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Effects of Xe ion irradiation and subsequent annealing on the structural properties of magnesium-aluminate spinel

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Abstract

Single crystals of magnesium-aluminate spinel $MgAl_2O_4$ were irradiated with 340 keV Xe^{++} ions at −173°C (~100 K). A fluence of 1×10^{20} Xe/m^2 created an amorphous layer at the surface of the samples. The samples were annealed for 1 h at different temperatures ranging from 130°C to 880°C. Recrystallization took place in the temperature interval between 610°C and 855°C. Transmission electron microscopy (TEM) images show two distinct layers near the surface: (1) a polycrystalline layer with columnar grain structure; and (2) a buried damaged layer epitaxial with the substrate. After annealing at 1100°C for 52 days, the profile of implanted Xe ions did not change, which means that Xe ions are not mobile in the spinel structure up to 1100°C. The thickness of the buried damaged layer decreased significantly in the 1100°C annealed sample comparing to the sample annealed for 1 h at 855°C. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Magnesium-aluminate spinel is a highly radiation-resistant material. Single crystals exhibit no swelling following neutron exposures up to 2×10^{26} n/m^2 at 925–1100 K [1]. Spinel has been proposed to be used in high-radiation environments such as fusion reactors and waste forms. Recent studies have examined the radiation response of spinel at very high ion doses (e.g. [2,3]). Under irradiation with 400 keV Xe ions at cryogenic temperatures (100 K), spinel first transforms into a crystalline metastable phase characterized by a cubic unit cell with a smaller repeat length (4 nm) than that of undamaged spinel (8 nm). At higher doses (25 displacements per atom), spinel transforms to an amorphous phase [2,3]. During the irradiation, there are at least two factors that may contribute to transformation of the material: (1) nuclear displacements; and (2) lattice distortions introduced by Xe ions implanted into the spinel structure.

Yu et al. [4] observed that electron irradiation at 300 keV of an ion irradiated spinel crystal, induced a phase transformation from an amorphous to a metastable crystalline structure. Crystallization of amorphous $MgAl_2O_4$ was observed both at the amorphous/crystalline interface by epitaxial growth and in the amorphous region by nucleation and growth. In contrast, thermal annealing at 600°C for 1 h produced negligible crystallization at the amorphous/crystalline interface.

The goal of this investigation was to determine if the amorphous layer formed in spinel by Xe ion implantation can be recrystallized by thermal annealing. Transformation of the surface amorphous layer during annealing was studied using optical absorption spectroscopy, Rutherford backscattering and ion channeling (RBS/C), and transmission electron microscopy (TEM). It was shown that the amorphous layer transforms into a polycrystalline layer at temperatures between 610°C and 855°C. Using TEM, it was shown that after annealing for 1 h at 855°C, two distinct layers form at the surface of the sample: (1) a near-surface layer having

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columnar grain structure; and (2) a buried crystalline layer epitaxial to the substrate.

It was further shown that after annealing at 1100°C for 52 days, the surface structure remains practically the same as after annealing for 1 h at 855°C. Moreover, the distribution of Xe ions implanted into the sample remains the same as before the annealing. Therefore, we can say that Xe ions implanted into spinel are not mobile up to 1100°C, and they do not prevent recrystallization of the material.

2. Experimental procedure

Single-crystals of $MgAl_2O_4$, were obtained from the Linde Division of Union Carbide Corporation. Both sides of 0.5-mm thick specimens were polished to optical quality for use in the optical absorption studies.

Ion-beam irradiations were performed in the Ion Beam Materials Laboratory at Los Alamos National Laboratory, utilizing a 200 kV ion accelerator. Xe^{++} ions of 340 keV energy were implanted into samples held at −173°C (100 K). Samples were exposed to a Xe^{++}-ion fluence of 1×10^{20} Xe/m^2. To minimize ion-channeling effects during exposure, the samples were tilted approximately 7°. Following irradiation, the samples were warmed to room temperature for optical and TEM studies.

Xe^{++}-ion induced microstructure changes in $MgAl_2O_4$ were examined using a Philips CM-30 transmission electron microscope operating at 300 kV. Cross-sectional TEM samples were prepared by using a combination of mechanical polishing and ion-thinning procedures, the latter with 4 keV Ar^+ ions.

Most samples were annealed for 1 h in an open furnace at varying temperatures ranging from 130°C to 880°C. One additional sample was annealed at 1100°C for 52 days.

Optical transmission measurements were carried out at room temperature using a Cary 5E spectrophotometer operating in the wavelength regime from 185 to 1000 nm (6.70–1.24 eV). Radiation damage accumulation was measured using RBS/C. RBS/C analyses were performed using a 2.0 MeV He^+ analyzing beam directed normal to the sample surface, with the detector located 13° from the sample normal. RBS/C measurements were performed ex situ at room temperature.

