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Radiation-induced swelling and softening in magnesium aluminate spinel irradiated with high-flux Cu^- ions

C.G. Lee [a,*], T. Ohmura [b], Y. Takeda [a], S. Matsuoka [b], N. Kishimoto [a]

[a] Nanomaterials Laboratory, National Institute for Materials Science, 3-13 Sakura, Tsukuba, Ibaraki 305-0003, Japan
[b] Materials Engineering Laboratory, National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan

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Abstract

Magnesium aluminate spinel of single crystal was irradiated with 60 keV Cu^- at a flux up to 6.2×10^{18} ions/m^2 s, to a total fluence of 3×10^{20} ions/m^2, in order to study changes in hardness and step-height swelling by high-flux implantation. Hardness determined by nano-indentation measurements steeply decreased with implantation. There is a strong negative correlation between flux dependences of the hardness and the step-height swelling: the former decreases as the latter increases. The Rutherford backscattering spectrometry (RBS)/channeling measurements showed that the spinel is not completely amorphized over the flux range in this study, and the radiation-induced softening observed is not due to amorphization. Results of optical absorbance suggested that radiation-induced point defects and their clusters on the anion sublattices of the spinel played an important role in the radiation-induced swelling under high-flux ion implantation.

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1. Introduction

Magnesium aluminate spinel is known to have radiation resistance with good insulating properties. The spinel is to be applied to dielectric windows of fusion reactors or electrical insulators in radiation environments [1]. The excellent radiation-damage resistance of spinel has been attributed to its structural characteristics. The spinel crystal contains numerous unoccupied interstices in the lattice, and these vacant interstices enhance interstitial mobility as well as interstitial–vacancy recombination. The recombination of radiation-induced interstitials with constitutional vacancies is believed to be the predominant mechanism for annihilation of the point defects [2].

Also, it has been demonstrated that cation disorder plays a significant role in the damage response of spinel. Cation disordering in spinel irradiated with neutrons has been quantitatively examined by neutron diffraction: disorder on the cation sublattices is the major damage retained in an irradiated spinel [3]. Spinels irradiated with heavy ions showed significant changes in the structure and their mechanical properties. A requirement for amorphization is the low mobility of radiation-induced defects [4], therefore amorphization would not be expected to occur in spinel above room temperature because of the effective recombination mechanism. Amorphization was observed in spinel irradiated with 400 keV Xe ions at 100 K to a peak damage level of 25 dpa [5], whereas amorphization did not occur in spinel irradiated with 300–400 keV Xe ion at 670 K to a peak damage level of 50 dpa [6]. These results indicate that, to some extent, a temperature effect is responsible for the

* Corresponding author. Present address: Department of Environmental Sciences, Japan Atomic Energy Research Institute (JAERI), Tokai-mura, Naka-gun, Ibaraki 319-1195, Japan. Tel.: +81-29 284 3667; fax: +81-29 284 3669.
E-mail address: cglee@clear.tokai.jaeri.go.jp (C.G. Lee).

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amorphization process in spinel. It was also shown that amorphization was accompanied by a change of the mechanical properties in spinel: decrease of 60% in hardness and 30% in Young's modulus [7].

