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He–vacancy interaction and multiple He trapping in small void of silicon carbide

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ABSTRACT

In fusion environment, large amounts of helium (He) atoms are produced by transmutation along with structural damage in the structural materials, causing material swelling and degrading of physical properties. To understand the microscopic mechanism of He trapping in vacancies and voids, we explored He–vacancy interactions in He_nVa_m (Va for vacancy) clusters (n, m = 1–4) and multiple He trapping in a 7-atom void of silicon carbide (SiC) by first-principles calculations. The binding energy between He and the He_nVa_m clusters increases with the number of vacancies, while the vacancy binding energy gradually increases with the number of He atoms. Furthermore, a small cavity of about 0.55 nm in diameter can accommodate up to 14 He atoms energetically and the corresponding internal pressure is estimated to be 2.5 GPa. The tendency of He trapping in small voids provides an explanation for the experimentally observed He bubble formation at vacancy defects in SiC materials.

1. Introduction

Silicon carbide (SiC) has been considered as a promising candidate for structural materials in future fusion reactor due to its high thermal conductivity, high-temperature stability, chemical inertness, and excellent resistance against irradiation [1–5]. SiC is a brittle material [6], but its fracture toughness can be improved by tailoring the fiber, the matrix and the interphase materials. The application of SiC/SiC composites in fusion power plant has to face a number of challenges such as irradiation stability, hermetic behavior and joining technology [5,7–9]. A widely accepted standard test method in the field of joining the SiC/SiC composites is missing [10]. So far, the performance of the SiC/SiC composite under neutron irradiation is still an open issue. A near-term understanding of the most appropriate application of SiC materials for fusion reactors, given its inherent strengths and limitations, will be carried out as part of international design studies [11].

It is well known that He impurities from neutron transmutation reactions have considerable effects on the properties of structural materials of fusion power reactor [12]. It was also found that point defects and cavity swelling strongly affect the stability of thermal and mechanical properties of SiC and SiC/SiC composites [1]. Zhang et al. [13] have investigated the recovery of lattice damage of SiC crystals that were implanted by 100 keV He ion at 600 K and subsequently annealed at different temperatures by Raman spectrometry and Fourier transform infrared spectrometry. Their results show that the damage induced by high energy He ion implantation in the lattice is closely related to the fluence [14,15]. Meanwhile, first-wall materials are also exposed to high energy neutrons and high fluxes of He escaping from the edge plasma inside reactor vessels [2]. As a consequence, the presence of He (in interstitial sites, point defects, or cavities) accumulates in the irradiated materials and accelerates swelling and creep of the materials [2,16,17]. Therefore, understanding the He behavior inside structural materials is a critical issue and has received certain amount of attention during the last three decades [6,18].

It was found that the population of He in SiC/SiC composite materials increases with increasing He ion energy and temperature by thermal helium desorption spectrometry [19]. Using dual-beam iron irradiation technology [1], potentially significant effects of He on swelling in SiC [20,21] for both the point-defect swelling and the cavity swelling temperature regimes have been investigated. These results indicate that the thermal conductivity decreases with

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increasing quantity of He in irradiated SiC composites due to the fact that helium triggers point-defect swelling [1]. The formation of He bubbles was observed in SiC crystals by irradiation with He ion at high temperature [12]. The size of helium bubbles increased with increasing irradiation temperature.

Despite the previous efforts, our current theoretical understanding on the trapping mechanism of He impurities inside SiC materials is still limited. Previous first-principles studies focused on the calculation of displacement-thresholds, electronic properties, atomic structures, etc. [22–26]. In realistic situations, the size of typical He bubbles is in the order of nm, which is larger than the monovacancies [27]. However, the behaviors of He inside monovacancy and multi-atom cavities (i.e., voids) for SiC materials have never been taken into consideration from a theoretical point of view. Therefore, a fundamental understanding of He behavior in voids of SiC is important for the development of materials for next-generation fusion reactors [28,29].

There are numerous polymorphs of SiC, among which the most stables are the cubic 3C, hexagonal 4H and hexagonal 6H polytypes. From crystallographic point of view, their structures differ only by the stacking sequence along the close-packed planes. In contrast to the hexagonal phases, it is rather difficult to prepare good quality single-crystal cubic phase, which is probably the reason why most of the experimental studies have been performed on the hexagonal polytypes. Recently, Debelle et al. [30] compared the ion-irradiated 3C–SiC and 6H–SiC single crystals, and found that the damage evolution is similar in these two polytypes. Similar conclusions were drawn by Jiang et al. [31] in their gold-ion irradiation experiments. Liu et al. [32] estimated the internal pressure of He bubbles in 6H–SiC materials in He ion implantation experiments. In order to be able to make a direct comparison between the present theoretical predictions and those reported by Liu et al. [32], here we also consider the 6H–SiC polytype as our base structure. Using first-principles calculations, we investigated the behavior of He impurities in vacancies and a small (7-atom) void of 6H–SiC in terms of structure, stability, and binding energy in order to elucidate the complex physical origin of He bubble formation. The tendency of multiple He trapping in a small void provides a valuable basis for further understanding the microscopic mechanism of He bubble formation at vacancy defects in SiC composite materials.

The rest of the paper is divided in two sections. In Section 2, we give a brief overview of the employed theoretical methodology including the computational details. The results are presented and discussed in Section 3.