Calculations of ion range and energy deposition were made using the Monte-Carlo code SRIM-2000 (version 2000.10) by Ziegler et al. [5]. For the calculations, a density of 3.58 g cm^{-3} was used for stoichiometric spinel (JCPDS file 21-1152 [6]). A threshold displacement energy of 40 eV was used for all target elements (this choice is arbitrary). The results of SRIM calculations are shown in Fig. 1. The projected range of 340 keV Xe^{++} ions was estimated to be ~88 nm. The peak concentration of Xe at the fluence of 1×10^{20} Xe/m^2 was about 1.7 at.%.

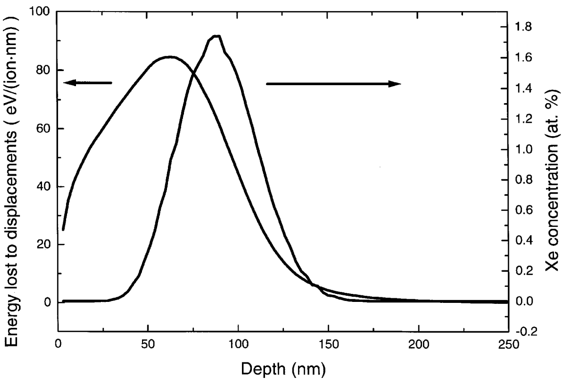

Fig. 1. SRIM Monte-Carlo simulation results for both the energy losses due to nuclear displacements, i.e., damage energy, (left-hand ordinate) and the concentration of implanted 340 keV Xe ions (right-hand ordinate) in $MgAl_2O_4$ spinel as a function of target depth. The concentration of implanted ions is given for the fluence of 1×10^{20} Xe/m^2.

3. Results and discussion

Fig. 2 shows the results of optical absorption measurements in spinel irradiated with Xe ions and subsequently annealed to different temperatures for 1 h. A detailed description of the effects of ion irradiation on the optical properties of magnesium-aluminate spinel can be found elsewhere [7]. Before irradiation, the

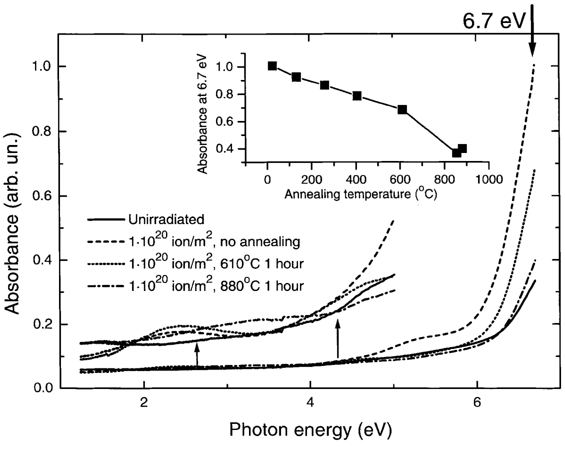

Fig. 2. Optical absorption spectra obtained from $MgAl_2O_4$ spinel crystals irradiated with 340 keV Xe ions and annealed for 1 h at different temperatures. A portion of each spectrum (between 1.24 and 5 eV) is magnified and plotted above the original spectra, to demonstrate oscillations in the absorbance. The inset shows absorbance at 6.7 eV vs. annealing temperature.

absorption spectrum of spinel does not show any significant absorption bands except for weak bands associated with impurity ions. After irradiation, two strong absorption bands develop at 5.35 and 6.9 eV. The band at 5.35 eV is caused by oxygen vacancies, which trap two electrons (F-centers). The band at 6.9 eV was assigned to the defects associated with amorphization of the material, possibly oxygen vacancies with local surroundings different from those in unirradiated $MgAl_2O_4$ [8]. The band at 6.9 eV serves as an indicator of the presence of an amorphous phase in magnesium-aluminate spinel.

As the maximum photon energy measurable in this experiment was 6.7 eV, this energy was used to study changes in the intensity of the 6.9 eV band. In the inset of the Fig. 2 one can see how the absorbance at 6.7 eV changes with annealing temperature. This absorbance returned to the same level as for an unirradiated sample at temperatures between 610°C and 855°C. This indicates recrystallization of the surface layer. Another element of the absorption spectrum leading to the same conclusion is the changes in interference patterns of the irradiated samples. Fig. 2 shows a magnified portion of the absorption spectra in the range of photon energies between 1.24 and 5 eV. After ion irradiation prior to annealing, one can observe oscillations in the absorption spectrum. These oscillations are caused by formation of a damaged layer with an index of refraction lower than that of an undamaged substrate [9–11]. After annealing to 610°C, the period as well as the intensity of the oscillations are nearly the same as in the irradiated spinel before annealing. However, after annealing to 855°C and 880°C, the structure of oscillations changes significantly. These results imply that the refractive index of the material is changed by annealing. The measured changes may also be indicative of recrystallization.

