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Swift heavy ion irradiation effect on the surface of sapphire single crystals

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Abstract

Surface changes in sapphire single crystals with four different orientations produced by irradiation with Kr (305 MeV), Xe (595 MeV) and Bi (710, 557, 269 and 151 MeV) ions have been studied by means of Atomic Force Microscopy (AFM) and Thermo-stimulated Exo-electron Emission (TS EEE). It was observed that individual surface defects with density corresponding to the ion fluence have been detected only for Bi ions with energy higher than 269 MeV. At the highest surface ionising density values of 41 keV/nm and 35 keV/nm these defects were found to have complicated structure- the hillock surrounded by border ring or hillock with cavity on the top. The TS EEE measurements show that all studied crystals are characterized by TS EEE curve depending on crystallographic orientation and irradiation dose. At the same time, some general features in the TS EEE data for all crystallographic orientation are observed.

Keywords

Heavy ions, sapphire, tracks, AFM, exoelectronic emission.

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1. Introduction

Aluminum oxide is one of the most radiation-resistant insulators, what makes it extremely useful for different nuclear-energy units. Therefore the investigations of radiation damage in sapphire are important for further development of nuclear technology.

Recent experiments have demonstrated the damage formation in aluminium oxide single crystals due to collective electronic excitations (Canut et al., 1993, 1995, Ramos et al., 1998a, 1998b). In particular, it was shown that the threshold energy deposition for extended defect creation is expected at of about 21 keV/nm. It was also found that extreme ionising density achieved by tens MeV fulleren irradiation leads to formation of latent tracks in material bulk and hillocks on the crystal surface. Track diameters for the energy loss rate of 76.2 keV/nm were measured (13 nm) with transmission electron microscope. AFM investigation of the topography of samples irradiated by 30 MeV fullerens showed the appearance of conical hillocks corresponding to individual latent tracks at the surface with diameter of 20 nm and height of 4.5±0.5 nm. The observed correlation between structural change on the surface and in bulk seems to be very important since it make it possible to apply the AFM-technique in such experiments. To our knowelege there are not actually any studies of the topography of Al_2O_3 crystal surface, irradiated at high level electronic stopping power, excepting the one by Ramos et al. (1998 b).

The TS EEE technique (Kortov et al,1986) was also applied to irradiated sapphire investigation. Because of its high sensitivity to the defect-formation processes and of the small depth of emergence of electrons, the TS EEE method seems to be very promising for the diagnostics of the physicochemical state of the surface layers of materials exposed to the ionic treatment. A correlation between the TS EEE and thermoluminescence methods has been established for these crystals (Petel and Holzapfel, 1973). The TS EEE method was applied to study the radiation-induced transformations on the surface of a sapphire crystal (Krylova,1998). However, only low-energy types of radiation (α, β, and γ) were used in that work, and the question of the influence of the crystallographic orientation of surface on the radiation effect was not raised at all.

Moreover, targets with only one crystallographic orientation –**c** (0001) were used in all the above-mentioned works. Sapphire is known to have complicated crystallographic structure with rather low symmetry and one can expect a different response from crystals with different orientation exposed to high energy heavy ion irradiation. The aim of the present work is the study the surface changes induced by 0.7-3.5 MeV/amu Kr, Xe and Bi ion irradiation in α-Al_2O_3 single crystals with different crystallographic orientation.

2. Experimental procedure

The leucosapphire single crystals were grown from the melt (horizontal crystallisation technique) and then annealed in vacuum at a temperature of about 1600 °C. The specimens of **c** (0001), **m** ($10\bar{1}0$), **a** ($11\bar{2}0$) and **r** ($10\bar{1}2$) orientations in the form of 2×1×0.5 mm plates have been used in the experiments. Before the irradiation the samples were optically polished and annealed in the room air at 1200 ^{0} C for 6 hours. The irradiation of targets with Kr (305 MeV), Xe (595 MeV) and Bi (710 MeV) ions at room temperature and normal beam incidence was performed at the JINR U-400 cyclotron facility. The Kr and Xe ion fluences were in the range of 10^{11} cm^{-2} - 10^{12} cm^{-2}. The irradiation fluence for the Bi ions was 10^{10} cm^{-2}.

During each irradiation samples of all orientations were mounted on one target holder. An ion beam homogeneity no worse than 5% on irradiating wafer surface has been achieved by using low-frequency beam scanning in horizontal and vertical directions (Skuratov et al., 1999). In order to modify the Bi ion energy and study possible effects at the same experimental conditions every target surface was divided into five parts – one part was open and the rest were covered with aluminium foils of 6, 18, 24 and 36 μm thickness. The main characteristics of the irradiation, such as absorber thickness, incident energy, surface electronic and nuclear stopping powers $(dE/dx)_{ion}$ and $(dE/dx)_{el}$, ion projected range R_p in aluminium oxide, calculated with the SRIM2000 code, are given in Table 1.

