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Ion Beam Synthesis of Nanocrystals and Quantum Dots in Optical Materials*

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Abstract—High-dose ion implantation has been used to synthesize a wide range of nanocrystals and quantum dots, and these structures can be encapsulated in a number of host materials using this technique.

I. INTRODUCTION

Nanocrystals and quantum dots have attracted considerable interest recently [1]. For sufficiently small structures, quantum confinement effects can arise when the electrons are confined to regions smaller than their delocalized length. A result of this quantum confinement is the modification of their optical, electrical, and physical properties that may lead to a series of unique optical, electrical, and magnetic devices. Many methods are being explored to synthesize nanocrystals and quantum dots. High-dose ion implantation is an ideal method to create high densities of encapsulated nanocrystals in the near surface of a wide range of host materials. Implantation produces a supersaturation of an impurity and subsequent annealing leads to precipitation and the formation of nanocrystals and quantum dots encapsulated in the host material.

This method of synthesis is applicable to the formation of a wide range of nanocrystals and quantum dots. Metallic nanocrystals such as Au [2–5] or Cu [6] have been formed in fused silica by ion implantation, and these lead to dramatic changes in the optical properties and give rise to a refractive index which depends on optical intensity. Elemental semiconductor nanocrystals Si and Ge have been formed in fused silica by ion implantation [7–12] and then can give rise to strong photoluminescence (PL) in the visible and near IR regions, although the mechanism responsible for luminescence remains under investigation [13]. Implantation can even be used to produce Si or Ge nanocrystals in α - Al_2O_3 , and these are three dimensionally oriented with respect

to the matrix [14]. Finally, by sequentially implanting various combinations of ions to high doses followed by annealing, a wide range of compound semiconductor and alloy nanocrystals have been synthesized in a range of host materials including fused silica, α - Al_2O_3 , and crystalline silicon [15–22]. The ability to synthesize such a wide range of nanocrystals and quantum dots, and to control easily the stoichiometry and depth distribution of the nanoparticles makes ion implantation a very attractive method for their fabrication. Implantation may be the simplest method to produce some of these materials due to their sensitivity to high temperatures or oxidizing conditions.

To form nanocrystals by ion implantation, doses of $\sim 1 \times 10^{17}/\text{cm}^2$ or greater are used at energies chosen to give a projected range of ~ 100 nm. To form compound semiconductors or alloys, various combinations of ions are implanted at energies chosen to give an overlap of the profiles. The stoichiometry of the compound is controlled by the relative doses of the individual constituents. In our work, implanted samples are subsequently annealed in Ar + 4% H_2 to induce precipitation and nanocrystal formation. Various methods have been used to characterize the nanocrystalline composites including x-ray diffraction, transmission electron microscopy (TEM), Rutherford backscattering - ion channeling, Raman spectroscopy, and various optical measurements (absorption, PL, and infrared reflectivity).

II. Si NANOCRYSTALS IN SiO_2

Silicon and Ge nanocrystals can be synthesized in both fused silica and Al_2O_3 by ion implantation [7–14]. Fig. 1 is a cross-section TEM micrograph showing individual Si nanocrystals formed in an SiO_2 film on silicon. Multiple energy implants were used to produce an excess Si concentration of $\sim 5 \times 10^{21}/\text{cm}^3$ throughout the film, and the implanted sample was annealed subsequently at $1100^\circ\text{C}/1$ h in

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Ar + 4% H₂. Under these conditions, the average nanocrystal diameter is ~4 nm, and there are very few nanocrystals larger than 8 nm in diameter. Si nanocrystals of this size encapsulated in SiO₂ give rise to strong PL in the wavelength range of 7500 Å.

Fig. 2 compares PL from Si (400 keV, $6 \times 10^{17}/\text{cm}^2$) implanted SiO₂ following annealing with that observed from porous Si. The PL intensity from the sample containing the Si nanocrystals is comparable in intensity to that from porous Si but shifted in wavelength as shown. The intensity of radiation from Si implanted SiO₂ is observed also to be much more stable than that from porous Si. In the case of porous Si, the PL intensity decreases significantly as a function of time each time a new part of the sample is exposed to the excitation beam. By contrast, the PL intensity

Fig. 1. Z contrast cross-section TEM micrograph showing Si nanocrystals in SiO₂.

Fig. 2. PL arising from porous Si and from Si implanted SiO₂ after annealing. The excitation wavelength was 514.5 nm.

from Si implanted SiO₂ is not affected by similar changes in sample position.

Strong PL in the wavelength range of 7500 Å is observed only after annealing the implanted sample, and the wavelength can be shifted slightly to higher energies by reducing the dose or by reducing the annealing time, both of which are expected to reduce the particle size. Fig. 3 shows the dependence on dose and demonstrates that the peak wavelength can be shifted from ~7600 Å to ~6900 Å by reducing the dose from $6 \times 10^{17}/\text{cm}^2$ to $3 \times 10^{16}/\text{cm}^2$ (at 400 keV energy). Strong optical absorption is also observed in Si implanted SiO₂ after annealing, and the dependence of absorption on dose is much stronger than the PL dose dependence. Fig. 4 shows the measured transmission as a function of wavelength. The absorption edge shifts to higher energy as the dose (and therefore the particle size) decreases. Results in Fig. 3 and 4 are in qualitative agreement with the behavior expected if the radiation arises from quantum confined excitations, but interface states at the nanocrystal/oxide interface cannot be ruled out as the states responsible for the emission. Optical absorption and PL emission occur at significantly different energies, so the radiation cannot be band edge emission.