Although there have been many reviews on the neutron- and ion-irradiation effects on spinel [8,9], limited information of radiation response to high-flux ions is available for spinel [10,11]. It has been observed that high-flux implantation induces spontaneous formation of nanospheres in insulators [12]. Intense Cu^- ions of 60 keV have induced nanoparticles embedded within a shallow depth in insulators [13,14], which exhibit optical nonlinearity with respect to surface plasmon resonance [15]. We have observed in both amorphous- and crystalline-SiO_2 substrates that flux dependent variations occur in nanoparticle formation and resultant optical properties [13,15]. This result implies that the variation in flux plays an important role in high-flux ion implantation. However, the high-flux implantation concurrently causes drastic atomic rearrangement of the implants. The metastable nature may cause phase instability of substrate materials. For crystalline-SiO_2 substrates, phase transformation from a crystalline to an amorphous phase occurred under high-flux implantation [14]. The formation process of colloids at low flux ($<10^{18}$ ions/m^2 s) has been successfully explained by quasi-equilibrium thermodynamics that assumed an extremely high fictitious temperature state is created by collisions of implanted ions with substrate ions [16,17]. However, the material kinetics at higher fluxes are still open to question. Therefore, it is necessary to understand radiation response of substrate materials under high-flux implantation. Since the radiation-induced processes are dominated by the point-defect kinetics, material response with changing flux is informative to study the kinetics. In particular, the radiation resistance of the Mg–Al spinel, associated with the interstitial–vacancy recombination, may be subjected to flux dependence.

In this study, we present the volumetric swelling (obtained from step-height measurements) and mechanical properties of spinel irradiated with high-flux negative Cu ions, by using nano-indentation technique, surface profilometer, Rutherford backscattering spectrometry (RBS) and optical absorbance. Particularly, we discuss the relationship between flux dependences of volumetric swelling and hardness in irradiated spinel.

2. Experimental

Single crystals of $MgO(1.0)Al_2O_3$ spinel with (1 0 0) plane supplied by Nakazumi Crystal Laboratory (Osaka, Japan) were used as substrate material. Size of the disk substrates, polished to the optical grade, is 15 mm in diameter and 0.5 mm in thickness. Negative Cu ions of 60 keV were irradiated into substrates at ambient temperature, where the sample stage during implantation was cooled with circulating water. The flux varied from 6.2×10^{16} up to 6.2×10^{18} ions/m^2 s, at a fixed total fluence of 3×10^{20} ions/m^2. Simulation with the TRIM code gave projectile ranges (R_p) and straggling ranges ($2\Delta R_p$) to be 30 and 20 nm, respectively [18]. A metal (Cu) mask of 6 mm diameter (four holes) was mounted on the sample surface to dissipate the beam load, and to assure the well-defined boundary between the irradiated and the unirradiated region on the sample.

Following the irradiation, nano-indentation measurements were conducted to evaluate the mechanical properties of irradiated and unirradiated spinel, by using a Hysitron Tribosocope with a Berkovich indenter (a three-sided pyramidal diamond). The indenter tip geometry was calibrated by the area function method [19]. For each sample, three indentation measurements normal to the irradiated surface layer were conducted by the load-controlled mode. The resolution limits of the loading and displacement system were 100 nN and 0.2 nm, respectively. For each indentation, a loading/unloading rate of 5 μN/s and 10 s hold time at the peak load of 50 μN were used during the load–hold–unload cycle. The standard deviation of hardness measured was less than 3%. More details on the measurement of hardness from load–displacement curves (for loading and unloading) can be found in Refs. [19,20]. The step-height was measured using a surface profilometer to evaluate volumetric swelling on the irradiated sample. Repetitive measurements were carried out on different positions across the boundary between the irradiated and the masked regions on the sample. The volumetric swelling was estimated from the step-height under the assumption that all of the swelling in the area of defined by $\pi \times r^2 \times R_p$, where r is the diameter of the irradiated region, occurred in the normal direction of the surface. The assumption is valid due to the strong lateral constraint by the unirradiated region. RBS with 2 MeV He^+ ions at a detector angle of 160° was used to study damage introduced by the high-flux ion implantation. Finally, optical absorption of the Cu^- irradiated samples were measured in a photon energy range from 0.5 to 6.5 eV with a dual beam spectrometer, where an unirradiated substrate was set for the reference beam.

