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Electronic excitation effects on radiation damage in insulators under ion irradiation

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Abstract

To extract electronic excitation effects from the synergistic damage processes, we have studied photon-irradiation effects on insulators under heavy ion irradiation. Copper ions (Cu^{2+}) of 3 MeV energy at an ion flux of 2 μA/cm^2 and 2.3 eV photons at 0.2 J/cm^{2}pulse were used to amorphous SiO_2 (KU-1) and spinel $MgO{\cdot}2.4(Al_2O_3)$, either sequentially or simultaneously to fluences up to 5×10^{17} ions/cm^2. Atomic force microscopy and cross-sectional TEM were conducted to study the surface morphology and internal microstructure, respectively. The simultaneous photon irradiation at high photon densities significantly enhanced surface damage for the insulators, but alleviated bulk defects. The electronic excitation gave rise to significant reduction in dislocation loops in $MgO{\cdot}2.4(Al_2O_3)$, whereas single ion irradiation produced copious dislocation loops. The results demonstrate that intense electronic excitation, coexistent with heavy ions, excite transient sub-gap states and the absorbed energy results in enhancement of atomic migration, either damaging the surface or annealing the internal defects.

PACS: 25.75.q; 32.80.t; 61.46.w; 71.23.Cq; 78.40.q

1. Introduction

Plasma-facing materials in fusion reactors are exposed to not only particle irradiation, neutrons and ions, but also intense photon irradiation from the burning plasma. Insulators for optical diagnostics and RF ports are subjected to both neutron and photon irradiation. Electronic excitation, due to either particle or photon irradiation, causes electronic transitions, then RIC (radiation-induced conductivity), and eventually relaxes to phonons, i.e., a heat flux. Besides the reversible processes, electronic excitation may influence atomic displacements via interaction with neutron/ion-induced electronic states. A key question is whether electronic excitation alleviates or enhances persistent defects.

It has been well known for some classes of nonmetals that electronic excitation by photon (alone) irradiation causes atomic displacements, typically in alkali halides [1] and a-SiO_2 [2], which are conventionally called DIET (desorption induced by electronic transition). In the cases of particle irradiation, electronic excitation (electronic stopping) may cause atomic displacements in insulators, such as stimulated atomic desorption, enhanced diffusion, defect annihilation and so on. The ionization-enhanced diffusion by electronic excitation was postulated by Bourgoin and Corbett [3] and the surface desorption by electronic excitation was done by Knotek and Feibelman [4]. Recently, Zinkle et al. systematically discussed electronic excitation effects on radiation damage [5,6], and Yasuda and Kinoshita observed that electron irradiation below displacement energy causes annihilation of dislocation loops in $MgO{\cdot}n(Al_2O_3)$ [7]. Accordingly, electronic excitation of

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particle irradiation, in general, may participate in atomic displacements, either enhancing or alleviating damage. It is, however, difficult to experimentally extract the electronic contribution under overwhelming recoil events. Also, the electronic energy given by particle irradiation ranges too widely to identify the mechanism (from subgap excitation to ballistic ionization). Here, we employ single-energy photons for subgap excitation under ion irradiation, and separate electronic excitation effects on radiation damage.

In this study, we focus on insulators of silica glass KU-1 and spinel oxide $MgO{\cdot}2.4(Al_2O_3)$. The former is known to be radiation-resistant due to OH passivation, and the latter has superb resistance to void swelling [8–10]. The radiation resistance of the spinel is believed to be due to effective recombination of radiation-induced interstitials with abundant structural vacancies and/or the large critical nucleus to form a dislocation loop [10]. The dislocation loop evolution is sensitive to ionizing to displacive portion of irradiation [11].

In this paper, we conduct photon irradiation under heavy-ion irradiation and study electronic and atomic changes in a-SiO_2 (KU-1) and $MgO{\cdot}2.4(Al_2O_3)$. We apply subgap excitation of a single energy (2.3 eV) and compare the material response with and without the photon excitation. The combined irradiation effects on surface morphology, electronic damage and microstructures are discussed with respect to electronic excitation effects.

