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Luminescence from Si nanocrystal grown in fused silica using keV and MeV beam

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Abstract

Embedded nanocrystals are grown using both keV and MeV energy ion beam followed by thermal annealing. Initially, 200 keV Si^+ ions were implanted in fused silica at various fluences varying from 2.5×10^{15} to 2.5×10^{16} ions cm^{-2}. A set of the implanted samples were irradiated using 70 MeV Si-beam and annealed at 900 °C for 3 h in nitrogen atmosphere. Photoluminescence (PL) studies were carried out by exciting the samples at room temperature with 514 nm line of an Ar ion laser. Implanted, irradiated and annealed samples showed a PL peak at 568 nm, whereas implanted and annealed samples had a PL peak at 580 nm. 70 MeV Si ion irradiation created tracks of about 2 nm diameter along its trajectory due to inelastic collision process. Nanocrystals are expected to be formed along the trajectory due to dense electronic excitation created by MeV Si beam around the tracks and subsequent annealing. The blue shift observed is attributed to quantum size effect in which reduction of the average nanocrystal size leads to emission at a shorter wavelength. The formation of Si nanocrystals has also been confirmed by complementary studies of UV-visible absorption spectra. Sharp absorption edges between 230 and 270 nm due to formation of Si nanocrystals were observed.

Keywords: Nanocrystals; Ion irradiation; Photoluminescence

1. Introduction

In recent years, there has been considerable interest in semiconductor nanostructures which exhibit visible luminescence. When the dimensions of crystallites approach the atomic scale, significant changes occur in the electronic, optical, magnetic and thermodynamic properties compared to those of bulk materials [1,2]. In the nanostructure, the band gap increases with decreasing size [3] and electronic states are predicted to be discrete. The synthesis of embedded nanostructures with size tunable optical and electronic properties by means of these nanoparticles is of immense interest.

Nanoparticles can be synthesized by different methods like RF sputtering, sol–gel method, ion implantation and other chemical routes [4]. Ion implantation method used to produce nanocrystals has some advantages, e.g., technical simplicity and compatibility with currently well-developed semiconductor technology, etc. It creates a supersaturated impurity concentration in the near surface of a host matrix. Subsequent annealing leads to precipitation and formation of nanocrystals, which are encapsulated in the host materials [5]. Moreover, the size of nanocrystals and the depth and depth distribution can be controlled by adjusting the parameters of the ion beam and post-annealing conditions. Ion implantation overcomes the restrictions imposed by the incompatibility of dopant and the host matrix ordinarily faced by the chemical routes and it can be used to dope any matrix with any element. Ion beam synthesis of semiconductor nanocrystals is a potential candidate for the manufacturing of pure nanocrystals not only for basic research but also for the application for

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optoelectronic devices [6]. However, the ion implantation method has some limitations. In this method, by forcing solute supersaturation inside the matrix and then annealing at a temperature where diffusion can occur leads to clusters that nucleate (and hence grow) at different times [7]. Subsequent precipitate evolution then leads to broad size distributions, with little control over the average cluster size and density. It is reported [7] that this problem may be overcome by using MeV ion irradiation along with implantation. MeV irradiation technique will decouple the nucleation and growth processes. Swift heavy ion irradiation leads to large deposition of energy into the target through electronic energy loss, which leads to structural phase transformation in the system thus not requiring further high-temperature annealing [8].

Over the decades, silicon is being used for the semiconductor industry. Irradiation-induced surface and electrical modification of silicon finds great application in industry [9]. Silicon has limited application in optoelectronic devices being as poor emitter of light even at liquid helium temperature. Formation of Si nanoclusters has opened a new area in optoelectronic industry. Silicon nanocrystals can emit red, green and even weak blue light when stimulated by light of shorter wavelength [10]. The efficiency of silicon nanocrystals (measured in photons emitted per incident photon) can exceed 1%, which is 10^4 times better than bulk silicon [11]. Si nanoclusters are direct band gap semiconductors and emits light in visible and infrared range at room temperature also. An exciting perspective of this discovery is that light-emitting devices based on this effect appear feasible within the well-established silicon technology. Ion beam synthesis of Si nanoclusters is a candidate for application in monolithically integrated Si-based optoelectronic devices.

