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Site preference and diffusion behaviors of H influenced by the implanted-He in 3C-β SiC

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ABSTRACT

SiC materials are potential plasma facing materials in fusion reactors. In this study, site preference and diffusion behaviors of H in the pure 3C-β SiC and in the He-implanted 3C-β SiC are investigated, on the basis of the first-principles calculations. We find that the most stable sites for H in the pure 3C-β SiC is the anti-bond site of Si—C at the side of C (ABc), while it becomes the bond-center (BC) site of Si—C in the He-implanted 3C-β SiC. Analysis on the electronic structures reveals that such change is attributed to the reduction of hybridization of C—Si bonds induced by the implanted He. Moreover, the presence of He strongly affects the vibration features of the system in the high frequency region, causing a blue shift of 3.10 meV for C—H stretch mode with H at ABc site and a red shift of 20.46 meV for that at BC site, with respect to that in the pure system. In the pure 3C-β SiC, H is diffusive with an energy cost of about 0.50 eV, preferring to rotate around the C atom in a Si—C tetrahedron with an energy barrier of just about 0.10 eV. In contrast, in the He-implanted 3C-β SiC, the energy barrier for H migration goes up to be about 0.95 eV, indicating that the implanted-He blocks the diffusive H to some extent. Our calculations also show that the influence of He on H diffusion works in a short range, just covering the nearest neighbors.

1. Introduction

SiC materials, possessing low induced-activation/low after-heat properties, creep resistance, especially exhibiting remarkable stability in high radiation environments, have been proposed as the prime candidates for plasma-facing materials in future fusion reactors [1–4]. Actually, SiC has recently been applied in the divertor of EAST (Experimental Advanced Superconducting Tokamak) [5,6]. Among various phases, the cubic beta-phase SiC (3C-βSiC) is the preferred material over the hexagonal alpha-phase SiC-based materials, because the latter usually experiences anisotropic swelling under irradiation, causing intergranular cracking eventually [4].

In practical applications, 3C-βSiC-based plasma-facing materials suffer strong bombardment from energetic He and H particles during their serving periods, and the retention and accumulation of He and H cause the structural damage and property degradation of the materials [7–10]. For instance, the transmission electron microscopy showed that significant amounts of helium (He) retained in 3C-βSiC, and the growth of helium clusters induced the swelling of the system to some extent [11]. O'Connell et al. reported that a number of smaller bubbles and the loop-like defects were observed in the H-implanted 3C-βSiC. They proposed the loop-like defects were attributed to the mobile H diffusing from the main damaged region deeper into SiC during the annealing process [12]. The behaviors of Hydrogen isotope in 3C-βSiC were studied by Oya et al., and it was found that the deuterium (D) only bound to C in SiC [13]. Recently, the effect of He pre-irradiation on the H retention in 3C-β SiC was paid attention [14,15]. It was revealed [14] by Raman spectroscopy that He irradiation leads to more structural damage in the host materials as compared to H irradiation, for the former induces an obvious increase in the relative height of the peak associated with the disordered carbon. Moreover, the distribution of the retained H was observed not to be affected by preceding He implantation in 3C-β SiC [14].

On the theoretical side, the retention features of H and He in 3C-βSiC were focused on [16,17]. Gail and Son reported that the most

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stable site for H in the pure 3C-βSiC was the anti-bond site of the C–Si bond, like H–C–Si [18–20]. Eddin et al. studied the insertion and diffusion of He in 3C-βSiC, and found that the most stable site of He in SiC was the tetrahedral interstitial site of four neighbouring Si (Tsi). They predicted the activation energies for migration in and around vacancies (silicon vacancy, carbon vacancy or divacancy) ranging from 0.6 to 1.0 eV [21–23].

In a fusion environment, 3C-βSiC, as the plasma-facing material, subjects to radiation of He and H particles simultaneously, causing co-existence of He and H in 3C-βSiC commonly, where some of H should interact with He nearby and such interaction changes the status of both the retention and the diffusion behaviors of H or He. This is an important issue in a fusion process, for it directly influences on the property degradation and serving lifetime of 3C-βSiC in a fusion reactor. Actually, it has been reported that diffusion barriers of He in the pristine 3C-βSiC are about 1.05 eV and 1.55 eV for the diffusion paths of Tc-Tsi and Tsi-Tc, respectively, while those in H-implanted 3C-βSiC decrease to be 0.26 and 0.68 eV [24], much lower than the related values in the pure system. We suppose that the implanted-He in 3C-βSiC may affect the retention and migration behaviors of H in it. Unfortunately, few theoretical study on diffusion behaviors of H in 3C-βSiC and that influenced by the implanted-He have not been reported to our best knowledge.

