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Evidence for cascade overlap and grain boundary enhanced amorphization in silicon carbide irradiated with Kr ions

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ABSTRACT

Evolution of amorphous domains in silicon carbide with 1 MeV Kr^{2+} irradiation is investigated using high-resolution transmission electron microscopy and simulations. An unusual morphology of highly curved crystalline/amorphous boundaries is observed in the images, which is identified as a result of cascade overlap and reproduced by a coarse-grained model informed by atomistic simulations. Comparison of local amorphization fractions near grain boundaries and within grain interiors provides experimental evidence for the interstitial starvation mechanism in SiC for the first time. As a competing effect to defect sinks, interstitial starvation increases the rate of local amorphization near grain boundaries and reduces the radiation resistance of nanocrystalline silicon carbide.

1. Introduction

Silicon carbide (SiC) has attracted considerable attention in the nuclear industry because of its outstanding properties, such as high-temperature stability, chemical inertness, high thermal conductivity and low neutron absorption cross-section [1]. In order to meet the reliability requirements during long-term service in a nuclear reactor, a material must be highly resistant to radiation damage. This is because radiation creates numerous point defects and defect clusters that accumulate and lead to the degradation of the material properties [2]. One of the responses of SiC to irradiation is radiation-induced amorphization (RIA) [3]. RIA reduces the hardness, elastic modulus and thermal conductivity of SiC and is accompanied by swelling of the material [4–6].

The mechanism for RIA in SiC has been extensively studied by both experimental and theoretical approaches [7–13]. Amorphization can proceed either homogeneously or heterogeneously [3]. In homogeneous amorphization, point defects accumulate progressively in the system until crystalline order is lost. This process is sometimes modeled as involving point defects raising the energy of the system until a critical energy density is reached, at which point the system transforms to a more stable amorphous state spontaneously [14]. For heterogeneous amorphization, several possible mechanisms have been proposed, including cascade overlap, direct impact/defect stimulated growth (DI/DS) at crystalline/amorphous (c/a) boundaries and a nucleation and growth model. The cascade overlap model assumes that irradiation produces regions of high defect concentration, i.e., displacement cascades, and the overlap of these cascades leads to localized amorphization. In contrast, in the DI/DS model, local disordered regions are formed directly by the incident particles and further growth at c/a interfaces is stimulated by the diffusion of generated defects. The amorphous phase may also nucleate and grow near extended defects, such as dislocations and grain boundaries. Experimentally, the amorphization fraction of SiC by ion irradiation has been measured as a function of irradiation dose [7–10]. The amorphization fraction – irradiation dose curve has a sigmoidal-like shape, which is consistent with all three mechanisms mentioned above. Molecular dynamics (MD) simulations have revealed that the completely amorphous state can be reached after generating a number of 10 keV Si or C atom recoils in a SiC crystal, which implies that an overlap of the displacement cascades may lead to the final c–a transition [12,15]. However, MD simulations also found the formation of nanoscale amorphous domains after a direct impact of 50 keV Au ions with SiC, suggesting that direct amorphization is also a possible mechanism for heavier irradiation ions [13].

Despite many studies dedicated to this topic, a complete understanding of the microscopic mechanism governing the c–a

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transition remains elusive, as the detailed amorphization process is likely to depend on the irradiation species, their energy, the sample temperature and the nano/microstructure of the SiC. Moreover, these effects are not necessarily independent of each other. Of particular interest is to understand how the specific amorphization mechanism is affected by the presence of grain boundaries (GBs). This interest is driven by recent efforts devoted to improving radiation tolerance by refining the grain size of SiC to the nanometer regime [16–21]. Nanocrystalline (nc) materials have a high volume fraction of GBs, which act as sinks for point defects generated during irradiation [22]. As a result one can expect nc materials to be more efficient at annealing radiation-induced damage. Indeed experiments found that nc SiC showed a higher dose to amorphization than single crystal SiC irradiated with high energy electron and Si ions [16,17]. Interestingly, however, reduction in radiation resistance of SiC due to grain refinement was also reported based on several irradiation experiments using 1 MeV Si, 2 MeV Au and 1 MeV Kr ions [18,20,21]. What is particularly puzzling is that the same low pressure chemical vapor deposited (LPCVD) nc SiC was used in Refs. [16] and [17] (showing improved resistance to amorphization) and in Ref. [21] (showing a decreased resistance). It appears that the answer to the question whether nc covalent ceramics have superior or inferior resistance depends not only on the nano/microstructural features (GBs, stacking faults, dislocation density, etc.), but also on the irradiation type. A summary of experimental results on the effects of radiation type and temperature on RIA in SiC can be found in Ref. [21]. The seemingly contradictory effects of grain refinement on resistance to amorphization reported in the literature also imply that GBs may play multiple roles in amorphization and general radiation damage process. Understanding the complex nature of RIA is important for utilizing nano-engineering to design materials with superior radiation resistance.

