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Ion Beam Synthesis and Optical Properties of Semiconductor Nanocrystals and Quantum Dots

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ABSTRACT

Nanocrystals of semiconductor materials have been fabricated in SiO_2 by ion implantation and subsequent thermal annealing. Strong red photoluminescence (PL) peaked around 750 nm has been observed in samples containing Si nanocrystals in SiO_2. The Si nanocrystals in the samples with optimized PL intensities are a few nanometers in diameter. Difference in the absorption bandgap energies and the PL peak energies are discussed. Significant influence of implantation sequence on the formation of compound semiconductor nanocrystals are demonstrated with the GaAs in the SiO_2 system. Optical absorption measurements show that Ga particles have already formed in the as-implanted stage if Ga is implanted first. A single surface phonon mode has been observed in the infrared reflectance measurement from samples containing GaAs nanocrystals.

INTRODUCTION

Ion implantation is a very useful technique for altering the near-surface properties of a wide range of materials. Desired elements can be injected into a solid in a controlled and reproducible manner by ion implantation [1]. Supersaturated impurity concentrations can be produced by high-dose implantation. Subsequent annealing leads to precipitation and the formation of nanocrystals which are encapsulated in the host material. Semiconductor nanocrystals and quantum dots have attracted considerable interest due to potential applications in novel optoelectronic devices [2]. Quantum confinement effects are expected when the sizes of the nanocrystals are smaller than the exciton diameters. For optical applications, for example, visible luminescence can be obtained from group IV nanocrystals due to quantum confinement effects [3]. Nonlinear optical properties can also be significantly enhanced for the nanocrystals compared to the bulk material [4].

We have studied the formation and properties of elemental (group IV) and compound semiconductor (III-V and II-VI) nanocrystals in different host materials [5-8]. The nanocrystal sizes can be controlled by the ion implantation dose and annealing temperatures. To form compound semiconductor nanocrystals, the constituent elements are implanted sequentially. Examples reported in this paper include Si and GaAs nanocrystals formed in amorphous SiO_2 matrices.

EXPERIMENTAL PROCEDURES

The semiconductor nanocrystals were formed by ion implantation of appropriate semiconductor species into a SiO_2 layer on (100) silicon substrate, followed by subsequent thermal annealing. The SiO_2 layer was ~ 750 nm thick, formed by thermally oxidizing a (100) Si wafer. Samples were also prepared by ion implantation into fused silica substrates (Corning 7940). Ion implantation was done at room temperature with doses in the range of $(3\text{-}30)\times10^{16}$

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ions/cm^2. The implant energies were chosen to put the peak concentration at the middle of the oxide layer. Samples were annealed isochronally for 1 h under Ar + 4%H_2 ambient at atmospheric pressure. The annealing temperatures were within the range of 600°C to 1100°C. The nanocrystalline structures were investigated by transmission electron microscopy (TEM) and X-ray diffraction. All the TEM specimens were prepared in cross sections, since the concentration distribution from ion implantation is a function of depth. Depth profiles were also examined by Rutherford backscattering spectrometry (RBS). Optical measurements include optical absorption, photoluminescence (PL) and infrared reflectance measurements.

Si NANOCRYSTALS IN SiO_2

Multiple implants of Si at different energies were performed to produce uniform concentration profiles of Si inside SiO_2. A TEM micrograph in Fig. 1 shows the Si nanocrystals are a few nanometers in size (in the 1-5 nm range, mostly ~ 2-3 nm) in the samples implanted with excess Si concentration of ~ 5×10^{21} cm^{-3} throughout a SiO_2 film on a Si substrate and annealed at 1100°C for 1 h. The formation of nanocrystals of different materials can be very different under similar annealing conditions [6]. It takes a higher annealing temperature for Si than that, e.g., for Ge to precipitate inside SiO_2. To achieve visible luminescence, the sizes of Si nanocrystals should be about a few nanometers in order to have sufficient quantum confinement effect [3].

