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Structure and optical properties of SiO_2 films with ZnSe nanocrystals formed by ion implantation

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ABSTRACT

ZnSe nanocrystals have been formed in the silicon dioxide matrix by the sequential high-fluence implantation of Zn^+ and Se^+ ions at 500 °C. After implantation a part of samples was annealed at 1000 °C for 3 min using rapid thermal annealing. Structural and optical properties of ZnSe/SiO_2 nano-composite films were analyzed by means of Rutherford Backscattering Spectrometry, cross-sectional Transmission Electron Microscopy, Raman scattering and photoluminescence techniques. It was shown that a sequence of implantation affects structural and optical properties of synthesized ZnSe clusters. Based on the Raman scattering and photoluminescence data the samples for which Zn ions were implanted first exhibited a better ZnSe crystalline quality than those of reverse sequence of implantation, i.e. with Se ions implanted at the beginning. The bands of blue ZnSe band edge emission and green-red ZnSe deep defect level emission were revealed in the PL spectra of the as-implanted and annealed nano-composites. The PL spectral features observed in the blue region are due to the quantum-size effects in the ZnSe nanocrystals embedded into the silicon dioxide matrix. The PL intensity ratio of the deep defect band to the near edge emission is higher in the samples first implanted with Se ions, and Zn ions implanted next. The effect of rapid thermal annealing on structural and light-emitting properties was discussed.

1. Introduction

Selenide-based nanostructural materials, such as wide-band gap A_2B_6 semiconductors, have been studied intensively due to their wide variety of practical application in the fields of light-emitting devices, solar cells, sensors, and optical recording materials. Following the demonstration of possible application of zinc selenide in photoelectronic devices, an intensive attention is paid to ZnSe as an alternative to the more toxic Cd-based materials. Indeed, ZnSe-based materials in such forms as thin films, nanocrystals (NCs), quantum wells, flower-shaped nanocrystals [1], nanoribbons [2], nanowires [3], hollow microspheres [4] and bulk crystals are applicable for fabrication of blue and green light-emitting diodes due to the direct band gap, infrared windows due to wide transmission wavelength range, lenses and prisms, and optically controlled switching devices due to giant photoresistivity.

Numerous investigations were focused on the synthesis of high-quality ZnSe nanocrystals (NCs). In most cases NCs were formed by a multistep chemical route [5–10]. For practical applications, however, the ion beam technique is very promising due to its compatibility to the common Si technology. Ion implantation is a suitable method of synthesis of nanostructured films and NCs embedded in different dielectric and semiconductor matrices. Formation of A_2B_6 nanocrystals such as CdS, CdSe, ZnS, ZnO [11–14] using ion implantation was previously reported. To our best knowledge, up to now no reports have been published on the ion-beam synthesis of ZnSe nanocrystals in SiO_2 layers except a brief notice in [15] concerning possibility of ZnSe precipitates creation in a-SiO_2. In this paper structural and optical properties of ZnSe nanocrystals synthesized in the amorphous SiO_2 matrix by ion implantation were studied.

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2. Material and methods

The $1 \times 1\ cm^2$ samples were cut from the thermally oxidized Si (100) wafer. According to Cross-sectional Transmission Electron Microscopy (XTEM), the thickness of SiO_2 film was 600 nm. Afterwards, these samples were sequentially "hot" implanted with Zn^+ and Se^+ ions at a target temperature of 500 °C. The energies of ions (150 keV for Zn^+ and 170 keV for Se^+) were chosen based on the computer simulation (TRIM code) to obtain overlapping concentration profiles of Zn and Se species. Both types of ions were implanted with the same fluence of 4×10^{16} ions/cm^2.

Two sets of samples were prepared. Those of the first set (samples A) were implanted at first with Zn ions and after that with Se ions. In the other set (samples B) the order of Zn and Se implantations was inverted. Rapid thermal annealing (RTA) at 1000 °C for 3 min in Ar atmosphere was performed on a part of the implanted samples. Rutherford Backscattering Spectrometry (RBS) using 2.5 MeV He^+ ions was employed to study the elemental composition of the implanted oxide films. The chosen energy of He ions was high enough to resolve Zn and Se peaks in the RBS spectra. Phase composition of the samples was investigated by means of Raman scattering (RS). RS measurements were performed in backscattering geometry with a Nanofinder High End micro-Raman spectrometer (LOTIS TII) using a 532-nm laser beam as the excitation source. Structural composition was studied by the cross-section technique of Transmission Electron Microscopy (XTEM) with a Hitachi H-800 electron microscope operating at 200 keV. Photoluminescence (PL) spectra were registered at room temperature using the He-Cd laser beam at the wavelength $\lambda = 325$ nm as the excitation source.

3. Results and discussion

Fig. 1 shows the impurity concentration profiles in SiO_2 calculated from the experimental RBS spectra for the as-implanted and annealed samples. The Zn and Se concentration profiles maxima simulated with TRIM are located at comparable depths near 112–114 nm (not shown in Figure). However, the maxima of concentration profiles of "hot" implanted impurities calculated from the experimental RBS spectra are shifted to the surface in comparison with the simulated ones. Thus in the case of the sample A (Fig. 1a), the "experimental" maxima of the Zn and Se concentration profiles are located at the depth of ~70 and 90 nm, respectively. For the sample B (Fig. 1b), the maxima of the Zn and Se concentration profiles are observed at ~70 and 60 nm, respectively. Rapid thermal annealing results in a noticeable diffusion of Zn and Se impurities towards the SiO_2/Si interface for both types of the samples (Fig. 1c, d). However, the diffusional redistribution is more essential for the sample A.