High-resolution transmission electron microscopy (HRTEM) provides insight into the role of GBs in RIA, since HRTEM can be used for direct observation of the evolution of nano/microstructural features during irradiation. For instance, Ishimaru et al. used *in situ* HRTEM to observe structural changes during electron irradiation of 3C-SiC with nanolayered planar defects [23]. It was shown that after receiving the same dose, GBs were highly damaged and disordered while the intragranular regions on both sides of the GB maintained crystalline order. This result suggested that irradiation-induced defects were preferentially trapped at GBs, driving amorphization in that region. For ion irradiation, Snead et al. analyzed the shape and orientation of the amorphized areas in single crystal 3C-SiC implanted with 0.56 MeV Si^+ [24]. Amorphous islands (or amorphous pockets), typically 10 nm in width and more than 30 nm in length, were formed in the region beyond the damage peak where the sample was only partially amorphized. These pockets had an elongated shape with the major axis aligned parallel to the surface of the specimen, regardless of the direction of the incident ion. The authors hypothesized that the orientation preference was either due to the strain field introduced by the amorphization or the free surface of the sample. However, the effects of microstructure (e.g., GBs) during the ion irradiation were not investigated.

In the present study, we use HRTEM to investigate the morphology of amorphous regions in polycrystalline 3C-SiC irradiated with Kr ions and to determine the role that GBs play in RIA. An unusual morphology with a very fine structure of highly curved c/a boundaries is found in the partially amorphized sample. To understand how such morphology can arise, we have developed a coarse-grained model for damage evolution, which reproduces the experimental observations based on the combined effects of cascade overlap and the two-dimensional projection inherent to HRETM. By comparing the c/a morphologies at GBs and within the grain interiors, the complex effects of GBs on the amorphization process are investigated. Our analysis is enabled by development of a new algorithm for automatic identification of the amorphous regions in HRTEM images. Our analysis demonstrates the existence of the "interstitial starvation" in SiC, which proposes that preferential annihilation of interstitials at the GBs leaves behind excess vacancies that lead to amorphization. This mechanism was previously only postulated to occur in SiC based on simulations [25]. The influence of the dual role of GBs as sinks for point defects and as a source for interstitial starvation on the radiation resistant of nanocrystalline material is also discussed.

2. Experiment

To obtain partially amorphous SiC samples, *in-situ* Kr^{2+} irradiation was conducted using the IVEM-Tandem facility at the Argonne National Laboratory. The TEM samples were prepared from polycrystalline CVD 3C-SiC sourced from Rohm & Hass with grain sizes ranging from 1 μm to 5 μm. The ion beam energy was 1 MeV and the flux was 6.25×10^{11} ions/cm^{2}s. The irradiation temperature was measured by a thermocouple within the heated specimen stage and the temperature was controlled at 100 °C, which is below the RIA critical temperature in SiC. During irradiation, electron diffraction patterns of the sample were recorded periodically and were used to determine the degree of crystallinity of the sample. The sample was regarded as fully amorphous when diffraction spots disappeared and only diffuse rings remained. The irradiation fluence for complete amorphization was 1.30×10^{15} ions/cm^2, corresponding to a dose of 1.35 dpa (displacement per atom). Another sample was then irradiated to half of the dose to amorphization (0.675 dpa) and therefore was considered partially amorphous. SRIM ("Stopping and Range of Ions in Matter") code was used to calculate the number of displacements per incident Kr ion as a function of specimen depth, and the average displacement number within the sample thickness was used to convert the fluence to dose in dpa [26]. Detailed settings for SRIM calculation are described in Section 3.1. For additional thinning, the partially amorphous sample was ion milled on both sides with Fischione 1050 set at 600 V for 15 min after the irradiation. Detailed procedures for sample preparation and irradiation experiment can be found in Refs. [17] and [21].

Ex-situ HRTEM images were taken using FEI Tecnai F30 microscope operated at 300 kV using the twin pole piece and with objective aperture radius of 47.3 mrad. Fig. 1 shows typical HRTEM images of an unirradiated sample and a sample that received half of the dose to amorphization. The insets show the corresponding selected area diffraction patterns (SADP). For the unirradiated sample, the HRTEM image has clearly visible columns of atoms (or lattice fringes) in the entire area of the image and the SADP shows only sharp crystalline diffraction spots. In the image of the partially amorphous sample, amorphous domains of mottled contrast are mixed with crystalline domains with periodic lattice fringes and the SADP contains diffuse rings indicative of amorphous material in addition to crystalline spots.

In order to quantify the c/a fractions and boundaries, we have developed an automated analysis method that is free from observer bias to distinguish consistently the amorphous and crystalline regions in all HRTEM images. The procedure consists of three steps, which are illustrated in Figs. 2–4, respectively. In Step I, we Fourier filter the image, retain only the crystalline spots in the Fourier transform and then do the inverse Fourier transform (Fig. 2). The goal of this Fourier filtering step is to preserve the intensity of the crystalline part of the image while eliminating the intensity of the amorphous part. In Step II, we calculate the local standard deviation of the filtered intensity. The filtered image is divided into