Formation of Si nanocrystals in ion implanted Si-SiO$_2$ structures by MeV electron irradiation

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Abstract. Si-SiO$_2$ structures implanted with Si$^+$ or O$^+$ ions were studied after high-energy (MeV) electron irradiation. 15 keV silicon or 10 keV oxygen ions with doses of $1.5 \times 10^{12}$ cm$^{-2}$ were implanted in n-type Si-SiO$_2$ structures. The ion-beam energy was chosen so that the maximum number of the implanted ions would be deposited close to or at the Si-SiO$_2$ interface. The reference (non-implanted) and ion implanted samples were simultaneously irradiated by 20 MeV electrons with a flux of about $1 \times 10^{15}$ cm$^{-2}$. The MeV electron irradiation effect on the redistribution of the implanted ions in Si-SiO$_2$ structures was studied using RBS spectroscopy. The SiO$_2$ surface roughness changes induced by ion implantation and high-energy electron irradiation of the structures were observed by atomic force microscopy (AFM).

1. Introduction

Silicon nanocrystals generated in a SiO$_2$ matrix have attracted considerable interest due to their excellent optical and electronic properties [1-2]. The most important property of these nanocrystals is the intense photoluminescence in the visible and the red/near-infrared ranges of the optical spectrum [2,3]. This is why Si nanocrystals are potential candidates for Si-based optoelectronic devices. Klimenkov et. al. investigated the influence of high-energy electron irradiation on high-dose ion-implanted Si-SiO$_2$ structures. They showed that high-energy electron irradiation can cause motion of clusters or atoms on the surface [4] and that, alternatively to the thermal treatment, the cluster formation can be stimulated by high-energy electron irradiation [5].

Using RBS/C spectra, it has previously been shown that the silicon and oxygen concentrations before and after high-energy electron irradiation are different [9]. As after electron irradiation both (oxygen and silicon) peaks of the RBS/C spectra widen in the same way, it can be assumed that the electron irradiation generates additional radiation defects, which are the reason for the radiation-

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enhanced diffusion of oxygen and an insignificant increase of the amorphous Si layer depth [9]. We compare here these results with AFM measurement of the same samples.

In this work, silicon nanocrystals generated by MeV electron irradiation are observed in a SiO₂ matrix of Si-SiO₂ structures implanted with silicon or oxygen ions (with a dose of 1.5×10¹² cm⁻²). The high-energy electron irradiation decreases insignificantly the oxygen concentration and increases slightly the silicon concentration and the amorphous layer thickness on the surface of the implanted Si-SiO₂ samples. We show that silicon accumulation is observed and silicon nanocrystals are formed at the SiO₂ surface after high-energy electron irradiation. We assume that during MeV electron irradiation (as a result of breaking Si-O bonds) free oxygen is generated and radiation-stimulated motion through defects takes place.

2. Experimental details

n-type CZ Si <100> wafers were cleaned and then oxidized in dry O₂ at 950 °C to oxide thickness of 20 nm. The oxide thickness was determined by ellipsometry. After oxidation, the Si-SiO₂ samples were implanted through the oxide by 15 keV silicon or 10 keV oxygen ions with the same dose of 1.5×10¹² cm⁻². The ion energy was chosen so as to produce maximum ion damage at the Si-SiO₂ interface. The implanted samples and non-implanted samples were simultaneously exposed to 20 MeV electrons perpendicular to the SiO₂ surface. The energy is sufficiently high for the electrons to penetrate through the entire sample (SiO₂ and Si wafer) to create radiation defects. The electron irradiation at a flux of 1.2×10¹⁵ el/cm² was carried out on Microtron MT-25 equipment in Flerov Laboratory of Nuclear Reactions of the Joint Institute of Nuclear Research, (FLNR, JINR) Dubna, Russia. The irradiation was performed in vacuum at a pressure of about 1×10² Pa. The sample temperature was controlled during all irradiation and kept close to room temperature. The distance between the Microtron window and the samples was 150 mm.

The microscopic morphology of reference sample SiO₂ surfaces and of implanted or irradiated Si-SiO₂ structures was observed by atomic force microscope (AFM) in the atmosphere. The AFM images were taken over areas of 1 μm×1 μm on the surface of the SiO₂-Si structures before and after MeV electron irradiation of each sample. AFM was used as a measurement technique to study the changes observed in the dynamic properties of a vibrating tip that interacts with the samples surface.

