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Structure and Optical Properties of Silicon Layers with GaSb Nanocrystals Created by Ion-Beam Synthesis

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We have studied the ion-beam synthesis of GaSb nanocrystals in Si by high-fluence "hot" implantation of Sb and Ga ions followed by thermal annealing. The Rutherford backscattering, transmission electron microscopy/transmission electron diffraction, Raman spectroscopy and photoluminescence were used to characterize the implanted layers. It was found that the nanocrystal size increases from 5 to 60 nm in the samples annealed at 900 °C up to 20–90 nm in those annealed at 1100 °C. For the samples annealed at 900 °C a broad band in the region of 0.75–1.05 eV is registered in the photoluminescence spectra. The nature of this photoluminescence band is discussed.

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1. Introduction

GaSb is a narrow-gap A^3B^5 semiconductor with a direct energy gap. Synthesis of GaSb quantum dots inside the crystalline Si is of interest for applications in light emitting diodes and photodetectors operating in IR range. InAs clusters have been formed on Si (001) by the MBE-technique [1]. Such clusters covered with a Si cap layer show intense luminescence at 1.3 μm at 7 K. The other technique for fabricating of III–V quantum dots is the ion-beam synthesis of nanocrystals by means of ion implantation followed by thermal treatment. In this technique, high-fluence ion implantation produces supersaturation of one or more implanted species in the near-surface of crystalline or amorphous matrix. The embedded impurities are then precipitates out of the host by thermal processing. InAs nanoclusters have been formed using this method in SiO_2 and Si [2–4].

The purpose of this paper is to investigate the effect of post-implantation thermal processing on the diffusion redistribution of embedded atoms and on the structural and optical properties of Si implanted with a large fluence of (Sb + Ga) ions.

2. Experimental

(001) Si wafers were implanted at 500 °C subsequently with Sb (250 keV, 5×10^{16} cm^{-2}) and Ga ions (350 keV, 5×10^{16} cm^{-2}). Afterwards, the samples were annealed using traditional annealing and rapid thermal annealing (RTA) in inert ambient gas. In order to analyze depth distribution of the implanted atoms as well as to evaluate damage of implanted material, we applied the Rurtherford backscattering spectrometry in combination with the channelling technique (RBS/C) with 1.3 MeV He^+.

The structure of implanted layers has been studied by means of transmission electron microscopy (TEM) and diffraction (TED) in plan view (PV) geometry using Hitachi H-800 microscope operating at 200 keV. In order to obtain information from different depths the PV-TEM sample preparation was combined with a precise etching technique. The optical properties of samples were investigated by the Raman spectroscopy (RS) and photoluminescence (PL). The Raman scattering experiments were carried out using a RAMANOR U-1000 dispersive spectrometer. The samples were excited by a laser with 532 nm wavelength. The Raman spectra were recorded in backscattering geometry at room temperature within the wave number range from 90 to 600 cm^{-1}. PL spectra were recorded in the spectral region of 0.7–2 eV using a 0.6 m grating monochromator and a cooled InGaAs detector. The samples were mounted in a liquid He immersion cryostat, and the 514.5 nm line of an argon ion laser was used to excite PL.

3. Results and discussion

The calculation of Sb and Ga concentrations in Si by the RBS spectra is complicated by the overlapping of

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peaks from Ga and Sb. To solve this problem, we measured RBS spectra at two angles of the incidence of He^+ onto the samples: 0° and 50°. The depth profiles were calculated by simulations of the spectra until they coincided completely with the experimental spectra obtained at two angles of the incidence of He^+ onto the samples.

Figure 1 shows the Ga and Sb depth profiles in the as--implanted and annealed samples simulated (SRIM'2003) and calculated from the RBS spectra. One can see that the "hot" conditions of implantation lead to depth profiles broadening and to significant reduction of impurity concentration as compared to the simulated data (Fig. 1a,b). A shown trend is weaker for Ga in comparison with Sb. The asymmetric broadening of Sb depth profile towards the sample surface is recorded.

