Atomic Modeling of Defects, Defect Generation and Multiple Ion-Solid Interactions

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Abstract. Understanding dynamic processes during ion-implantation requires fundamental knowledge on defect properties, defect generation in atomic collision processes and multiple ion-solid interactions. The defect properties calculated using density functional theory (DFT) in SiC are consistent with multi-axial channeling measurements. Molecular dynamics (MD) methods have been employed to study defect generation and clustering due to ion interactions with SiC and structural evolution. The surviving defects are dominated by C interstitials and vacancies, and the number and size of clusters are very small, in agreement with those observed experimentally. The multiple ion-solid interaction, defect accumulation and disordering on Si and C sublattices are studied by simulating a large number of cascade overlap events. The damage accumulation, relative disordering and volume swelling obtained experimentally and from molecular dynamic simulations are in good agreement. Thus, the present studies provide atomic-level insights into the interpretation of experimentally observed features in SiC.

INTRODUCTION

Ion implantation is an important technique for acceptor and donor doping in semiconductors, particularly in those with a low diffusivity of dopants, such as SiC [1]. This method not only offers the advantage of precise control of dopant concentrations over well-defined depth distributions, but also provides an alternative tool for near-surface modification of the physical and chemical properties of materials. However, the process of ion implantation creates defects, defect clusters and lattice disordering, the level of which depends on the experimental parameters, such as ion fluence and temperature. These atomic-level defects and disordering by ion-solid interactions can lead to microstructure changes, and affect the eventual performance or lifetime of the devices.

A fundamental understanding of defect properties, defect generation and damage accumulation is important in using ion-implantation techniques for device fabrication. Ion-solid interactions encompass elastic collision, defect formation, the nucleation and growth of lattice disordering and damage accumulation, which are associated with multiple physical phenomena. Therefore, understanding these phenomena demands the development of multiscale modeling techniques to study microstructural evolution during ion-implantation and thermal annealing. The present paper is concerned with the recent progresses of atomic-level simulations that relate to the nature of defects, damage production by displacement cascades, defect accumulation and amorphization due to multiple ion-solid interactions in SiC.

SIMULATION METHOD

Density functional theory (DFT) has been used to calculate the formation energy of defects, and to determine the most stable configurations of interstitials. This method is based on the pseudopotential plane-wave method within the framework of the local density approximation, as described in detail elsewhere [2]. The results for vacancies and antisite defects were obtained using a 32-atom supercell, while a 64-atom or 128-atom supercell, depending on configurations, was used to calculate interstitials. These results, together with some physical properties of SiC, were used to fit an empirical many-body interaction potential using a lattice relaxation fitting approach [3]. The potential form employed is based on the Brenner potential formalism [4], which takes into account the chemical environment of the atoms as well as their geometrical relationships with on another. The defect properties calculated using this potential were compared with those given by DFT calculations. Molecular dynamics (MD) methods have been employed to simulate defect production as a function of energy and damage accumulation by cascade overlap. All of the MD simulations were performed using a modified version of the code MOLDY [5], with either constant volume or constant pressure and periodic boundary conditions. The interactions between atoms were described by an optimized form of the repulsive potential for short interatomic separations, as discussed previously [6]. A single cascade was simulated by given a primary recoil atom a kinetic energy equal to the damage energy, and the
subsequent evolution was followed for 10 ps. The cascade overlap events were evolved by creating a second cascade and subsequent cascades with similar procedure, except the atoms and directions were selected randomly.

RESULTS AND DISCUSSION

Defect Properties. DFT calculations have determined the formation energies of native defects in 3C-SiC. Vacancies form on both sublattices. Two types of antisite defects form by atoms located on the wrong sublattice. For interstitial defects, there are ten possible configurations, four tetrahedral and six dumbbell (split) configurations. The most stable configurations for C interstitials are C+C and C-Si split interstitials along the <100> and <110> directions [2]. For Si interstitials, the most stable configuration is the tetrahedral site surrounded by C atoms. The defect formation energies in 3C-SiC are summarized in Table 1. The most stable configurations of interstitials are consistent with multi-axial channeling measurements [8] that indicate C and Si interstitials are well aligned along the <0001> axis in 6H-SiC. Based on these results, an empirical many-body interaction potential for SiC has been developed, and the defect properties in both 3C-SiC [3] and 4H-SiC [7] have been studied by classical MD simulations. The MD results for 3C-SiC are also listed in Table 1 and show good agreement with the DFT calculations, particularly for interstitial defects. Defects in 4H-SiC have similar formation energies to the corresponding defects in 3C-SiC. The number of non-equivalent defect configurations in 4H-SiC is much larger than in 3C-SiC. In 4H-SiC there are four vacancy and four antisite defects, and 40 possible interstitial configurations. However, many compact defects in 4H-SiC have similar structures as the corresponding defects in 3C-SiC. In general, the most stable configurations for C interstitials are C+C and C-Si split interstitials on C and Si sites, respectively, along the <103> and <1110> directions in 4H-SiC [8] that are equivalent directions of <100> and <110> in 3C-SiC [8]. For Si interstitials, the most stable configuration is the tetrahedral site surrounded by C atoms, as predicted by DFT calculations.

