FORMATION OF LUMINESCENT NANOSTRUCTURES BY REDUCTION OF SiO_2 IN TRACKS OF SWIFT HEAVY IONS

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320 nm-thick SiO_2 layers were thermally grown on the Si substrates. The layers were irradiated with 167 MeV Xe ions or with 700 MeV Bi to the doses ranging between 10^{12} cm^{-2} and 10^{14} cm^{-2}. After irradiation the yellow-orange photoluminescence (PL) band appeared and grew with the ion doses. In parallel, optical absorption, Raman scattering and X-ray photoelectron spectroscopy were carred out. The results obtained are interpreted as the formation of the light-emitting nanostructures inside the tracks of swift heavy ions through the disproportionation of SiO_2. Ionization losses of the ions are regarded as responsible for the processes observed. Difference between the dependences of the PL intensity on the doses of Xe and Bi ions are ascribed to their different stopping energy, therewith the diameters of the tracks of Xe and Bi ions were assessed as <3 nm and ~10 nm, respectively. Shift of the PL bands, induced by Xe and Bi ions, agrees with the predictions of the quantum confinement theory.

Introduction

Today silicon nanostructures gained worldwide much interest [1]. From one side it is related to the down-scaling of semiconductor devices, while, from the other side, to the capability of quantum-size Si nanocrystals to emit intensive light in the visible and infrared spectral ranges. This last observation gives hopes for developing of silicon–based integrated circuits with combined electronic and optical functions. As it is well known, bulk Si, the dominating material in electronics, is not the best matter for photon generation because of too low probability of the radiative recombination in the indirect-bandgap semiconductors.

At present Si nanocrystals are usually prepared by processing at high temperatures (>1000^o C) of the SiO_2 layers containing overstoichiometric amount of silicon. Along with furnace treatments, the employing pulsed annealing has also proven feasible [2–4]. Pulsed anneals are of high practical importance, as they enable one to perform high-temperature heat treatment locally while insignificantly affecting the adjacent regions. This is particularly advantageous for the processing of ultra-large-scale integrated circuits. Moreover, pulsed anneals substantially reduce the thermal budget of the heat treatment. Irradiation with swift heavy ions (SHI) may be considered, to a certain extent, as a kind of pulse treatment. When SHI penetrate in solid-state targets, their stopping in thin near-surface layers occurs predominantly by electronic (ionization) losses. If the deposited energy density exceeds ~1 keV/nm, tracks may be forming with the nm-scale diameters, where the carrier concentrations may reach ~10^{22} cm^{-3} or even more. The temperature inside the tracks may exceed 5000 K for 10^{-13}–10^{-11} s [5]. Such extreme parameters are interesting for the material processing. It is tempting to employ the SHI irradiation for formation of the light-emitting nanostructures in stoichiometric SiO_2, the material widely used in microelectronics owing to its excellent dielectric properties and to the perfect Si-SiO_2 interface. In the present work we attempted to form the light-emitting nanostructures by disproportionation of stoichiometric SiO_2 in the tracks of SHI.

Experimental

320 nm-thick SiO_2 layers were thermally grown on the Si substrates. The layers were irradiated with 167 MeV Xe ions to the doses ranging between 10^{12} cm^{-2} and 10^{14} cm^{-2}, or with 700 MeV Bi ions in the dose range of $3x10^{12}$ – $1x10^{13}$ cm^{-2}. According to the SRIM code (www.srim.org), the ionization losses of Bi ions in the SiO_2 layers were ~24 keV/nm, or 99.7% of the total ones, while for Xe the ionization and nuclear (elastic) losses were 14.5 keV/nm and 0.3 displacements/nm, respectively. Photoluminescence (PL), optical FTIR absorption, ellipsometry, Raman scattering and X-ray photoelectron spectroscopy (XPS) were used for the characterizations. The PL signal was excited by the laser radiation lines at the wavelengths of 488 nm. The PL spectra were corrected for the spectral response of the registering system.

Results

The ellipsometry measurements have shown that in the as-grown layers the refractive index at the wavelength of 632.8 nm was 1.45, i.e. the layers were of stoichiometric SiO_2. Fig. 1 shows the PL spectra of the samples before and after irradiation with SHI. With growing ion dose the yellow-orange PL band at ~560 nm arose and grew up. The similar behavior was seen for the Raman scattering spectra – gradual increase in the scattering at the wavenumbers band of ~ 480 cm^{-1} with increase in the ion dose. The line is typical of atomic vibrations in

