EFFECT OF LOW TEMPERATURE ION IRRADIATION ON THE MICROSTRUCTURE OF NITRIDE CERAMICS – S.J. Zinkle, L.L. Snead, W. S. Eatherly, J.W. Jones and D.K. Hensley (Oak Ridge National Laboratory)

OBJECTIVE

The objective of this study is to gain some insight into point defect mobilities in silicon nitride and aluminum nitride by examining the low-temperature irradiated microstructure.

SUMMARY

Cross-section transmission electron microscopy was used to investigate the microstructure of polycrystalline silicon nitride (Si_3N_4) and aluminum nitride (AlN) following 2 MeV Si ion irradiation at 80 and 400 K up to a fluence of $4x10^{20}$ ions/m^2 (maximum damage of ~10 displacements per atom, dpa). A buried amorphous band was observed at both temperatures in Si_3N_4 in the region corresponding to the peaks in the implanted ion and displacement damage. From a comparison of Si_3N_4 specimens irradiated at different fluences, it is concluded that the amorphization is primarily controlled by the implanted Si concentration rather than the displacement damage level. Si_3N_4 amorphization did not occur in regions well-separated from the implanted ions for doses up to at least 3 dpa at 80 K, whereas amorphization occurred in the ion implanted region (calculated Si concentration >0.01 at.%) for damage levels as low as ~0.6 dpa. The volumetric swelling associated with the amorphization of Si_3N_4 is <10%. Amorphization was not observed in any of the irradiated AlN specimens. A moderate density of small (~3 nm) defect clusters were observed in the crystalline damaged regions of both the Si_3N_4 and AlN specimens at both irradiation temperatures. Aligned network dislocations were also observed in the AlN specimen irradiated to high dose at 80 K.

PROGRESS AND STATUS

Introduction

AlN and Si_3N_4 are being considered for ceramic insulator applications in magnetic fusion reactors. Both of these materials have high strength and high electrical resistivity at moderate temperatures. Despite the widespread interest in these materials for electronic and structural ceramic applications, relatively little is known about their point defect behavior. We are unaware of any studies on self-interstitial atom (SIA) mobility in Si_3N_4. Atobe and coworkers found that the nitrogen vacancies (F centers) in AlN accumulated linearly with fast neutron fluence during irradiation at 20 K, whereas the accumulation was sublinear (proportional to the square root of fluence) at 360 K [1]. This indicates [2] that nitrogen SIAs are immobile in AlN at 20 K and mobile at 360 K.

Examination of the irradiated microstructure of ceramics, and in particular the temperature-dependent amorphization behavior, can provide insight into the mobility of point defects [3-5]. Several previous microstructural investigations of irradiated AlN and Si_3N_4 have been performed. Elevated temperature neutron irradiations of AlN [6,7] and Si_3N_4 [8] have observed faulted dislocation loops on basal and prism habit planes, respectively. Amorphization did not occur during 1 MeV electron irradiation at 140 K up to a fluence of $3x10^{26}/m^2$ (~0.5 dpa) in AlN [9] or during 1-2 MeV electron irradiation at 100-170 K up to fluences of $3\text{-}18x10^{26}/m^2$ (~0.5-4 dpa) in Si_3N_4 [9-11]. AlN and Si_3N_4 were found to remain crystalline following room temperature bombardment with 3 MeV Kr ions up to a fluence of $2x10^{21}/m^2$ (~150 dpa peak damage) [12]. Conversely, numerous ion irradiation studies at temperatures from 80 to 450 K have found that Si_3N_4 can be amorphized after ~1 to 2 dpa in the region corresponding to the peak in the implanted ion (Ni, Ti, Si, Fe, Cr) and displacement damage profiles [3,13-17]. The discrepancy in the Si_3N_4 amorphization behavior observed by Cartz et al. [12] and the implanted Ni, Ti, Si, Fe, Cr studies [3,13-17] highlights the importance of obtaining amorphization data under conditions where implanted ion effects are negligible [3]. Silicon nitride was recently shown to be resistant to amorphization up to 7 dpa during room temperature 3.6 MeV Fe ion irradiation in regions well separated from the implanted ions, whereas amorphization occurred readily in ion-implanted regions for doses of ~2 dpa [3]. Unfortunately, many ion beam amorphization studies have not attempted to separate implanted ion and displacement damage effects, with the notable exceptions of in-situ thin foil [18] and cross-section [3] MeV ion irradiation studies.

