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Surface modifications of sapphire single crystals and PET polymer induced by swift heavy ions.

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ABSTRACT

Surface changes in sapphire single crystals with four different orientations produced by irradiation with Kr , Xe and Bi swift ions and in polyethelenetherephtalate thin films produced by Xe ions have been studied by means of Atomic Force Microscopy. It was observed that individual surface defects with density corresponding to the ion fluence have been detected for sapphire samples only for Bi ions with energy higher than 269 MeV. These defects were found to have complicated structure- the hillock surrounded by border ring or hillock with cavity on the top: the type of structure depends on irradiation energy. The surface track shape in polymer was found to depend on polymer treatment: small cavity just after the irradiation, bigger cavity after low-temperature annealing and the hillock after high-temperature annealing. It was shown that annealing of the polymer allows to visualise different areas around the track axis. The possible mechanism of such behaviour (amorphisation and crystallisation) was discussed.

1. Introduction

Aluminum oxide is one of the most radiation-resistant insulators, what makes it extremely useful for different nuclear-energy units. Polyetheleneterephtalate (PET) is the base material for production of track membranes (nuclear filters). Therefore the investigations of radiation damage in sapphire and PET are important for further development of nuclear technology and applications. The surface after the irradiation is usually investigated by electronic microscopy methods. But the resolution of these techniques is not high enough to detect initial, virgin surface defects: the chemical treatment (etching) is usually needed. The highest resolution of AFM-technique gave possibility of track and surface defects investigation just after the irradiation.

The AFM studies of the topography of Al_2O_3 crystal surface, irradiated with high-energy particles, were carried out in [1,2] : 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 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. The first results for swift high ion accelerated sapphire crystals obtained by authors, is described in [3]. Using AFM the initial defects at the surface of irradiated polycarbonate (CR-39) were investigated in [4] and it was found that the track area has complicated structure. Three different zones were detected (after some sort of chemical treatment) at the surface of Xe-irradiated PET –zones of carbonisation, destruction and cross-linking [5,6].

2. Experimental procedure.

The **sapphire** single crystals were grown from the melt, annealed in vacuum and then cut out into thin sheets with different orientations. The specimens of c (0001), m (10 $\bar{1}$0), a (11 $\bar{2}$0) and r (10 $\bar{1}$2) orientations were used in the experiments. Before the irradiation the samples were optically polished and annealed. The irradiation of targets with Kr (305 MeV), Xe (595 MeV) and Bi (710). **).** 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 mcm thickness**.** This make it possible to obtain 557,269, 151 MeV ions energies at the entrance in crystal. Ionisation was performed at the U-400 cyclotron (JINR, Dubna). The irradiation fluence was varyed from 10^{10} cm^{-2} to 10^{12} cm^{-2} .

Biaxially oriented **polymer (PET)** film with thickness 10 mcm was used. After the irradiation with Xe ions (150 MeV and fluence $2{\cdot}10^9$ $ions{\cdot}cm^{-2}$)) samples were annealed during 2 hours at two temperatures- 100 ^{0} C and 160 ^{0} C. So, three types of samples were investigated- initial (just after the irradiation), and developed at the temperatures of 100 and 160 ^{0} C.

All samples were investigated by AFM. 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.

It must be mentioned that “tapping regime” was used both for crystal and polymer samples and showed better results (to compare with “contact regime”).

3. Results and discussion

Crystal. The AFM investigations showed that no individual defects exist for Kr, Xe and low-energy Bi ion irradiation. Only integral changes of the surface were detected - for example, increasing of the roughness. For highest irradiation energy –for Bi ions with energy of 710, 557 and 269 MeV the individual surface defects with density corresponding to the fluence used (10^{10} cm^{-2}) were detected. An example of the surface changes of **m-**oriented sapphire irradiated with 710 MeV and 269 MeV Bi ions is shown in Fig. 1 together with line cross-sections through the images. For the irradiation energy of 710 and 557 MeV the defects look as craters containing in their central part hillocks of 15 nm mean basal diameter and 2 nm mean height surrounded by border "splash" rings (Fig.1 a and Fig. 1 b –cross-sections). For less energetic ions (269 MeV) craters appear quite different - as hillocks of 1 nm height and 22 nm basal diameter with small central holes (Fig.1c,d). Geometrical parameters of craters for all energies depends on crystallographic orientations. For example, the ratio of the hillock height and the border height is different for all four orientation under investigation. To our opinion this parameter may be taken as a characteristic of orientation. We can also 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 or different reticular density of the crystallographic planes.

