# GaAs Nanocrystals Fabricated by Ga and As Ion Implantation

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## **1. Introduction**

Nanometer-sized semiconductor crystallites (nanocrystals) have attracted much attention because they exhibit a wealth of quantum phenomena and have a potential as future optoelectronics devices [1]. Recent advances in controlling and characterizing semiconductor nanocrystals have generated considerable interest in exploring new synthesis techniques. Several approaches have been developed for producing nanostructured materials, including colloidal chemistry [2], self-assembled dot growth [3], and electrochemical etching [4], and so on.

Ion implantation technique is an integral part for practical semiconductor device fabrication. In addition, high-dose ion-implantation and thermal annealing technique has been shown to provide a versatile technique for creating semiconductor nanocrystals in the surface region of a substrate material, since almost any ions can be implanted into any solid substrates [5,6].

In this paper, we have fabricated GaAs nanocrystals by means of Ga<sup>+</sup> and As<sup>+</sup> co-implantation into SiO<sub>2</sub> matrices and applied selective excitation spectroscopy to clarify the origin of photoluminescence (PL) from GaAs nanocrystals in SiO<sub>2</sub> matrices. The structural and optical properties of GaAs/SiO<sub>2</sub> nanocomposites are discussed.

### 2. Experiment

The nanocrystals were formed in the 100-nm SiO<sub>2</sub> films on (100) crystalline Si substrates. The nanocrystals were synthesized by  $3 \times 10^{16}$ /cm<sup>2</sup> Ga<sup>+</sup> and  $2 \times 10^{16}$ /cm<sup>2</sup> As<sup>+</sup> co-implantation at 75 keV into SiO<sub>2</sub>. The implanted Ga and As concentration profiles coincide with each other within the oxide film, with the peak concentration lying 30-40 nm from the surface. Subsequent annealing in vacuum resulted in precipitation of GaAs nanocrystals [7]. We tried to change the annealing temperature and annealing time in order to control the nanocrystal size: For a fixed annealing time of 10 min, the annealing temperatures were changed between 800 °C and 1100 °C. For a fixed annealing temperature of 900 °C, the annealing time was ranged between 0 min and 300 min. After thermal annealing, hydrogen passivation experiments were performed by means of low energy (600 eV) deuterium implantation using a Kauffman ion source and the deuterium dose was determined by elastic recoil spectrometry using a 2.0 MeV <sup>4</sup>He<sup>++</sup> beam.

Under 2.707 eV laser excitation at room temperature, we measured the PL spectra and selected samples showing efficient visible luminescence. The highest PL intensity was observed from samples passivated by deuterium implantation at a dose of  $3 \times 10^{15}$ /cm<sup>2</sup> after annealed at 900 °C for 10 min. Hydrogen passivation is important for efficient luminescence. In these samples, the presence of nanocrystalline GaAs was

verified from lattice images of high-resolution electron transmission micrographs and x-ray diffraction patterns. We will discuss luminescence properties of these "bright" samples.

## 3. Results and Discussion

Figure 1 shows PL spectra under the 2.707-eV laser excitation at 2 K. Under blue laser excitation, the sample shows broad luminescence in the red spectral region. The full PL spectrum can be divided by three Gaussian bands and the peak energies of the PL bands are 1.78 eV (band A), 1.62 eV (band B), and 1.52 eV (band C), as denoted by dotted lines in the figure. Ion implantation often introduces structural damage into SiO<sub>2</sub> thin films. Even after thermal annealing, there exist defects at the GaAs/SiO<sub>2</sub> interface and in SiO<sub>2</sub> matrices and the broad PL due to the defects has been reported observed in other nanocrystals/SiO<sub>2</sub> systems [4]. Therefore, it is considered that the defect states cause the complicated PL spectrum in GaAs/SiO<sub>2</sub> nanocomposites, as shown in Fig. 1.



Fig. 1. PL spectra of GaAs nanocrystals in  $SiO_2$  matrices under 2.707 eV laser excitation energies at 2 K. The full PL spectrum can be divided by three Gaussian bands, whose peaks are located at 1.78 eV (band A), 1.62 eV (band B) and 1.52 eV (band C).