3. Results and discussion

Figure 1 shows AFM images of the same non-implanted sample before (a) and after 20 MeV electron irradiation (b). The first sample does not show any ordered surface structures before electron irradiation (figure 1 a). Accumulation of nanostructures at the SiO₂ surfaces is observed only after electron irradiation. We assume that the MeV electron irradiation breaks Si-O bonds and the free oxygen atoms move through radiation defects, so that Si nanostructures are generated in the SiO₂. This is in good agreement with our earlier results [7-9] where we showed that oxygen accumulates at the SiO₂-Si interface. We also assume that the radiation defects (created by the MeV electron irradiation) act as a source for Si nanostructures generation in the SiO₂.

![Figure 1. Surface morphology of Si-SiO₂ sample before and after electron irradiation.](image-url)
Figures 2 and 3 present AFM images of silicon- and oxygen-implanted non-irradiated samples (a), and such samples irradiated by 20 MeV electrons (b), respectively. It is obvious that a dose of $1.5 \times 10^{12}$ cm$^{-2}$ for both types of implanted ions is not sufficient to create nanostructures in the oxide. The AFM observation shows structural modifications on the SiO$_2$ surface after the ion implantation. We assume that the implanted Si atoms (figure 2) migrate and form small precursor precipitations in the SiO$_2$ matrix, because the implanted ions and the implantation-induced damages are in an activated state. The following 20-MeV electron irradiation (flux of $1.2 \times 10^{15}$ el/cm$^2$) generates a new silicon nanostructure in SiO$_2$ with different appearance and mode. We assume that these nanostructures are silicon nanocrystals generated in SiO$_2$ by MeV electrons. The AFM images show that the nanocrystal sizes are different depending on the ions implanted in SiO$_2$. The lateral size and height of these structures are presented in table 1. The silicon nanocrystal size vary with the implantation dose as well [10]. The variation of the nanocrystal size can be related to the reduction of the oxygen ion concentration at the oxide surface. The nanocrystals are larger in silicon implanted samples, but have lower density. The nanocrystals in oxygen implanted samples (figure 3) are narrower and with higher density. This means that the effect of the ion implantation is to rearrange the Si-O-Si groups in a different form. The ion implantation breaks many of the Si-O bonds and may also knock atoms from their sites. However, most of the atoms, silicon or oxygen, bond again shortly after being dislodged.

### Table 1. Structural parameters of the nanocrystals observed on the surface of the electron irradiated samples.

| Sample           | $l_{\text{mean}}$ [nm] | $h_{\text{mean}}$ [nm] | $l_{\text{max}}$ [nm] | $h_{\text{max}}$ [nm] |
|------------------|------------------------|------------------------|------------------------|------------------------|
| 20 MeV           | 30                     | 2.2 to 3.2             | 223                    | 4.2                    |
| Si$^{+10^{12}}$ + 20 MeV | 50                     | 2.3 to 4.2             | 50 to 124              | 4.2                    |
| O$^{+10^{12}}$ + 20 MeV | 30                     | 2.3 to 3.2             | 50                     | 6                      |

![Figure 2. Surface morphology of silicon implanted ions Si-SiO$_2$ sample: (with dose of $10^{12}$ cm$^{-2}$) before (a) and after electron irradiation (b).](image)
Conclusions
Structural changes at the silicon surface of the implanted Si-SiO$_2$ samples are observed after high-energy electron irradiation. The MeV electron irradiation effects on the surface morphology of Si-SiO$_2$ structures implanted with silicon or oxygen ions (with dose of $1.5\times10^{12}$ cm$^{-2}$) are by AFM. It is demonstrated that MeV electrons (at a flux of $1\times10^{15}$ cm$^{-2}$) generate additional radiation defects in the entire Si-SiO$_2$ structure and radiation-enhanced diffusion of oxygen takes place which can be the reason for the creation of Si nanocrystals in the SiO$_2$ films in both kinds of implanted samples. The shape and density of these Si nanocrystals depend on type of implanted ions. The SiO$_2$ surface morphology yields additional evidence that Si nanocrystals are created in SiO$_2$ films after electron irradiation only.

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