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AMORPHIZATION AND THE EFFECT OF IMPLANTED IONS IN SiC

L. L. SNEAD and S. J. ZINKLE
Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37831-6376

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ABSTRACT

The effects of implanted ion chemistry and displacement damage on the amorphization threshold dose of SiC were studied using cross-section transmission electron microscopy. Room temperature as well as 200 and 400°C irradiations were carried out with 3.6 MeV Fe, 1.8 MeV Cl, 1 MeV He or 0.56 MeV Si ions. The room temperature amorphization threshold dose in irradiated regions well separated from the implanted ions was found to range from 0.3 to 0.5 dpa for the four different ion species. The threshold dose for amorphization in the He, Si and Fe ion-implanted regions was also ~0.3 to 0.5 dpa. On the other hand, the amorphization threshold in the Cl-implanted region was only about 0.1 dpa. The volume change associated with amorphization was ~17%. No evidence for amorphization was obtained in specimens irradiated at 200 or 400°C.

INTRODUCTION

An understanding of the microstructural evolution of SiC under irradiation is critical to the application of these materials in fusion energy systems. At the anticipated operation temperatures for SiC (<1200°C), the most significant microstructural changes are expected to occur within the lower temperature range. Specifically, at temperatures under 100°C, the volumetric swelling due to point defect induced strain in neutron-irradiated SiC approaches 3%.[1] At these low temperatures amorphization of SiC is also possible, leading to a reported dramatic volumetric expansion[2,3] of 15 to 30%, along with a correspondingly large change in mechanical properties such as hardness, fracture toughness and elastic modulus.[2-4]

Numerous studies[2,3,5-11] have shown that SiC becomes amorphous during ion-beam irradiation at temperatures between 77 K and room temperature for damage levels in excess of 0.1 to 0.5 displacements per atom (dpa). To date there has been no demonstration of neutron-induced amorphization of SiC, although it is worth noting that neutron irradiation of SiC to damage levels in excess of 0.5 dpa at temperatures below 100°C apparently has not yet been performed. Relatively little is known about the susceptibility of SiC to amorphization during irradiation at elevated temperatures. Amorphization did not occur in SiC specimens irradiated with Cr, N or He ions at 750°C to doses in excess of 10 dpa at damage rates near 10^{-4} dpa/s.[2,3,10] However, partial amorphization was reported for SiC specimens irradiated to ~0.6 dpa at 600°C with Si ions at a damage rate of ~10^{-4} dpa/s.[11] Amorphization was not observed in SiC irradiated with fission neutrons (damage rate ~10^{-7} dpa/s) at ~150°C to damage levels in excess of 1 dpa.[11]

The majority of studies relating to SiC amorphization have utilized low-energy (<0.3 MeV) ion-beams[2,3,5-9], with one study investigating the amorphization threshold using high-energy electrons.[12] A possible complication arising from using low-energy ion beams is the difficulty in separating out the effects of the ion-induced displacement effects and any implanted-ion chemical effects. Such chemical effects have been shown to have a large effect on the threshold dose to produce amorphization in ceramics. For example, the threshold dose to produce amorphization in alumina during room temperature irradiation is ~600 dpa for 150 keV Cr ions, and ~100 dpa for 170 keV Zr ions.[13] Likewise, in covalently bonded Si_3N_4, the microstructure becomes amorphous during room temperature irradiation with 1.8 MeV Cl ions at ~0.5 dpa in the Cl ion implanted region while the structure does not amorphize even after ~7 dpa in the unimplanted region.[14] The main objectives of the present study were to determine the room temperature threshold dose for amorphization of ion-irradiated SiC in regions well-separated from the implanted ion region, and to determine if implanted ions alter this threshold dose. An additional objective of this study was to determine the maximum temperature that SiC can be amorphized during ion irradiation at high (~10^{-3} dpa/s) damage rates.

