POLYGONISATION OF IONIC SINGLE CRYSTALS — A NEW EFFECT OF SWIFT ION BOMBARDMENT*

A. Turos†, L. Nowicki

The Andrzej Soltan Institute for Nuclear Studies
Hoża 69, 00-681 Warsaw, Poland

F. Garrido, L. Thomé

Centre de Spectrométrie Nucléaire et de Spectrométrie de Masse
CNRS-IN2P3, 91405 Orsay Campus, France

R. Fromknecht

Research Center Karlsruhe, INFP
PO Box 3640, 75636 Karlsruhe, Germany

and J. Domagała

Institute of Physics, Polish Academy of Sciences
Al. Lotników 32/46, 02-668 Warsaw, Poland

(Received July 4, 1998)

Isostructural oxide single crystals of the fluorite structure: stabilized cubic zirconia and UO2 were bombarded at room temperature with 72 MeV iodine ions or 340 MeV Xe ions, respectively. The aim of this paper was the study of structural transformations induced by ion bombardment in two different regimes: at 72 MeV where the radiation damage production is strongly influenced by collision cascades and at higher energies where the ionization mechanism prevails. The structure of as-grown and implanted single crystals was examined using the RBS/channeling technique and X-ray diffraction analysis. Some of the samples were also investigated by transmission electron microscopy. It was observed that the residual damage depends strongly on energy loss mechanism, and hence on the incident ion energy. At high incident energies solidification of latent tracks in UO_2 leads to their polygonisation. Since the energy of 72 MeV is too low for latent track formation, the resulting damage is composed of dislocation and clusters and is similar to that created by the ion bombardment at low energies. The amount of defects was strongly enhanced by the interaction of ionised regions with collision cascades.

PACS numbers: 61.16.–d, 61.16.Fk, 61.80.Jh

* Presented at the International Conference "Nuclear Physics Close to the Barrier", Warszawa, Poland, June 30–July 4, 1998.

† and the Institute of Electronic Materials Technology, Warsaw, Poland.

1. Introduction

Bombardment of solids with energetic ions is becoming increasingly important in material engineering. In microelectronic technology it is used to modify electrical parameters and microstructure of surface layers, or to synthesize surface and buried layers. Although the mechanisms of radiation damage produced by ion irradiation at energies below 2 MeV are quite well known, the processes occurring at higher energies are still extensively studied. To the fairly good approximation processes occurring during the low energy ion bombardment can be described by the model of a linear cascade resulted from binary collisions of impinging ions and recoils with target atoms. On the other hand, swift heavy ions produce along their trajectory highly defected or amorphous regions, called latent tracks. Latent tracks are principally due to the extremely high ionization density in the wake of primary ions.

In the present paper, the results of a study of structural transformations in ionic single crystals of the fluorite structure bombarded at energies below and above the threshold of the latent track formation are presented. Uranium dioxide UO_2 is today's fuel for electricity production, whereas the isomorphic stabilized cubic zirconia (ZrO_2 +10 mol% Y_{23}) is considered as a promising inert matrix for transmutations of highly active actinides by in pile neutron irradiation. Both materials are therefore subjected to the irradiation with swift fission products. Since the response of these two materials to the low energy ion bombardment is almost identical [1-4] one can expect that also at high energies their behavior will be similar.

2. Models of latent track formation

It can be useful to briefly recall the basic processes associated with the interaction of an energetic ion with atoms and electrons of the target. Here we will focus exclusively on the Coulomb interactions leaving all nuclear processes out of consideration. In the first step, occurring in less than 10^{-16} s, electronic excitations and ionization along the track of the projectile occurs. Local thermalization of the electronic system is completed at about 10^{-14} s. Energy transfer from electrons to atoms takes place principally between 10^{-14} and 10^{-12} s depending on the magnitude of electron–phonon coupling. For intense electronic excitations induced by an electronic stopping power exceeding a few keV/nm, a cylindrical region around the track of the ion becomes fluid and reaches its maximum diameter of several nm within some ps [5]. In this stage the system has virtually lost the "memory" of its initial stage. Upon next 100 ps the surplus energy has been dissipated and the latent track is cooled down to ambient temperature. However, after completion of the solidification the final stage differs from the initial one. Basing

