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Study of Si implanted with Zn and irradiated with swift Xe ions using X-ray absorption spectroscopy

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The change in the structure of zinc nanoparticles (NPs) in the Si matrix after irradiation with swift Xe ions is analyzed. Silicon wafers were implanted with $^{64}Zn^{+}$ ions at a dose of $5 \cdot 10^{16}$ cm^2 and energy of 50 keV at a temperature of 350°C. After implantation in Si, zinc NPs with a size of about 10 nm were formed. Then the samples were irradiated with swift Xe ions with an energy of 167 MeV and fluences of 10^{13} and 10^{14} cm^{-2}. The samples were studied by X-ray absorption spectroscopy (XAS) on the K-edge of Zn. According to XANES data, in samples with different Xe fluences, zinc has a similar local environment and exists in the metallic phase. According to EXAFS data, the intense peak of the Fourier transform is in the range of 2–3 Å and corresponds to the split first coordination sphere in the Zn structure. After irradiation with Xe, the intensity of this peak noticeably decreases compared to the sample after Zn implantation, which indicates a very strong disordering of the local structure, which is characteristic of small NPs with sizes less than 5 nm.

Keywords: silicon, hot Zn implantation, swift heavy ion irradiation, nanoparticles, XANES, EXAFS.

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A method for modifying metallic nanoparticles in semiconductor or oxide matrices via irradiation with swift heavy ions has been proposed in [1]. This irradiation induces the formation of latent tracks (nanosized disordered regions around the trajectory of a heavy ion [2,3]), thus altering the shape and size of metallic nanoparticles. It is commonly believed that these changes in the shape and size of metallic nanoparticles occur if they are implanted into dielectric matrices with a relatively low heat conductivity. This should not be observed in such semiconductor matrices as Si: since it features a higher heat conductivity, heat released in the propagation of a heavy ion is transferred rapidly away from the ion propagation channel [4]. The pattern changes when the heat conductivity of a semiconductor matrix decreases [5]. These changes may be caused by the presence of various defects (e.g., twins, grain boundaries, dislocations, point defect clusters, and large metallic nanoparticles themselves) in it. This is exactly the case with our experimental system that was chosen to be the model one in the study of fundamental aspects of modification of materials by irradiation with swift heavy ions. In the present study, changes in the structure of Zn nanoparticles in a Si matrix induced by irradiation with swift Xe ions are analyzed.

Czochralski-grown *n*-type (100) silicon wafers (with electron density $n_0 = 5 \cdot 10^{16}$ cm^{-3} at $T = 300$ K) were implanted with $^{64}Zn^{+}$ ions with a fluence of $5 \cdot 10^{16}$ cm^{-2} and an energy of 50 keV at a temperature of 350°C at a High Voltage Engineering heavy-ion accelerator. Zinc nanoparticles with a size on the order of 10 nm formed in Si after implantation [6]. Implanted samples were then irradiated with swift Xe ions at an ITs-100 cyclotron. The irradiation parameters were as follows: energy — 167 MeV; fluence — $2 \cdot 10^{13}$ and $5 \cdot 10^{14}$ cm^{-2}.

Samples were examined by XAS (X-ray absorption spectroscopy) at the Zn *K*-edge. Measurements were performed at the „Structural Materials Science “ end-station of the Kurchatov Synchrotron Radiation Source [7,8]. Spectra were recorded in the fluorescence mode with an air ionization chamber and an Amptek X123 SDD detector. A single-crystal „channel-cut“ Si (111) monochromator was applied to scan over the energy. Parallel to the sample spectrum, the spectrum of a reference specimen (zinc foil), which is needed to calibrate the energy scale, was measured with a beam transmitted through the sample in the transmission mode using two free air ion chambers. XAS spectra were processed using the IFEFFIT suite [9,10]. EXAFS (extended *X*-ray absorption fine structure) Fourier transforms were extracted with weight coefficient $kw = 2$ within the interval of wave numbers $k = 2–8$ Å^{-1} and modeled within the range of interatomic distances $R = 1–3$ Å.