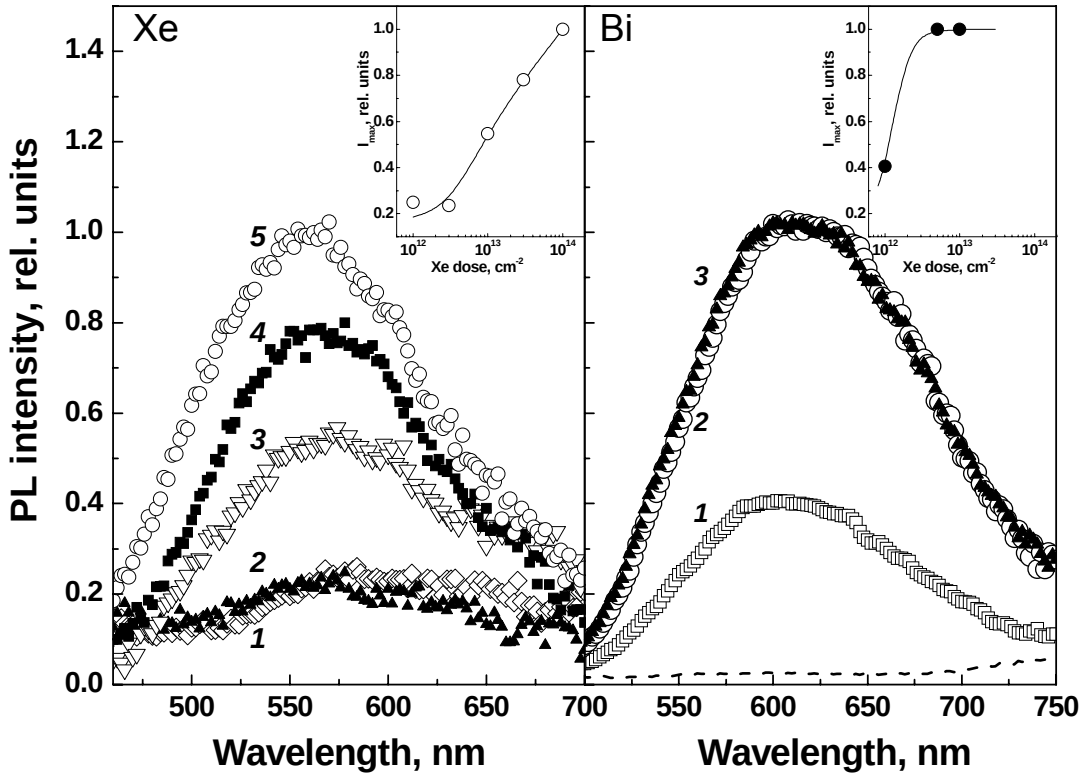

Fig.1. PL spectra after irradiation with Xe ions, doses, 10^{12} cm^{-2}: 1- 1; 2- 3; 3- 10; 4- 30; 5- 100 and Bi ions, doses, 10^{12} cm^{-2}: 1- 3; 2- 5; 3- 10. Dashed line – before irradiation. Insets – dependences of the PL maxima on the ion doses.

the amorphous Si. The appearance of the Si-enriched (O - deficient) regions after Xe bombardement was confirmed by the XPS spectroscopy. Before irradiation only one line at the binding energy of 103.6 eV was seen. This line is characteristic of the **Si-**4O bonds in stoichiometric SiO_2. After the irradiation the intensity of the line dropped down and its maximum shifted towards lower energies, evidencing formation of Si-Si bonds.

The irradiation with Bi ions gave the results resembling in general those obtained after Xe bombardment. The light-emitting centers were found to appear in the irradiated layers and their PL intensity grew with the ion dose (Fig. 1). However, one can see some differences comparing to the spectra measured after Xe irradiation. First of all, the intensity of the luminescence saturates by the Bi ion dose about $5x10^{12}$ cm^{-2} (Fig. 4), while at the Xe irradiation the PL intensity continues to increase up to the dose of 10^{14} cm^{-2} (Fig. 1). The second difference is in the position of the PL maximum – it is shifted to ~610 nm. In the FTIR spectrum of the as-grown sample the single absorption band ~1090 cm^{-1} was seen. Traditionally this band is ascribed to the absorption of the Si-O bonds in stoichiometric SiO_2. The irradiation with Bi ions led to diminishing of the absorption and to a shift of the band toward the long waves. The post-bombardment spectrum may be deconvoluted rather precisely into the two components – bands ~1090 cm^{-1} and ~1040 $см^{-1}$. The first one relates to the vibration of the Si-O bonds in stoichiometric SiO_2, and the second band reflects the enrichment of the oxide network with Si.

The XPS data of the samples before irradiation by Bi ions consisted of the single Si 2p line at 103.6 eV. This line is characteristic of the **Si-**4O bonds in stoichiometric SiO_2. After irradiation the line became less intensive, broader and shifted to the lower energies. This may be interpreted as a decrease in number of $Si-O_4$ bonds in favour of Si-coordinated Si atoms. Thus SHI irradiation provides the disproportionation of stoichiometric SiO_2.