In order to clarify the origins of these PL bands, we applied selective excitation spectroscopy to our GaAs nanocrystal samples. Under selective excitation at energy within the A band, fine structures are observed in the PL band. Figure 2 shows PL spectra under various excitation photon energies at 13.5 K. The pronounced fine structures in the A band are marked by an open circle ( $\bigcirc$ ), a solid circle ( $\bigcirc$ ), and a solid triangle ( $\blacktriangle$ ). These peaks shift to lower energy side with a decrease of excitation photon energies. In the A band, the peak positions of fine structures depend on the nanocrystal size. Moreover, when excitation energy decreases and the B and C bands are

selectively excited, the first and second peaks ( $\bigcirc$  and  $\blacktriangle$  in the figure) gradually diminish. These behaviors suggest that the origins of the *B* and *C* PL bands are due to defect states in SiO<sub>2</sub> matrices. Selectively excited PL spectra suggest that the origin of the *A* band is different from the defect-like *B* and *C* bands.



Fig. 2. PL spectra of GaAs nanocrystals in  $SiO_2$  matrices under various excitation energies at 13.5 K. The excitation laser energies are shown in the figure. Fine structures in the PL spectrum are observed under selective excitation at energies within the *A* band.

The energy difference between the second peak ( $\bigcirc$ ) and  $E_{\text{ex}}$  is  $\sim$ 36 meV, which does not depend on the excitation energy, where  $E_{\text{ex}}$  is the excitation laser energy. The observed energy difference of  $\sim$ 36 meV is in fairly good agreement with LO-phonon energy of bulk GaAs (36.5 meV). The  $E_2$  peak structure is probably due to Raman scattering from GaAs nanocrystals.

On the other hand, the energy differences between the first peak ( $\bigcirc$ ) and  $E_{ex}$ , and between the third peak ( $\triangle$ ) and  $E_{ex}$  decrease with a decrease of  $E_{ex}$ . With a decrease of  $E_{ex}$ , the first ( $\bigcirc$ ) and the third ( $\blacktriangle$ ) peaks converge to the same energy,  $\sim 1.5$  eV, at  $E_{ex}=1.515$  eV. The fine structures ( $\bigcirc$  and  $\bigstar$  in Fig. 2) are only observed in nanocrystals, but not in bulk crystal. Moreover, the peak energy depends on the excitation energy (i.e., size-dependent). These observations imply that the luminescence fine structures are caused by radiative recombination in quantum confinement in GaAs nanocrystals.

From theoretical calculations [8], it is speculated that the two peak structures ( $\bigcirc$  and  $\blacktriangle$  in Fig. 2) are attributed to recombination between the ground state of electron and the first excited-state of hole  $(e_1-hh_2)$  and between the ground state of electron and the ground state of hole  $(e_1-hh_2)$  and between the ground state of hole  $(e_1-hh_1)$ , respectively. The  $e_1-hh_2$  transition is the optically forbidden one because of the parity selection rules. However, similar forbidden transitions have been experimentally observed in InGaAs [9] and CuCl [10] nanocrystals. The forbidden transition is observed probably due to some internal perturbations or asymmetry which can break the parity selection rules. Further theoretical studies are needed for understanding the optical transitions in nanocrystals.

### 4. Conclusion

We have fabricated GaAs nanocrystals by Ga<sup>+</sup> and As<sup>+</sup> co-implantation into  $SiO_2$  matrices and studied their PL properties. Efficient and broad PL spectra with multipeaks are observed in the red spectral region. From selectively excited PL spectra, it is concluded that one of the PL bands is attributed to quantum confinement states in GaAs nanocrystals. Visible luminescence is attributed to both quantum confinement states in GaAs nanocrystals and defects in SiO<sub>2</sub>. We observed for the first time efficient luminescence of GaAs nanocrystals in SiO<sub>2</sub> matrices fabricated by ion-implantation and thermal annealing technique.

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