Different forms of defects reflect, in our opinion, the different stages of track formation in crystal: for higher energy the expansion of the middle part of the track (which forms the hillock) related to decrease in the density of amorphised central zone of track in 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 (which is depends on the irradiation energy), associated with the hillock appearance in the crater, is laying in limits of 35 keV/nm < $(dE/dx)_{ion.}$ ≤ 40 keV/nm. Rough estimates of the track size as diameter of the hillocks measured at half-maximum of their height (see, for example,[2,7]), 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 [2].

Craters of other type (Fig.1c,d), registered for the 269 MeV ion energy (which corresponds to 35 keV/nm ionising density), reflect, in our opinion, the structural modifications preceding continuous tracks appearance, in particular, discrete or discontinuous track formation..

Polymer. For polymer samples just after the irradiation small cavities with diameter 7 nm were found – in accordance with the results of the work [8]. Their surface densities corresponds to the irradiation fluence. For annealed PET films surface defects were also detected, and their shape was found to depend on annealing temperature. After 100 ^{0} C treatment these defects look like cavities with diameter approx. 25-30 nm and depth 4 nm (Fig.2a). Different types of defects were found after 160^0 C annealing: the hillocks with diameter 25-35 nm and the height 3-5 nm (Fig.2b).

The small cavities (diameter 7 nm) at the non-annealed surface caused with polymer destruction at the "track core" [8]. The temperature development of polymer leads to different processes at the zones of "track cover" : processes of polymer crystallisation took place in track area at the temperature 100^0C. As a result , the density of these areas increase; this process leads to "compression" of track substance and formation of cavities at the surface. On the other hand, the dominant process at 160^0C is amorphisation. Extraction of gaseous products out of track zone was also detected. All these processes leads to decreasing of track area density and expansion of the track material. The IR- spectra of polymer just after the irradiation and irradiated polymer after annealing confirmed these conclusions: the ratio of bands D_{1473}/D_{1455} was measured. (D_{1473} – band is connected with trans-conformation and D_{1455} – band is connected with gosh-conformation of molecule). It was shown that after 100^0 C treatment this ratio was increased , which reflects the macromolecules orientation and crystallisation, while the 160^0 C annealing leads to decreasing of D_{1473}/D_{1455} –ratio , which confirms the polymer amorphisation.

4. Conclusions

It was shown that AFM method is a fine tool for surface track areas in crystal and polymer investigation. For the first time the fine, complicated structure of track in sapphire was found. For the first time the different stages of track degradation during annealing were detected and correlated with the complicated track structure. In both cases – for crystal and for polymer –hillock formation is caused by track area amorphisation and expansion.

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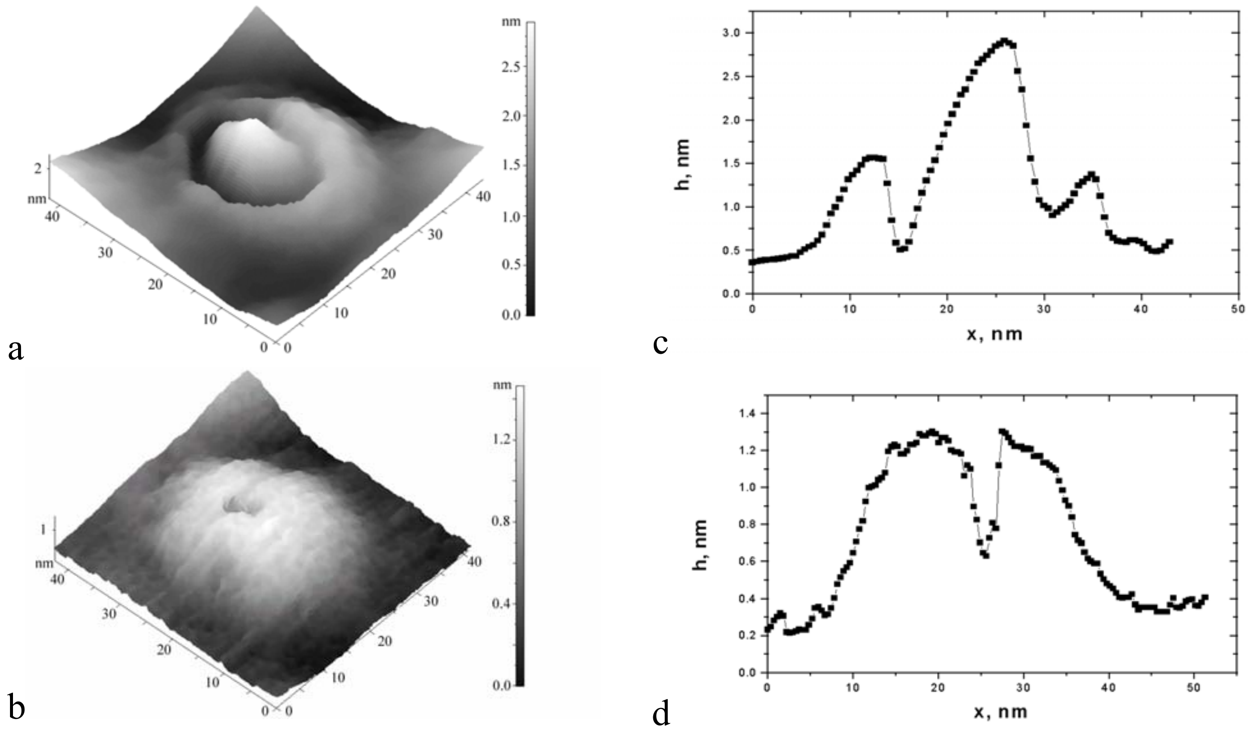