TEM images (not shown here) obtained from the spinel samples after irradiation with Xe ions to a fluence of 1×10^{20} Xe/m^2, reveal formation of an amorphous layer near the surface of a sample. A uniform amorphous layer of $\sim$155 nm in thickness is present at the sample surface. A detailed description of microstructural changes in spinel samples irradiated with Xe ions at cryogenic temperature can be found elsewhere [3]. Fig. 3 shows a TEM bright-field (BF) micrograph obtained from the implanted region of a spinel single crystal irradiated to the fluence of 1×10^{20} Xe/m^2 and annealed at 855°C for 1 h. The implanted layer is viewed edge-on in this cross-sectional image. The implanted region of the irradiated sample exhibits two distinct layers. According to microdiffraction patterns (Fig. 3)

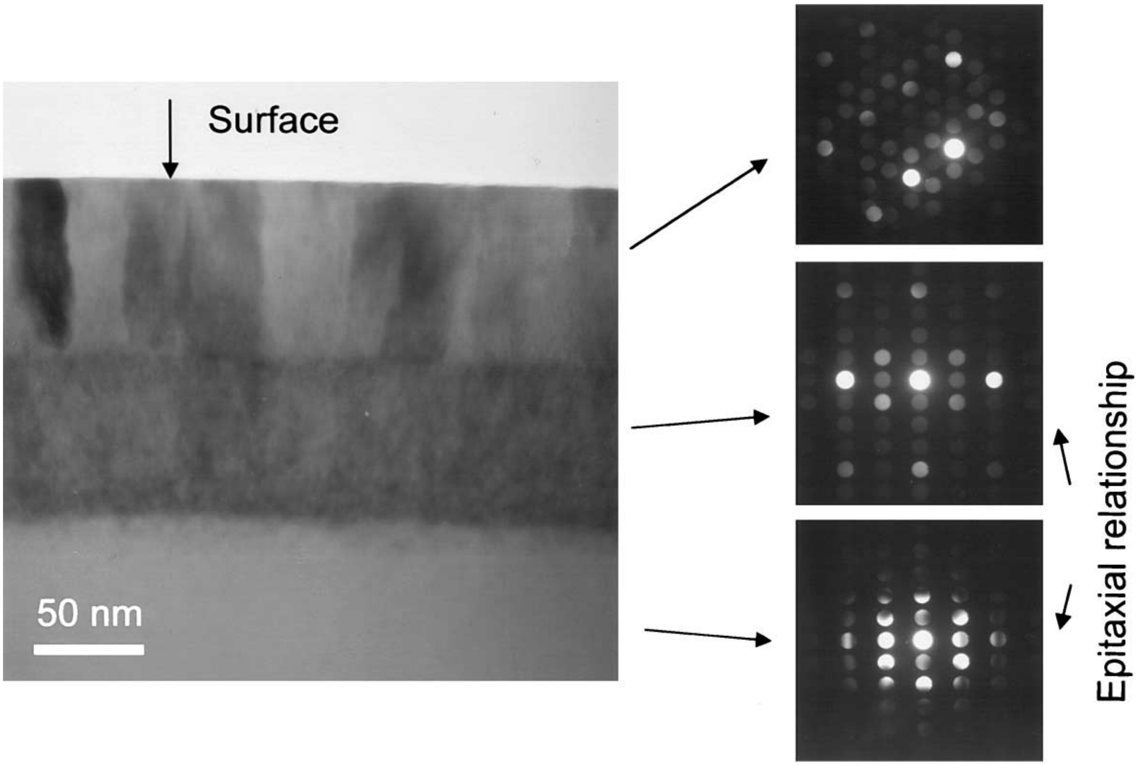

Fig. 3. TEM bright-field image obtained from a spinel crystal irradiated at −173°C (100 K) with 340 keV Xe ions to a fluence of 1×10^{20} Xe/m^2 and annealed for 1 h at 855°C. Also shown are microdiffraction patterns from the near-surface layers and the substrate.

