-implanted composites [8, 78]. For example, a [110]-oriented specimen of YSZ was implanted with Fe to a dose of 8×10^{16} ions cm^{-2} and annealed in Ar + 4% H_2 in a two-step process (1 h at 1000°C with a slow cool, followed by 2 h at 1100°C, after which the sample was quenched). This produced a layer of Fe nanocrystals that were crystallographically aligned in one of three possible orientations. A single [100] axis of the Fe was oriented with one of the three [100] axes of the YSZ, and the other two equivalent $[100]_{\text{Fe}}$ axes were aligned with the [110] directions in the YSZ [8]. Computer simulations of the magnetic hysteresis of a layer of interacting, crystallographically oriented “nanocubes” of α -Fe closely matched the experimental results, whereas simulations for noninteracting particles did not [78]. The orientation dependence of the magnetic hysteresis was found to be consistent with the concept of frustration among groups of particles.

Further experimental evidence in favor of the interacting-particle model comes from the temperature dependence of the coercivity. For small particles, the relationship between temperature and coercive field, H_c , is:

$$\frac{H_c(T)}{H_c(0)} = 1 - \left(\frac{T}{T_B} \right)^n. \quad (5)$$

Here, T_B is the blocking temperature and the exponential term n is close to 0.5 (it is exactly 0.5 for uniaxial anisotropy). T_B is proportional to the particle volume (V) and the anisotropy constant (K) and can be estimated for a specific experimental condition (for example, $T_B \cdot KV/100k_B$ for cubic anisotropy, a measurement interval of 100 s, and a flip attempt frequency of 10^9 s^{-1}). Sorge et al. [8] found that the temperature dependence of oriented α -Fe nanoparticles deviated strongly from the expected $T^{0.5}$ relationship, further supporting the interacting nature of the composite.

Estimates were made of the ratio $4\pi M_{\text{sat}}^2 f : 2K_{\text{eff}}$, where M_{sat} is the saturation magnetization, f is the volume fraction of particles in the implanted layer, and K_{eff} is the effective anisotropy constant. The first term is an estimate of the nanoparticle interaction, and the second is the energy contribution from the magnetic anisotropy. Making reasonable estimates for the contributions to K_{eff} leads to a ratio of almost 4:1, further evidence in favor of strongly interacting particles [8]. Schulthess et al. [78] also point out that the changes in the hysteresis loops from magnetostatic interactions are qualitatively similar to those that result from random orientations of the magnetic anisotropy. Nevertheless, the story is probably not complete, nor by any means universally accepted.

With respect to magnetic recording media, ion implantation offers the possibility of fine control over the magnetic properties of the nanoclusters. The first clear example of high-coercivity ferromagnetic nanoparticles made by ion implantation was demonstrated for Fe nanoparticles formed by implantation of high-purity copper [79]. In that work, coercivities as high as 1150 G were reported, and were attributed to stress in the particles, interstitial impurities, and increased anisotropy due to the cubic shape of the precipitates. More recently, it has become possible to obtain experimental control over the coercivity of ion-implanted nanocomposites (Fig. 6). By implanting 140-keV Co^+ at ambient temperature to a fluence of $8 \times 10^{16} \text{ ions cm}^{-2}$ into [0001]-oriented sapphire and subsequently annealing for two hours at 1100°C, well-faceted and crystallographically oriented Co nanoclusters were produced [80]. X-ray diffraction showed that the Co was a nearly 50:50 mixture of the cubic and hexagonal phases. Nanoparticles with the hcp Co structure were aligned with their c -axis parallel to the c -axis of the host sapphire; whereas, the ccp nanocrystals were aligned with a [111] axis parallel to the sapphire c -axis. This composite demonstrated the low coercivities more typical of specimens produced by ion implantation.

The magnetic hysteresis of this Al_2O_3 -Co composite can be modified by subsequent ion irradiation. By implanting Xe to various fluences through the Co nanoparticle layer, the coercivity of the composite can be increased from 50 to 460 G (Fig. 6) [80]. Implantation of Pt has an even more dramatic effect, with the coercivity increasing up to 1500 G. These results allow the nanocomposite to be tailored for a specific coercivity ranging from 50 to 1500 G. Further work has used coimplantation of Co and Pt to create CoPt alloy particles with the tetragonal L_{10} structure. This is an extremely hard magnetic material, and the specimens reach coercivities as high as 10,000 G at 5 K [81].