3. Results and discussion

Fig. 1 shows load–displacement curves measured from $MgO(1.0)Al_2O_3$ irradiated at different fluxes, fixing the total fluence of 3×10^{20} ions/m^2. It is readily seen that the load–displacement curves of spinel irradiated are greatly dependent on flux. Plastic deformation depths h_c obtained by extrapolation of an initial unloading stiffness to the x-axis are 14.6, 4.7 and 8.2 nm for fluxes of 1.9×10^{17}, 3.1×10^{18} and 6.2×10^{18} ions/m^2 s, respectively.

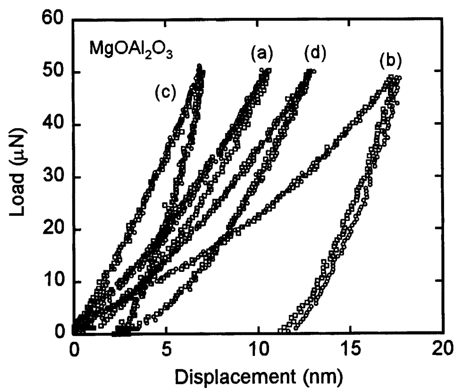

Fig. 1. Load–displacement curves under nano-indentation on $MgO(1.0)Al_2O_3$ irradiated with 60 keV Cu^- of various fluxes to a total fluence of 3×10^{20} ions/m^2, before irradiation (a), at 1.9×10^{17} ions/m^2 s (b), at 3.1×10^{18} ions/m^2 s (c), and at 6.2×10^{18} ions/m^2 s (d).

It is generally accepted that the indentation depth should not exceed 10–25% of the layer thickness in order to minimize the influence of the unirradiated substrate [20]. Since thickness of the layer modified by irradiation is about 60 nm from TRIM simulation, significant effects from the unirradiated substrate on the measured hardness are avoided. Hardness of the each specimen was calculated from the load–displacement curve. Using the plastic deformation depth h_c and the indenter geometry, size of the contact area between the indenter and the specimen was calculated, and then the applied load was divided by the contact area to get the hardness according to the conventional hardness definition.

Fig. 2 shows the flux dependence of the hardness obtained from load–displacement curves in Fig. 1. It is clearly seen that hardness steeply decreases with implantation; the hardness is about 15–64% of that of unirradiated spinel. In the low flux region, the hardness decreases with flux and then reaches a minimum value at a flux of 1.9×10^{17} ions/m^2 s, which is about 15% of the value for unirradiated spinel. With increasing flux, the hardness increases up to a flux of 3.1×10^{18} ions/m^2 s and decreases with further increasing the flux. The maximum value of hardness of the irradiated spinel is about 13.5 GPa at a flux of 3.1×10^{18} ions/m^2 s, which is 64% of the unirradiated spinel. A detailed discussion concerning the nano-indentation measurement on spinel irradiated with high-flux implantation will be published. As for the decrease of hardness, it has been reported to occur in spinel irradiated with 370 keV Xe ions at 120 K: hardness drastically decreases at a peak displacement damage of about 28 dpa [21]. The decrease is due to transformation to an amorphous phase. Radiation-induced amorphization in ceramics occasionally leads to substantial volume expansion along with changes in mechanical properties. We evaluate the volumetric swelling due to high-flux implantation below.

Fig. 3 shows the flux dependence of step-height in spinel irradiated with 60 keV Cu^- to a total fluence of 3×10^{20} ions/m^2. The step-height strongly depends on flux. Step-height increases with flux and reaches a maximum at 1.9×10^{17} ions/m^2 s. The magnitude of this increase falls with increasing flux and reaches a minimum at a flux of 3.1×10^{18} ions/m^2 s. At the highest flux of 6.2×10^{18} ions/m^2 s, the step-height increases again. Figs. 2 and 3 show a strong correlation between flux dependences of the hardness and the step-height. The hardness becomes minimum when the step-height is maximum. Volumetric expansions induced by ion irradiation in insulators are common phenomena and have been observed in several materials [22]. There are three main mechanisms of radiation-induced expansion: (1) the interstitials created by the ion irradiation diffuse to the surface and regrow at the surface [23], (2) density change due to lattice disordering or amorphization and (3) radiation-induced defects accumulation. Among the