Primary Damage. The primary damage state of a typical 50 keV cascade in SiC is shown in Fig. 1, where only interstitial atoms are plotted for clarity. As observed in many MD displacement cascades, there is a rapid build-up in the number of displaced atoms during the collisional phase, and recovery occurs during the subsequent relaxation stage. The Si primary knock-on atom (PKA) travels along the [001] direction a considerable distance before it comes to rest in the lattice and generates multiple branches along its path. The final damage state of the cascade is dominated by interstitials and vacancies rather

<table>
<thead>
<tr>
<th>Defect Type</th>
<th>$E_f$ [eV] (DFT)</th>
<th>$E_f$ [eV] (MD)</th>
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<tr>
<td>$V_C$</td>
<td>5.48</td>
<td>2.76</td>
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<tr>
<td>$V_{Si}$</td>
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<td>$C_{Si}$</td>
<td>1.32</td>
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<td>$Si_C$</td>
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<tr>
<td>$C^{-}-Si&lt;110&gt;$</td>
<td>3.28</td>
<td>3.95</td>
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</table>

Fig. 1. Illustration of a typical 50 keV cascades at the final damage state in 3C-SiC, where dark gray spheres represents Si interstitials and light gray spheres C interstitials.
than antisite defects. The C defects outnumber Si defects. Similar behavior is observed for C PKAs. Higher-energy cascades show that cascades are more linear as opposed to the spherical morphology (vacancy rich core surrounded by interstitial rich region) reported previously in metals [9]. Localized melting in the cascade, which occurs in metals, does not take place in SiC.

Most interstitials produced in SiC are single interstitials, and a few small defect clusters. The largest interstitial cluster in SiC contains only four interstitials [10]. The relative numbers of mono, di- and tri-vacancies produced at various damage energies are shown in Fig. 2. The overwhelming majority (nearly 90%) of the vacancies are produced as single vacancies, and defect clusters containing more than three defects are very rarely seen. The present findings concerning defect clusters are in general agreement with the results of Perlado et al. [11], who found most vacancies produced by Si recoils in SiC, with energies up to 5 keV, are isolated. The formation of dispersed cascades and the very short lifetime of the thermal spike in SiC [10], which prevents the short-range diffusion of atoms during the first few ps after the collisional stage, may reduce the probability of forming large clusters.

However, the concentration of small clusters increases with increasing dose and these clusters are distributed randomly inside the MD block. During continued cascade overlap, the small clusters coalesce and grow to form larger clusters or amorphous domains, which are surrounded by many small clusters, as illustrated in Figs. 3(b). Thus, the amorphization process appears to be consistent with the defect-stimulated cascade-induced growth of small clusters. The coalescence and growth of clusters gives rise to the formation of larger amorphous regions, as seen in Fig. 3(c). A completely amorphous state is reached at a dose of about 0.28 MD-dpa, as shown in Fig. 3(d), where interstitials, vacancies and antisite defects are distributed homogeneously. Such homogeneous-like amorphization is associated with several possible processes during cascade overlap: (a) the production and accumulation of point defects and small clusters that act as amorphous nuclei at low dose; (b) the nucleation of additional small clusters due to local high defect concentration; and (c) the local growth and coalescence of clusters to form amorphous domains. Under these conditions, the primary driving force for irradiation-induced amorphization is the accumulation of both interstitials and antisite defects.

**Damage Accumulation.** MD methods have been employed to study damage accumulation processes in 3C-SiC by randomly overlapping 10 keV Si cascades at 200 K in a simulation cell containing 40,000 atoms until a fully disordered state was achieved after 140 cascades [12]. At the low dose, the dominant defects are single interstitials and mono-vacancies, and some small clusters are nucleated, as shown in in Fig. 3(a). The size of the clusters is very small, similar to those found in a single cascade.

**Fig. 2.** The relative numbers of mono, di- and tri-vacancies produced by a Si recoil as a function of PKA damage energy.

**Fig. 3.** Computer plots showing the process of damage accumulation as a function of dose, the nucleation of small clusters and the coalescence of clusters, where only interstitials and antisite defects are presented. The legend identifies the four possible defect type: C interstitial (C\textsubscript{I}), Si interstitial (Si\textsubscript{I}), C sublattice antisite (Si\textsubscript{C}) and Si sublattice antisite (C\textsubscript{Si}).
Comparison with Experiments. The average relative disorder from the MD simulations exhibits a sigmoidal dependence on dose, as shown in Fig. 4, that is in good agreement with the experimental measurements, also shown, for 6H-SiC irradiated at 190 K with 550 keV Si$^+$ [13]. The interpretation of the MD results is consistent with the direct-impact, defect-stimulated model for amorphization [14], which has been used to fit the data in Fig. 4 based on the average relative cross sections determined previously for single 10 keV Si cascades [13]. The evolution of structural and mechanical properties of materials in high-radiation environment, and in particular irradiation-induced swelling, are important issues in nuclear applications. The volume expansion in the MD simulation as a function of dose is shown in Fig. 5. The swelling increases rapidly with dose and saturates at a value of 8.2%, which is slightly greater than the volume of the MD melt-quenched state relative to the crystalline state.

**CONCLUSIONS**

The present paper summarizes the recent progress in atomic-scale developing fundamental understanding of defects, defect processes and damage accumulation in SiC. DFT calculations have been used to determine the stable native defect configurations in SiC. MD simulations have been used to study both the energy dependence of defect production and the effects of cascade overlap processes. Because of the consistent agreement of the computational results with experimental observations, the simulations are providing atomic-level insights into the interpretation of experimentally observed features.

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**REFERENCES**