Discussion

The obtained results point out, that SHI irradiation of stoichiometric SiO_2 creates the PL centers, emitting in the yellow-orange region. The intensity of the PL grew with the ion dose, suggesting the radiation-induced origin of the centers. Earlier, the PL bands between 500 nm and 700 nm were observed in the cases where either the annealing temperature and time, or the concentrations of excess Si were insufficient for the formation of perfect Si nanocrystals. Such PL bands were attributed to a lot of different Si nanoprecipitates. The positions of the PL maxima in were slightly varying, that was supposed to be due to the differences in size, structure or shape of the precipitates. We believe the PL centers result from the partial reduction of SiO_2 in the SHI tracks. All the observed changes in the layer properties support this idea. Those are: i) an increase of the Raman scattering at ~480 cm^{-1}, typical of atomic vibrations in the amorphous Si; ii) XPS spectra directly show O depletion of the layers and formation of the Si-Si bonds; iii) FTIR data demonstrate the enrichment of the oxide network

with Si. Thus, Si or O-deficient nanoinclusions should be considered as the source of the yellow-orange PL. They are supposed to be just of the nanometer size, because really may appear inside the highly excited and the short-living SHI tracks, which diameters are known as being of several nm.

In spite of the similar response of the dioxide layers to the irradiation with both sorts of SHI, changes in the optical properties under Bi bombardment reached saturation by the dose of about $5x10^{12}$ cm^{-2}, while under Xe irradiation they are traced up to the dose of 10^{14} cm^{-2} (Fig. 1). It is usually accepted, that the structural transformations under SHI bombardment take place within a separate ion track. Thus, the saturation with the ion dose suggests a full coverage of the sample surface by the tracks. The irradiated part of a sample surface S is determined by an expression: $S = S_0 [1- \exp (– c \cdot Q)]$, were S_0 – the full sample area, c stands for the cross-sections of the tracks, and Q denotes the ion dose . Fig. 2 shows the dependence of the irradiated part of the sample surface on the SHI dose. At the dose of $5x10^{12}$ cm^{-2} the sample surface will be completely overlapped with the tracks of 10 nm in diameter. While for the dose of 10^{14} cm^{-2} the full coverage will not be attained if the diameter of the tracks will less than 3 nm. It should be remembered that ionization losses of 167 MeV Xe ions in the oxide layer were ~14.5 keV/nm, and for the 700 MeV Bi ions they were ~24 keV/nm. That means the Bi ions deposited much more energy, providing more intense heating, longer the track cooling time and therefore higher diffusion length of heat. The increase of ionization losses results in enlargement of the SHI tracks diameters. It is worthy to note, that the PL band induced by Bi ions is centered at ~610 nm, while after Xe ions the PL intensity is peaking at ~560 nm. Quantum confinement theory just predicts a redshift with the size enlargement of the light-emitting nanostructures.

Contrary to the ionization losses, the nuclear ion stopping cause the structural transformations by the sequential accumulation of the defects with the dose. To saturate SiO_2 with the defects the total nuclear energy deposition has to be about 10^{23} eV/cm^{-3}. In our case the nuclear losses and the ion doses provided the maximal energy deposition not more than $\sim 7x10^{20}$ eV/cm^3. This is too low value to induce the processes observed.

Conclusions

320 nm-thick SiO_2 layers were thermally grown on the Si substrates. The layers were irradiated with 167 MeV Xe ions to the doses ranging between 10^{12} cm^{-2} and 10^{14} cm^{-2}, or with 700 MeV Bi ions in the dose range of $3x10^{12}$ – $1x10^{13}$ cm^{-2} . The PL bands peaking at 560 nm and at 610 nm appeared and grew with the doses of Xe and Bi ions, respectively. In parallel optical absorption in the region of 950-1150 cm^{-1}, Raman scattering and X-ray photoelectron spectroscopy evidenced a decrease in the number of Si-O bonds and an increase in the number of Si-coordinated atoms. The results obtained are interpreted as the formation of the light-emitting Si nanostructures inside the tracks of swift heavy ions through the disproportionation of SiO_2. Ionization losses of the ions are regarded as responsible for the processes observed. Difference between the dependences of the PL intensity on the doses of Xe and Bi ions are ascribed to their different stopping energies. From the dose dependences the the track diameters for Xe and Bi ions were assessed as <3 nm and ~10 nm, respectively. Shift of the PL bands, induced by Xe and Bi ions, agrees with the predictions of the quantum confinement theory.

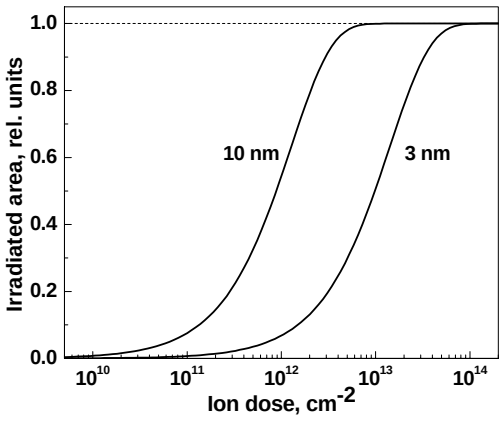

Fig.2. Dependence of the irradiated area on the ion dose for the track diameters of 10 nm and 3 nm.

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