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Combined experimental and computational study of the recrystallization process induced by electronic interactions of swift heavy ions with silicon carbide crystals

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The healing effect of intense electronic energy deposition arising during swift heavy ion (SHI) irradiation is demonstrated in the case of 3C-SiC damaged by nuclear energy deposition. Experimental (ion channeling experiments) and computational (molecular dynamics simulations) studies provide consistent indications of disorder decrease after SHI irradiation. Furthermore, both methods establish that SHI-induced recrystallization takes place at amorphous-crystalline interfaces. The recovery process is unambiguously accounted for by the thermal spike phenomenon.

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Research on ion-solid interactions usually focuses on predicting and mitigating detrimental effects on materials from particle irradiation, as in nuclear reactors, space applications, and ion-implantation doping of electronic devices. Such destructive effects are often the result of collision cascades induced by low-energy ions. Swift heavy ions (SHIs) have high energies ($>$100 MeV) and interact with solids primarily by inelastic collisions with electrons of target atoms. This energy-transfer process results in a state of intense electronic excitations along the ion path that can, particularly in insulating materials, lead to the formation of cylindrical damage regions, commonly referred to as latent ion tracks,[1,2] which correspond to permanent structural modifications on the nanometer scale along the ion trajectory. The effect of SHIs on semiconducting materials, on the other hand, is more subtle and significantly less studied. Irradiation of pristine SiC with SHIs has shown that latent ion tracks do not form,[3,4] but there is some production of point defects.[5] Notably, in 6H-SiC irradiation damaged with low-energy ions, which predominantly lose energy through ballistic collisions processes (nuclear energy deposition), it has been observed that SHI irradiation in the GeV energy range can induce, at room temperature (RT), recovery of the preexisting damage;[6] this phenomenon has been labeled SHIBIEC, which stands for swift heavy ion-induced epitaxial recrystallization.

Silicon carbide (SiC) is a wide-band-gap semiconductor with broad applications and an expanding range of functionality due to unique defect-based quantum states, excellent thermal conductivity, large breakdown voltage, high strength, as well as outstanding chemical, mechanical, and nuclear properties. There has been significant research and development on utilizing SiC in high-power, high-frequency, and high-temperature electronics and sensors for energy efficiency, nuclear and space applications,[7–9] in nuclear structural applications,[10] and as an accident-tolerant cladding to prevent Fukushima-type accidents.[11] Energetic ion beams used in the fabrication of SiC devices usually induce defect formation that eventually leads to a crystalline-to-amorphous transition,[12] and high-energy ions in nuclear environments and cosmic radiation in space can disrupt or damage SiC-based devices.

In this Rapid Communication, we report on the use of integrated experimental and molecular dynamics (MD) simulation methods to investigate the effects of swift heavy ion irradiation on model damage states in 3C-SiC. The results demonstrate that highly ionizing particle irradiation can, via a thermal spike phenomenon, promote self-healing rather than defect production in SiC.

The experimental work was performed using (001)-oriented 3C-SiC single crystals obtained from HAST Corporation. The samples were initially irradiated with 100 keV Fe ions at RT to fluences of 2×10^{14} cm^{-2} (0.36 dpa) and 4×10^{14} cm^{-2} (0.72 dpa) to create specific irradiation damaged states[13] that are discussed in detail below. Under these conditions, the irradiation damage is due to ballistic displacement cascades from the nuclear energy loss, and the ion fluence corresponds to a peak Fe concentration of only $\sim$0.1 at. %, which can be disregarded. The damaged crystals were subsequently irradiated with 0.87 GeV Pb ions at RT at the GANIL facility in Caen (France). For this ion energy, the nuclear energy loss ($<$0.1 keV/nm), and hence displacement damage, is negligible compared to the electronic energy loss (33 keV/nm). Two Pb ion fluences were used, 7.5×10^{12} cm^{-2} and 2×10^{13} cm^{-2}, and the ion flux was kept below 5×10^8 cm^{-2} s^{-1} to minimize target heating. The crystals were tilted off any major direction during irradiation to avoid channeling effects. Before and after each irradiation step, the crystals were analyzed by Rutherford backscattering spectrometry in the channeling mode (RBS/C) at RT using a 1.4 MeV He ion beam at the ARAMIS accelerator of CSNSM in Orsay. The energy resolution was on the order of 12 keV, which corresponds to a depth resolution of ~10 nm. The resulting spectra were analyzed with the McChasy Monte Carlo code developed at the Soltan Institute of Nuclear Studies (SINS) in Warsaw.[14] In this code, the disorder is accounted for by considering that a fraction of atoms f_D are randomly displaced from their regular crystallographic site. This assumption is particularly appropriate in the case of SiC, since the disordering process up to amorphization is, under the present irradiation conditions, due to the accumulation of point defects and very small point defect clusters.[15] In this study, only the disorder in the Si sublattice is investigated. Additionally, high-resolution cross-sectional transmission electron microscopy (X-HRTEM) characterization and associated fast-Fourier transform (FFT) analysis were carried out on a microscope operated at 300 keV.