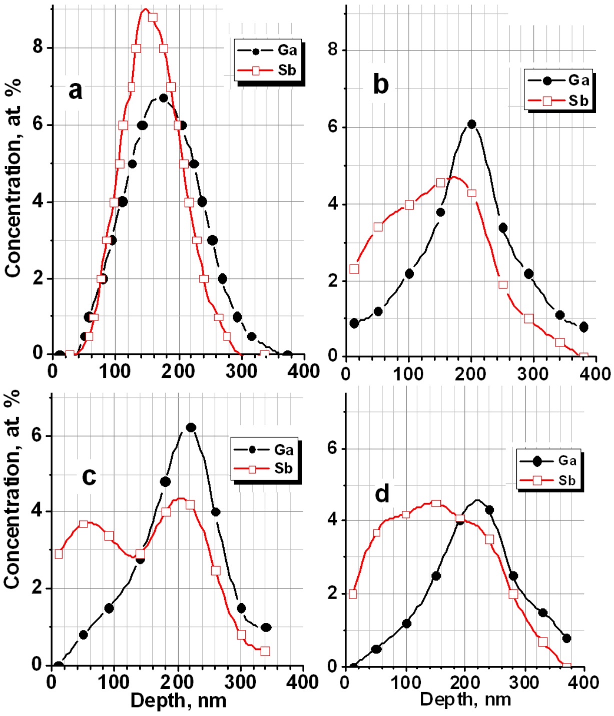

Fig. 1. Simulated (SRIM 2003) (a) and calculated from the RBS spectra (b)–(d) depth profiles of impurities in Si, implanted with Sb (350 keV, 5×10^{16} cm^{-2}) and Ga ions (250 keV, 5×10^{16} cm^{-2}) at 500 ℃. The sample as-implanted (b), the sample after furnace annealing (900 ℃, 45 min) (c), the sample after RTA (900 ℃, 30 s) (d).

A GaSb melting temperature is 712 ℃. In order to achieve as complete recovery of Si crystalline structure as it is possible without GaSb melting, at first a set of samples was annealed at 700 ℃ for 45 min.

The PL spectra of the implanted samples are presented in Fig. 2. One can see that in the PL spectrum of the as-implanted sample a broad asymmetric band with a maximum at 0.91 eV dominates (Fig. 2a). Annealing at 700 ℃ leads to disappearance of the band at 0.91 eV and to appearance of a narrow intensive line of exciton emission in Si peaked at 1.09 eV and less intensive bands at 1.03 and 1.14 eV. We failed to get channelled RBS spectra from the samples annealed at 700 ℃ that indicated insufficient structure recovery of implanted layers. Then the samples were annealed at the temperature exceeding the GaSb melting point.

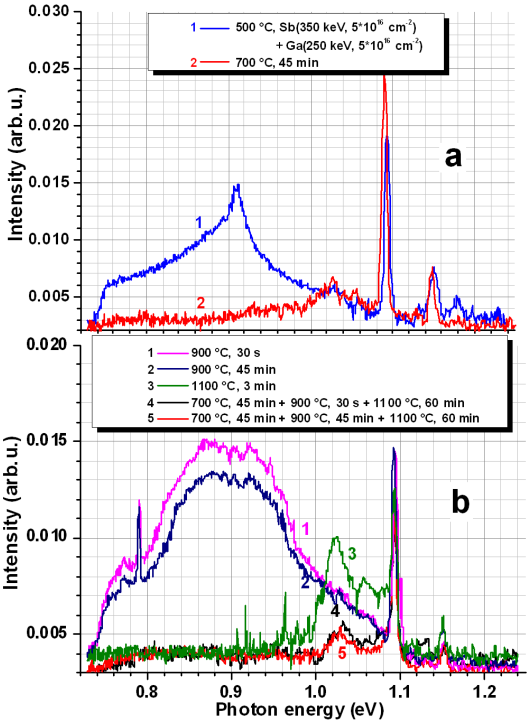

Fig. 2. PL spectra of Si samples implanted with Sb and Ga and annealed in different modes.

The depth profiles of implanted species annealed at 900 ℃ are presented in Fig. 1c,d. One can see that RTA leads to some more broadening of Sb depth profile towards the surface in comparison with the as--implanted sample. Increase of thermal processing duration to 45 min leads to bimodal distribution of Sb atoms in the samples with the maxima at 50 and 200 nm. A similar bimodal distribution of species in Si implanted at 550 ℃ with a high fluence of a number of impurities and annealed at 1000 ℃ for 1 h was reported by Meldrum et al. [5].

