Available online at www.sciencedirect.com

ScienceDirect

Acta Materialia 62 (2014) 162–172

Acta MATERIALIA

www.elsevier.com/locate/actamat

Structures and stabilities of small carbon interstitial clusters in cubic silicon carbide

Chao Jiang *, Dane Morgan *, Izabela Szlufarska *

Department of Materials Science and Engineering, University of Wisconsin, Madison, WI 53706, USA

Received 6 June 2013; received in revised form 23 September 2013; accepted 23 September 2013
Available online 18 October 2013

Abstract

Knowledge of the configurations and stabilities of defect clusters in SiC is important for understanding radiation damage in this material, which is relevant to its nuclear and electronic applications. Such information is, however, often difficult to obtain experimentally. In this study, we perform Monte Carlo basin-hopping simulations with both empirical potential and density functional theory (DFT) calculations to search for the ground state (GS) configurations of small carbon interstitial clusters and carbon–antisite-based defects in cubic SiC (3C–SiC). Educated guesses of possible GS configurations have also been made. Our new approach can successfully identify many hitherto unknown GSs and energetically highly competitive metastable structures. For carbon penta- and hexa-interstitials, the GS structures predicted by DFT and empirical potential differ, and the plausible origin of this discrepancy is discussed from the chemical bonding point of view. Surprisingly, the GS structures of large carbon interstitial clusters in SiC are disjointed and composed of di- and tri-interstitial clusters as fundamental building blocks. Based on the present results, a possible mechanism for the carbon tri-interstitial defect to grow into the extended {1 1 1} planar interstitial defects observed in neutron-irradiated 3C–SiC is proposed. Furthermore, we show that C interstitial clusters can get trapped at a carbon antisite and form very stable complexes in SiC.

Keywords: Silicon carbide; Interstitials; Irradiation effect; Monte Carlo simulations; First-principles calculations

1. Introduction

Cubic silicon carbide (3C–SiC) with a zinc-blende crystal structure is a promising structural and cladding material for nuclear fission and fusion reactors due to its excellent mechanical strength, high-temperature stability and low neutron capture cross-section [1,2]. Its hexagonal polytype (4H–SiC) is also a wide-band-gap semiconductor for high-temperature, high-power and high-frequency devices [3,4]. Under thermodynamic equilibrium conditions, the concentrations of point defects in SiC are extremely low due to their high formation energies [5]. However, when exposed to displacive radiation environments (e.g. during neutron irradiation or ion implantation), lattice defects are created in amounts significantly greater than their equilibrium concentrations. If left unchecked, the accumulation of irradiation-induced lattice damage can lead to unwanted microstructural changes such as crystalline-to-amorphous transformation [6,7] and volume swelling [8], as well as degradation of the mechanical [9,10] and electrical [11] properties of SiC. Therefore, to fully exploit the potential of SiC for both nuclear and electronic applications, a fundamental understanding of the production and long-time evolution of radiation damage in this material is crucial.

Radiation damage is an inherently multiscale phenomenon that spans many time and length scales [12–14]. Irradiation by light particles such as electrons creates single Frenkel defects (interstitial–vacancy pairs). In cubic SiC, the average threshold displacement energy (i.e. the minimum kinetic energy necessary to create a stable Frenkel pair) for the C and Si sublattice was calculated to be 19 and 38 eV, respectively [15]. For C atoms, a threshold

* Corresponding authors.
E-mail addresses: cjiang32@wisc.edu (C. Jiang), ddmorgan@wisc.edu (D. Morgan), szlufarska@wisc.edu (I. Szlufarska).

1359-6454/$36.00
http://dx.doi.org/10.1016/j.actamat.2013.09.044

displacement energy of 21.8 eV was experimentally observed in 6H–SiC [16]. In contrast, heavy ions and neutrons produce cascade displacement damage. The primary damage in SiC due to collision cascades has been investigated using molecular dynamics (MD) simulations [17,18] with a modified Tersoff [19] potential. It was found that defects surviving 10 and 50 keV Si displacement cascades in SiC are mostly single point defects, including C and Si Frenkel pairs as well as antisite defects on both Si and C sublattices. For high-energy cascades, multiple subcascades can lead to in-cascade formation of interstitial clusters containing up to four interstitials [18]. Over longer time scales, irradiation-induced point defects and their complexes can migrate and recombine harmlessly with their anti-defects (e.g. vacancy–interstitial recombination [20–22]), annihilate at internal sinks such as grain boundaries [23,24] or aggregate with each other to form larger defect clusters such as interstitial Frank loops and voids. Since such processes are inaccessible to MD simulations due to their intrinsic time-scale limitations (ps to ns), higher-level modeling techniques such as object kinetic Monte Carlo (OKMC) [13,25] and mean field rate theory model [25,26] are needed to extend the simulation time and length scales to the meso-scale regime.

