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AMORPHIZATION IN β -SiC

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Temperature dependence of ion-beam-induced amorphization in β -SiC

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The ion-beam-induced crystalline-to-amorphous transition in monolithic β -SiC has been studied as a function of irradiation temperature using the HVEM-Tandem Facility at Argonne National Laboratory. Specimens were irradiated with 1.5 MeV Xe⁺ ions over the temperature range from 40 to 550 K, and the evolution of the amorphous state was followed *in situ* using the HVEM. At 40 K, the displacement dose for complete amorphization in β -SiC is 0.34 dpa and increases with temperature in two stages. The simultaneous recovery process associated with the high-temperature stage (above 100 K) has an activation energy of 0.097 ± 0.019 eV. The critical temperature above which complete amorphization does not occur is 498 K under these irradiation conditions.

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1. Introduction

Silicon carbide (SiC) is a widely studied material with high-temperature semiconducting properties, high thermal conductivity, high-temperature stability, extreme hardness, and chemical inertness that make it a potential candidate for use in a wide range of advanced technological applications. It is a promising wide-gap semiconductor for high-temperature, high-power, and high-speed electronic devices. Because of its small neutron capture cross-section, it is a candidate material for structural components in fusion reactor systems. There is also interest in SiC for use as a high-temperature structural material in other applications, such as advanced heat engines. Electronic device fabrication, predicting behavior in a fusion reactor environment, and ion-beam modification/processing of high-temperature structural components all require a more detailed understanding of irradiation effects in SiC than presently exists. The temperature dependence of irradiation-induced amorphization in SiC is one area where there is limited understanding and is the subject of the present paper.

Silicon carbide is a largely covalently bonded material that exists in well over 100 polymorphs. The SiC phases of technical interest are the alpha phase (6H polytype) and the beta phase (cubic). Electron-beam-induced amorphization has been studied in some detail for both α -SiC [1-3] and β -SiC [4]. Under electron irradiation, where displacement cascades are not present, chemical disordering apparently plays an important role in the crystalline-to-amorphous transition in α -SiC [3] and β -SiC [4]. In the study of 2 MeV electron-irradiated α -SiC, the dose for complete amorphization increases with temperature in two stages, with a temperature independent regime from ~ 75 to 200 K [1]. Above 200 K, the dose for complete amorphization in α -SiC rises rapidly [1,2], and the critical temperature, T_c , above which complete amorphization cannot be induced is estimated to be 290 K [1]. The dose for complete amorphization in β -SiC

is nearly identical to that measured in α -SiC at 150 K; however, the increase in amorphization dose with temperature is slightly slower in β -SiC, with the critical temperature for amorphization in β -SiC estimated to be 340 K [4]. There is limited data on the temperature dependence of amorphization in α -SiC or β -SiC under ion irradiation, where displacement cascades dominate the irradiation-damage processes. In one study, the dose for complete amorphization in β -SiC under 130 keV Al^+ and 87 keV Si^+ irradiation is reported to be 50 to 60% higher at 300 K than at 77 K [5]. The present paper addresses the temperature dependence of amorphization in β -SiC under Xe^+ irradiation. Future studies will address ion-beam-induced amorphization in α -SiC.

2. Experimental procedures

The monolithic β -SiC used in this study was prepared by a bulk chemical vapor deposition (CVD) process by Morton Advanced Materials. The high-purity polycrystalline sample (99.9995% SiC) was theoretically dense (3.21 g/cm^3), with no voids or microcracks. Specimens were cut as thin sections from the bulk sample and prepared as TEM specimens by Ar^+ ion milling. The irradiations were carried out at the HVEM-Tandem Facility at Argonne National Laboratory. This facility consists of a modified Kratos/AEI EM7 high voltage electron microscope (HVEM) and a 2 MV tandem ion accelerator [6]. The irradiations were performed with 1.5 MeV Xe^+ ions, 5 to 10° off the surface normal, over the temperature range from 40 to 550 K to investigate the temperature dependence of amorphization. The ion fluence for complete amorphization in the electron transparent thickness ($\sim 200 \text{ nm}$) of the specimens was determined *in situ* by complete loss of the crystalline diffraction pattern under selected area electron diffraction conditions. Post-irradiation characterization of the structural changes at intermediate dose levels was carried out by high-resolution transmission electron microscopy (HRTEM).