Figure 3 shows the TEM-images of implanted Si. It should be noted that annealing does not lead to acceptable structure recovery. In the surface region of the samples annealed at 900 ℃ for 45 min a badly damaged layer with microtwins and precipitates is formed (Fig. 3a). Existence of a great number of microtwins may be caused by subsurface Sb atoms accumulation registered by the RBS technique (Fig. 1b). As one can see, most of the precipitates has sizes from 10 to 60 nm (inset in Fig. 3a). According to the RBS data a maximum of embedded atoms is located at the depth of about 200 nm. In order to investigate a structure of implanted layer at this depth in detail we etched 190 nm from the surface of a part of samples.

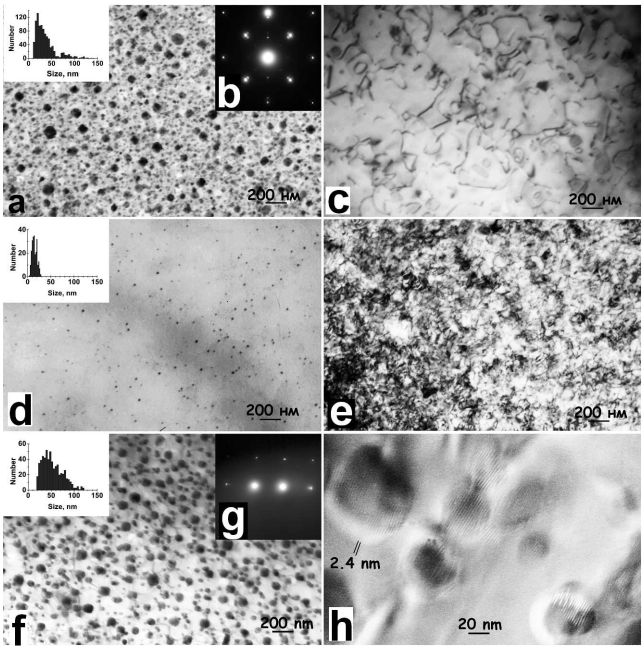

Fig. 3. Bright-field TEM-images (a, c, d, e, f, h) and microdiffraction patterns (b, g) from the silicon layers after implantation of Sb (350 keV, 5×10^{16} cm^{-2}) and Ga (250 keV, 5×10^{16} cm^{-2}) and heat treatment: 900 °C, 45 min (a, b, c, d), 900 °C, 30 s (e), 1100 °C, 60 min (f, g). Micrographs (c, d, e) were obtained from the thinned samples after removal of the surface layer of 190 nm thickness. Insets in (a, d, f) depict size distribution of precipitates in silicon matrix.

In the thinned sample after long (45 min) annealing at 900 °C, there may be distinguished precipitates and dislocation-like defects (Fig. 3c,d). In accordance with the size distribution (inset in Fig. 3d) in the deeper region of sample the precipitates size and size distribution are remarkably reduced and are equal to 5–30 nm. In the thinned sample after RTA (900 °C, 30 s) it is impossible to distinguish precipitates and secondary defects. Hence, the total damage level in the sample after RTA is substantially higher in comparison with the sample after long time annealing. However, the PL spectra of both samples are the same and characterized with a narrow line of exciton emission in Si at 1.09 eV and a broad band at 0.75–1.05 eV (Fig. 2b). A similar band was observed in the PL spectra of InAs nanocrystals grown by MBE on Si wafers [1] or ion implantation in Si matrix [3, 4]. That band was ascribed to InAs nanocrystals. In our experiment the same band is registered in the PL spectra of Si implanted with (Sb + Ga).

A question about the discussed band nature arises. Let us suggest that basic contribution to luminescence in this region enters from carrier recombination into GaSb nanocrystals. Then luminescence intensity should be higher in the more recovered sample after long time annealing in comparison with the sample after RTA. The suggestion that band under discussion attributes to radiative recombination on the nanocrystal/Si interfaces seems to be more probable. In such interpretation it may be suggested that a position of the nanocrystal-related band in the PL spectrum for GaSb and InAs is independent of the method of synthesis (MBE or implantation) and defined by nanocrystal/Si interface properties, while a quantum confinement effect in PL is a minor one.