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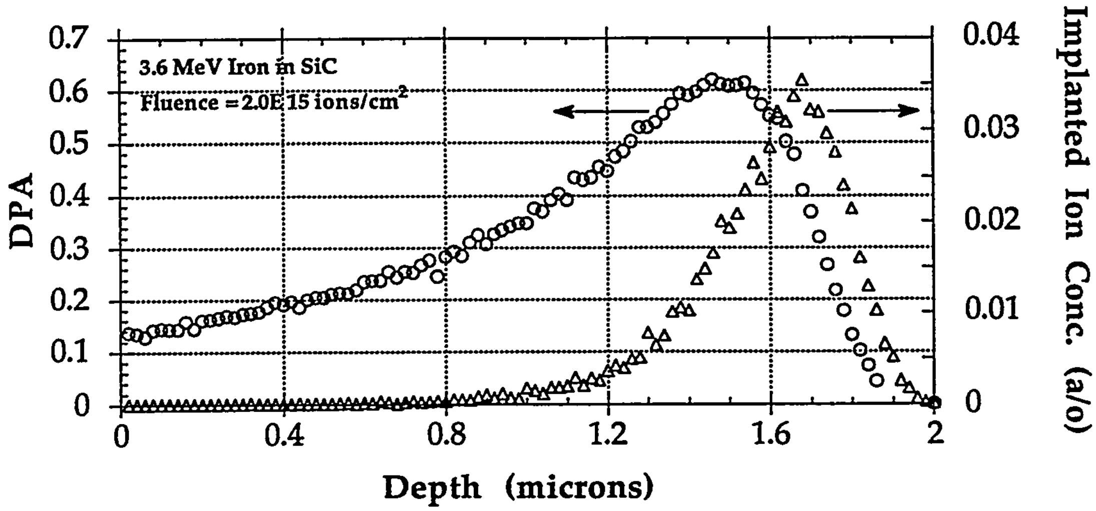

Fig. 1. Calculated displacement and ion implantation profile of 3.6 MeV Fe ions in SiC at a fluence of 2×10^{15} ions/cm^2.

EXPERIMENTAL PROCEDURE

Three SiC-based materials were used in this study: Cree Systems single crystal 6-H alpha SiC, chemically vapor deposited (CVD) beta-SiC produced from methyltrichlorosilane at Oak Ridge National Laboratory (ORNL), and Cercom (Coors) direct sintered beta-SiC. Most of the specimens were irradiated with single beams of 3.6 MeV Fe or 0.56 MeV Si ions. The sintered beta-SiC specimens were irradiated with a simultaneous dual beam of 1.8 MeV Cl and 1.0 MeV He ions. The Si ion beam was produced by the NV-500 accelerator at the SMAC user facility at ORNL while the Fe, Cl and He ion beams were produced by the Triple Ion Beam Facility at ORNL. In both facilities, samples were heat sinked to a thermalizer block and temperatures were measured using thermocouples either in the thermalizer block itself or a backing to which the block was clamped. The beam currents were about 30 nA/cm^2 for the Cl ion beam, ~100 nA/cm^2 for the Si and Fe ion beams, and 3 μA/cm^2 for the He ion beam. Cross sectional transmission electron microscopy was used for all samples. Samples prepared for microscopy were mechanically thinned and ion milled with 6 keV Ar ions at an angle of 15° using a liquid nitrogen-cooled ion milling stage.

RESULTS AND DISCUSSION

Shown in Fig. 1 are displacement and ion implantation profiles for the medium dose (2.0×10^{15} ions/cm^2) Fe ion irradiation. These profiles were calculated using the TRIM-92 code[15] assuming a sublattice-averaged threshold displacement energy of 40 eV. It is seen from these profiles that implanted ion concentrations are negligible up to the mid-range of the ions (0.7 μm depth) while there is a significant concentration of implanted ions over the second half of the range. The calculated peak displacement level and peak Fe concentration both occur at a depth near 1.6 μm with values of ~0.68 displacements per atom (dpa) and 0.036 atomic percent, respectively for a fluence of 2.0×10^{15} Fe^+/cm^2.