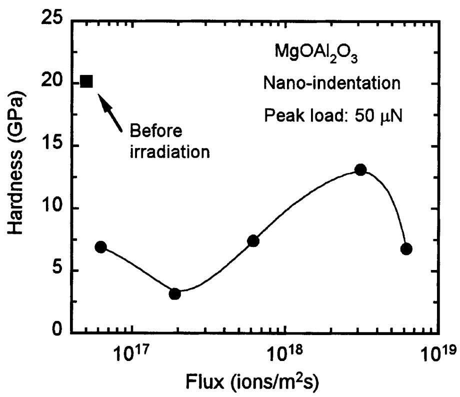

Fig. 2. Flux dependence of hardness on $MgO(1.0)Al_2O_3$ irradiated with 60 keV Cu^- to a total fluence of 3×10^{20} ions/m^2.

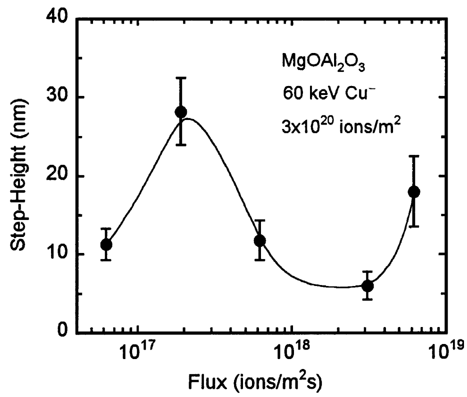

Fig. 3. Flux dependence of step-height on $MgO(1.0)Al_2O_3$ irradiated with 60 keV Cu^- to a total fluence of 3×10^{20} ions/m^2.

three possibilities, the volumetric expansion observed is likely caused by the types associated with (2) and (3), which is supported by the results of RBS and optical measurement, as will be discussed later. In addition, long-range migration of radiation-induced point defects in spinel is not be expected [24].

To study a structural change associated with the step-height increase, RBS/channeling measurement was carried out. The good mass resolution provided by the RBS/channeling enables the separate analysis of disorder on each sublattice. Fig. 4 shows the RBS/channeling spectra of spinel irradiated with 60 keV Cu^- at 1.9×10^{17} ions/m^2 s. The minimum backscattering yield (χ_{min}), i.e., the RBS yield ratio of aligned to random spectrum, is about 4% for the Al damage peak prior to implantation, which indicates good crystallinity of the unirradiated specimen. With the ion implantation, the Al and O damage peaks appear in aligned spectra that are clearly resolved for each sublattice. Fig. 5 shows the flux dependence of the damage peak in spinel irradiated with 60 keV Cu^-, fixing the total fluence at 3×10^{20} ions/m^2. The Al damage peak at a flux of 1.9×10^{17} ions/m^2 s reaches about 90% of the random yield. After implantation at 3.1×10^{18} ions/m^2 s, where hardness reaches a maximum, the Al damage peak is about 65% of the random yield. Even at the highest flux of 6.2×10^{18} ions/m^2 s, the damage peak shows 63% of the random yield. The anion(O) damage peak remains at about 48–54% of the random yield. Maximum values of Al and O damage peaks appeared at a flux of 1.9×10^{17} ions/m^2 s. RBS/channeling measurements indicated that spinel was not completely amorphized over the flux range examined, although the crystalline lattice is significantly damaged. This result agrees with several studies of spinel irradiated with lower flux at room temperature [24,25]. The resistance of spinel against amorphization at high-flux may also arise from the recombination of radiation-induced interstitials with structural vacancies in the spinel structure. It is considered that the recombination mechanism is enhanced by high-flux implantation. The fluence dependence of a damage peak in $MgO(1.0)Al_2O_3$, ranging from 3×10^{15} to 6×10^{20} ions/m^2, fixing a flux of 1.9×10^{17} or 6.2×10^{18} ions/m^2 s, indicates that the damage peak is smaller for the higher flux and fluence [26]. This result implies that the recombination mechanism is effective even under high-flux implantation. It should be noted here that radiation-induced softening is not always due to amorphization. The radiation-induced softening observed is primarily associated with the lattice disordering, including point defects and clusters.

