Defect structure and properties of Zn diffusion doped Si after swift Xe ion irradiation

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Abstract. The electronic and optical properties of Si doped by Zn diffusion have been studied for a long time. Recently the defect structure and properties of n-Si (111) compensated by Zn during high-temperature diffusion annealing with subsequent quenching were investigated. The large-scale rod-like defects with μ-sizes have been observed. These defects were connected with Zn precipitates or/and dislocations. In the present paper we study the modification of defect structure and properties of Zn diffusion doped Si after swift heavy ion (SHI) irradiation. The SHI irradiation is known to lead to the formation of latent tracks (nanometer-sized disordered regions around ion trajectory) in many semiconductor and oxide crystals. It was established that the craters with a size of about 100nm surrounded by hillocks are fixed on the Si surface. The traces of dislocation group along Xe ion beam direction were revealed on Si surface. The small-angle boundaries and interstitial-type planar defects have appeared. After Xe ion irradiation with a fluence of 5×10¹² cm⁻² the number of radiating centres in dislocation core increasing so, that increasing the dislocation-related luminescence (DRL) from the lines D₁ and D₂. When the Xe ion irradiation fluence is increased to a value of 1×10¹⁴ cm⁻² the DRL in the Si sample is almost extinguished.

Keywords: Si; Zn high temperature diffusion; quenching; defect clusters; dislocations; swift Xe ion irradiation

1. Introduction.
The electronic and optical properties of Zn diffusion doped Si have been studied for a long time [1, 2]. Recently the defect structure and properties of n-Si (111) compensated by Zn during high-temperature diffusion annealing with subsequent quenching were investigated by the electron beam induced current method in a scanning electron microscope (SEM) [3], by X-ray diffraction (XRD) [4], transmission electron microscopy (TEM), atomic force microscopy (AFM) and other methods. The large-scale rod-
like defects with $\mu$-sizes have been observed. These defects were connected with Zn precipitates or/and dislocations. Apart from them, there are revealed likewise another small-scale type defects with sizes 50nm, namely, chaotically distributed dislocations and dislocation loops or spherical clusters of vacancy-type. In addition, there are observed the Si crystalline with dimension 5-20nm divided by disordered damage regions. Recently it was proposed the new technique for modifications of a crystal lattice subsurface layer by swift heavy ion (SHI) beams [5]. As known SHI irradiation leads to the formation of the so-called latent tracks (nanometer-sized disordered regions around ion trajectory) in many semiconductor and oxide crystals [6-7]. In the present communication, we analyse defect structure and properties in Zn diffusion doped Si after the influence of SHI irradiation.

2. Experimental.
The single crystalline n-type Cz-Si(001) substrate was Zn diffusion-doped up to the Zn concentration of $1\times10^{14}$ cm$^{-3}$ at the temperature of 900°C and quenched subsequently to a room temperature at a rate of about 100°C/s. After quenching, a 50μm-thick layer was ground on both sides of the Si substrate. Then, the substrate surface was prepared by chemical mechanical polishing. After that, the samples were irradiated by $^{132}$Xe$^{26+}$ ions with fluences $1\times10^{12}$-$7.5\times10^{14}$ cm$^{-2}$ and energy of 167MeV.

The surface topology was investigated by SEM MIRA3 (TESCAN) and AFM MFP-3D (Asylum Research) in a semi-contact mode (AC Air Topography). A defect crystal structure of subsurface layers was characterized by XRD and TEM techniques. XRD measurements were performed using D8 Discover (Bruker-AXS) X-ray diffractometer. JEM 2100 (JEOL) unite at accelerating voltage of 200kV was used for TEM investigation of the cross-sectional samples. The photoluminescence (PL) spectra were recorded at 10K using a conventional lock-in technique. For infrared (IR)-region PL was excited by photons at the wavelength $\lambda=920$nm (which were generated by a GaAs-laser at a power of 1W/cm$^2$) and cooled Ge photoresistor was used as a detector. For a visible range of spectra, the PL was excited by a HeCd-laser with a wavelength of 325nm and a pump power of 0.5W/cm$^2$. The photoluminescence spectra were recorded using an FEU-79 photomultiplier.