2. Experimental procedures

Heavy ions of 3 MeV Cu^{2+} and photons of 2.3 eV (Nd: YAG laser with second harmonic generator) were used to irradiate amorphous (a-) SiO_2 (KU-1: 820 ppm OH^-) and a single crystal of $MgO{\cdot}2.4(Al_2O_3)$ oriented along (100)-plane, whose shape was 15 mm in diameter and 0.5 mm thick. The projected ranges of Cu ions were estimated by the SRIM2003 code [12] to be 2.2 and 1.4 μm in a-SiO_2 and $MgO{\cdot}2.4(Al_2O_3)$, respectively. The ion flux and the photon density were 2 $\mu A/cm^2$ (1 particle-$\mu A/cm^2$) and 0.05–0.2 J/cm^{2}pulse (pulse width of 20 ns at 10 Hz). Electronic-energy deposition rate within R_P is calculated by the SRIM code to be $\dot{E}_{Ion} \sim 5 \times 10^6$ Gy/s (1×10^{23} eV/cm^3 s) at 2 $\mu A/cm^2$. The incident laser density of 0.2 J/cm^{2}pulse corresponds to $I_0 = 2$ W/cm^2 in time average and $I_{peak} = 10^7$ W/cm^2 at the peak. If all incident laser were absorbed within R_P, $\dot{E}_{Laser}$ would be 4×10^6 Gy/s (9×10^{22} eV/cm^{3}s) in average, which is comparable with $\dot{E}_{Ion}$. However, it should be noted that the absorbed laser energy is determined by the absorbance (see the text later). The total ion fluence was varied from 3×10^{16} to 5×10^{17} ions/cm^2. Spatial distribution of the laser power was adjusted to a uniform profile of about 6 mm diameter by means of the image-relay technique. The irradiation was conducted in three modes: (1) single ion irradiation (Ion), (2) simultaneous irradiation of ions and photons, i.e., the co-irradiation (Co.), and (3) sequential-photon irradiation (Seq.) after single ion irradiation, for the same period of the ion irradiation. Thermal effects by the laser irradiation are negligible, since the absorbed power is much smaller than the incident power of 2 W/cm^2. The combined irradiation effects on surface morphology, electronic damage and microstructures were evaluated by atomic force microscopy (AFM), optical absorption (0.5–6.5 eV) and cross-sectional TEM, respectively.

3. Results and discussion

Since ion irradiation in itself carries an electronic-excitation component (electronic stopping), comparative study with and without photon irradiation, under heavy-ion irradiation, gives information of enhancement of existing electronic-excitation effects. Furthermore, comparison between sequential and co-irradiation clarifies whether the phenomenon is caused by the cumulative electronic energy or by the dynamically combined process.

Previously, we have observed significant co-irradiation effects on the surface morphology of a-SiO_2 depending on photon density and fluence [13]. The photon co-irradiation gave rise to surface pitting (atomic desorption), whereas either the single ion- or the sequential irradiation showed few discernible changes in surface morphology. The pit formation implies photon-enhanced atomic loss, that is, desorption induced by electronic transitions (DIET) [2,13]. The phenomenon is similar to stimulated desorption postulated by Knotek and Feibelman [4] but the Auger process may not take place by the present subgap photons. As far as residual defects as energy absorbers, i.e., accumulated defects or solutes, are concerned, the sequential energy deposition should be absorbed more efficiently than the co-irradiation, and the cumulative photon effects should increase with increasing ion fluence. The experimental result of a-SiO_2 that only the co-irradiation gives distinct effects on the surface morphology implies that transient defects during ion irradiation are responsible for electronic effects on atomic desorption. Recently, an in situ absorption measurement revealed a transient defect band around 2.3 eV [14] and suggested that STH (self-trapped hole) states [15] are likely to be responsible for absorbing the photon energy.