on these considerations, two models of the conversion of energy transferred to electrons into atomic motion were developed [6]:

a. Coulomb explosion model focuses on excited electrons and on processes by which their energy dissipates in the lattice, it considers creation of a cylinder of highly ionized matter which is very unstable due to the electrostatic repulsion,

b. thermal spike model deals with the response of ionized atoms which rapidly gained by the efficient energy transfer from hot electrons to lattice atoms; a strong electron phonon coupling is necessary.

3. Experimental

Zirconia single crystals of (100) orientation and of 1 mm thickness were polished on one side to a mirror finish. They were bombarded with 72 MeV I ions to the fluences ranging from 5×10^{14} to 5×10^{15} at/cm^2 at Chalk River Laboratory, Canada. Damage accumulation was assessed by Rutherford Backscatering Spectroscopy in the channeling mode (RBS/c) using 2 MeV ^{4}He ions. Some of the samples were also examined by cross-sectional transmission electron microscopy [7].

UO2 single crystals 1.5 mm thick were polished with a diamond paste and subsequently annealed at 1500°C in Ar/(8%)H_2 in order to remove the remnant damage. The samples were irradiated with 340 MeV Xe ions to the fluence of 1×10^{13} at/cm^2 at Hahn–Meitner Institute in Berlin, Germany. The virgin and irradiated crystals were analyzed by RBS/c using 3.045 MeV ^{4}He ions and high resolution X-ray diffraction (XRD) [8].

Fig. 1 shows the range distribution, electronic and displacive energy loss for 340 MeV Xe ions in UO_2 calculated using the Monte Carlo TRIM code [9]. TRIM simulations showed that the ion range is 15 μm and the longitudinal range straggling is 0.86 μm. The magnitude of the electronic energy loss in the near surface region is about 35 keV/nm and decreases linearly with increasing depth. It is 38000 times larger than the collisional energy loss. For lower energy of impinging ions these values are much smaller: ion range is 6.8 μm, range straggling is 0.4 μm, and the electronic stopping power at the surface is 19 keV/nm.

The ranges of primary ions are in all cases beyond the thickness accessible for the RBS/c analysis which is 2.5-4 μm. Also the probing depth of the XRD analysis does not exceed 6 μm. Only by means of cross-sectional Transmission Electron Microscopy (TEM) the whole depth of the bombarded region can be visualized.

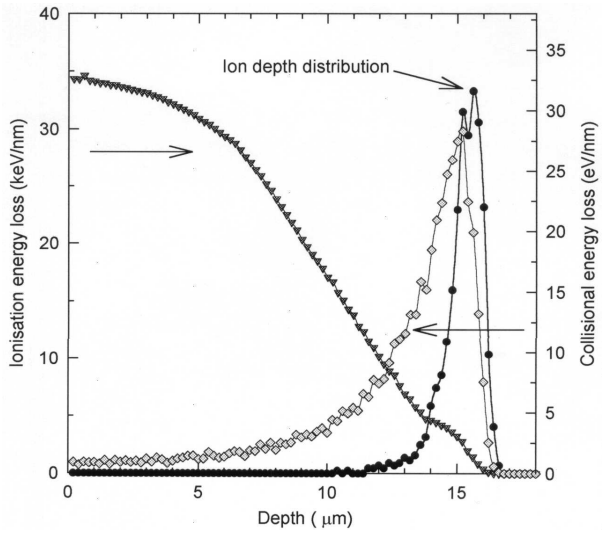

Fig. 1. Range distribution of impinging ions, electronic and collisional energy loss for 340 MeV Xe ions in UO_2 calculated using the Monte Carlo SRIM code.