Figure 1 presents the obtained XANES (*X*-ray absorption near edge structure) spectra, while Fig. 2 shows the EXAFS Fourier transforms at the Zn K-edge. According to the XANES data, Zn has similar local environments and exists in the metallic phase in all irradiated samples. The EXAFS data reveal differences between samples. The

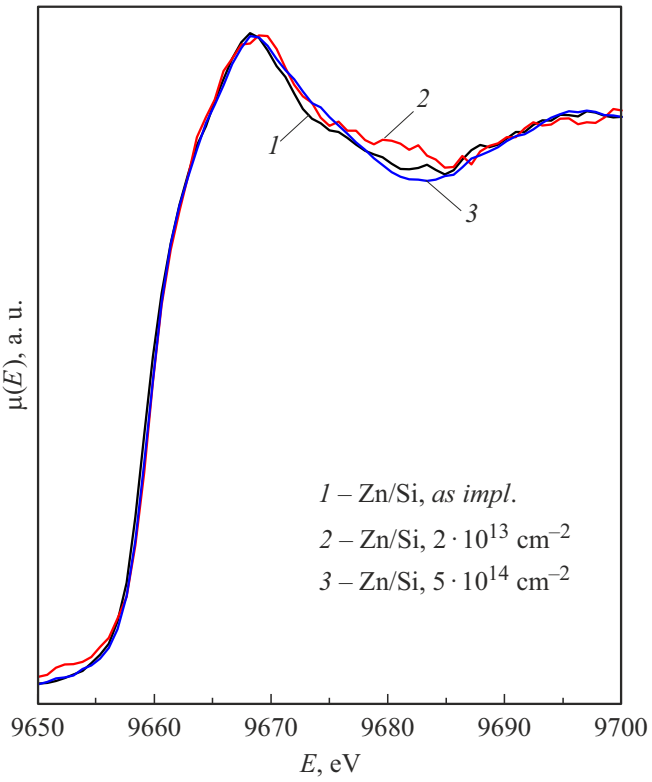

Figure 1. Zn *K*-edge XANES data for silicon implanted with zinc ions prior to (*1*) and after irradiation with Xe ions with a fluence of $2 \cdot 10^{13}$ (*2*) and $5 \cdot 10^{14}\,\mathrm{cm}^{-2}$ (*3*). E is the energy of an X-ray radiation quantum and $\mu(E)$ is the absorption coefficient that is calculated from the fluorescence intensity and normalized to the magnitude of the jump at the absorption edge.