Very strong PL has been observed in the samples containing Si nanocrystals about a few nanometers in size. Figure 2(a) shows PL spectra, excited by an Ar laser at 514.5 nm wavelength, from a samples implanted with Si at a dose of 1.5×10^{17} cm^{-2} before and after thermal annealing. There is some luminescence with a broad peak centered at ~ 650 nm from the as-implanted sample. These luminescence centers are presumably due to the ion-implantation damage of the SiO_2 matrix. The PL intensity is significantly reduced after the sample is annealed at 800°C. After annealing at a higher temperature of 1100°C, Si nanocrystals in sizes of a few nanometers have been formed and a very strong PL peak center at ~ 750 nm have been observed. For samples annealed at different temperatures, the PL peak intensity is the highest for the sample annealed at 1100°C.

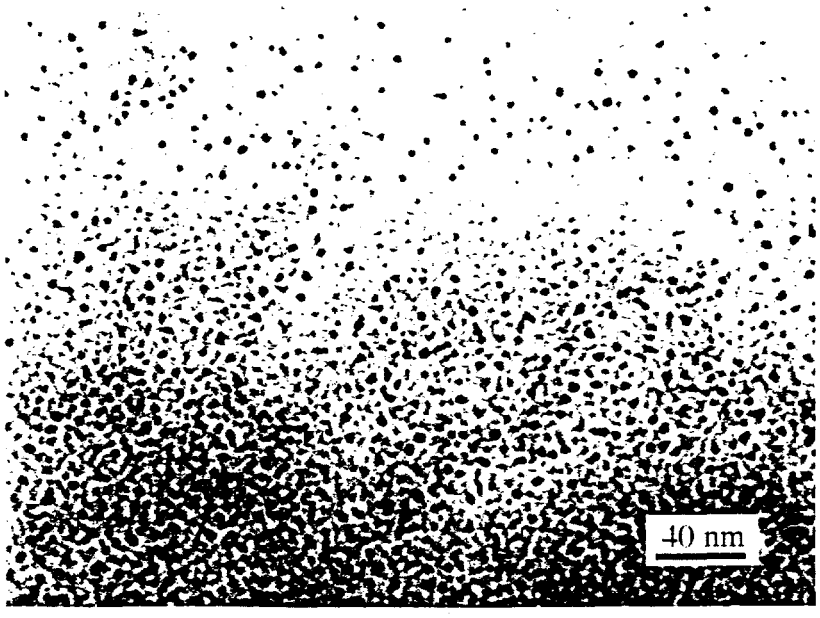

Fig. 1. TEM micrograph showing the Si nanocrystals formed inside a SiO_2 matrix.

GaAs NANOCRYSTALS IN SiO_2

For the formation of compound semiconductors, such as GaAs, where there is more than one element involved, the sequence of Ga and As implantation was found to influence the size distributions of GaAs nanocrystals dramatically [12]. Figure 3 shows cross-sectional TEM images from samples implanted with the same doses, 1.5×10^{17} ions/cm^2, but different implantation sequences and annealed at 1000°C for 1 h. The GaAs nanocrystals in Fig. 3(a) were formed in the sample implanted with Ga first and then As, and have sizes ranging from a few nanometers to ~ 30 nm. These nanocrystals are nearly spherical and randomly oriented with respect to each other, as expected for amorphous matrices. Some voids are observed in the region near the oxide surface. In the sample implanted with As and then Ga, the GaAs nanocrystals formed after annealing at the same temperature are much smaller with sizes in the range of 1 - 10 nm as shown in Fig. 3(b). The difference between the two samples shown in Fig. 3 (a) and (b) is very striking considering they have been through the same processing except the implantation sequence of Ga and As.