The photon co-irradiation effects on $MgO{\cdot}2.4(Al_2O_3)$ up to the higher fluence are of interest, with respect to dislocation-loop formation or metal precipitation. Fig. 1 shows AFM images of $MgO{\cdot}2.4(Al_2O_3)$ that was ion irradiated with 3 MeV Cu^{2+} ions to 5×10^{17} ions/cm^2 (a), sequentially irradiated with Cu^{2+} ions to 5×10^{17}

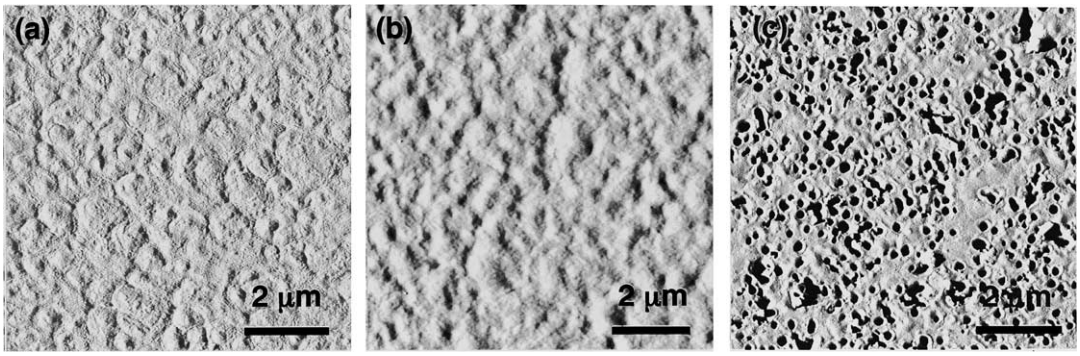

Fig. 1. Surface morphology of MgO·2.4(Al_2O_3) that was single ion irradiated with 3 MeV Cu^{2+} ions to 5×10^{17} ions/cm^2 (a), sequentially irradiated with Cu^{2+} ions and 2.3 eV photons to 5×10^{17} ions/cm^2 (b), and co-irradiated with Cu^{2+} ions and 2.3 eV photons (c). The ion flux and photon density are 2 μA/cm^2 and 0.2 J/cm^{2}pulse, respectively.

ions/cm^2 and 2.3 eV photons (b) for the same period as the co-irradiation and co-irradiated with Cu^{2+} ions and 2.3 eV photons (c) to the same fluence. The ion flux and photon density are 2 μA/cm^2 and 0.2 J/cm^{2}pulse, respectively. As seen in Figs. 1(a)–(c), the co-irradiation causes deep and sharp pits, whereas the single ion- or the sequential irradiation gives only slightly roughened texture. Consequently, the electronic excitation effect on surface morphology is strikingly large for spinel MgO·2.4(Al_2O_3) as well as for a-SiO_2. One difference of MgO·2.4(Al_2O_3) from the case of a-SiO_2 is that the single ion and the sequential irradiation yield surface roughening. Fig. 2 shows power spectral density of the surface textures of MgO·2.4(Al_2O_3) that were co-irradiated with Cu^{2+} ions and 2.3 eV photons (thick solid lines), sequentially irradiated with Cu^{2+} ions and 2.3 eV photons (dashed line), and single ion irradiated with Cu^{2+} ions (thin solid line). The overall roughing due to the photon co-irradiation is two orders of magnitude larger than the single ion irradiation, except in the small wavenumber region (large wavelength). As was seen in Figs. 1(a) and (b), some roughing occurs also in the single ion-and the sequential irradiation for MgO·2.4(Al_2O_3). The roughing effect in the sequential irradiation is by one order of magnitude larger than that in the single ion irradiation.

The MeV ions, in general, do not cause significant surface sputtering, but combination of the high ion fluence with the photon irradiation causes catastrophic surface damage on MgO·2.4(Al_2O_3). The difference between the co-irradiation and the sequential irradiation is ascribed to a dynamic electronic-excitation effect on atomic desorption. Although the Mg–Al spinel has been believed to have superb radiation resistance [10,11], the surface damage enhancement by electronic excitation is of concern. Here, the difference between the single ion and sequential irradiation can be regarded as a photon irradiation effect for cumulative defects. Since the morphology of Figs. 1(a) and (b) is similar to each other, it