2. Computational methods

All DFT calculations were performed under periodic boundary conditions, using the plane-wave pseudopotential method implemented in the well-established Vienna *Ab initio* Simulation Package (VASP). Exchange–correlation interactions were described using the generalized gradient approximation (GGA) with the Perdew and Wang (PW91) functional. We used $5 \times 5 \times 1$ supercell of 300 atoms for modeling the 6H–SiC solid. A kinetic energy cutoff of 400 eV was used for the plane-wave basis. A Monkhorst–Pack **k**-point mesh was used in all calculations after careful convergence tests [33]. The calculated equilibrium lattice constants (a = 3.087 Å and c = 15.139 Å) of the 6H–SiC crystal are in good agreement with the experimental data (a = 3.081 Å and c = 15.120 Å) [34]. Based on the equilibrium lattice parameters, all internal atomic positions were fully relaxed at constant cell volume and shape until the force on each atom was less than 0.005 eV/Å.

The formation energy of a He interstitial in the 6H–SiC supercell is defined as

$$E^f(\mathrm{He}_n) = E(\mathrm{He}_n) - E(\mathrm{perfect}) - nE(\mathrm{He}), \quad (1)$$

where E(perfect) is the energy of the perfect 6H–SiC supercell with 300 atoms, $E(\mathrm{He}_n)$ is the energy of the supercell containing n He atoms, and E(He) is the energy of an isolated He atom in vacuum. By definition, a system with positive formation energy means its formation process is endothermic, while negative formation energy means exothermic.

The binding energy between a helium–vacancy cluster ($\mathrm{He}_n\mathrm{Va}_m$) and a vacancy ($E^b(\mathrm{Va}_1)$) is described as

$$E^b(\mathrm{Va}_1) = E(\mathrm{Va}_1) + E(\mathrm{He}_n\mathrm{Va}_m) - E(\mathrm{He}_n\mathrm{Va}_{m+1}) - E(\mathrm{perfect}), \quad (2)$$

where $E(\mathrm{Va}_1)$ is the energy of the supercell with a vacancy; $E(\mathrm{He}_n\mathrm{Va}_m)$ is the energy of the supercell containing a $\mathrm{He}_n\mathrm{Va}_m$ cluster with n He atoms and m vacancies. Here and in the following, Va stands for vacancy.

In the other case, the binding energy between a helium–vacancy cluster ($\mathrm{He}_n\mathrm{Va}_m$) and an interstitial He ($E^b(\mathrm{He}_1)$) is described as

$$E^b(\mathrm{He}_1) = E(\mathrm{He}_1) + E(\mathrm{He}_n\mathrm{Va}_m) - E(\mathrm{He}_{n+1}\mathrm{Va}_m) - E(\mathrm{perfect}), \quad (3)$$

where $E(\mathrm{He}_1)$ is the energy of the supercell with an interstitial tetrahedral He atom; $E(\mathrm{He}_n\mathrm{Va}_m)$ is the energy of the supercell containing a $\mathrm{He}_n\mathrm{Va}_m$ cluster with n He atoms and m vacancies. Positive binding energy denotes attractive interaction, and negative binding energy denotes a repulsive interaction.

To systematically investigate the microscopic mechanism for He trapping in vacancy-type defects, we chose a small void model as shown in Fig. 1. This small void was created by removing four carbon atoms and three silicon atoms in the middle of the 6H–SiC supercell with 300 atoms. In real metals, the size of He bubbles can be as small as ~1 nm in diameter [35,36], which is comparable to the size of the current small void (0.55 nm in diameter). We defined the trapping energy E^{trap} to characterize the energy required for moving a He atom from a remote stable site (R site) into the space of small void. The choice of a stable site will be discussed in detail later.

We placed the He atoms into the 7-atom cavity one by one. For the first He atom (n = 1) and the rest He atoms (n > 1) trapped in the void, the trapping energy was calculated as

$$E^{\mathrm{trap}}(1) = E(\mathrm{Va},\mathrm{He}) - E(\mathrm{Va},\mathrm{He_R}), \quad (4)$$

and

$$E^{\mathrm{trap}}(n) = E(\mathrm{Va},n\mathrm{He}) - E[\mathrm{Va},(n-1)\mathrm{He}] - [E(\mathrm{Va},\mathrm{He_R}) - E(\mathrm{Va})], \quad (5)$$

respectively. Here E(Va, He) is the energy of the supercell with a vacancy and a He atom; $E(\mathrm{Va}, \mathrm{He_R})$ is the energy of the supercell with a vacancy and a He atom at an R site far from the vacancy; E(Va) is the energy of the supercell with a vacancy; E(Va, nHe) is the energy of the supercell with a vacancy and n He atoms. By definition, a negative trapping energy indicates an exothermic process for a He atom moving from a remote R site to the vacancy region.

3. Results and discussion

3.1. Interstitial He in bulk SiC

We first investigate the solution properties of a single He impurity in the possible interstitial positions in 6H–SiC. Fig. 2 shows ten possible interstitial sites in the 6H–SiC host lattice [37]. The 6H–SiC lattice has two nonequivalent tetrahedral (T) sites: $\mathrm{T_{si}}$ has four nearest neighbors (NN) Si atoms and six second NN C atoms, and the reverse holds for $\mathrm{T_c}$. $\mathrm{T'_{si}}$ and $\mathrm{T'_c}$ are different from the previous ones due to second neighbor difference and they are separated by the "E site". There is an empty channel along the c axis, and the center of empty channel is the "R site". The hexagonal interstitial (H) site is the center of the hexagon that is made up