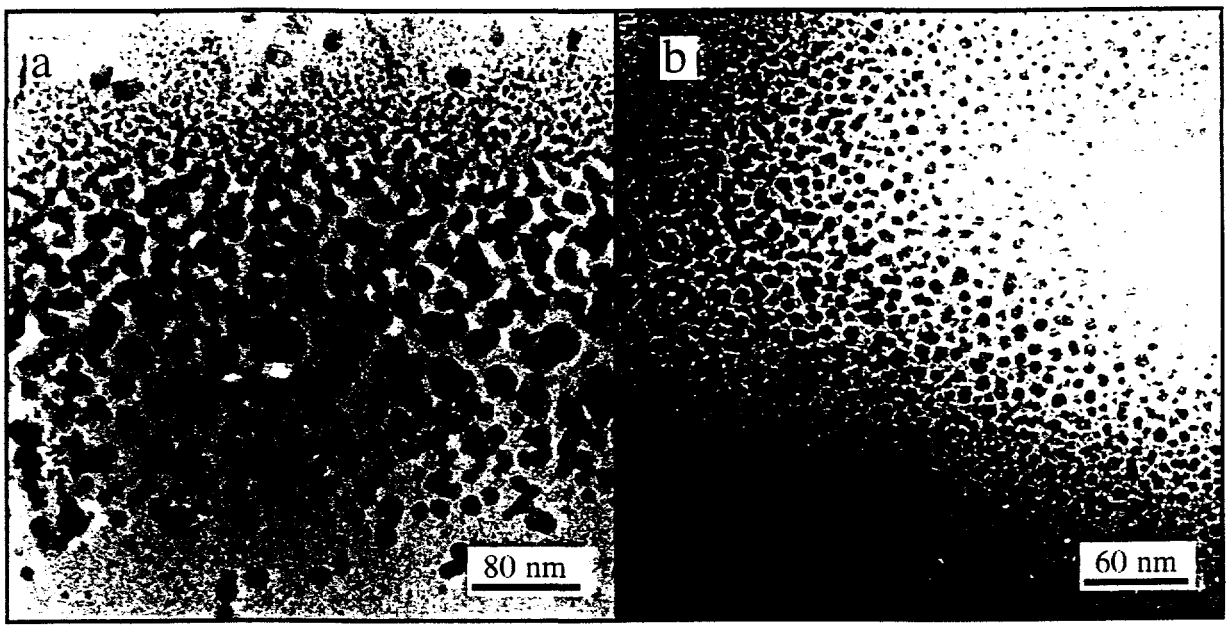

Fig. 3. Cross-sectional TEM images from samples implanted with equal doses, 1.5×10^{17} cm^{-2}, of Ga and As, but different implantation sequence: (a) Ga first and then As and (b) As first and then Ga. Both samples have been annealed at 1000°C.

RBS measurements of the implanted ion profiles reveal that the As implanted in SiO_2 is thermally stable, while Ga implanted in SiO_2 is very mobile during implantation and annealing. Optical absorption spectra from samples implanted with Ga along or As along into silica glass wafers are shown in Fig. 4. A strong absorption peak at 220 nm has been observed in the as-implanted sample implanted with Ga only. This absorption peak is attributed to the surface plasmon resonance of Ga particles in SiO_2. Details on surface plasmon resonance of metal particles, such as Ag, in a dielectric matrix can be found elsewhere [13]. The optical density decreases after annealing at 1000°C, which is in agreement with the Ga loss observed in the RBS spectra. TEM from a sample implanted with Ga first and then As confirms the formation of Ga particles in the as-implanted stage. The optical absorption spectrum for the sample implanted with As only is virtually unchanged after annealing at 1000°C. The thermal stability of the As profile helps to interpret the thermal stability of the ion-concentration profile of As + Ga in the samples implanted with As first. When Ga ions are implanted after the implantation of As, they bond with

the As atoms due to the chemical affinity between Ga and As. In the samples implanted with Ga first and then As, there is much more diffusion involved since Ga is very mobile in SiO_2. Consequently, the GaAs nanocrystals grow much bigger.

In the samples implanted with As first and then Ga, the GaAs nanocrystals formed after annealing are smaller than the bulk exciton radius. Therefore, quantum confinement effect is expected. An infrared reflectance spectrum is shown in Fig. 5 recorded from a sample implanted with equal amount, 1.0×10^{17} ions/cm^2, of As and then Ga and annealed at 1000°C for 1 h. A strong reflectance at 278 cm^{-1} has been observed. A Raman spectrum measured from the bulk GaAs is also plotted in Fig. 5. The single peak from the GaAs-nanocrystal-containing sample lies in between the transverse (267 cm^{-1}) and longitudinal (291 cm^{-1}) optical phonon modes of bulk GaAs. Observation of a similar single mode between the bulk transverse and longitudinal optical modes in the infrared spectrum has been reported for microcrystallites of MgO and GaP [14]. This peak is attributed to the excitation of surface phonon modes. A single surface phonon mode has also been detected for GaAs nanocrystals formed in single crystalline Al_2O_3 matrix, where GaAs nanocrystals are faceted and very well aligned with the crystalline matrix [7].