Table 1. Summary of properties of the investigated AlN and Si_3N_4 ceramics [7,19].

Material	Crystal structure	Lattice parameters	Density (g/cm^3)	Thermal conductivity (W/m-K)	Ionicity	Sublimation temperature
AlN (Cercom)	Hexagonal (wurtzite)	a=0.311 nm c=0.498 nm c/a=1.60	3.25	115	0.40	2790 K
β-Si_3N_4 (Kyocera)	Hexagonal ($P6_3$ space group)	a=0.760 nm c=0.290 nm c/a=0.290	3.21	29	0.28	2151 K

EXPERIMENTAL PROCEDURE

Small blocks of hot isostatically pressed Si_3N_4 (Kyocera SN733) and sintered AlN (Cercom) were obtained from commercial vendors. Table 1 summarizes some of the physical properties of AlN and Si_3N_4 [7,19]. Transmission electron microscope (TEM) specimens (3 mm diameter by 0.5 mm thick) were machined by a combination of diamond sawing and ultrasonic cutting. The top surfaces of the specimens were mechanically polished using 0.05 μm diamond paste.

The specimens were thermally anchored to a copper block using either silver paint or Aquadag™ adhesive. Duplicate specimens of each material were simultaneously irradiated for each irradiation condition using a 1.2 cm diameter beam spot. The irradiations were performed using 2 MeV Si beam currents of 0.3-1 $\mu A/cm^2$ at the Surface Modification And Characterization (SMAC) facility in the Solid State Division at ORNL. The irradiation temperature was continuously monitored by a thermocouple embedded in the support block. The maximum calculated beam heating was <1°C. Specimens were irradiated to fluences of either $4x10^{19}$ or $4x10^{20}/m^2$ at 78-82 K and 400 K. The displacement damage and implanted ion profiles were calculated using the TRIM96 program [20]. Figure 1 shows the calculated results for Si_3N_4; similar profiles were calculated for AlN. All calculations assumed a sublattice-averaged displacement energy of 40 eV.

Following the irradiation, cross-section TEM specimens were prepared by gluing the irradiated disks to polished unirradiated disks, sectioning, grinding to 0.1 mm, dimpling to 20 μm, and then dual-gun ion beam thinning at ~80 K with 6 keV Ar ions until perforation occurred near the interface. The specimen surfaces were cleaned using 3 keV Ar ions at an angle of 11° and then coated with a thin (~5 nm) layer of carbon prior to examination. The specimens were examined using conventional bright-field and dark-field imaging techniques in a Philips CM-30 microscope operating at 300 kV.

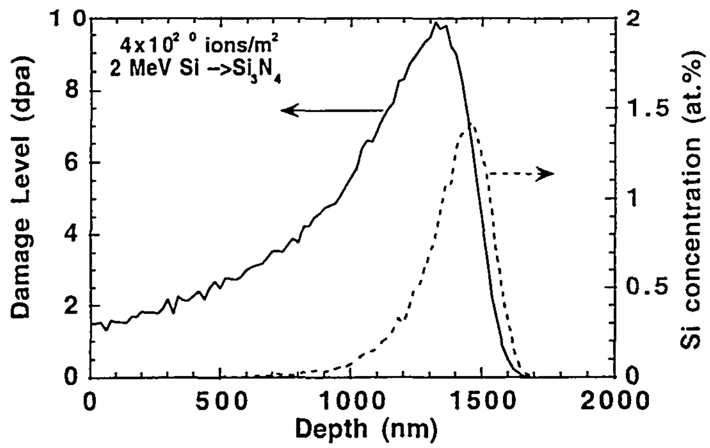

Fig. 1. Calculated damage and implanted ion distributions for 2 MeV Si ions in Si_3N_4.