III. FORMATION OF COMPOUND SEMICONDUCTOR NANOCRYSTALS

The synthesis of compounds by sequential implantation represents a new direction of research for high-dose ion beam synthesis. In most of the previous work on compound formation by ion implantation, the matrix material was one of the major components of the compound [23]. However, it has been demonstrated that compounds can be formed by implanting both constituents at energies chosen to give an

Fig. 3. PL arising from Si (400 keV) implanted SiO₂ after annealing at 1100°C/1 h/Ar + 4%H₂.

Fig. 4. Optical transmission measured through fused silica samples implanted by Si (400 keV) and annealed at 1100°C/1 h/Ar + H₂. Results from the implanted samples were compared with those from unimplanted fused silica.

overlap of the profiles [15–22]. Fig. 5 demonstrates that GaAs nanocrystals can be formed in SiO₂, by the implantation of equal doses ($1.5 \times 10^{17}/\text{cm}^2$) of Ga (at 470 keV) and As (at 500 keV) followed by annealing (1000°C/1 h/Ar + H₂). The strong diffraction peaks arising from GaAs are observed in addition to scattering from the amorphous substrate (SiO₂) and the Si (200) multiple scattering peak from the underlying substrate. The sizes of nanoparticles in Fig. 5 extend to several hundred angstroms in diameter, but the nanoparticle size depends strongly on the dose, the annealing conditions, and the order of the implant [24].

Group II–VI compound semiconductor nanocrystals can also be formed by the sequential implantation of various combinations of Group II and Group VI ions [19]. The X-ray diffraction results in Fig. 6 show that CdSe nanocrystals are formed by the implantation of Cd and Se, and that CdS nanocrystals result from the implantation of overlapping profiles of Cd and S. For the case of Cd + 0.5Se + 0.5S, the diffraction peaks are intermediate between those of CdSe and CdS, suggesting that the mixed chalcogenide Cd₁Se_{0.5}S_{0.5} has been formed by the implantation of three ions. Results from Fig. 6 are supported by Raman measurements on the same samples.

A wide range of nanocrystals can be formed also in single-crystal silicon by sequential implantation of the individual constituents [15–17, 21, 22]. One example is the formation of GaAs encapsulated in crystalline silicon [21]. Fig. 7 is a

θ -2 θ scan along the [001] diameter of silicon showing strong peaks arising from the encapsulated GaAs in addition to the expected Si (004) reflection. In this case, implantation at elevated temperatures was used to preserve the crystallinity of the matrix during implantation, and elevated temperature annealing was used to reduce residual damage and promote nanocrystal growth. Detailed studies show that the GaAs nanocrystals formed in Si are three dimensionally oriented with respect to the matrix.

Fig. 5. X-ray diffraction demonstrating the formation of GaAs nanocrystals in SiO₂ by the implantation of Ga and As.

Fig. 6. Compound semiconductor nanocrystals formed by the implantation of equal doses ($1 \times 10^{17}/\text{cm}^2$) of Group II and Group VI ions into SiO₂, followed by annealing (1000°C/1 h/Ar + H₂).

Fig. 7. X-ray diffraction results showing GaAs nanocrystals formed by the implantation of equal doses ($1 \times 10^{17}/\text{cm}^2$) of Ga and As into crystalline silicon, followed by annealing ($1000^\circ\text{C}/1 \text{ h}/\text{Ar} + \text{H}_2$).

The synthesis of compounds by sequential ion implantation is a new direction of research for high-dose ion implantation because it presents opportunities to form many more compounds than previously demonstrated. These compounds can be synthesized in a variety of matrices. Table I shows a list of the compound semiconductor nanocrystals we have synthesized in SiO_2 , Al_2O_3 , and crystalline Si [18–21], and results of others are reported in [15–17,22]. Nanocrystal size and size distribution depend on the dose, the annealing conditions, and the order of the implant. In amorphous SiO_2 , the nanocrystals are randomly oriented, but in crystalline matrices, the nanocrystals are three dimensionally oriented with respect to the matrix. Ion implantation may be the most convenient method to produce most of these nanocrystals, and the method can be used to encapsulate them in a wide range of host matrices.

TABLE I
NANOCRYSTAL COMPOUNDS FORMED BY SEQUENTIAL IMPLANTATION. AN X INDICATES THAT THE COMPOUND WAS FORMED IN THE GIVEN MATRIX.

Nanocrystal	Substrate		
	SiO_2	Al_2O_3	Si
SiGe	x	x	
GaAs	x	x	x
InAs	x		
GaP	x		x
InP	x		
CdS	x	x	x
CdSe	x	x	x
$\text{CdSe}_{0.5}\text{S}_{0.5}$	x		
GaN		x	

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