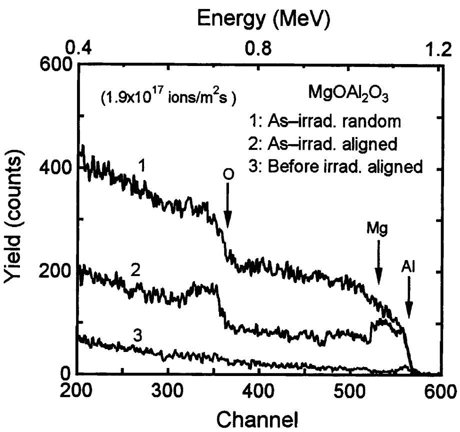

Fig. 4. Random and aligned RBS spectra of $MgO(1.0)Al_2O_3$ irradiated with 60 keV Cu^- at a flux of 1.9×10^{17} ions/m^2 s.

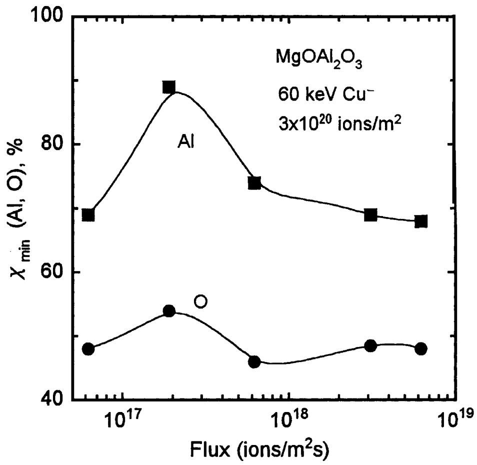

Fig. 5. Flux dependence of disorders (χ_{min}) for Al and O sublattice on $MgO(1.0)Al_2O_3$ irradiated with 60 keV Cu^- to a total fluence of 3×10^{20} ions/m^2.

Optical absorbance after implantation is informative to understand the nature of point defects produced by high-flux implantation. The insert of Fig. 6 shows optical absorbance of Cu^- irradiated spinel at various fluxes, to a total fluence of 3×10^{20} ions/m^2. The absorption spectra consist of a plasmon peak at 2.2 eV and F-centers at 5.3 eV. Another broad band around 3.2 eV appears after implantation at a flux of 6.2×10^{18} ions/m^2 s. More detailed discussion about absorption spectra including the plasmon peak at 2.2 eV was reported elsewhere [27]. The origin of F-centers at 5.3 eV is known as an oxygen vacancy with two trapped electrons i.e., defects band [28]. Fig. 6 shows the flux dependence of the F-center intensity calculated from the absorption spectra, which is normalized by each absorbance at 2.4 eV to minimize the influence of absorbance by Cu implants. As seen in Fig. 6, the intensity of F-center in $MgO(1.0)Al_2O_3$ irradiated is largest at the flux of 1.9×10^{17} ions/m^2 s and then decreases with further increasing flux. The variation of F-centers intensity with flux correlates with the flux dependence of the damage