A part of samples was additionally annealed at 1100 °C for 1 h to achieve more recovery of structure. In the TEM images of these samples the crystal precipitates are also observed which is proved by the Moiré contrast presence (Fig. 3g). As can be seen, the sizes of most precipitates are in the range of 20–90 nm (inset in Fig. 3f). After the annealing at 1100 °C the band at 0.75–1.05 eV disappears from PL spectrum (Fig. 2b). Like for the samples annealed at 700 °C, in a PL spectra of the samples processed at 1100 °C the narrow intensive line of exciton emission in Si at 1.09 eV and less intensive bands at 1.03 and 1.14 eV are registered.

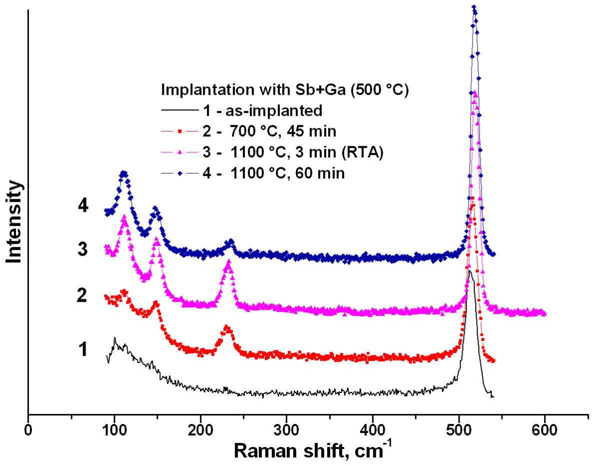

Fig. 4. RS spectra of Si samples implanted with Sb and Ga and annealed in different modes.

In order to identify nanocrystals the RS technique was used. Figure 4 depicts the RS spectra of implanted samples. The Raman spectrum of an as-implanted sample (curve 1) reveals a narrow peak at 512 cm^{-1} corresponding to the zone-center phonons scattering of crystalline silicon. The presence of this peak confirms the crystalline state of the silicon matrix after the “hot” high-fluence implantation of heavy Sb and Ga ions. There should be noted its significant shift towards low frequencies in comparison with undamaged Si (521 cm^{-1} [6]). We suggest that the shift indicates existence of significant mechanical stresses in the implanted layer. Probably, these stresses are caused by the accumulation of heavy impurity atoms (for the most part, Sb) in the subsurface layer.

Annealing leads to a high-frequency shift (up to 518 cm^{-1} after processing at 1100 °C) and increases the intensity of the peak under discussion. Though, the tested regimes of annealing do not eliminate stresses in the implanted layer completely.

We have recorded RS spectrum of the sample annealed at 900 ℃ for 45 min after etching of 190 nm layer from its surface and registered the discussed peak position at 521 cm^{-1} (not shown in the figure). Hence, thickness of the stressed layer is less than 190 nm. Annealing results in the appearance of bands in the region 110–235 cm^{-1}. A peak at 233 cm^{-1} is attributed to LO-phonon scattering of crystalline GaSb [7]. Its intensity varies with the annealing temperature and duration. In addition to the GaSb characteristic line, two peaks at 112 and 149 cm^{-1} are registered in the RS spectra of the annealed samples. We attribute them to the characteristic LO- and TO-phonon scattering of crystalline Sb [6]. Probably the thermal processing of the samples with high Sb and Ga concentrations leads to the formation of both GaSb and Sb crystals in Si matrix. A similar situation was reported by the authors of Ref. [3] for Si implanted at 500 ℃ with a high fluence of As and In. In the annealed samples both InAs phase and In crystals were detected by X-ray diffraction.

4. Conclusions

We have demonstrated a possibility of GaSb nanocrystals formation in Si by implantation of (Sb + Ga) ions. The implantation at 500 ℃ with Sb^+ (250 keV, 5×10^{16} cm^{-2}) and Ga^+ (350 keV, 5×10^{16} cm^{-2}) followed the annealing (900 ℃, 45 min) results in the formation of GaSb-phase precipitates sized from 5 to 60 nm. Annealing temperature increasing to 1100 ℃ leads to the precipitates growth to 20–90 nm. It was found that character of PL spectrum of Si with nanocrystals is defined by annealing temperature. For the samples annealed at 900 ℃ a broad band in the region 0.75–1.05 eV is registered. For the samples processed at 700 or 1100 ℃ the narrow line of exciton emission in Si at 1.09 eV and bands at 1.03 and 1.14 eV are observed.

Acknowledgments

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