The irradiated samples were subjected to AFM and TS EEE studies. The tapping mode AFM measurements were performed in air on Solver P47 (NT-MDT) device using ULTRASHARP cantilevers supplied by MikroMasch and NT-MDT cantilevers . We used cantilevers of different types: low-frequency with rectangular lever (NSC12-C, f=150 kHz), high-frequency with rectangular lever (NSC12-B, f=315 kHz) and high-frequency with triangle lever (NSC11-B, f=315 kHz) with different oscillation amplitude and damping. All measurements have shown similar results.

The method of thermally stimulated exoelectronic emission (TS EEE) consists in studying a non-stationary electron emission from the surface of a solid in a nonequilibrium (excited) state. The emission is stimulated by heating the solid up to a temperature just below the threshold of the appearance of steady-state thermal emission. The electrons emitted from the excited surface layer of material can provide essential information. The measurement of the temperature dependence of the TS EEE current gives a characteristic curve (the so-called "glow curve"). The temperature positions of glow curve maxima are determined by the type of structural failures (disturbances), while the amplitude is proportional to the concentration of active-emission centers.

The equipment for TS EEE was constructed by the authors using a standard heater and amplifier (secondary electron multiplier with an open input; the amplification factor of 10^{6} - 10^{9}, temporary resolution of 10^{-9} - 10^{-10} s and intrinsic background of 1 pulse/s). Before the TS EEE measurement, sapphire plates were preliminarily activated by the corona-discharge plasma in air. The samples were then placed into a vacuum chamber (vacuum better than 10^{-1} Pa) and heated up with a special device at a constant rate of 5 K/min. The measurements were performed in the pulse regime.

3. Results and discussion

The AFM investigation showed that Bi ions with energy of 710, 557 and 269 MeV have caused the individual surface defects with density corresponding to the fluence used (10^{10} cm^{-2}) while for ions with energy of 150 MeV and less no surface effects were found (Fig.1). Also no defects were detected for irradiations with Xe (595 MeV) and Kr (305 MeV) ions. An example of the surface changes of **m-**oriented sapphire irradiated with 710 MeV and 269 MeV Bi ions is shown in Fig. 2 together with line cross-sections through the images. As it can be seen, the structure of the observed defects crucially depends on the electronic stopping power of the incident ions near the surface. For the value of $(dE/dx)_{ion.}$ = 41 keV/nm the defects look as craters containing in their central part hillocks of 15 nm mean basal diameter (d in Table 2) and 2 nm mean height (H in Table 2) surrounded by border “splash” rings of 1.1 nm mean height (h in Table 2) and 27 nm basal diameter (D in Table 2). For 557 MeV Bi ions having about the same electronic stopping power (40 keV/nm) the crater structure is similar. For less energetic ions (269 MeV, $(dE/dx)_{ion.}$ = 35 keV/nm) craters appear quite different - as hillocks of 1 nm height (h in Table 2) and 22 nm basal diameter (D in Table 2) with small central holes of 5 nm diameter (d in Table 2) and 0.7 nm depth. Geometrical parameters of craters for all surface ionising densities and crystal orientations are listed in Table 2.

The present AFM images and data given in Table 2 lead to the following important observations. First of all, craters of complicated form produced by Bi ion bombardment at high electronic stopping power have been observed on sapphire surface for the first time. As known, high-energy heavy ion irradiation usually results in the creation of either craters or hillocks on the surface of oxide crystals. Ramos et al., (1998b) have suggested that the conical hillocks observed on the 30 MeV fullerene irradiated aluminium oxide surface could be described as a partial emergence of the ``track’s head". It was suggested that the hillock structures result from an out of plane expansion of the amorphous core tracks related to a relative decrease in the density of amorphized α-Al_2O_3. Following this suggestion and taking into account our experimental data, it can be stated that the electronic stopping power threshold for continuous tracks formation in sapphire, associated with the hillock appearance in the crater, is 35 keV/nm < $(dE/dx)_{ion.} \leq$ 40 keV/nm. Rough estimates of the track size as diameter of the hillocks measured at half-maximum of their height (see, for example, Audouard et al., 1998, Ramos et al., 1998b) give us a reliable value of about 7 nm. One should note that this value is in good agreement with the track size of 8 nm, which was found under TEM observation in sapphire irradiated with 15 MeV fullerens at very close ionizing density of 41.4 keV/nm (Ramos et al., 1998b).

Craters of other type, registered at 35 keV/nm (see Fig. 1), reflect, in our opinion, the structural modifications preceding continuous tracks appearance, in particular, discrete or discontinuous track formation. As for possible mechanisms responsible for the track formation, on the base of our experimental results we can not prove which model - thermal spike or ion explosion spike – play the dominant role. This question remains to be answered.

