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Surface and structure modification induced by high energy and highly charged uranium ion irradiation in monocrystal spinel

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ABSTRACT

Due to its high temperature properties and relatively good behavior under irradiation, magnesium aluminate spinel ($MgAl_2O_4$) is considered as a possible material to be used as inert matrix for the minor actinides burning. In this case, irradiation damage is an unavoidable problem. In this study, high energy and highly charged uranium ions (290 MeV U^{32+}) were used to irradiate monocrystal spinel to the fluence of 1.0×10^{13} ions/cm^2 to study the modification of surface and structure. Highly charged ions carry large potential energy, when they interact with a surface, the release of potential energy results in the modification of surface. Atomic force microscopy (AFM) results showed the occurrence of etching on surface after uranium ion irradiation. The etching depth reached 540 nm. The surprising efficiency of etching is considered to be induced by the deposition of potential energy with high density. The X-ray diffraction results showed that the (440) diffraction peak obviously broadened after irradiation, which indicated that the distortion of lattice has occurred. After multi-peak Gaussian fitting, four Gaussian peaks were separated, which implied that a structure with different damage layers could be formed after irradiation.

1. Introduction

Due to its excellent high temperature properties (high thermal conductivity and high melting point), good resistance to neutron irradiation and good electrical insulation, magnesium aluminum spinel ($MgAl_2O_4$) is considered as a possible material to be used as inert matrix for the minor actinides burning, or as an electrical insulator in future fusion reactor [1,2]. In radiation environment, the stability of materials in structure is one of the important problems. The studies performed in the past decades have shown that spinel shows a good resistance to neutron irradiation and an acceptable behavior to low and medium energy heavy ion irradiation as well as structural stability to alpha particles irradiation [1,3,4]. However, investigations on the stability against fission product impacts revealed a poor behavior of spinel, large swelling and amorphization were observed [5]. In this study, uranium (U) ions with high energy were used to irradiate the monocrystal spinel to study the change in structure. In addition, the incident U ions were also highly charged. Highly charged ions carry large potential energy, when they interact with a surface, the release of potential energy results in the modification of surface. Therefore, the modification of U ion irradiation on surface morphology was also investigated.

2. Experimental

The samples used in experiment were monocrystal spinel ($MgAl_2O_4$ (1 1 0)). One surface of the sample was polished carefully by the manufacturer to obtain a smooth surface. Subsequently, the polished samples were irradiated with 290 MeV U^{32+} ions at room temperature to the fluence of 1.0×10^{13} ions/cm^2 at an irradiation terminal of the separate-fan cyclotron in the national laboratory of heavy-ion accelerators in Lanzhou, China. The direction of incident ions was perpendicular to sample surface. The energy loss of 290 MeV U ions with depth obtained from SRIM 2012 simulation is shown in Fig. 1 [6]. The electronic energy loss (S_e) at surface reaches 34.4 keV/nm. The projected range is about 14.8 μm. After irradiation, atomic force microscopy (AFM, Veeco, Dimension 3100) and X-ray diffraction (XRD, Philips X' Pert MRD) were used to characterize the change in surface morphology and structure, respectively.

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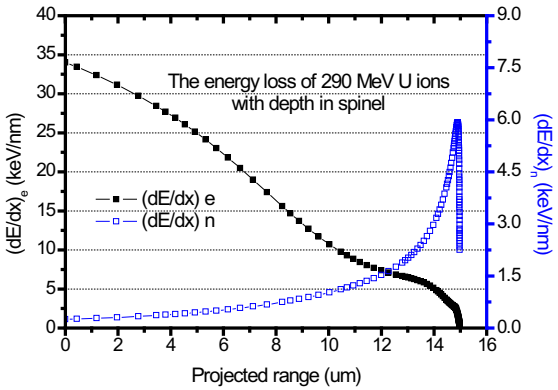

Fig. 1. The energy loss of 290 MeV U ions with depth in spinel.

3. Results and discussion

3.1. Surface morphology

Due to limited beam time, only one data point of ion fluence is obtained in experiment, the evolution of surface morphology with ion fluence does not be achieved in this study. From AFM results, surface etching is observed in the irradiated area. A clear step can be seen at the boundary of irradiated and un-irradiated area (Fig. 2c). The surface of etched area becomes rough (R_{q_irrad} = 3.59 nm, R_{q_virgin} = 0.46 nm), as shown in Fig. 2a and b. The cross section of etching depth is shown in Fig. 2d. It is seen that etching depth reaches 540 nm. One should keep in mind that the irradiation fluence of 1.0×10^{13} ions/cm^2 corresponds to only 10 ions/(10×10 nm). From the etched depth and irradiation fluence, the estimated sputtering yields are 0.8, 1.6 and 3.2×10^5 atoms/ion for Mg, Al and O atoms, respectively. The efficiency of sputtering is surprising. SRIM 2012 was used to simulate the sputtering yields on surface of spinel irradiated by U ions with different kinetic energy [6]. The simulated results are shown in Fig. 3. It is seen that sputtering yields for different atoms (Mg, Al and O) have a similar evolution trend, which initially increases sharply and then decreases gradually with increase of kinetic energy. The sputtering yields are only 0.18, 0.21 and 0.61 (atoms/ion) for Mg, Al and O atoms, respectively, when the kinetic energy of U ions reaches 290 MeV. Therefore, the direct sputtering from kinetic energy cannot lead to the surface etching with such high efficiency.