The density of atomic displacements produced per ion as a function of depth in the electron transparent thickness (~ 200 nm) is shown in Fig. 1 and was calculated using TRIM-95 (full cascades) [7], a specimen thickness of 200 nm, and an assumed displacement energy of 25 eV for both Si and C. (The displacement energy for C in α -SiC is reported to be ~ 22 eV [8], and the displacement energy for Si is expected to be similar.) The average displacement dose (dpa) corresponding to the ion fluence for complete amorphization was calculated at a depth of 100 nm (center of the electron transparent thickness) to allow comparison to the electron-irradiation results of Inui et al. [4], which also have been converted to an equivalent displacement dose assuming a displacement energy of 25 eV.

3. Results and discussion

In Fig. 2, a typical sequence of selected area electron diffraction patterns, obtained *in situ* during the irradiation, show the progression of the amorphization process in β -SiC under 1.5 MeV Xe^+ ion irradiation at 300 K. A single crystal pattern is always obtained in unirradiated specimens [Fig. 2(a)]. At 0.22 dpa, a faint diffuse halo associated with the presence of amorphous material is apparent in the electron diffraction pattern [Fig. 2(b)]. The intensity of this diffuse halo increases with further increases in dose, while the intensity of the diffraction maxima from the remaining crystalline material decreases [Fig. 2(c)]. At a dose corresponding to 0.68 dpa, the specimen appears completely amorphous under electron diffraction [Fig. 2(d)].

The microstructural changes observed by post-irradiation HRTEM of specimens irradiated at 300 K with 1.5 MeV Xe^+ ions to different dose levels are shown in Fig. 3. Stacking faults on the $\{111\}$ planes are present in the unirradiated specimen [Fig. 3(a)]. At an intermediate dose of 0.22 dpa [Fig. 3(b)], the lattice fringes are discontinuous and twisted as the amorphous regions,

which exhibit mottled contrast, overlap; in addition, stacking faults are no longer apparent. After irradiation to a dose of 0.68 dpa, which corresponds to the fully amorphous state under electron diffraction [Fig. 2(d)], only a mottled contrast is observed under HRTEM [Fig. 3(c)].

The effects of irradiation temperature on the dose to completely amorphize β -SiC under 1.5 MeV Xe^+ ion irradiation are shown in Fig. 4. For comparison, the results for 2 MeV electron irradiated β -SiC single crystals [4] also are shown. At 40 K, the dose for complete amorphization under 1.5 MeV Xe^+ irradiation is 0.34 dpa and rises rapidly to 0.48 dpa at 100 K. This step increase between 40 and 100 K is outside the experimental error and is similar in magnitude and temperature to the step increase observed in electron-irradiated α -SiC [1]. Between 160 K (the lowest temperature under 2 MeV electron irradiation [4]) and 250 K, the dose for complete amorphization under 1.5 MeV Xe^+ irradiation (~ 0.50 dpa) is slightly less than under 2 MeV electron irradiation (~ 0.68 dpa). The results in Fig. 4, along with the previous results for α -SiC [1], suggest that within experimental error ($\pm 10\%$) the amorphization dose is nearly independent of temperature between ~ 100 and 250 K. For the 1.5 MeV Xe^+ irradiated β -SiC in this study and for the 2 MeV electron-irradiated α -SiC [1], the dose for complete amorphization increases with temperature in two stages. Stage I (below ~ 100 K) is probably associated with close-pair recombination. In Stage II (above ~ 100 K), the amorphization dose increases more rapidly with temperature for the 2 MeV electron-irradiated β -SiC than for 1.5 MeV Xe^+ irradiated β -SiC. The more rapid increase in amorphization dose with temperature for the 2 MeV electrons is probably due to the larger fraction of recoverable defects (isolated Frenkel pairs) produced by the electrons, as compared to the 1.5 MeV Xe^+ ions, which produce primarily cascade-type damage. At 500 K, only partial amorphization could be produced under 1.5 Xe^+ irradiation to 13 dpa.