Fig. 2 shows the XTEM images of the as-implanted and annealed samples A and B. One can see two spatially separated layers in the as-implanted sample A (Zn + Se) (Fig. 2a). No clusters are observed on the surface and in the subsurface layer up to 40 nm deep. Underneath that cluster-free region, the layer with small (2–15 nm) clusters is located in the depth range of (40–190 nm). The bigger clusters of 8–15 nm are concentrated at a depth of 80–100 nm (near the maximum of the impurity concentration – Fig. 1a). Such precipitate size distribution is typical of the clusters formed by ion implantation [14,16]. Similar features are observed for the sample B (Se + Zn) (Fig. 2b). However, the layer with the clusters is thinner (0–150 nm), and the size of clusters at the concentration maximum of embedded impurities is bigger (10–20 nm at depths of 60–100 nm in this case) in comparison with the sample A. It can be supposed that the firstly implanted Se ions prevent diffusion of the secondly implanted Zn ions to the depth of oxide film via the formation of Zn—Se bonds. This results in a higher concentration of both embedded impurities in a narrower region of SiO_2 matrix compared to the sample A. Accordingly, the larger clusters are revealed in this region.

RTA results in a structural rearrangement for both samples (Fig. 2c, d). The number of small inclusions decreases significantly, and large precipitates of regular shape appear. The size of such precipitates varies from 50 to 60 nm, and the secondary defects (stacking faults, twin boundaries) are registered inside them. It should be noted that in the case of the annealed sample A (Fig. 2c) the layer with large precipitates is located at the depth of 20–100 nm. Smaller clusters (20–40 nm) are registered in the other regions of the SiO_2 layer and even at the SiO_2/Si interface. This is in agreement with the impurity diffusional redistribution deep into the silicon dioxide layer observed in the concentration profiles of the sample A (Fig. 1c). In the case of the sample B (Fig. 2d), RTA results in the formation of larger clusters predominantly at a depth of 40–110 nm while there are no single small clusters in the other regions of oxide matrix. Segregation of impurities (presumably Se) is observed at some points of the surface for the sample B.

Fig. 3 depicts the Raman spectra of the samples A and B. The second order 2TA (transverse acoustical) phonon mode of Si substrate at ~301 cm^{-1} is observed in all spectra. The Raman spectra of the as-implanted samples A and B are characterized with the band at ~252 cm^{-1} assigned to the LO (longitudinal optical) phonon of crystalline ZnSe [5,7,17]. Thus the clusters observed in the TEM images of as-implanted samples correspond to the ZnSe nanocrystals. The TO (transverse optical) phonon line at 205 cm^{-1} is probably too weak to be resolved for the geometry of our experiment [18] in the Raman spectra. It should be noted that the ZnSe band intensity is higher for the sample A than for the sample B. Based on the RBS and TEM data, the amount of the implanted species involved in clusters formation is almost similar in the samples A and B. Taking it into account the observed difference of ZnSe signal intensity in the RS spectra can be explained via the difference of crystalline quality of synthesized ZnSe NCs in the samples A and B. Based on the results of Refs [16,19], it is obvious that impurity atoms embedded in the first implantation stage should be agglomerated in the Zn or Se clusters (in the case of the samples A and B, respectively). In the second step of implantation, the implanted species should be embedded in the Zn or Se clusters already formed in the SiO_2 matrix in the first stage of implantation. According to the RS data, one can conclude that the incorporation of Se ions into the Zn clusters leads to the formation of ZnSe nanocrystals of higher crystalline quality than the incorporation of Zn ions in Se clusters. Thus, the implantation order (Zn ± Se) is more preferable for creation of high-quality ZnSe NCs in comparison with the inverted implantation order (Se ± Zn). RTA results in a slight decrease of ZnSe band intensity in the RS spectrum of the sample A. This can be explained by the formation of large nanocrystals with secondary defects during annealing as can be seen in the TEM images (Fig. 2).

Let us consider light-emitting properties of the ZnSe nanostructures. It is known that the room temperature PL spectrum of ZnSe nanostructures is typically dominated by two characteristic emission peaks. They are a near band edge (NBE) emission peak in the blue spectral range and a broad deep defect (DD) emission band in the wavelength range of 500–680 nm (green-red spectral region) [3,20]. The NBE emission is generally assigned to the excitons bound to neutral and charged acceptor and donor of different chemical nature and donor-acceptor pairs. The lines of donor-bound (I_2) and acceptor-bound excitons (I_1) in the bulk ZnSe crystals ($T = 10$ K) are observed in the energy range of (2.794–2.802) eV and (2.78–2.794) eV, respectively [21]. In the case of pure, "not-intentionally" doped ZnSe, Zn interstitials and Se vacancies can play the role of donors, and Zn vacancies can play the role of acceptors [3]. On the other hand, the deep level defect emission is mainly due to the intrinsic point defects such as vacancies, interstitials, stacking faults, and antisites [20]. Also, the green emission band was ascribed to imperfections such as dislocations and vacancies on the nanocrystal surface [22,23]. Additionally, the DD emission band can be assigned to the donor-acceptor pair (DAP) recombination mechanism involving Zn vacancies as the acceptor species and Zn interstitials as the donor species with large separation between