It can be seen from Table 2 that the crater parameters differ for the different crystal orientations, nevertheless more experiments are needed to obtain the definite orientation dependence. We can note that most clear and significant changes were observed for m- and c-orientations, that might be due to the higher oxygen atom packing in these directions. At the same time, for a- and r- orientations height of defects is smaller and no surface defects were detected for $(dE/dx)_{ion}$ =35 keV/nm.

The TS EEE curves for four orientation of Kr-irradiated samples are presented on Fig. 3 (for the fluence $3 \cdot 10^{11}$ cm^{-2}). After irradiation glow-curves for each orientation change in common way: the intensity of low-temperature peak (200-300 ^{0}C) decreases, while the high-temperature (400-500 ^{0}C) peak intensity increases and its position shifts to the higher temperature value. Nevertheless, each orientation has a specific, characteristic glow-curve shape.

Fig. 4 demonstrates results obtained for Bi-irradiated samples. All the peaks (low-temperature and, especially, high-temperature) become more intensive. Doubling of high-temperature peaks for **r** and **c** orientation is observed. In this case for all orientation under investigation “middle” peak appears at the temperature ≈ 320^0 C.

It is easy to see that the character of the TS EEE spectra depends on both crystallographic orientation of the surface under irradiation and on the bombardment ion energy. This may be attributed to the fact that surface traps associated with radiation structural defects have different energy states for different orientations. This effect can be connected with different reticular density of the surfaces under investigation.

4. Conclusions

The surface defects of complicated form attributed to the latent track formation in sapphire as a result of high-energy heavy ion irradiation have been observed for the first time. The dependence of structure of these defects on electronic stopping power has been found. Threshold ionising density necessary for track formation would be in the range from 35 to 40 keV/nm. Mean track diameter is estimated to be of about 7 nm. The present AFM images and data given in the tables lead to the following conclusions: craters of complicated form produced by Bi ion bombardment associated with high level of electronic stopping power – they appear under certain threshold ionizing density value. These defects could not be due to the elastic collisions, since the $(dE/dx)_{el.}$ values are rather small and these values decreased with increasing of ion energy (see Table 1).

The dependence of the TS EEE curve on crystallographic orientation and irradiation parameters was found to be significant.

Acknowledgements

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Table1.
The characteristics of the Bi ion irradiation in α-Al_2O_3 specimens.

Absorber thickness, μm	Energy of Bi ions, MeV	$(dE/dx)_{ion.}$, keV/nm	$(dE/dx)_{el.}$, keV/nm	Projected range, μm
0	710	41	0,08	24
6	557	40	0,12	21.5
18	269	35	0,19	13
24	151	27	0,35	9.5
36	0	0		0

Table 2.
Geometrical parameters of structural defects on sapphire surface (**m**, **c**, **a**, **r** – orientation) caused by Bi ion irradiation. D – external basal diameter of the defect, d – basal diameter of the middle hillock or middle cavity (for $(dE/dx)_{ion}$ =35 keV/nm), H – height of the central hillock, h- height of the border "splash" ring.

Crystal orientaion	**m**			**c**			**a**			**r**		
$(dE/dx)_{ion.}$, keV/nm	41	40	35	41	40	35	41	40	35	41	40	35
D, nm	27±2	27±2	25±2	25±2	26±2	27±2	30±2	30±2	-	22±2	27±2	-
d, nm	15±2	15±2	5±1	17±2	17±2	5±1	20±2	20±2	-	17±2	-	-
H, nm	2.0 ±0.2	2.0 ±0.2	-	2.5 ±0.2	1.9 ±0.2	-	1.2 ±0.2	1.2 ±0.2	-	0.8 ±0.2	1.0 ±0.2	-
h, nm	1.1 ±0.2	0.6 ±0.2	1.0 ±0.2	0.6 ±0.2	0.7 ±0.2	1.0 ±0.2	1.2 ±0.2	1.2 ±0.2	-	0.1 ±0.1	0.1 ±0.1	-

Figure captions

Fig. 1. AFM images of sapphire surface irradiated with Bi ions of different energies: a-710 MeV, b – 557 MeV, c – 269 MeV, d – 151 MeV; scan size 200x200 nm. Vertical scale is shown in the scalebars right to each image.

Fig. 2. 3D AFM images (scan size 40x40 nm) and corresponding cross-sections of two crater types on irradiated sapphire surface:
a, b – crater induced by 710 MeV Bi ion; c,d – crater induced by 269 MeV Bi ion.

Fig. 3. Temperature dependence of TS EEE for different crystallographic orientation of sapphire A – **c,** B - **m,** C- **a**, D- **r**. Dotted line – initial sample, solid line- Kr irradiation, fluence $3 \cdot 10^{11}$ cm^{-2}.

Fig. 4 .Temperature dependence of TS EEE for different crystallographic orientations of sapphire A – **m,** B - **c,** C - **a**, D - **r**. Bi –irradiation, fluence 10^{10} cm^{-2}.