Fig. 1.

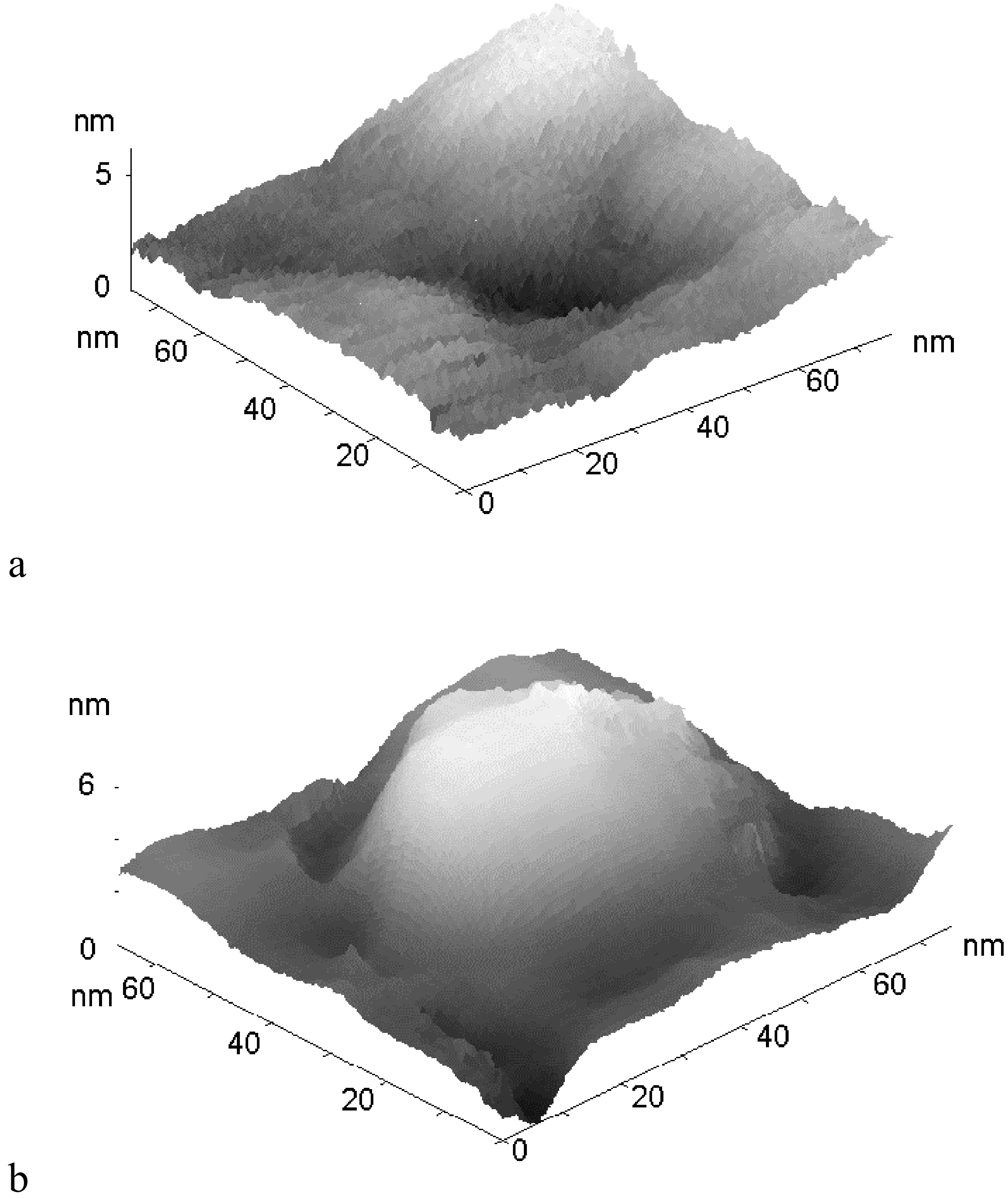

Fig. 2.