In order to study the effect of SHIs on an atomistic level, molecular dynamics simulations have been performed to simulate single and multiple SHI impacts in SiC cells with two different irradiation damaged states that mimic the experimental ones. The simulations were carried out with the MD code PARCAS (Ref. 16) using the Gao-Weber SiC potential.[17] This potential has previously been used to study defect formation energies,[17] defect migration,[18] epitaxial recrystallization, and phase transitions[19,20] in SiC, and it is therefore expected to describe well the damage production and recovery processes occurring along the trajectory of a SHI. The structure of the damaged simulation cells is analyzed before and after ion impact by a structure factor method,[21] where defects are defined based on deviation from the bond angles in the ideal zinc blende structure of 3C-SiC. The simulation cell was cubic with a side length of 24 nm and contained 1 300 000 atoms. The damaged layers were created in the horizontal xy plane by randomly giving 50 eV of kinetic energy to atoms in the confined layer, which is sufficient energy to permanently displace both Si and C atoms.[22] This process was repeated until the desired level of damage was reached. To mimic the distribution of damage production, positions of recoil atoms in the z direction (i.e., perpendicular to the damaged layer) were chosen according to a Gaussian distribution centered in the middle of the cell with a standard deviation of 2 nm. In the subsequent SHI simulations, the direction of the ion was perpendicular to the damaged layers, i.e., in the z direction. To simulate the local heating from a swift heavy ion, the inelastic thermal spike model[23,24] was used to determine the kinetic energy distribution given to atoms via electron-phonon coupling from the excited electronic system. This gives rise to a cylindrically symmetric radial profile of kinetic energy added to the lattice (exceeding 1 eV/atom within a 2-nm radius of the ion path), with heating most intense closest to the ion path and decreasing with distance from it. Similar to other studies,[25,26] kinetic energy determined from the radial profile was added in random directions to atoms in the MD environment to simulate the heating from a thermal spike and to study the impact of the SHI on the damage states. The heat was dissipated to thermally controlled boundary layers at the x and y boundaries (given the ion path in the z direction), and the changes in the structure after 100 ps were analyzed. More precisely, the short-range structure in the most affected area, a cylinder of radius 8 nm, was analyzed both prior to and after the SHI simulation.

As previously mentioned, two different damage states have been investigated. Disorder depth profiles extracted from RBS/C spectra are displayed in Fig. 1(a) for crystals that have been irradiated to the highest Fe fluence prior to SHI irradiation. Complete amorphization is observed in this damaged state, since the disorder fraction reaches the random level (i.e., $f_D = 1$) over a thickness of approximately 50 nm [solid line in Fig. 1(a)]. After SHI irradiation [dashed and dotted lines in Fig. 1(a)], a decrease in thickness of the amorphous layer from the buried amorphous-crystalline (a-c) interface is clearly evident. This finding suggests a recrystallization process. A TEM analysis (not shown here) confirms that the thickness of the amorphous layer decreased after SHI irradiation, while no noticeable modification of the remaining amorphous region is observed. The corresponding MD simulated amorphous layer (obtained after 70 000 recoils) is by necessity thinner than the actual experimental layer, but is very similar in structure: a central inner amorphous layer