The properties of ferromagnetic nanocomposites produced by ion implantation are only just beginning to be understood from a fundamental perspective. A considerable amount of work will be required to obtain a more detailed understanding. The magnetic simulations recently performed by Schulthess et al. [78] are a step forward in this direction. A more detailed model that in-

Fig. 6. Plan-view TEM images of Co nanocrystals in sapphire and corresponding magnetic hysteresis, modified after [1]. (Co): 140-keV Co ions implanted to a fluence of 8×10^{16} ions cm^{-2} at 30°C . The specimen was subsequently processed at 1100°C for 2 h under flowing Ar + 4% H_2 , (Co:Xe): same as in (Co) but with a subsequent implantation of Xe (244 keV, 2×10^{16} ions cm^{-2}), and (Co:Pt): same as in (Co) but with an additional implantation of Pt (320 keV, 6.4×10^{15} ions cm^{-2} , 30°C). The different particle number densities in the TEM images are due to differing specimen thickness. After [80]

incorporates a dynamical spin-rotation method based on the Landau–Lifshitz–Gilbert equation and that includes a larger number of particles interacting in three dimensions, while computationally challenging, would provide considerable further understanding of the magnetic properties of these materials. Some of this work has already been started, and some unexpected results have been found, including ultrafast magnetic relaxation in iron nanocrystals formed by ion implantation that was attributed to cluster–cluster interactions [82], and a very large Faraday rotation [83]. With respect to applications, the ability to control the orientation and crystal structure of the ferromagnetic precipitates and the durable nature of the composites themselves are important advantages of the ion-implantation technique. Control over the magnetic hardness of the composite has now been obtained, although the exact mechanisms responsible for the increased coercivity have not been unambiguously identified. Another critical challenge will be in the creation of uniformly sized

particles patterned into a 2D array. Nanosensors based on the magnetostrictive effect have also been proposed (e.g., [84]). If ion implantation is to have applications in magnetic recording, this challenge will almost certainly have to be met. In Sect. 5, some of the future research directions toward these objectives are discussed.

4.4 Smart Nanocomposites

In the previous sections, some of the most promising applications for nanocomposites synthesized by ion implantation were outlined. Several other potential applications are being actively explored. One example of “smart” nanocomposite material developed by ion implantation is nanocrystalline VO_2 embedded in a SiO_2 matrix (Fig. 7) [85]. VO_2 is a transition-metal oxide that shows abrupt changes in electronic and optical properties at 67°C . On heating above this critical temperature the material undergoes a semiconductor-to-metal phase transition with a 10,000-fold increase in electrical conductivity and a significant decrease of the near-infrared optical transmission. It is precisely this near-room-temperature transition and the associated large optical and electrical property changes that have also made VO_2 a candidate material for a wide variety of technological applications such as thermochromic coatings, optical or holographic storage, laser scanners, and ultrafast optical switching. It is considered a particularly “smart” material because the switching/sensing functions are integrated in the intrinsic nature of the oxide without the need of external circuitry, control, or modular design.

VO_2 nanocomposites can be fabricated using the ion-implantation techniques described above. In particular, small VO_2 particles in the nanoscale regime have been produced in SiO_2 and Al_2O_3 substrates by coimplanting vanadium and oxygen ions at room temperature in a stoichiometric proportion. The implantation energies were 150 keV for vanadium and 55 keV for

Fig. 7. Transmission electron microscopy images of VO_2 precipitates in SiO_2 and their optical transmission vs. temperature at a $1.5\text{-}\mu\text{m}$ wavelength for selected annealing times. Shorter annealing times produced smaller precipitates and produce wider hysteresis loops. The samples were prepared by implanting SiO_2 with 1.5×10^{17} V ions cm^{-2} at 150 keV and 3.0×10^{17} O ions cm^{-2} at 55 keV and then annealing in argon at 1000°C . After [85]

Fig. 8. Linear optical transmittance at $\lambda = 800$ nm of a nanocrystalline VO_2/SiO_2 composite and a standard VO_2 thin film cycled through their phase transition. After [89]

oxygen ions, to ensure overlapping concentration profiles within 200 nm from the specimen surface. Thermal processing at 1000°C in a flowing high-purity argon atmosphere induced the precipitation of the VO_2 nanocrystals whose size was controlled by varying the growth time in the furnace from 2 to 60 min.