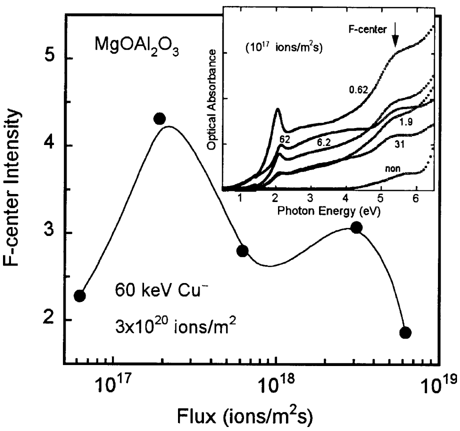

Fig. 6. Flux dependence of absorbance of the F-center at 5.3 eV. The data is obtained by normalizing the absorbance at 2.4 eV. Insert: Optical absorbance of the $MgO(1.0)Al_2O_3$ irradiated with 60 keV Cu^- at various fluxes to a total fluence of 3×10^{20} ions/m^2.

peak shown in Fig. 5. The qualitative agreement implies that radiation-induced F-centers can also be responsible for the variations in lattice damage. A peculiar feature of the flux dependence of step-height, lattice damage (χ_{min}) and F-centers appears at a flux of 1.9×10^{17} ions/m^2 s: radiation-induced point defects, swelling and lattice disordering reach a maximum around 1.9×10^{17} ions/m^2 s and then decreases with increasing flux. As for this peculiar feature around 1.9×10^{17} ions/m^2 s, it is considered for $MgO(1.0)Al_2O_3$ that a high-flux-enhanced recovery of defects overcomes the defect production beyond a flux of 1.9×10^{17} ions/m^2 s. It is probable that thermal diffusion by beam heating has some contribution to the enhanced recovery of defects at higher fluxes. High-flux implantation is subjected to a significant increase in temperature for insulators, as a result of the electronic excitation. A temperature rise of a specimen due to the electronic excitation may be one of the important factors that affect the recovery of radiation-induced defects under high-flux implantation. The decrease in radiation-induced damage with increasing flux may allow the $MgO(1.0)Al_2O_3$ spinel to be suitable as the optical substrates or insulating components for high-flux ion implantation.

As seen in Figs. 3 and 6, the flux dependence of the step-height and the intensity of F-centers exhibit similar characteristics up to a flux of 3.1×10^{18} ions/m^2 s. At the highest flux of 6.2×10^{18} ions/m^2 s, the step-height increases though the intensity of F-centers decreases. The different behaviors with flux can be ascribed to difference in the type of radiation-induced defects: radiation-induced defects contributing to the step-height are different between until 3.1×10^{18} and 6.2×10^{18} ions/m^2 s. A broad band at 3.2 eV is also seen in the detailed spectrum of 6.2×10^{18} ions/m^2 s, which is inserted in Fig. 6. This band is known as V-type centers that are associated with O^- adjacent to a cation site deficient in positive charge [29]. And this band is seen only in the spectra of 6.2×10^{18} ions/m^2 s. Thus, it is concluded that increase of the step-height at a flux of 6.2×10^{18} ions/m^2 s is mainly due to the V-type centers at 3.2 eV. This result implies that point defects in the anion sublattice of stoichiometric spinel played an important role in the volumetric swelling under high-flux ion implantation.

4. Conclusions

Radiation-induced swelling and softening of $MgO(1.0)Al_2O_3$ spinel single crystals by high-flux 60 keV Cu^- implantation were evaluated by using nano-indentation, step-height measurements, Rutherford backscattering spectrometry and optical absorbance. Volumetric swelling and hardness of spinel irradiated with high-flux implantation strongly depend on flux. There is a strong negative correlation between flux dependence of the hardness and the volumetric swelling produced by point defects accumulation. The hardness decreased as the swelling increased. No amorphization is observed in the spinel over the flux range studied, although volumetric swelling is discernible by the step-height measurement. The radiation-induced softening observed is not due to amorphization but to lattice disordering associated with point defect aggregates. Radiation-induced point defects in the anion sublattice play an important role in the radiation response under high-flux ion implantation. The decrease in radiation-induced damage with increasing flux suggests that the $MgO(1.0)Al_2O_3$ spinel is applicable for optical substrates or insulating components for high-flux ion implantation or radiation environments, respectively.

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