The effects of temperature on amorphization can be described by simultaneous recovery

processes with activation energies, E_a , that decrease the average defect density produced per particle and, consequently, the rate at which the amorphous fraction, f_a , accumulates at a constant particle flux. In the model described by Weber et al. [9,10], the relationship between temperature and dose required for complete amorphization is shown to be given by the expression:

$$\ln(1 - D_0/D) = C - E_a/kT \quad (1)$$

where D_0 is the dose for complete amorphization at 0 K for each recovery process (each stage) and C is a constant dependent on ion flux and amorphization cross section. Equation 1 is similar to the expression derived by Morehead and Crowder [11]; however, in their model, D_0/D in Eq. 1 would be replaced by $(D_0/D)^{1/2}$ or $(D_0/D)^{1/3}$.

By applying the above model (Eq. 1) to the data in Fig. 4, the activation energy, E_a , for the Stage II recovery process can be determined from an Arrhenius type plot of $\ln(1 - D_0/D)$ versus $1/kT$ (there is insufficient data to determine E_a for the Stage I process). The amorphization dose, D_0 , associated with Stage II is 0.50 and 0.68 dpa for 1.5 MeV Xe^+ ions and 2 MeV electrons, respectively. The results of this analysis, along with a linear fit, are shown in Fig. 5. The activation energies determined for Stage II are 0.097 ± 0.019 eV and 0.064 ± 0.016 eV for the 1.5 MeV Xe^+ and 2 MeV electron irradiations, respectively. Within experimental error, these activation energies are similar suggesting similar recovery processes associated with the presence of similar irradiation-produced defects, although the relative concentrations are different. These activation energies are similar in magnitude to activation energies previously reported for irradiation-enhanced epitaxial recrystallization in other materials [9-12].

In addition to the activation energies, the critical temperature, T_c , above which complete

amorphization does not occur ($D = \infty$), can be determined from the linear fit to the Stage II data in Fig. 5. Since $\ln(1 - D_0/D) \rightarrow 0$ as $D \rightarrow \infty$, Eq. 1 yields the following expression for T_c :

$$T_c = E_a / kC. \quad (2)$$

Based on the activation energy, E_a , and intercept, C , determined for the Stage II data, T_c in β -SiC is estimated to be ~ 336 K under 2 MeV electron irradiation and ~ 498 K under 1.5 MeV Xe^+ irradiation. The value of T_c determined by a fit of the model to the 2 MeV electron data is nearly identical to the value (340 K) originally estimated by Inui et al. [4]. The observed increase in T_c with projectile mass (average recoil energy transferred) in β -SiC is similar to behavior previously reported in $\text{Ca}_2\text{La}_3(\text{SiO}_4)_6\text{O}_2$ [10], Si [11], and CuTi [13].

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Figure Captions

Fig. 1. Calculated damage in β -SiC from 1.5 MeV Xe^+ irradiations based on TRIM-95 [7].

Fig. 2. Electron diffraction patterns of monolithic β -SiC before and during irradiation with 1.5 MeV Xe^+ ions at 300 K: (a) unirradiated, (b) 0.22 dpa, (c) 0.56 dpa, and (d) 0.68 dpa.

Fig. 3. High-resolution TEM images of β -SiC before and after irradiation with 1.5 MeV Xe^+ ions at 300 K: (a) unirradiated, (b) 0.22 dpa, and (c) 0.68 dpa.

Fig. 4. Temperature dependence of the dose for complete amorphization in β -SiC under 1.5 Xe^+ ion irradiation [this study] and under 2 MeV electron-irradiation [4]. The half-filled data point at 500 K indicates that only partial amorphization is observed at this dose.

Fig. 5. Arrhenius-type plot of $\ln(1 - D_0/D)$ versus $1/kT$ for the β -SiC results in Fig. 4.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5