Figure 8 illustrates the linear optical transmittance at $\lambda = 800$ nm for both VO_2 nanoparticles and a 210-nm thick standard VO_2 thin film undergoing the same phase transition. The VO_2 phase transition is manifested by a decrease in optical transmission when the metallic phase is formed in both thin-film and nanocrystalline samples; however, the magnitude of the change is larger in the film since it contains five times more VO_2 by mass than the nanocrystalline composite. When normalized to an equal mass, the VO_2 nanoparticles present an enhanced optical contrast compared with thin films [86] and exhibit a significantly wider hysteresis than the thin-film sample. Systematic size-controlled studies have shown that the width of the hysteresis loop is, in fact, a size-dependent property. The origin of this behavior is rooted in the heterogeneous nature of the phase transition. Smaller precipitates show larger hysteresis due to the statistically small probability of finding a phase-transition nucleation site within a smaller nanoparticle volume [87].

When the nanoparticles are in the metallic phase, a strong surface-plasmon resonance is present – a feature that is absent in bulk VO_2 . According to (1), the large absorption coefficient at the surface-plasmon frequency can be calculated from the classical Mie formula for the polarizability of a spherical particle, for particle sizes much smaller than the wavelength of light. The surface-plasmon resonance in VO_2 nanoparticles can be observed only when the particles are in the metallic phase, in which the real part of the dielectric constant is negative. The relative change in transmission, $\Delta T/T$, as a function of wavelength in the case of large-aspect-ratio nanoparticles is well described by Mie scattering theory (solid curves of Fig. 9). According to Mie theory, the resonance condition for nonspherical particles depends on their orientation relative to the electric-field polarization. For ellipsoidal nanoparticles with their major axes parallel to the plane of incidence, Mie

Fig. 9. Relative change of transmission as a function of wavelength for several aspect ratios (*top to bottom*: 1, 1.5, 2, 3.5) as obtained by varying the annealing time (3, 7, 10, and 45 min, respectively). *Squares*, measured at a delay of 200 fs after photoexcitation; *solid curves*, calculations based on Mie scattering theory. As a comparison, *dashed curves* show the prediction of Mie theory for spherical particles (aspect ratio, 1; the same as in the topmost figure). Representative TEM pictures of the corresponding samples are shown *at the right*. After [88]

theory predicts absorption features at longer wavelengths for polarization parallel to the major axis. Therefore, the continuous angular distribution of randomly oriented rods in the ion-implanted samples results in an overall broadening of the absorption spectrum toward longer wavelengths.

Additional interesting features of the switching behavior of these ion-implanted nanocomposites include room-temperature operation, compatibility with fiber-optic environment, and high efficiency at telecommunication wavelengths (1.3–1.5 μm). Furthermore, the phase transition can be induced by infrared light pulses of less than 200 fs duration [88]. Indeed, the phase transition can be optically triggered by electronic excitation on a timescale shorter than that of a thermal path. The threshold for the photoinduced phase transition is 300 mJ cm^{-2} , which is equivalent to a 150-pJ pulse for a typical $50\text{-}\mu\text{m}^2$ size single-mode fiber, making possible the use of nanoscale VO_2 in all-optical switching schemes. In the particles with the highest aspect ratio, a switching efficiency of $\sim 25\%$ was observed at $1.55 \mu\text{m}$ over a propagation length of less than 100 nm and for a VO_2 filling factor of less than 10% [89]. One might achieve higher switching contrasts by increasing aerial filling factors or interaction length, although the nanosecond lifetime of the metallic state may limit the suitability of VO_2 for all-optical switching at high bit rates.

Ion implantation allows easy doping of the VO₂ nanoparticles with other ions by coimplanting them with the oxygen and vanadium prior to the heat thermal processing. The addition of other species is useful since they can help to tailor the critical temperature and hysteresis width of the phase transition. Tungsten in low atomic concentrations can decrease the phase-transition temperature below room temperature without producing a significant deterioration of the switching characteristics. In contrast, while titanium has little effect on the onset value of the transition temperature, it is found that it can significantly reduce the width of the hysteresis loop. Ion implantation may be one of the most attractive ways to produce nonequilibrium doping of smart nanocomposites in order to further control their properties.