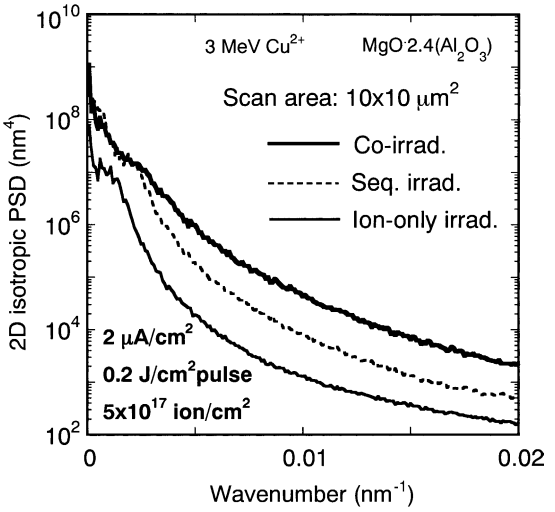

Fig. 2. Power spectral density of the surface texture of MgO·2.4(Al_2O_3) that was co-irradiated with 3 MeV Cu^{2+} ions and 2.3 eV photons (thick solid line), sequentially irradiated with Cu^{2+} ions and 2.3 eV photons (dashed line), and single ion irradiated with Cu^{2+} ions (thin solid line). The ion flux and photon density are 2 μA/cm^2 and 0.2 J/cm^{2}pulse, respectively.

may be speculated that the surface roughing of the single ion irradiation is also associated with the electronic stopping component of ions.

Fig. 3 shows optical absorption spectra of MgO·2.4(Al_2O_3) that was irradiated in the three irradiation modes at the ion flux of 2 μA/cm^2 to 5.0×10^{17} ions/cm^2. The photon density is again 0.2 J/cm^{2}pulse. The absorption spectrum of single ion irradiation has three features: a hump around 2.2 eV, a slope from 2–5 eV and a broad band around 5.5 eV. The hump around 2.2 eV is ascribed to surface plasmon resonance of Cu nanoparticles [16], and the wide slope is due to optical transitions from the Cu d to s band [17] including widely spread defect bands such as V-type centers at 3.2 eV [18].

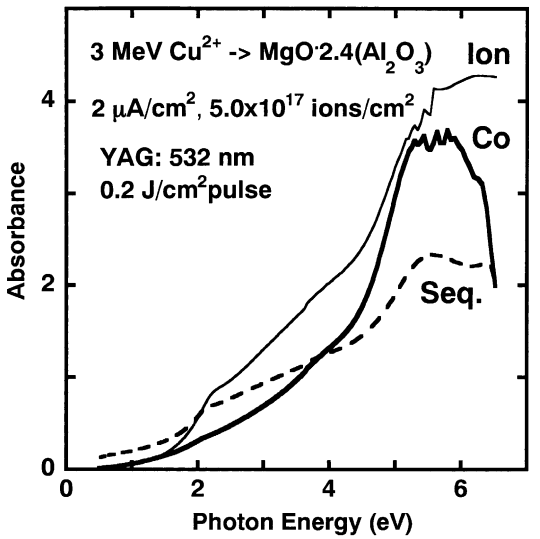

Fig. 3. Optical absorption spectra of $MgO{\cdot}2.4(Al_2O_3)$ that was co-irradiated with 3 MeV Cu^{2+} ions and 2.3 eV photons (thick solid line), sequentially irradiated with Cu^{2+} ions and 2.3 eV photons (dashed line) and single ion irradiated with Cu^{2+} ions (thin solid line). The ion flux and photon density are 2 $\mu A/cm^2$ and 0.2 J/cm^2pulse, respectively.

The broad bands in the high-energy region are assigned to F^+ centers at 4.8 eV and F centers at 5.3 eV [19]. In comparison with the single ion irradiation, the co-irradiation gives overall reduction in the SPR peak, the wide slope and the F-center bands. The co-irradiation-induced changes are interpreted as dynamic dissolution of Cu precipitation and annihilation of radiation-induced defects. On the other hand, the sequential photon irradiation sustains the SPR peak and greatly suppresses the F-center band. It is natural that the photon irradiation after the growth of metal nanoparticles cannot easily dissolve the metal particles. The co-irradiation effect observed at high fluence is in contrast to that at lower fluence of a-SiO_2 where co-irradiation just enhanced precipitation [13]. Since the photon energy used roughly coincides with the SPR due to Cu precipitates, the energy absorption in $MgO{\cdot}2.4(Al_2O_3)$ seems to result in dissolution of the precipitates. Consequently, not only defect states but also solute/precipitate states take part in absorbing electronic excitation energy by the co-irradiation. A common feature, irrespective of the fluence, is atomic migration enhancement by electronic excitation.