The ion used in irradiation is not only swift heavy ion, but also is highly charged ion (U^{32+}). Highly charged ion carries large potential energy, for example, the potential energy for Th^{32+} and Th^{90+} are about 13.5 and 775 keV [7], respectively. Upon surface impact, highly charged ions will regain its missing electrons to become fully neutralized again. During the neutralization process, large amount of electrons are extracted in a short time within a small area of the target. If the electronic relaxation time within the target is slow compared to the ionic neutralization time, a volume with net positive charges can be formed in surface-near region, which could result in a coulomb repulse. If the coulomb repulse is strong enough, it could cause ejection of ions and neutrals as well as significant lattice damage [8]. The energy for the ejection of target atoms and ions results from the potential energy of incident ion, therefore, this kind of sputtering has been termed "potential sputtering" [7]. In this study, the incident U ions carry large potential energy (the atomic number of U (92) is close to that of Th (90), so it is considered that the potential energy of U^{32+} is also close to that of Th^{32+} (13.5 keV)), which could be mainly response for the surface etching.

The kinetic energy of incident ions (290 MeV) in this experiment is considered to have small contribution directly to the sputtering yields, but it probably has an indirect contribution to the sputtering yields. The charge equilibrium for highly charge ion is determined by its velocity and the target material [8]. Usually the time for the neutralization of highly charged ion is in the order of femto-second (10^{-15} s) [9]. The velocity of incident U ions is 1.53×10^7 m/s. The critical distance R_c where the neutralization sequence begins on metal surface can be simply estimated from the formula [10],

$$R_c \approx \frac{1}{2W}(8q+2)^{\frac{1}{2}} \quad (1)$$

W is the work function of metal surface, q is the charge of incident ion. For example, for the ion of U^{32+} on Au surface, the critical distance $R_{c\text{-}Au}$ is about 2.2×10^{-9} m. The time is only 1.53×10^{-16} s to pass through the distance of $R_{c\text{-}Au}$, which is shorter than that for neutralization of highly charged ions (10^{-15} s). The sample used in this experiment is insulating material, the critical distance $R_{c\text{-}spinel}$ should be smaller than $R_{c\text{-}Au}$. Therefore, the time should be much shorter for 290 MeV U^{32+} ions to pass through $R_{c\text{-}spinel}$. In other words, the number of U^{32+} ions approaching the surface in the same time increases, which results in the increase of deposition density of potential energy comparing with that on Au surface. Moreover, the electronic relaxation time in insulator is longer than that in metal. All these factors could cause a huge accumulation of net positive charges within a small area, which can lead to stronger coulomb repulse in surface-near region. Therefore, the indirect effect from the kinetic energy should also be another factor for the high-efficiency surface etching induced by irradiation with high energy and highly charged ions. In addition, strong electronic excitation induced by high energy heavy ion irradiation can also produce specific damage on sample surface, e.g. hillocks and craters. The hillocks have been observed on spinel surface irradiated with various heavy ions ($S_e \geqslant 15.5$ keV/nm) [11]. The density of these hillocks increased with increase of ion fluence. On sapphire surface, it was observed that the isolated hillocks started to overlap at the fluence about 10^{11} ions/cm^2, and formed completely disordered surface layer at the fluence about 10^{12} ions/cm^2 [12]. In our experiment, the electronic energy loss reached 34.4 keV/nm at surface and the ion fluence reached 1.0×10^{13} ions/cm^2, a completely disordered surface layer could be formed in irradiation process. This completely disordered surface layer could be sputtered more easily by the subsequent bombardment of incident ions.

3.2. Structure

Fig. 4 shows the (440) ($2\theta = 65.319°$) diffraction peak for the samples before and after irradiation. It is seen that the diffraction intensity decreases and the diffraction peak broadens after irradiation. The diffraction peak extends along both low and high angle direction, and the extension is asymmetric. After multi-peak Gaussian fitting, four Gaussian peaks labeled A, B, C and D are separated, the corresponding peak positions are 65.231, 65.263, 65.315 and 65.353°, respectively. From the Bragg equation ($2d\sin\theta = n\lambda$), the shift of peak to low or high angle direction corresponds to the expansion or compression of lattice, respectively. Therefore, the extension of diffraction peak along low and high angle direction implies that the expansion and compression of lattice exist simultaneously in the irradiated sample.

Defects are produced in materials under irradiation. These defects could result in an expansion of lattice, which is the main factor leading to the shift of diffraction peak to low angle direction. In addition, ion track, which is consisted of a trail of defective or even amorphous material along ion incident direction [13], could be formed for the sample irradiated with high energy ion. The