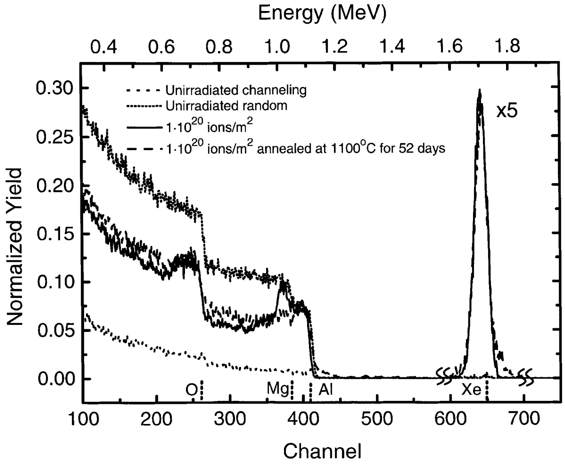

Fig. 4. RBS/C spectra obtained from a spinel crystal irradiated at −173°C (100 K) with 340 keV Xe ions to 1×10^{20} Xe/m^2, before and after annealing for 52 days at 1100°C. Also plotted are aligned and random spectra obtained from the sample prior to irradiation. The Xe ion profile is scaled by 5× in the plots.

both layers are crystalline. There is no evidence for the presence of an amorphous phase in this sample. The near-surface layer exhibits a columnar grain structure whose orientation is unrelated to the substrate. The buried layer bears an epitaxial relationship to the substrate.

To examine the recrystallization process over a longer period of time, an annealing experiment was performed at 1100°C for 52 days. Fig. 4 shows RBS/C spectra obtained from spinel samples: (1) before irradiation; (2) after irradiation with Xe ions; and (3) after annealing of the irradiated sample. A minimum yield (the ratio of the backscattering yield of an aligned spectrum to that of a random spectrum) of ∼6% was obtained from the unirradiated spinel, indicating good single crystalline quality of the substrate. Following irradiation to a fluence of 1×10^{20} Xe/m^2, the aligned RBS/C spectra exhibit additional dechanneling yields for Al, Mg, and O below the surface due to the accumulation of radiation-induced lattice disorder. The minimum yield of the as-implanted crystals (in the irradiated region of each RBS/C profile) was found to be ∼100%.