The key issue in the growth process is to synthesize Si nanocrystals in an insulating matrix, preferably SiO_2 films with a narrow size distribution. This would enable one to increase the band gap of Si from 1.1 to 4 eV in small increment energies by decreasing the particle size in small steps allowing wide range applications of Si as detectors and light-emitting devices from infrared to visible UV radiation. The origin of the PL band in silicon nanocrystals (Si-nc) is still controversial [12]. There is a general consensus that an incident photon in Si-nc excites an electron to a higher energy state in the nanocrystal, but the origin of the electron-hole recombination that results in visible light emission remains is not clearly explained.

In this work, detail studies on precipitation of Si-nanoclusters in SiO_2 using swift heavy ion (SHI) irradiation in MeV energy range are reported. SHI beam on passing through matter loses its energy in two ways: electronic energy loss (S_e) due to inelastic collisions with electrons and nuclear energy loss (S_n) due to elastic collisions of atoms of the solid with the projectile ion [13]. Subsequent momentum and energy transfer creates a trail of defects along the ion trajectory called latent track. The nature of the defects depends on S_e of ion beam and the target material. A threshold value of the electronic energy loss S_e^{th} is required to generate extended latent track in solid. In fused silica, S_e^{th} is 1.8 keV nm^{-1} [14]. Nanoprecipitation is expected to occur along the track as well as in a tubular area surrounding the track. Confining the nanostructures inside the track will help to control their size.

2. Experimental

Silicon nanocrystals are grown on fused silica using both keV and MeV energy ion beam followed by annealing. Initially 200 keV Si^+ ions from ECR ion source were implanted in optical grade fused silica at various fluences varying from 2.5×10^{15} to 2.5×10^{16} ions cm^{-2}. The size of the matrix is 10×10×1 mm. The samples were kept at room temperature during the whole process. The projected range of the ion implantation is about ~300 nm calculated by using the TRIM code [15]. Using the high fluence of Si beam, supersaturation of Si atom is created at that depth. Both annealing at high temperature and athermal annealing using swift heavy ion beam were carried out for nanoprecipitation to occur. A set of the implanted samples was irradiated using 70 MeV Si-ion beam from 16 MV Pelletron tandem accelerator [16] at Nuclear Science Centre, New Delhi. Ion beam was magnetically scanned on (10×10 mm) area on sample surface for uniform irradiation. The samples were mounted on a copper target ladder with silver paste giving good thermal conductivity between them. This prevents sample heating during SHI irradiation. The ion flux was 10^9 ions cm^{-2} s^{-1}. All the samples were irradiated at a particular fluence of 5×10^{11} ions cm^{-2}. Care was taken such that latent tracks do not overlap each other. The irradiated samples were annealed at 900 °C for 3 h in nitrogen atmosphere. The annealed samples along with pristine sample were characterized by Ultraviolet/Visible optical absorption spectroscopy, photoluminescence (PL) measurements. Optical absorption spectra of the defects were taken using Hitachi 330 UV/Visible spectrophotometer. Photoluminescence spectra were taken using 514 nm line of Argon ion laser.

3. Results and discussion

PL spectra were taken for two sets of samples. One set was implanted, irradiated, annealed and the other set was implanted and annealed samples. Implanted and annealed samples had a PL peak at 580 nm (Fig. 1), whereas implanted, irradiated and annealed samples showed a PL peak at 568 nm (Fig. 2). In both cases, the PL peak increases with fluence. Shifting of the PL peak occurs with increasing fluence. But the variation is very small. Visible luminescence, seen at 580 and 568 nm, is mainly due to Si nanocrystals [17]. The PL peak corresponding to these