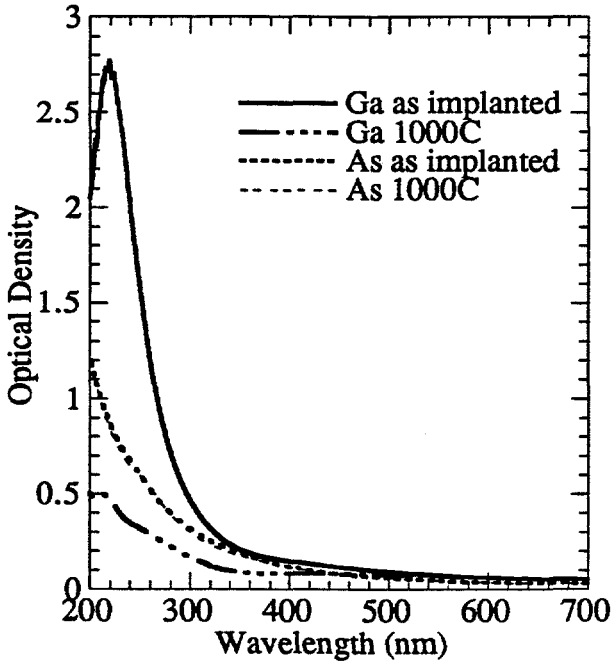

Fig. 4. Optical absorption spectra from samples implanted with 1.0×10^{17}/cm^2 of Ga or As only, before and after annealing.

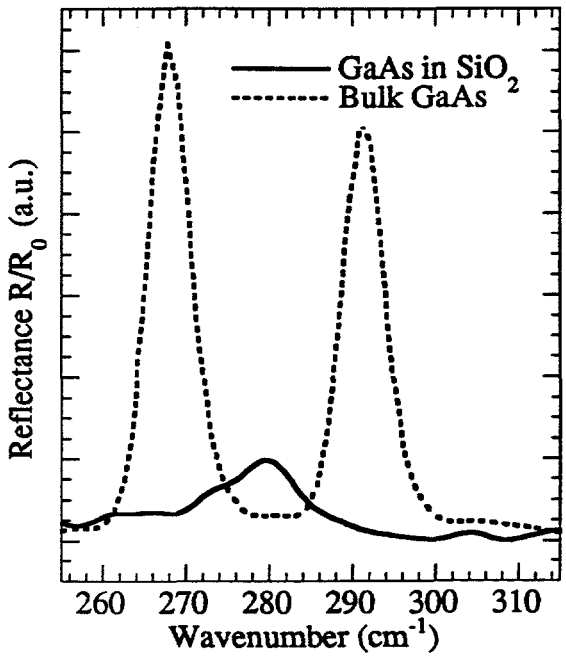

Fig. 5. Infrared reflectance spectrum (solid curve) from a GaAs-nanocrystal-containing sample with the Raman spectrum (dashed curve) from bulk GaAs superimposed.

CONCLUSIONS

Semiconductor nanocrystals of Si and GaAs have been formed in SiO_2 by ion implantation and subsequent thermal annealing. The microstructure has been characterized extensively by TEM. A broad range of nanocrystal sizes can be produced through the control of ion implantation and annealing processes. Strong PL peaked at around 750 nm is observed in Si-nanocrystal-containing samples. The absorption bandgap energies measured are consistent with the quantum confinement effect, while the PL peak energies are considered to be associated with the surface/interface states. For the formation of compound semiconductor GaAs nanocrystals, it is demonstrated that the sequence of Ga and As ion implantation affects the size distributions of GaAs nanocrystals significantly. The nanocrystal sizes are much bigger in the samples with Ga

implanted first than those with As implanted first. This phenomenon is explained by the different diffusion behaviors of Ga and As species. Optical absorption measurements show that Ga particles have already formed in the as-implanted stage with the absorption peak at 220 nm due to a surface plasmon resonance of metal particles in SiO_2. Single surface phonon mode has been observed from samples containing GaAs nanocrystals in the infrared reflectance measurement. We have also fabricated and characterized nanocrystals of other semiconductor materials in different matrices using the ion implantation technique, which is beyond the scope of this paper.

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