Amorphization of single crystal SiC due to 3.6 MeV Fe ion irradiation at room temperature is shown in Figure 2 for three separate fluences. The upper cross-section micrograph shows the highest fluence specimen (5.7×10^{15} ions/cm^2), which has amorphized over the entire range (spot-free, diffuse diffraction rings were used as an indicator of amorphization in all cases). The electron diffraction pattern for the amorphous region is inset into the upper micrograph of Fig. 2. At a

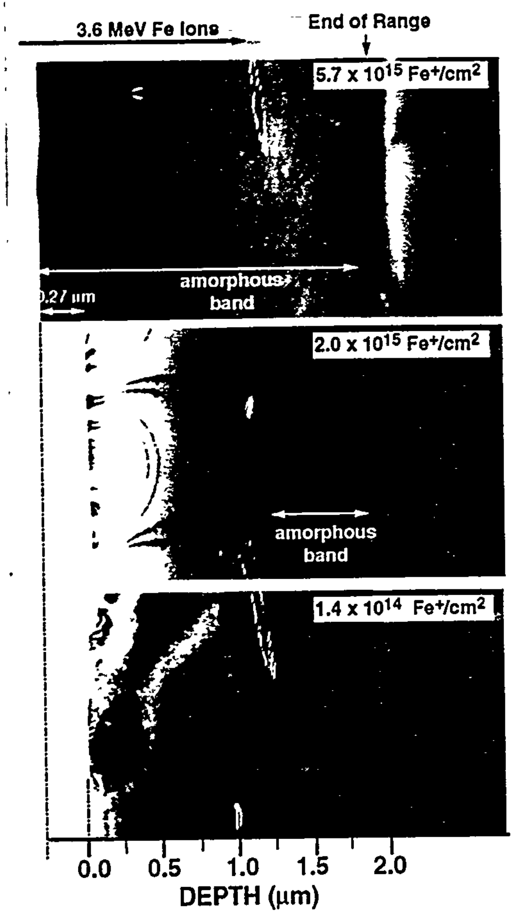

Fig. 2. Cross-section TEM bright field micrographs of SiC irradiated at room temperature with three different fluences of 3.6 MeV Fe ions.

Fig. 3. Cross-section TEM bright field micrographs of SiC irradiated simultaneously with dual beams of 1 MeV He and 1.8 MeV Cl ions at 50°C to two different fluences.

lower fluence of 2.0×10^{15} ions/cm^2 (middle micrograph of Fig. 2), amorphization only occurred over a ~0.7 µm wide band centered near the peak damage region. Amorphization was not observed at any depth at the lowest Fe ion fluence shown in Fig. 2 (1.4×10^{14} ions/cm^2), which produced 0.05 dpa in the peak damage region. Similar results were obtained for CVD SiC irradiated with Fe ions at the same three fluences. In general, no significant difference was found in the amorphization behavior of the three types of SiC used in this irradiation study, so material differences will not be further discussed.

Figure 2 also demonstrates the volumetric expansion associated with the amorphization of SiC. By comparison of the upper (completely amorphized) micrograph of this figure with the bottom (completely crystalline) micrograph, it is seen that amorphization has caused a significant volumetric expansion, with a resultant 0.27 µm movement of the free surface to the left. From this free surface "step-height" movement a volumetric swelling of ~15% was calculated due to the crystalline to amorphous transformation. Part of the original surface is missing in the middle micrograph of Fig. 2, so the volumetric expansion associated with the 0.7 µm amorphous band is not evident. Damage range TEM measurements made on micrographs with the original surface intact indicated that the swelling associated with the amorphous band was 17% for this specimen.

Figure 3 shows the effect of a room temperature simultaneous irradiation of 1.8 MeV Cl and 1.0 MeV He ions into a beta-SiC sample. The Cl beam had a damage range of nearly 1 µm, and the He beam produced damage up to ~2 µm. The upper micrograph of this figure is for the higher dose condition, and it is seen that amorphization has occurred over all but the near-surface regions of the Cl plus He ion irradiated region (~ 1.0 µm) and over the last third of the He ion irradiated region (maximum range ~2.4 µm due to density decrease associated with amorphization). The