Significant photon irradiation effects on dislocation loops were also observed either in the co-irradiation or sequential irradiation mode. Fig. 4 shows cross-sectional TEM images of $MgO{\cdot}2.4(Al_2O_3)$ that was single ion-irradiated (a), sequentially irradiated (b) and co-irradiated (c) at 2 $\mu A/cm^2$ to 5.0×10^{17} ions/cm^2. The photon density was 0.2 J/cm^2pulse. The images were taken around the projected range. The single ion irradiation at room temperature creates dislocation loops and gives the contrasts of black lobes. The high-fluence irradiation caused random orientation of the loops. As is seen in Figs. 4(a)–(c), the dislocation loops are significantly annihilated by the photon irradiation. It is considered that electronic excitation enhances atomic migration, with some similarity to ionization enhanced diffusion [3], and that interstitials are dissolved into sinks, probably structural recombination centers of the spinel. For the loop morphology, there is apparently little difference between the sequential and co-irradiation, but the crystallinity (lattice image) is somewhat better for the co-irradiation than for the sequential irradiation. While $\dot{E}_{\mathrm{Ion}} = 5\times10^6$ Gy/s, the absorbed laser energy $\dot{E}_{\mathrm{Laser}}$ greatly depends on the absorbance A. A preliminary measurement of the in-beam absorbance yielded $A = 0.02$ on ion irradiation even in the lower fluence region. The in-beam absorbance is significantly large because of transient defect states, as compared to the off-

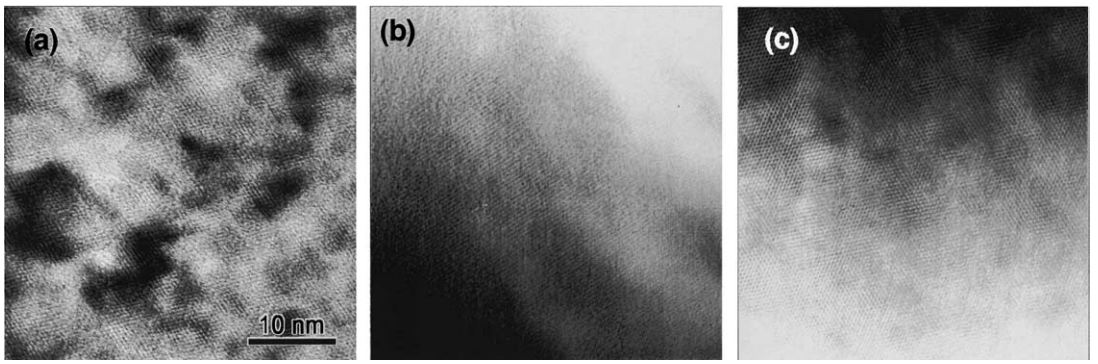

Fig. 4. Cross-sectional TEM images of $MgO{\cdot}2.4(Al_2O_3)$ that was single ion irradiated to 5.0×10^{17} ions/cm^2 with 3 MeV Cu^{2+} ions (a), sequentially irradiated with Cu^{2+} ions and 2.3 eV photons (b) and co-irradiated Cu^{2+} ions and 2.3 eV photons (c) to the same fluence. The ion flux and photon density are 2 $\mu A/cm^2$ and 0.2 J/cm^2pulse, respectively.

beam absorbance. The laser density absorbed within R_P is given to be $\dot{E}_{Laser} = I_0[1 - 10^{-A}]/R_P = 2 \times 10^5$ Gy/s. Since the absorbed energy density of laser is much smaller than that of ions, the co-irradiation effects observed are clearly not due to a thermal process of the input energy. On the other hand, the peak laser density during 20 ns is by five orders of magnitude higher than the electronic energy of ions. It is accordingly concluded that the co-irradiation effects dynamically take place during the laser-on time and that the electronic energy is converted to atomic displacements. The electron irradiation study of Mg–Al spinel by Yasuda and Kinoshita [7] pointed out the importance of electronic energy on loop evolution. The present study has advantage of well-defined selectivity of electronic energy by using a single photon energy combined with optical measurements, and has revealed that even subgap electronic excitation with little momentum enhances atomic displacements.