4. Results

Fig. 2 shows RBS/c random and aligned spectra obtained for an UO2 single crystal prior and after irradiation with $1x10^{13}$Xe/cm2 at 340 MeV. The spectra are divided into two parts: high energy part related to the backscattering from U atoms located in the 0-700 nm depth region, and the low energy part where peaks reflecting the resonant scattering by O atoms are superimposed on a continuos background due to backscattering from U atoms located below the first region. Aligned spectrum for the virgin crystal presents a very low normalized minimum yield just behind the surface peak indicating high crystalline perfection of the crystal. After irradiation the sample exhibits an important increase of the surface peak and strong enhancement of the bascattering yield extending towards the greater depth. Moreover, the dechanneling rate remains constant over the whole analyzed depth indicating an uniform concentration of defects. The detailed discussion of the principles of the RBS/c analysis can be found in Ref. [10].

Fig. 3 displays the XRD map in the reciprocal space recorded for the bombarded UO_2 crystals. It consists of the combination of two scans: the (Θ-2(Θ) scan, (G_{220}), that is usually applied for the lattice parameter determination, and the Ω-scan, (G_{001}), revealing the misalignement of grains in the crystal. The contours on the map represent the lines of equal intensity of X-ray diffraction. The two region are depicted in Fig. 3: the region labeled surface corresponds to the surface peak in the RBS/c spectrum whereas

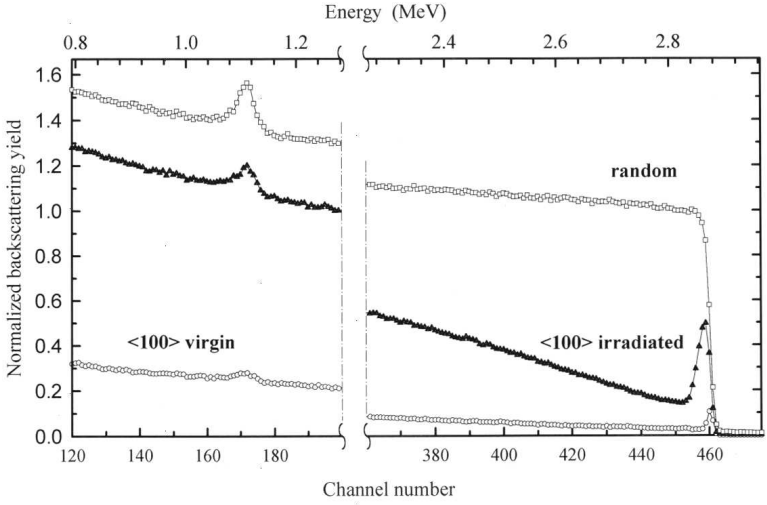

Fig. 2. Random and aligned spectra recorded with 3.045 MeV 4He ions for the virgin and irradiated UO_2 single crystal. Irradiation was performed using 340 MeV Xe ions to the fluence 1×10^{13} at/cm^2.

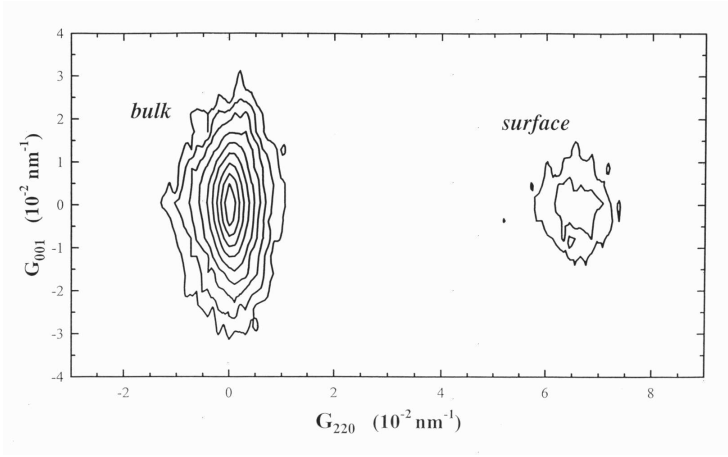

Fig. 3. X-ray diffraction contour map in the reciprocal space displaying bulk and surface regions of an UO_2 single crystal irradiated as in Fig. 2.