Results

Figure 2 shows the general cross-section microstructure of silicon nitride irradiated at 80 K to fluences of $4x10^{19}$ and $4x10^{20}$ ions/m^2. A buried amorphous band was observed at both fluences, with a width of 0.7 µm at the lower fluence and 1.0 µm at the higher fluence. The residual dark contrast in the amorphous regions is due to Y_2O_3-enriched grain boundaries (0.5 µm mean grain diameter). The amorphization dose was comparable at grain boundaries and in the grain interior. The measured maximum damage range at both fluences was 1.70 $\pm$0.02 µm. The similarity in damage range for the two doses implies that the volumetric swelling associated with amorphization of Si_3N_4 is <10%, which is much less than the value of 22-25% suggested in some previous ion irradiation studies [15,16]. A recent modeling study found that the crystalline and amorphous Si_3N_4 densities were comparable [21], in agreement with the present results. From a comparison with the calculated TRIM profiles (Fig. 1), amorphization occurred at 80 K when the damage level was >0.6 dpa and the implanted Si concentration was c_{Si}>0.01 at.% in the lower fluence specimen and when the damage level was >3.3 dpa and c_{Si}>0.01 at.% in the higher fluence specimen. This implies that the implanted ion concentration is the controlling factor in the low temperature amorphization of Si_3N_4 (for damage levels >0.6 dpa).

Small defect clusters (~3 nm diameter) were visible in the crystalline damaged regions of Si_3N_4 irradiated at 80 K to a fluence of $4x10^{20}$ ions/m^2, whereas these defect clusters were not visible in the lower fluence specimen. This implies that these defect clusters were formed as the result of nucleation and growth (or perhaps multiple overlapping cascades), as opposed to direct formation within a single cascade.

Irradiation of Si_3N_4 at 400 K also produced a buried amorphous layer, although the band width at a given fluence was smaller than at 80 K. For example, the amorphous layer was ~0.17 µm wide for irradiation at 400 K to a fluence of $4x10^{19}$ ions/m^2. Analysis of the amorphization behavior at 400 K showed a good correlation with implanted Si concentration and a poor correlation with damage level. Amorphization of Si_3N_4 at 400 K occurred when the calculated Si concentration exceeded 0.1 at.% (for damage levels >0.9 dpa). Small defect clusters (~3 nm diameter) were observed in the damaged crystalline regions of Si_3N_4 at both of the 400 K irradiation fluences.

Fig. 2. Cross-section microstructures of Si_3N_4 irradiated with 2 MeV Si ions at 80 K.

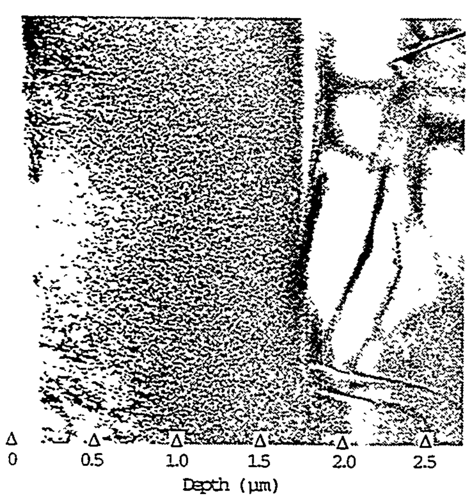

Fig. 3. Cross-section microstructure of aluminum nitride irradiated with 2 MeV Si ions at 78 K to a fluence of $4x10^{20}$ ions/m^2.

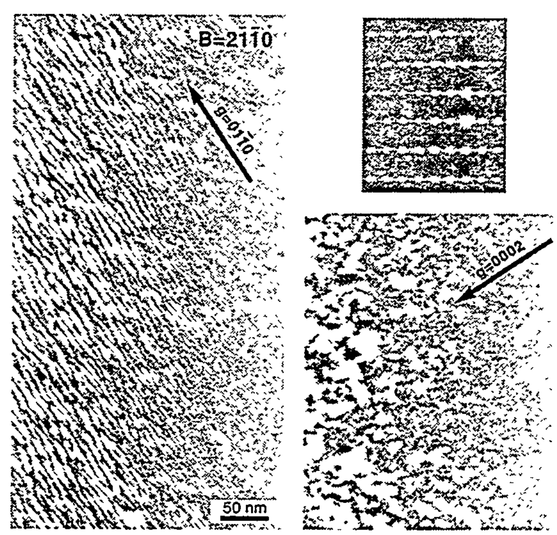

Fig. 4. Aligned network dislocations and defect clusters in AlN irradiated at 78 K to a fluence of $4x10^{20}$ ions/m^2.

Figure 3 shows the general cross-section microstructure of aluminum nitride irradiated at 78 K to a fluence of $4x10^{20}$ ions/m^2. A high density of small defect clusters (mean diameter of ~3 nm) was formed up to a maximum depth of 1.74 μm, with no evidence for amorphous regions in the grain interior (~8 μm grain diameter). A similar damage range and defect microstructure was observed in the specimen irradiated at 400 K to the same fluence. The initially crystalline grain boundary phase in AlN (easily visible at grain boundary triple points) was amorphized during irradiation at 78 K.