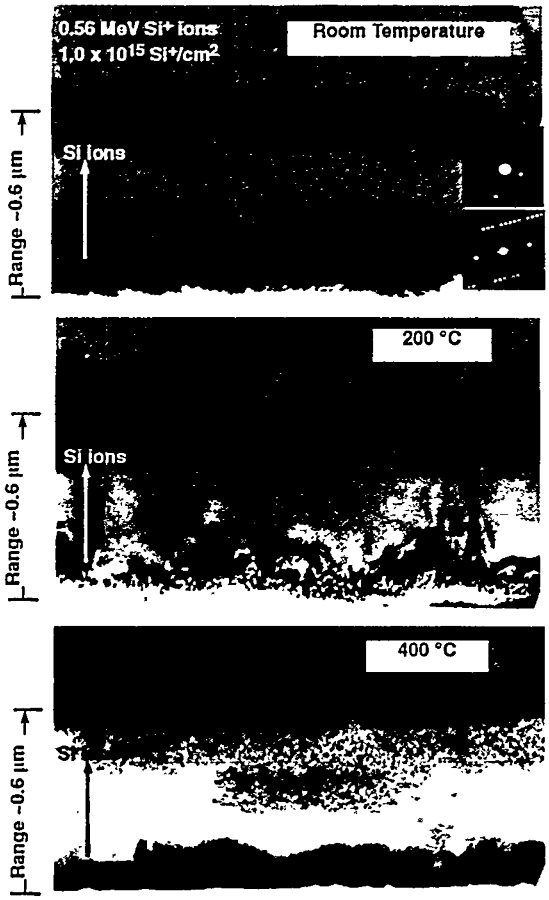

Fig. 4. Cross section TEM bright field micrographs of SiC irradiated with 0.56 MeV Si ions to the same fluence at three different temperatures.

lower ion doses shown in the bottom of this figure exhibit amorphization only near the end of the Cl and He ion ranges. Figure 3 also shows the effect of volumetric expansion, visible through the free surface movement. A measured swelling associated with amorphization of 17% (±3%) was measured for these specimens. The measured volume change associated with amorphization in SiC of 17% for the Fe, Cl and He ion irradiations is somewhat lower than the maximum reported[2] value of 30%, but is in good agreement with the revised value of 15% recently reported by McHargue and Williams[3].

The effect of 0.56 MeV Si ion irradiation at three different temperatures is shown in Figure 4. These specimens were irradiated to the same ion fluence (1.0x10^{15} ions/cm^2) at room temper-ature, 200 and 400°C. The room temperature specimen contained a band of material starting at about mid-range that appeared to be amorphous under ordinary bright field imaging conditions. However, it can be seen by inspection of the inset diffraction pattern that this region exhibits crystalline diffraction spots as well as the diffuse rings from the amorphous phase. Therefore, this region is partially, though not fully, amorphous. It should be noted that since the maximum damage range is ~0.6 µm at all three temperatures in Fig. 4, significant swelling has not occurred for the room temperature irradiation even though the structure is very close to the amorphous state. This suggests that the crystalline lattice contains a tremendous amount of potential energy due to the constraint of the low-density amorphous phase. As the irradiation temperature is increased to 200°C and 400°C, diffuse rings are no longer apparent in the electron diffraction patterns, suggesting that enhanced dynamic recovery of the crystal occurs at these temperatures. Amorphization also did not occur at 400°C for a fluence of 1 x 10^{16} Si^+/cm^2, which is ten times the dose needed to induce partial amorphization at room temperature (upper micrograph in Fig. 4).

A series of weak beam dark field micrographs were taken in the irradiated regions of the samples irradiated with Si ions at the three different temperatures. From these it was apparent that the size of the "black spot" defects increased significantly at 200°C and further increased at 400°C. Such results are consistent with an increased interstitial mobility inhibiting amorphization above room temperature. It is well established that the dose required to produce amorphization in SiC and other ceramic materials is nearly independent of temperature at low temperatures, but rises rapidly once a critical threshold temperature is reached.[12,16] The temperature threshold for amorphization in SiC has so far only been measured after 1 MeV electron irradiation, with a reported threshold occurring slightly below room temperature.[12] The apparent discrepancy between the temperature threshold for amorphization of SiC obtained in the present study with heavy ions (T_a<200°C) and the electron irradiation value (T_a<0°C) implies that an irradiation spectrum effect may be present, i.e., the displacement cascades associated with ion irradiation may allow amorphization to occur up to higher temperatures than would normally be possible with point defect accumulation effects alone.