3. Results and discussion

3.1. SEM study

Fig. 1.a shows an image in the SEM-SE mode (topological contrast) (a) and TEM image of near-surface cross-section after Xe irradiation with a fluence of $7.5\times10^{14}$/cm$^2$ (b).

![Figure 1](image-url)

**Figure 1.** SEM-SE images of Si surface after Xe irradiation with the fluence of $7.5\times10^{14}$/cm$^2$ (a) and TEM image of near surface cross-section after Xe irradiation with the fluence of $7.5\times10^{14}$/cm$^2$ (b).

From Fig.1.a, it follows that on the sample surface the craters with a size of about 100nm are created. They surrounded on edge by hillocks a few tens of nm thick. From SEM-BSE study (figure not shown) follows that the craters are filled with the material, which is lighter than Si. It can be hydrocarbon contamination. Hillocks along the crater edge in the SEM-BSE study do not give the contrast, hence follows that they consist of Si matrix material. The formation of these craters and hillocks we associate with radiation effects due to Si surface irradiation with swift Xe ions.
3.2. TEM study
In Fig. 1,b shows a TEM image of the near-surface layer of silicon. The good visible dark lines are dislocations. They appeared after Xe irradiation. According to SRIM simulation, the projective range of Xe ions implanted with the energy of 167 MeV in Si is about 20μm. It is apparent that the cylindrical amorphous defects with a diameter of 5-10nm were formed during irradiation in the Si matrix. They created stresses in the matrix lattice, which relaxed through the generation of dislocations.

3.3. AFM study
In Fig. 2,a is presented the 2D-image of the sample surface after irradiation with Xe ions in phase contrast. Wherein the surface topology is characterized by the following parameters: Rms=1.9nm and Ra=1.5nm. During the topological study, the revealed dark spots on a 2D-image (not shown) correspond to craters on the Si surface (compare with Fig.1,a). On some dark spots, one can distinguish light (with a higher altitude) hillocks, surrounding craters on the surface. Concerning phase contrast it should be noted next: during cantilever oscillation, it is tip touches the specimen surface; it experiences not only repulsive but other forces. As a result of such interaction, a shift occurs in the oscillations phase too. The distribution of the phase shift along the surface will reflect the distribution of the material characteristics. These properties may represent clusters of radiation-induced point defects or a dislocation group emerging on the surface.

3.4. XRD study
The reciprocal space map (RSM) Si(224) measured for Zn diffusion-doped Si sample after Xe+ ion irradiation is presented in Fig. 2,b. The X-ray diffuse scattering (XRDS) halo around Si(224) reciprocal lattice point is likely caused by agglomeration of SiOx clusters that formed during 900°C annealing and quenching. The Xe+ ion irradiation with the energy of 167MeV generates a large number of radiation induced point defects (the order of 10^4 displacements per ion, according to SRIM simulations). It introduces distortions in the crystal structure of the layer and leads to the formation of the small-angle boundaries (the region with strong intensity blurred across the diffraction vector (224) (Fig. 2,b). XRDS associated with planar interstitial-type defects (blue and dark blue areas) is also observed.

3.5. PL study
Fig.3,a shows the spectra of photoluminescence (PL) at a temperature of 10K after Zn diffusion doped Si (curve 1) and after SHI irradiation at fluences of 5×10^{12} (curve 2) and 1×10^{14}cm^{-2} (curve 3) in the visible region. All spectra are wide unstructured bands in practically the entire range. As seen from Fig.3,a, the Xe irradiation with a fluence of 5×10^{12}cm^{2} leads to a very slight increase in the PL intensity, while it increases up to 1×10^{14}cm^{-2} this leads to a strong increase in the PL intensity with a
maximum of about 2.9 eV. Earlier [8], we showed that the Zn implantation in Si leads to the appearance of a large number of radiation-induced point defects and its clusters in Si. They are a source of intense PL in the visible region of the spectrum. An increase in the Xe fluence leads to an increase in the number of radiation-induced defects, which leads in turn to an observed increase in the intensity PL signal (Fig. 3, a).