The irradiated microstructure of AlN is shown in finer detail in the centered dark field images of Fig. 4. A network of aligned dislocations were visible with a diffraction vector of $g = 01\bar{1}0$ but were not present for g=0002. Streaking was observed along the 0002 systematic row in the diffraction pattern.

Discussion

According to ionicity model for amorphization susceptibility [22], Si_3N_4 and AlN would both be expected to have moderate resistance to radiation-induced amorphization due to their largely covalent bonding. However, both of these materials have an amorphization resistance at 80 K that is comparable or superior to the predominantly ionic bonded Al_2O_3 which is amorphized after ~5 dpa [23,24]. Similarly, according to structural freedom considerations [25], Si_3N_4 should become amorphous at lower doses than Al_2O_3. As discussed elsewhere, point defect mobility is another important factor for amorphization [4]. In particular, amorphization generally does not occur in irradiated ceramics if the anion and cation SIAs are mobile.

The observation of a well-developed network dislocation structure in AlN at 80 K (Fig. 4) is evidence for significant SIA mobility. This conclusion is based on the assumption that the network dislocation structure was formed by the growth and unfaulting of interstitial dislocation loops produced at lower doses. As discussed in the introduction, the earlier optical absorption study by Atobe et al. [1] suggested that nitrogen SIAs in AlN are immobile at 20 K and mobile at 360 K. The present microstructural observations suggest that both the anion and cation interstitials in ion irradiated AlN are mobile at a temperature as low as 80 K. Further work is needed to determine if there is any possible influence of ionization induced diffusion [26] which could produce enhanced point defect mobility during ion irradiation.

There is a lack of microstructural data to which the present low-temperature irradiation results can be compared. It is interesting to note that the predominant habit plane for dislocation loops observed in previous high-temperature neutron irradiation studies were [0001] and $\{10\bar{1}0\}$ for AlN and Si_3N_4, respectively [7,8]. This difference may be due to the large difference in c/a lattice parameter ratios for these two materials (Table 1). The microstructural evolution in AlN irradiated to ~10 dpa at 80 K in the present study appeared to be more advanced than in a previous neutron irradiation study to a similar dose at ~770 K [7]. The neutron irradiation study reported the presence of interstitial dislocation loops on the basal plane with a Burgers vector of c/2[0001], but a network dislocation structure was not observed. The formation of network dislocations in irradiated materials generally requires high doses at elevated temperatures. Work is in progress to investigate the dose and temperature dependence of the microstructure of ion-irradiated AlN.

As summarized in the introduction, there are no known observations of amorphization in AlN, although relatively few studies have been performed [9,12]. In contrast, numerous studies have reported ion beam amorphization of Si_3N_4. The results of the present study and ref. [3] demonstrate that certain implanted ions have a pronounced effect on promoting amorphization of Si_3N_4. One possible mechanism for the implanted ion effect is that the impurity atoms may effectively trap migrating SIAs in Si_3N_4. The physical reason why AlN is able to accommodate >1% Si without amorphization whereas Si_3N_4 becomes amorphous for implanted metal ion concentrations above 0.01-0.1 at.% is worthy of further study. From the present study and previous work, strong implanted ion effects on the amorphization of Si_3N_4 appear to exist for Ni, Ti, Si, Fe, and Cr ions [3,13-17]. Amorphization has not been observed in Si_3N_4 irradiated at room temperature to moderate (3.5 dpa) or high (150 dpa) damage levels with He [3] or Kr [12] ions, respectively.

Conclusions

Aluminum nitride exhibits a high resistance to ion beam amorphization at temperatures as low as 80 K. The pronounced microstructural evolution of the defect clusters in the irradiated AlN specimens suggests that there is high mobility of the self interstitial atoms on both sublattices at 80 K. Therefore, amorphization is not expected to occur at temperatures ≥80 K even at higher doses (>10 dpa) unless implanted ions begin to trap point defects or the composition becomes significantly different from AlN due to the implanted ions.

The amorphization of beta-silicon nitride is extremely sensitive to small concentrations of implanted ions (Cr, Ti, Fe, Si). Amorphization at 80 K occurred when the implanted Si concentration exceeded ~100 appm for damage levels greater than ~0.5 dpa. Amorphization did not occur at 80 K outside of the implanted ion region (c_{Si}<100 appm) for damage levels as high as 3 dpa. Amorphization at 400 K was also sensitive to the implanted ion concentration, with a critical concentration of Si needed to induce amorphization of ~0.1 at.% for damage levels >0.9 dpa.