For a predictive multiscale modeling of defect kinetics in irradiated SiC, detailed knowledge of the diffusion, recombination, clustering and dissociation mechanisms of point defects and their complexes is critical. For SiC, explicit consideration of defect clustering is particularly important since point defects are known to have a strong tendency to agglomerate in this material. For example, the binding energy between two C interstitials in SiC is ~5 eV [27–29], which is over sixfold larger than that between two Fe interstitials in body centered cubic (bcc) Fe (0.8 eV [13]). The formation of defect clusters can strongly influence damage evolution in irradiated materials, as has been demonstrated by Ortiz and Caturla [25] using bcc Fe as an example. It was shown that the damage recovery process becomes kinetically hindered when point defects are immobilized into clusters.

In typical OKMC simulations, defect clusters are assumed to be point-like and their detailed atomic configurations are ignored. Consequently, only the most stable (hence thermodynamically most probable) defect configurations are considered. For covalently bonded materials such as SiC, the situation is, however, more complicated since rearrangements of defect structures can be kinetically difficult. It is thus likely that metastable defect configurations can co-exist with the stable ones even at high temperatures, leading to different mechanisms of their migration and reaction.

The purpose of the present study is to systematically investigate the structures and stabilities of small carbon interstitial clusters (I_n, cluster size n up to 6) as well as carbon interstitial clusters centered on an antisite defect ($(C_n)_{Si}$, n up to 4) in cubic SiC using a combination of empirical potential and density functional theory (DFT) modeling techniques. Findings of both ground-state (GS) and energetically competitive metastable defect configurations are presented. Here, we focus on the clustering of C interstitials since C Frenkel pairs are produced in much higher quantities than Si Frenkel pairs during irradiation [17,18] and the C interstitials are highly mobile (migration barriers are 0.74 eV [30], 0.5 eV [22]). The abundance of mobile C interstitials means that clusters of C interstitials are likely to be important defects over a wide range of temperatures and irradiation conditions. Our search unveils new GS structures for carbon penta- and hexa-interstitial clusters as well as tetra-carbon antisite that are previously unknown. Surprisingly, even for small clusters such as carbon di-, tri- and tetra-interstitials, our search identifies many energetically highly competitive metastable structures that were not found in our previous study [29]. These new structures are likely to be observed experimentally because of their large stability. Based on the present results, we propose a possible mechanism for the carbon tri-interstitial defect to grow into the experimentally observed planar interstitial clusters lying on {1 1 1} planes in neutron-irradiated 3C–SiC [31–33]. The interactions between C interstitial clusters and a C antisite have also been investigated in this study.

2. Global optimization strategy

The determination of the GS geometry of a cluster of atoms is a formidable global optimization task due to the enormous number of local minima on the potential energy surface (PES), which tends to grow exponentially with cluster size [34–36]. In the case of defect clusters embedded in a crystal, the situation is even more complicated due to the interplay of electronic and elastic interactions of the defect cluster with the underlying lattice, the interactions of which can be long range in nature. Large supercells are needed to minimize artificial defect–defect interactions due to the periodic boundary conditions, especially for large clusters. Furthermore, in SiC, the energy barriers for transitions between different defect cluster configurations are very high, which can prevent a satisfactory sampling of the PES by MD simulations. From the DFT calculated cohesive energies (see Section 3.3 for computational details) of diamond and cubic SiC divided by the total number of nearest-neighbor bonds (two per atom), we estimate that breaking a C–C and Si–C single bond would cost an energy of 4.4 and 3.6 eV, respectively. This estimate is of course approximate because it ignores any bond-order effects. However, it does illustrate that bond breaking and reconfiguration in SiC is a rare event on the time scales of classical MD simulations.

In our previous study [29], we employed a combination of random structure searching [37–39] and MD simulated annealing [35,40–42] with empirical potential, followed by DFT structural optimizations, to search for the GS defect cluster geometries in SiC. By performing simulated annealing runs starting from many randomly generated defect