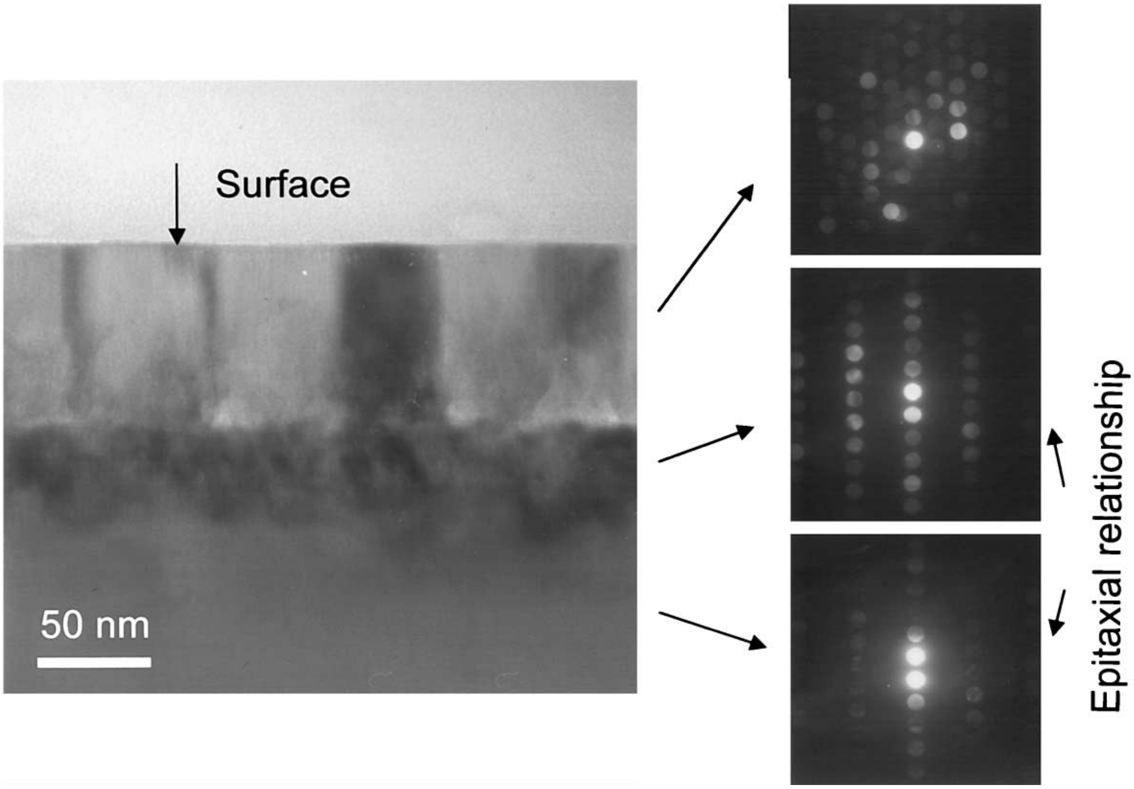

Fig. 5. TEM bright-field image obtained from a spinel crystal irradiated at −173°C (100 K) with 340 keV Xe ions to a fluence of 1×10^{20} Xe/m^2 and annealed for 52 days at 1100°C. Also shown are microdiffraction patterns from the near-surface layers and the substrate.

This is the expected result for an amorphized sample. The RBS/C spectrum of the annealed sample (52 days at 1100°C) indicates a slight decrease in the backscattering yield from Mg. The yields from Al and O are essentially unchanged. This demonstrates that this long-term anneal does not return the crystal to its original state.

Another interesting feature of the RBS/C spectra is that the profile of the implanted Xe ions did not change, even after annealing for 52 days at 1100°C. This indicates that implanted Xe ions are not mobile in the spinel structure at this annealing temperature (1100°C).

Fig. 5 shows a TEM BF image obtained from the damaged region of a spinel crystal annealed for 52 days at 1100°C. The structure of the surface layers remained the same as in a sample annealed for 1 h at 855°C. The near-surface layer possesses a columnar grain structure, and based on microdiffraction measurements (Fig. 5), the buried layer is epitaxial to the substrate. The only apparent change in structure is the reduced thickness of the epitaxial layer. These results indicate that a portion of the irradiated layer recrystallized by epitaxial growth. Our annealing results suggest that lattice distortion effects due to implanted Xe ions, do not play a major role in the recrystallization of an irradiation-induced amorphous phase in magnesium-aluminate spinel.

4. Conclusions

We have demonstrated that recrystallization of an irradiation-induced amorphous layer in Xe ion implanted spinel, occurs in the temperature region between 610°C and 855°C. Two distinct layers replace the amorphous layer following recrystallization: (1) a near-surface polycrystalline layer exhibiting a columnar grain structure; (2) a buried crystalline layer possessing an epitaxial relationship to the substrate.

After annealing for 52 days at 1100°C, the two-layer structure remained unchanged. However, the epitaxial buried damage layer became narrower; this indicates that part of this layer completely recovered and became a part of the substrate.

Rutherford backscattering measurements revealed that Xe ions implanted in magnesium-aluminate spinel are not mobile (to 1100°C). After annealing for 52 days at 1100°C, the implanted Xe ion profile remained the same as before annealing. We conclude that the Xe ions introduced into the spinel lattice by implantation do not influence the crystalline state of this material.

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References

[1] F.W. Clinard, G.F. Hurley, L.W. Hobbs, J. Nucl. Mater. 108 (1982) 655.
[2] N. Yu, K.E. Sickafus, M. Nastasi, Phil. Mag. Lett. 70 (1994) 235.
[3] N. Yu, R. Devanathan, K.E. Sickafus, M. Nastasi, J. Mater. Res. 12 (1997) 1766.
[4] N. Yu, K.E. Sickafus, M. Nastasi, Mater. Chem. Phys. 46 (1996) 161.
[5] J.F. Ziegler, J.P. Biersak, U. Littmark, The Stopping and Range of Ions in Solids, Pergamon Press, New York, 1985.
[6] Powder Diffraction File, Joint Committee on Powder Diffraction Standards, Philadelphia, PA, 1974-present.
[7] I.V. Afanasyev-Charkin, V.T. Gritsyna, D.W. Cooke, B.L. Bennett, C.R. Evans, M.G. Hollander, K.E. Sickafus, Nucl. Instr. and Meth. B 148 (1999) 787.
[8] I.V. Afanasyev-Charkin, V.T. Gritsyna, D.W. Cooke, B.L. Bennett, K.E. Sickafus, in progress.
[9] I.V. Afanasyev-Charkin, D.W. Cooke, M. Ishimaru, B.L. Bennett, V.T. Gritsyna, J.R. Williams, K.E. Sickafus, Opt. Mater. (submitted).
[10] I.V. Afanasyev-Charkin, D.W. Cooke, V.T. Gritsyna, M. Ishimaru, K.E. Sickafus, Vacuum (in press).
[11] P.D. Townsend, P.J. Chandler, L. Zhang, Optical Effects of Ion Implantation, Cambridge University Press, Cambridge, 1994, p. 151.