The development of resolvable defect clusters (and a network dislocation structure in the case of AlN) during irradiation at ~80 K is an indication that both anion and cation self-interstitial atoms are mobile in these two nitride ceramics. Further work at temperatures <80 K is needed to determine the migration kinetics of self-interstitial atoms in these materials.

REFERENCES

1. K. Atobe, M. Honda, N. Fukuoka, M. Okada, and M. Nakagawa, Jap. J. Appl. Phys. **29** (1), 150 (1990).
2. S.J. Zinkle and C. Kinoshita, J. Nucl. Mater. **251**, 200 (1997).
3. S.J. Zinkle and L.L. Snead, Nucl. Instr. Meth. B **116**, 92 (1996).
4. S.J. Zinkle and G.P. Pells, J. Nucl. Mater. **253**, 120 (1998).
5. A. Meldrum, S.J. Zinkle, L.A. Boatner, and R.C. Ewing, Phys. Rev. B, in press (1999).
6. T. Yano, M. Tezuka, H. Miyazaki, and T. Iseki, J. Nucl. Mater. **191-194**, 635 (1992).
7. T. Yano and T. Iseki, J. Nucl. Mater. **203**, 249 (1993).
8. R.A. Youngman and T.E. Mitchell, Radiat. Eff. **74**, 267 (1983).
9. A. Matsunaga, C. Kinoshita, K. Nakai, and Y. Tomokiyo, J. Nucl. Mater. **179-181**, 457 (1991).
10. H. Inui, H. Mori, and H. Fujita, Acta Metall. **37** (5), 1337 (1989).
11. H. Mori, T. Sakata, H. Yasuda, and M. Maeda, J. Vac. Sci. Technol. B **12** (4), 2376 (1994).
12. L. Cartz, F.G. Karioris, and R.A. Fournelle, Radiat. Eff. **54**, 57 (1981).
13. R.S. Bhattacharya, A.K. Rai, and P.P. Pronko, J. Appl. Phys. **61** (10), 4791 (1987).
14. R.G. Vardiman, in *Processing and Charaterization of Materials using Ion Beams*, MRS Symposium Proceedings, edited by L.E. Rehn, J. Greene, and F.A. Smidt (Materials Research Society, Pittsburgh, 1989), Vol. 128, p. 369.
15. W. Bolse, S.D. Peteves, and F.W. Saris, Appl. Phys. A **58**, 493 (1994).
16. F. Brensheidt, E. Wieser, W. Matz, A. Mücklich, and W. Möller, Appl. Phys. A **65**, 281 (1997).

17. F. Brensheidt, S. Oswald, A. Mücklich, E. Wieser, and W. Möller, Nucl. Instr. Meth. B **129**, 483 (1997).
18. L.M. Wang, S.X. Wang, W.L. Gong, R.C. Ewing, and W.J. Weber, Mater. Sci. Eng. A **253**, 106 (1998).
19. C.-M. Wang, X. Pan, M. Rühle, F.L. Riley, and M. Mitomo, J. Mater. Sci. **31**, 5281 (1996).
20. J.F. Ziegler, J.P. Biersak, and U. Littmark, *The Stopping and Range of Ions in Solids* (Pergamon Press, New York, 1985).
21. F. de Brito Mota, J.F. Justo, and A. Fazzio, Phys. Rev. B **58** (13), 8323 (1998).
22. H.M. Naguib and R. Kelly, Radiat. Eff. **25**, 1 (1975).
23. H. Abe, S. Yamamoto, and H. Naramoto, Nucl. Instr. Meth. B **127/128**, 170 (1997).
24. R. Devanathan, K.E. Sickafus, W.J. Weber, and M. Nastasi, Nucl. Instr. Meth. B **141**, 366 (1998).
25. L.W. Hobbs, A.N. Sreeram, C.E. Jesurum, and B.A. Berger, Nucl. Instr. Meth. B **116**, 18 (1996).
26. S.J. Zinkle, in *Microstructure Evolution During Irradiation*, MRS Symposium Proceedings, edited by I.M. Robertson, G.S. Was, L.W. Hobbs, and T. Diaz de la Rubia (Materials Research Society, Pittsburgh, 1997), Vol. 439, p. 667.