that labeled bulk reflects the deeper region. Let us focus first on the bulk region. One notes relatively small broadening of the peak in the (G_{220}) direction indicating a spread of crystal lattice parameter which is typical for ion implanted crystals. On the other hand, the spreading along the (G_{001}) direction is much larger than that along the perpendicular direction. This can

be attributed to the formation of grains with a small misalignment ($\sim 1^\circ$) with respect to the principal crystallographic direction of the crystal. This effect is called polygonisation.

Fig. 4 shows the RBS/c spectra for zirconia single crystals bombarded to different fluences of 72 MeV I ions. In contrast to previously discussed results the dechanneling for all applied fluences is surprisingly high. The spectra in Fig. 4 suggest that zirconia crystals have suffered rather extensive microstructural changes like partial amorphisation or polygonisation. The cross-sectional TEM micrographs and the microdiffraction patterns from the irradiated region indicated that it remains epitaxial with the underlying substrate. Since TEM failed to reveal evidence for a structural transformation, the high magnitude of the RBS/c dechanneling yield is apparently due to a high concentration of extended defects and defect clusters.

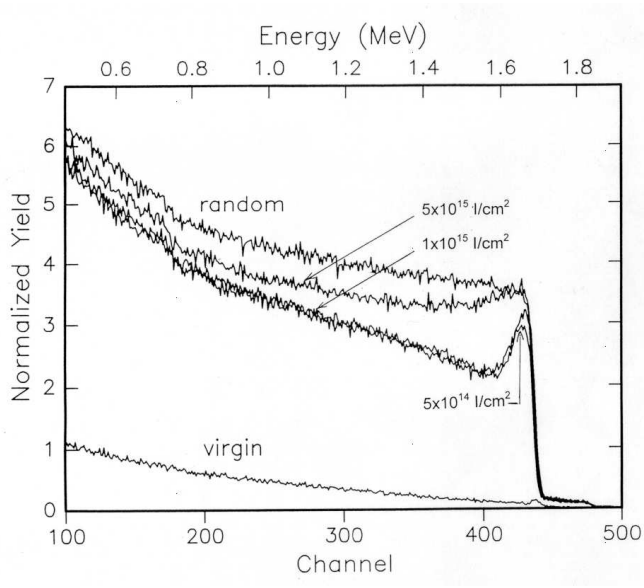

Fig. 4. Random and aligned spectra recorded with 2 MeV ^{4}He ions for the virgin and irradiated zirconia single crystal. Irradiation was performed using 72 MeV I ions to different fluences as indicated in the drawing.

5. Discussion and conclusions

The irradiation with ions of similar mass Xe (131) and I (127) produced different defect structures in two isostructural compounds UO_2 and cubic zirconia, depending primarily on the energy of impinging ions. Let us consider the electronic stopping power first. The ionization energy deposited

by 72 MeV I ions amounts to 19 keV/nm at the surface and decreases to 8 keV/nm at the depth of 4 μm. The corresponding values for 340 MeV Xe ions are: 34 keV/nm and 32 keV/nm.

Recently, it was demonstrated that the threshold for latent track formation in UO_2 ranges between 22 and 29 keV/nm [11]. Thus, the formation of latent tracks in UO_2 upon Xe-ion bombardment is highly probable. Typically, the latent tracks remain coherent and eventually become amorphous. Only in insulators the break up of the cylindrical region into a "string of elastically independent pearls" [12] was observed [13]. The other factor to be concerned is the stress imposed on the hot region by its cool surroundings. In the case of long cylindrical inclusion the stress is no longer hydrostatic but contains also shear components. These considerations provide a sound explanation of the UO2 polygonisation by high energy heavy ions. Moreover, such an effect was observed at low energies, *i.e.* by 300 keV Xe-ion bombardment [14]. It was demonstrated that the large amount of defects can induce polygonisation only if the implanted atoms are insoluble in the UO_2 matrix and form bubbles or inclusions. It is known that these object introduce large strain fields in the implanted region.