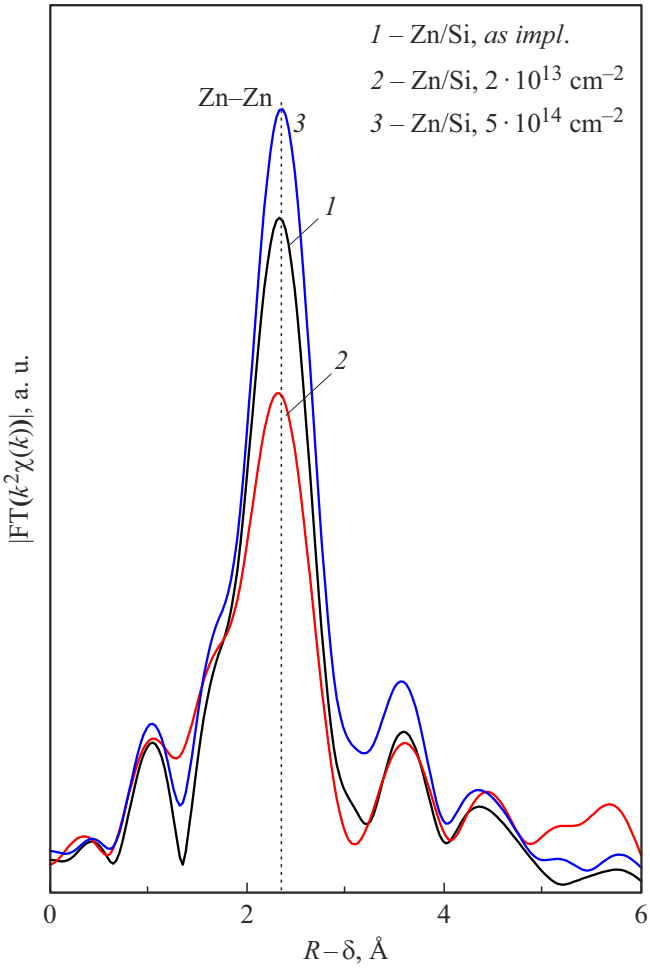

Figure 2. EXAFS Fourier transforms (radial distribution curves of atoms) at the Zn *K*-edge for silicon implanted with zinc ions prior to (*1*) and after irradiation with Xe ions with a fluence of $2 \cdot 10^{13}$ (*2*) and $5 \cdot 10^{14}\,\mathrm{cm}^{-2}$ (*3*). R is the interatomic distance, $\chi(k)$ is the EXAFS function (beyond-the-edge $\mu(E)$ oscillations isolated from the spectrum and re-plotted with respect to electron wave number k), and δ is the difference between the real coordination sphere radius and axis R in the EXAFS Fourier transform emerging due to the phase shift of an electron wave upon scattering of a photoelectron.

most intense peak of Fourier transforms lies within the 2–3 Å interval and corresponds to the split first coordination sphere in the Zn structure. The intensity of this peak in samples subjected to irradiation with Xe decreases considerably relative to the corresponding intensity in the sample implanted with Zn. This is indicative of very strong disordering of the local structure, which is characteristic of small nanoparticles.

The hexagonal structure of metallic zinc features two closest distances between metal atoms, which differ by less than 0.2 Å. Therefore, at least two Zn–Zn paths of scattering of photoelectrons need to be used in EXAFS modeling. The results of modeling are presented in the table.

Both coordination numbers assume the bulk value of 6 in the as-implanted sample. Local structure disordering, which is attributable to a reduction in the nanoparticle size, is observed after irradiation with Xe ions with a fluence of $2 \cdot 10^{13}\,\mathrm{cm}^{-2}$. This is evidenced by the fact that the coordination number corresponding to the greater Zn–Zn interatomic distance decreases. The near-constancy of Debye factors, which should increase significantly in the case of disordering, provides further evidence in favor of size reduction as opposed to structure disordering. The irradiation with Xe ions with a fluence of $5 \cdot 10^{14}\,\mathrm{cm}^{-2}$ induces local structure disordering that is similar in nature to the one observed at a lower Xe fluence, but is greater in magnitude, since both coordination numbers decrease in this case (such behavior is typical of small metallic nanoparticles 1–5 nm in size).

The following conclusions may be inferred from the results of the study.

1. Zinc implanted into silicon at a temperature of 350°C forms relatively large metallic nanoparticles with a coordination number that is equal to bulk values corresponding to nanoparticles larger than 10 nm.

EXAFS modeling results

Sample	N_{Zn-Zn}	R_{Zn-Zn}, Å	σ^2, Å^2	R_f, %
Implanted with Zn ions	6 ± 1 6 ± 1	2.59 2.72	0.0163 0.0125	1.9
Irradiated with Xe ($2 \cdot 10^{13}$ cm^{-2})	6 ± 1 1 ± 1	2.63 2.80	0.0104 0.0017	0.7
Irradiated with Xe ($5 \cdot 10^{14}$ cm^{-2})	4 ± 2 4 ± 2	2.58 2.78	0.0071 0.0072	2.8

Note. N is the coordination number (averaged over all Zn atoms), R is the interatomic distance, σ^2 is the Debye factor (spread of interatomic distances due to thermal fluctuations or structural disorder), and R_f is the R-factor (quadratic residual).

2. Considerable disordering of the local structure of metallic zinc is observed after irradiation with swift Xe ions with a fluence of $2 \cdot 10^{13}$ cm^{-2}. This change is attributable to a reduction in the nanoparticle size (10 nm or smaller).

3. The irradiation with swift Xe ions with a fluence of $5 \cdot 10^{14}$ cm^{-2} induces an even stronger local structure disordering in Zn nanoparticles, which decrease in size to 5 nm (or smaller diameters) in this case.

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Conflict of interest

The authors declare that they have no conflict of interest.

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