5 Controlling Nanocrystal Size, Spacing, and Location

Despite the many potential applications, there are currently no commercial nanoparticle-based devices that make use of the ion-implantation concept. New ideas and advances are in various stages of development, and in some cases prototype devices have been built and tested. The major and most critical experimental difficulty yet to be overcome is control over the size distribution and spacing of the precipitates. Key research in a number of areas related to these problems is underway. This research is making use of newly developed focused ion beams, multiple-beam implanters, and submicrometer lithographic masking.

Focused ion beams (FIBs) are a readily available technology, with manufacturers claiming beam diameters of under 10 nm. Commercial FIBs have been developed primarily as thinning and cutting tools and are typically limited to Ga sources with a maximum beam energy of 35 kV, which are currently major limitations to their use as ion 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”. Accessories can now be obtained that permit a wider range of ions to be implanted. Some laboratories do have high-energy focused ion-beam machines, although these are often home-built and are not readily available commercially. Even if the voltage and source issues are overcome, FIB implantation is still a serial technique. Implantation of relatively large areas will, therefore, be a slow and costly procedure.

Lithographic masking is another technique that offers promise for controlling the distribution of nanoparticles within an implanted layer. The technique has been employed for decades in industry for precision doping of silicon wafers. The main difference in nanoparticle research is that the film material will have to withstand high heavy-ion-implantation fluences without physical degradation. A first example of patterned ferromagnetic nanoparticles was recently demonstrated [90], and subsequently the patterning of luminescent silicon nanocrystals via an ion-implantation mask was shown (Fig. 10) [91].

Fig. 10. Luminescent silicon nanocrystals array produced by high-fluence implantation through a metal mask. The letters in the “U of A” sign in the inset at the lower right are ~ 68 micrometers high. The image color images were obtained with a fluorescence microscope using an Ar ion laser as the pump. From [91]

In this example, a thick molybdenum mask was patterned directly on a fused silica wafer, using conventional deep UV lithography. The specimen was subsequently implanted $>10^{17}$ ions cm^{-2} (silicon and iron were tested in the references cited above). The results showed that the masking material did not observably degrade due to ion implantation, and micrometer-scale spatial control was obtained. By using finer-scale lithographic techniques, it may be possible to create considerably smaller features, with the ultimate goal of creating one particle at each mask hole, although certain technical challenges will have to be overcome in order to accomplish this objective (e.g., lateral straggling of the implanted ions).

One of the current technological advancements pursued in several laboratories is the production of a multibeam implantation instrument. Parallel implantation using many focused ion beams on a single machine would significantly speed the pattern-generating capabilities of the current generation of FIB instruments. Ion-beam projection through a stencil mask is a further promising idea under investigation. A conventional ion beam first impinges on a durable patterned mask, so that only the patterned regions are “projected” down the beamline. The subsequent “beamlets” are focused and demagnified until they impinge on a specimen. Other multifocused-beam instruments will be maskless, instead using a stacked multiaperture electrode–insulator structure to accelerate each parallel beam with the same accelerator electrodes. As these technologies are developed, it will become possible to control the spacing, and even possibly the particle size, in a relatively inexpensive, reproducible fashion that avoids time-consuming lithography and makes practical high-volume manufacturing of ion-implanted nanostructured materials.

6 Conclusion

In the past decade, ion implantation has been demonstrated to be a versatile and flexible method for creating single-element or compound nanocryst-

tals embedded in one of many possible host materials. To date, numerous nanocrystal–host combinations have been synthesized and their optical, electronic, magnetic, and microstructural properties investigated. A variety of possible applications has been identified that are being actively explored. The utility of the technique for creating an enormous variety of nanocrystalline composites is now well established. The research directions in the next decade will focus less on demonstrating the creation of new nanocrystal–host combinations, and more on solving the well-known difficulties associated with the technique and on developing new *classes* of materials with new properties (e.g., smart materials, micromechanical materials, or buried superconducting layers and wires). In the great majority of potential applications, it will be critical to narrow the size distributions. Advanced nucleation and growth techniques such as inverse Ostwald ripening or temporal separation of the nucleation and growth stages offer promise for improving size distributions. Lithography and parallel focused ion-beam instruments provide another means for potentially narrowing size distributions and patterning nanocrystal arrays on the submicrometer scale.

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