It is not yet clear for the spinel what defect states, besides the precipitates (SPR), are responsible for capturing electronic excitation of photons and what absorption band corresponds to the dislocation loops. However, comparison between the variation of absorption spectra and the reduction in loops suggests that the widely spread slope around 2–5 eV may be associated with dislocation loops. Further systematic study is necessary to clarify the concrete mechanism.

4. Summary

Electronic excitation effects on radiation damage of a-SiO_2 (KU-1) and $MgO{\cdot}2.4(Al_2O_3)$ were studied by using 2.3 eV photon irradiation under heavy ion irradiation of 3 MeV Cu^{2+}. The co-irradiation at high fluence exhibited significant effects on surface morphology, bulk defects and precipitates in the insulators. Whereas either the single ion or the sequential irradiation did not distinctly alter the surface morphology, the electronic excitation at high photon density strikingly enhanced surface damage due to DIET (atomic desorption induced by electronic transition). Optical absorption spectra at high fluence showed that co-irradiation promoted not only reduction in radiation-induced defects but also dynamic dissolution of metal precipitates. The dislocation loops were significantly annihilated by the photon irradiation, especially by the co-irradiation. Although the spinel is radiation resistant against void swelling, the surface of $MgO{\cdot}2.4(Al_2O_3)$ is susceptible to electronic excitation under heavy ion irradiation. It is concluded that intense electronic excitation, coexistent with heavy ions, is absorbed by transient electronic states and results in atomic displacements, that is, enhancement of surface damage, relaxation of electronic defects and dissolution of precipitates.

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References

[1] R.T. Williams, J.N. Bradford, W.L. Faust, Phys. Rev. B 18 (1978) 7038.
[2] C. Itoh, T. Suzuki, N. Itoh, Phys. Rev. B 41 (1990) 3794.
[3] J.C. Bourgoin, J.W. Corgett, J. Chem. Phys. 59 (1973) 4042.
[4] M.L. Knotek, P.J. Feibelman, Surf. Sci. 90 (1979) 78.
[5] S.J. Zinkle, Nucl. Instrum. and Meth. B 91 (1994).
[6] S.J. Zinkle, V.A. Skuratov, D.T. Hoelzer, Nucl. Instrum. and Meth. B 191 (2002) 758.
[7] K. Yasuda, C. Kinoshita, Nucl. Instrum. and Meth. B 191 (2002) 559.
[8] L.W. Hobbs, F.W. Clinard Jr., J. Phys. 41 (1980) C6-232.
[9] C. Kinoshita, J. Nucl. Mater. 191–194 (1992) 67.
[10] C. Kinoshita, K. Fukumoto, F.A. Garner, G.W. Hollenberg, J. Nucl. Mater. 219 (1995) 143.
[11] S.J. Zinkle, J. Nucl. Mater. 219 (1995) 113.
[12] J.F. Ziegler, J.P. Biersack, U. Littmark, The Stopping and Range of Ions in Solids, Pergamon, New York, 1985 (Chapter 8).
[13] N. Kishimoto, N. Okubo, C.G. Lee, N. Umeda, Y. Takeda, Nucl. Instrum. and Meth. B 175–177 (2001) 426.
[14] N. Okubo, N. Kishimoto, Y. Takeda, Nucl. Instrum. and Meth. B 219–220 (2004) 830.
[15] Y. Sasajima, K. Tanimura, Phys. Rev. B 68 (2003) 14204.
[16] N. Kishimoto, N. Takeda, Y. Umeda, N. Gritsyna, V.T. Lee, T. Saito, J. Nucl. Instrum. and Meth. B 166&167 (2000) 840.
[17] Y. Takeda, C.G. Lee, N. Kishimoto, N. Umeda, V.T. Gritsyna, Nucl. Instrum. and Meth. B 148 (1999) 1029.
[18] R. Boscaino, Nucl. Instrum. and Meth. B 116 (1996) 373.
[19] G.S. White, K.H. Lee, J.H. Crawford, Appl. Phys. Lett. 35 (1979) 1.