Table 1 compares the threshold dose to induce amorphization in SiC during room temperature irradiation obtained by previous studies and the present study. The displacement

Table I. Amorphization threshold dose of SiC at room temperature

Ion	Energy (MeV)	Peak dose rate (dpa/s)	Calculated threshold dose (dpa)	Reference
N	0.062	$\sim10^{-4}$-10^{-3}	0.1	Williams [6]
Cr	0.260	$\sim10^{-4}$-10^{-3}	0.13	Williams [6]
H	0.080	2×10^{-7}	0.21	Spitznagel [7]
N	0.075	2×10^{-5}	0.19	Spitznagel [7]
Al	0.750	5×10^{-5}	0.26	Spitznagel [7]
Al	0.130	---	0.58	Edmond [8]
Si	0.87	---	0.45	Edmond [8]
Al	0.90	2×10^{-3}	0.28	Chechenin [9]
Cl	1.8	3×10^{-5}	0.12 implanted $\geq$0.4 unimplanted	this study
He	1.0	1×10^{-4}	~0.5 implanted ~0.6 unimplanted	this study
Fe	3.6	1×10^{-3}	>0.4 implanted 0.5 unimplanted	this study
Si	0.56	1×10^{-3}	>0.25	this study

levels for the previous studies have been recalculated with the TRIM-92 code using the threshold fluence data provided by the authors and assuming 40 eV for the sublattice-averaged threshold displacement energy. The previous published studies (utilizing relatively low energy ions) indicate that the amorphization threshold ranges from 0.1 to 0.58 dpa. Separate values for the amorphization threshold obtained in the present work are listed for the ion-implanted and unimplanted regions in order to assess the importance of chemical effects. These values were determined by comparing the widths of the amorphized regions for the different fluence irradiations with the TRIM-92 calculated displacement damage profiles. For unimplanted regions in SiC, the amorphization threshold dose ranges from 0.4 to 0.6 dpa.

An effect of implanted ion species in reducing the amorphization threshold was clearly seen only for the Cl ion beam. The amorphization dose was reduced from approximately 0.4 dpa for unimplanted regions of SiC to approximately 0.12 dpa in the Cl-implanted regions of SiC. On the other hand, He and Fe did not have a significant effect on the amorphization threshold. The effect of implanted Si on the amorphization threshold could not be determined due to the low fluences in this study (insufficient damage to induce amorphization outside of the implanted Si region), but Si clearly does not cause a large reduction in the threshold dose for amorphization.

The results summarized in Table I indicate that the threshold dose to produce amorphization in ion-irradiated SiC at room temperature is insensitive to variations in the damage rate over the range of 10^{-7} to 10^{-3} dpa/s. This implies that neutron irradiation (typical damage rates $\sim10^{-7}$ dpa/s) should produce amorphization in SiC at room temperature. Since amorphization of SiC is apparently very difficult at temperatures $\geq$ 200°C even for high damage rates of $\sim10^{-3}$ dpa/s (Fig. 4), damage rate effects may be expected to become more significant as the irradiation temperature approaches 200°C, which would explain the absence of amorphization in SiC irradiated with neutrons ($\sim10^{-7}$ dpa/s) at 150°C.[11]

CONCLUSIONS

(1) Previous work on the amorphization threshold dose for SiC using low energy ion beams has been reviewed and results recalculated using a consistent calculational method. The threshold measured in previous low-energy ion studies ranges from 0.1 to 0.58 dpa, which is in general agreement with the values found for the higher energy ions in this work of 0.4 to 0.6 dpa.

(2) Chlorine ion implantation assists the amorphization of SiC, reducing the room temperature amorphization threshold dose from approximately 0.4 dpa to 0.12 dpa.

(3) The density of the amorphous phase is about 17% less than the crystalline phases of SiC.

(4) A temperature effect on amorphization was observed, suggesting that the maximum temperature for ion beam-induced amorphization of SiC occurs between room temperature and 200°C. Amorphization was not observed at 200°C and 400°C, at least up to damage levels of 0.25 dpa and 2.5 dpa, respectively.

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