Regarding the damage production in zirconia crystals by 72 MeV I-ion bombardment, one notes that the highest ionization energy deposited by 72 MeV I ions amounts to 19 keV/nm and is lower than the presumed threshold of the latent track formation. On the other hand, each 72 MeV I ion produces 2 vac(ancies)/nm at the surface and 6 vac/nm at 4 nm. For 340 MeV Xe ions these numbers are 0.8 vac/nm and 1.1 vac/nm, respectively. In such a case the damage in the zirconia crystals is created by the interplay of high ionization and intensive collisional displacements. In such circumstances the displacement threshold can be lowered leading to the large damage concentration in zirconia crystals.

These considerations prompt one to couple the structure of residual damage to the latent tract formation. At high enough incident energies the solidification of latent tracks results usually in formation of amorphous zones or as in the reported case, leads to the polygonisation. If the incident energy is too low and ionization energy is below the threshold of the latent track formation, the resulting damage is similar to that created by the ion bombardment at low energies. However, the amount of defects can be strongly enhanced by interaction of ionization fields with collision cascades.

These considerations are valid for the bulk crystal. In the near surface region (about 200 nm thick), where large surface peaks were observed (*cf.* Figs 2 and 4), the cylindrical geometry along the ion trajectory does not hold any longer. Consequently, the electrical field has non-vanishing component perpendicular to the surface leading to the mixing of atoms and enhanced sputtering at the free surface.

This work was performed in the frame of the Collaboration between IN2P3–Polish Laboratories. The authors thank Dr. Hj. Matzke, ITU, Karlsruhe for supplying the zirconia samples.

REFERENCES

[1] Hj. Matzke, A. Turos, *J. Nucl. Mater.* **188**, 285 (1992).

[2] A. Turos, Hj. Matzke, M. Wielunski, L. Nowicki, *Nucl. Instrum. Methods* **B80/81**, 1259 (1993).

[3] N. Yu, K.E. Sickafus, P. Kodali, M. Nastasi, *J. Nucl. Mater.* **244**, 266, (1997).

[4] K. Yasuda, M. Nastasi, K.E. Sickafus, C.J. Maggiore, N. Yu, *Nucl. Instrum. Methods* **B** (in press).

[5] Z.G. Wang, C. Dufour, E. Paumier, M. Toulemonde, *J. Phys. Condens. Matter* **6**, 6733 (1994).

[6] D. Lesuer, A. Dunlop, *Radiat. Eff. Defects Solids* **126**, 163 (1993).

[7] K.E. Sickafus, Hj. Matzke, K. Yasuda, R. Verall, A. Turos, R. Fromknecht, N. Baker, *Nucl. Instrum. Methods* **B** (1998) (in press).

[8] F. Garrido, C. Choffel, J.-C. Dran, L. Thomé, L. Nowicki, A. Turos, *Nucl. Instrum. Methods* **B127/128**, 634 (1997).

[9] J.F. Ziegler, J.P. Biersack, U. Littmark, *The Stopping and Range of Ions in Solids*, Pergamon Press, New York 1985.

[10] L.C. Feldman, J.W. Meyer, S.T. Picraux, *Materials Analysis by Ion Channeling*, Academic Press, New York 1982.

[11] T. Wiss, Hj. Matzke, C. Trautmann, S. Klaumünzer, M. Toulemonde, *Nucl. Instrum. Methods* **B122**, 583 (1997).

[12] H. Trinkaus, A.I. Ryazanov, *Phys. Rev. Lett.* **74**, 5072 (1995).

[13] T.A. Tombrello, C.R. Wie, N. Itoh, T. Nakayama, *Phys. Lett.* **100A**, 42 (1984).

[14] Hj. Matzke, A. Turos, G. Linker, *Nucl. Instrum. Methods* **B91**, 294 (1994).