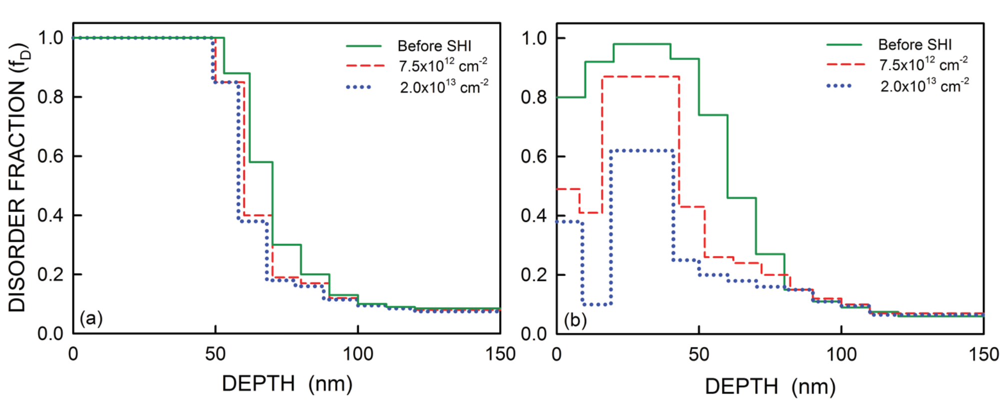

FIG. 1. (Color online) Experimental depth distributions of the disorder fraction in the 3C-SiC crystals damaged by low-energy recoils and subsequently heat treated by a thermal spike due to 0.87 GeV Pb ion irradiation: Case of (a) fully amorphous and (b) partially amorphous layers.

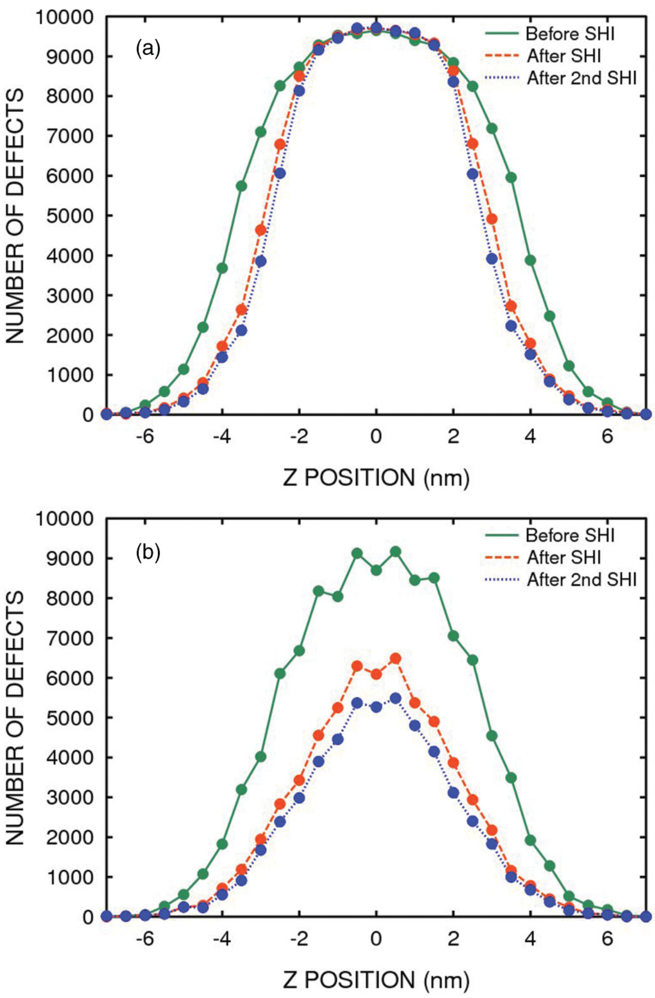

FIG. 2. (Color online) Simulated depth distributions of the damage in the 3C-SiC cells damaged by low-energy recoils and subsequently heat treated by a thermal spike due to 0.87 GeV Pb ion irradiation: Case of (a) fully amorphous and (b) partially amorphous layers.

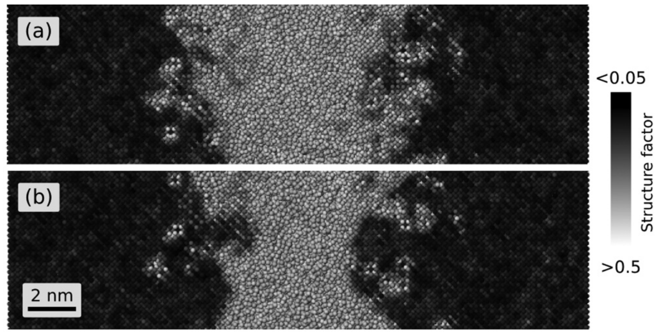

FIG. 3. Atomistic model of the fully amorphous layer (a) before and (b) after the thermal spike. The grayscale represents the structure factor of the atoms, i.e., the deviation from the zinc blende bond angle. The cross section is chosen from the area within the effective track recovery radius.

surrounded on each side by partially disordered interfacial layers that merge with the pristine, crystalline matrix. In this fully amorphous layer, the thermal spike is found to induce recrystallization at the *a-c* interfaces, with minor additional recrystallization for a second overlapped impact [Fig. 2(a)], consistent with experimental observations. This recrystallization is illustrated in Fig. 3, where a section of the amorphous layer is shown before and after the SHI energy is deposited as a thermal spike and allowed to relax.