![Figure 3. PL spectra in the visible (a) and IR –range (b).](image)

Fig.3,b shows the PL spectra at a temperature of 10K of the samples in the near IR-region. The high-temperature diffusion of Zn in Si and subsequent quenching leads to the appearance of a characteristic dislocation-related luminescence (DRL) due to the dislocations generation after these processes. As is known, DRL in Si is a series of D1-D4 bands in the energy range 0.8-1.0 eV [9]. As follows from Fig. 3,b, the short-wave part of the DRL, consisting of the D4 (1.0 eV) line and its phonon repetition D3 (0.934 eV) line are practically absent in the PL spectra shown. In this part of the spectrum, we observe a superposition of a broad luminescence band centred at 1.07 eV and various phonon repeats of an exciton bound on phosphorus (BE\textsuperscript{TO} and BE\textsuperscript{TA}). Since the lines D3 and D4 are associated with carrier recombination at the straight segments of split 60°-dislocations [10], the absence in the PL spectra of these lines indicates a corresponding morphology of dislocations. At the same time, the low-energy part of the DRL contains of D1 line (0.81 eV) and a barely detectable D2 (0.87 eV) line, whose sources are certain structural defects in the dislocation core (Fig.3,b, curve 1). After Xe irradiation with the fluence of 5×10\textsuperscript{12} cm\textsuperscript{-2}, a more intense DRL spectrum is observed in the energy range 0.75-1.1 eV, and the D1 and D2 line intensity increase noticeably (Fig.3,b, curve 2). These facts indicate an increase in the dislocation density due to Xe irradiation. In turn, the line BE\textsuperscript{TO} and BE\textsuperscript{TA} practically disappeared in the PL spectrum. With an increasing of Xe ion irradiation fluence up to 1×10\textsuperscript{14} cm\textsuperscript{-2}, the DRL in the sample is almost completely extinguished (Fig.3,b, curve 3). In contrast to luminescence in the visible spectral region, which increases its intensity as a result of the increase in the dose of Xe (Fig.3,a), the DRL, in this case, behaves oppositely. At the same time, we can expect a continued increase in the dislocation density with an increase in the Xe radiation fluence, by analogy with the B\textsuperscript{+} ions implantation [11]. This behaviour of DRL can be explained as follows: with an increase in the dose of Xe, an increase in the number of defects in the volume of silicon occurs. The most of these defects are centres of radiationless recombination, and only parts of them are centres of radiative recombination. In both cases, they are competing for recombination channels concerning dislocations, which lead to a strong extinction of DRL. It is worth noting that such DRL behaviour has already been observed earlier in [11], where with increasing dose of implantation of B\textsuperscript{+} ions into the silicon crystal intensity of DRL extinction occurred.
4. Conclusions
After fast Xe ion irradiation the craters with a size of about 100 nm surrounded by hillocks are fixed on the Si surface as a result of lattice damage. The traces of dislocation group along the Xe ion beam direction were revealed and the small-angle boundaries and planar defects of interstitial-type have appeared. Implantation of Zn leads to generation of a set of radiation defects in silicon volume, including dislocations. Additional Xe irradiation with a fluence of $5 \times 10^{12} \text{ cm}^{-2}$ leads to an increase in the intensity of D1 and D2 lines of DRL associated with an increase in the dislocation density. With a further increase in the dose of Xe ions up to $1 \times 10^{14} \text{ cm}^{-2}$ due to the increase in the concentration of radiation defects, and, as a consequence, the appearance of additional channels of recombination of charge carriers, there is a extinction of DRL.

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