For the samples irradiated to the lower Fe ion fluence, full amorphization is incomplete at the damage peak ($f_D \sim 0.98$) and, while a high degree of disorder is present over the entire damaged thickness, some crystallinity remains [solid line in Fig. 1(b)]. This structure is represented in Fig. 4(a), which shows a high-resolution TEM image of the SiC crystal prior to SHI irradiation. The image has been recorded in the vicinity of the damage peak (i.e., at a depth of ∼25 nm), and it shows a lattice with strongly disturbed (originally) crystalline regions which can be considered as amorphous pockets. The corresponding FFT displayed in the inset supports this description. Upon SHI, this partially amorphous structure behaves in a completely different manner than that observed for fully amorphous crystals. Indeed, a decrease in f_D over the whole damaged thickness is readily evidenced after Pb ion irradiation [dashed and dotted lines in Fig. 1(b)], meaning that the recovery is not only localized at the buried *a-c* interface (which is consistent with previous results; see Ref. 6). The observed recovery process is furthermore corroborated by a high-resolution TEM analysis. The initial damage state [Fig. 4(a)] contains substantial amorphous pockets; however, following SHI irradiation, the amorphous pockets are clearly less numerous [Fig. 4(b)] and have been superseded by disturbed, crystalline regions. The partial vanishing of the diffuse scattering component in the FFT pattern, shown in inset of Fig. 4(b), is consistent with this interpretation. The corresponding MD partially amorphous layer (obtained after 30 000 recoils) also shows significant recovery, within the central effective SHI track radius, over the whole damaged thickness [Fig. 2(b)], in good agreement with the experimental results.

Despite the apparently different behavior between the two sets of experimental samples, it is believed that the same recovery and recrystallization processes take place. In the fully amorphous sample, recovery of point defects and recrystallization occurs primarily at the buried *a-c* interface region, which TEM indicates (not shown here) to be rather coarse, leading to sharpening of the disordered interface. A similar mechanism occurs in the partially amorphous crystal, where crystalline areas are present over the entire damaged

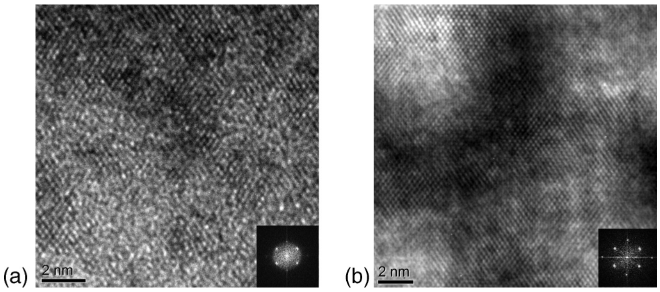

FIG. 4. X-HRTEM micrograph and corresponding FFT of a partially amorphous SiC structure before (a) and after (b) energy deposition via swift heavy ion irradiation.

thickness. Consequently, it is conjectured that discontinuous *a-c* interfaces act as seeds for recrystallization. Owing to the exceptionally good agreement between experiments and simulations, it is very likely that the observed damage recovery induced by swift heavy ions can, in fact, be explained by a thermal spike annealing mechanism.

In conclusion, experimental and molecular dynamics simulation methods demonstrate that room-temperature SHI irradiation induces recovery of preexisting irradiation damage in SiC by a thermal spike phenomenon. Considering that ion-beam-induced epitaxial crystallization (IBIEC), which generally occurs with lower ion energy at temperatures above RT, has been previously reported in semiconductors,[27] insulators,[28] or metal silicides,[29] it is believed that the room-temperature SHI-induced recovery processes (SHIBIEC) reported here may also take place in materials other than SiC. Thus, whether controlled in a laboratory or as a consequence of a radiation environment, SHIBIEC may have beneficial healing effects on damaged structures. Furthermore, it would be interesting to investigate the occurrence of this effect in chalcogenide materials that are used in phase-change data-storage media.[30] Indeed, laser or electrical current pulses are currently preferred to ion irradiation to induce local phase changes because of a lack of understanding of physical mechanisms occurring during ion irradiation; this lack is partially filled in with the results presented in this Rapid Communication.

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