In this work, we explore the site preference and diffusion behaviors of H in the pure 3C-β SiC, as well as in the He-implanted 3C-β SiC, on the basis of the density functional theory (DFT) calculations. We find that H favorably locates at the anti-bond site of Si–C (from the side of C) in the pure 3C-β SiC, whereas it prefers to stay at the bond-center site of Si–C in the He-implanted 3C-β SiC. Moreover, the implanted He blocks the migration of H to some extent. In addition, the local vibration features of H influenced by the implanted-He are addressed.

2. Computational method

All calculations are performed by using Vienna ab initio simulation package (VASP 5.3.3) based on the local density approximation [25]. The interaction between ions and valence electrons is described with using projector augmented wave (PAW) potentials [26], and the Perdew-Burke-Ernzerh of GGA expression is employed for the exchange-correlation functional [27]. A 64-atom supercell consisting of $2 \times 2 \times 2$ primitive unit cells is employed, and the kinetic energy cutoff of 500 eV is used for all calculations. In addition, the k–point sampling of $4 \times 4 \times 4$ within the Monkhorst-Pack special k-point scheme in the Brillouin zone is considered [28]. The energy relaxation iterates until the forces acting on all the atoms are less than 10^{-3} eV/Å. With these settings, we obtain the optimal crystallographic parameters of 3C–SiC, c = 4.379 Å, which are in good agreement with the experimental values (4.360 Å) [29]. Since H is a light-mass particle, the zero-point energy (ZPE) of H is taken into account in the calculation [30]. In the present work, the ZPE of H atom is calculated by summing up the normal modes of each H atom $\mathrm{ZPE} = \sum_i h\upsilon_i/2$, where υ_i is the *ith* normal mode frequency.

The climbing image nudged elastic band (CI-NEB) method [31–33] is used to determine the minimum energy paths for diffusion of H atoms in the concerned SiC system.

3. Results and discussions

3.1. Site preference of H in 3C-βSiC and in the He-implanted 3C-βSiC

We begin by exploring the favorite site of H in 3C-βSiC (for convenience, we just call it as SiC in the following). Four typical sites in SiC are considered, and they are the bond-center (BC) site of Si–C, the anti-bond site of Si–C (AB), the tetrahedral interstitial site of four neighboring Si (Tsi), and the tetrahedral interstitial site of four neighboring C(Tc), as shown in Fig. 1. The formation energy of H at a site is defined as

$$E_f = E_s - E_{SiC}^{bulk} - E_H^{atom},$$

where E_S is the total energy of the system containing H, E_{SiC}^{bulk} is the total energy of the related pure SiC, and E_H^{atom} is the energy of a single H atom. Of these concerned sites, anti-bond of Si–C at the side of Si (ABsi) for H is not stable, at which H will move to Tsi spontaneously. Table 1 lists the calculated formation energy of H at the considered sites, in which the ZPE has been taken into account. From Table 1, one can see that the anti-bond site of Si–C at the side of C (ABc) is the energetically favorite site for H in the pure SiC, and the bond-center site of Si–C is also a preference site, at which the formation energy is only 0.06 eV higher than that at ABc site. This is in good consistence with previous reports [34,35]. We then consider the influence of He retention on the site preference of H in SiC. By introducing He into the pure SiC at various sites, we find the favorite site for He in SiC is the interstitial site of Tsi, being in consistent with the literatures [21–23]. For convenience, we denote the He-implanted SiC as SiC + He. Similarly, the four typical sites for H around the implanted He in the pure SiC mentioned above are also taken into account (see Fig. 1), and the calculated formation energies (E_f') are summarized in Table 1. As seen in Table 1, the most stable site for H is not ABc site but the nearest BC site around He, with the formation energy being lower than that at ABc site by about 0.39 eV. Moreover, H at the Tc site is not stable, due to the presence of He around it. The H atom at Tc site moves to ABc site spontaneously. Interestingly, our calculated formation energies of H at the concerned sites of next neighbouring from He are almost the same as those in the pure SiC. This means that the presence of He in SiC can alter the distribution features of H within the scope of the nearest neighboring region, which gets well with the experimental observation that the retained H distributions can be affected slightly by preceding He implantation in 3C-β SiC [14].

We now discuss why the implanted He influences the site preference of H in SiC. By checking the configuration of SiC, we find

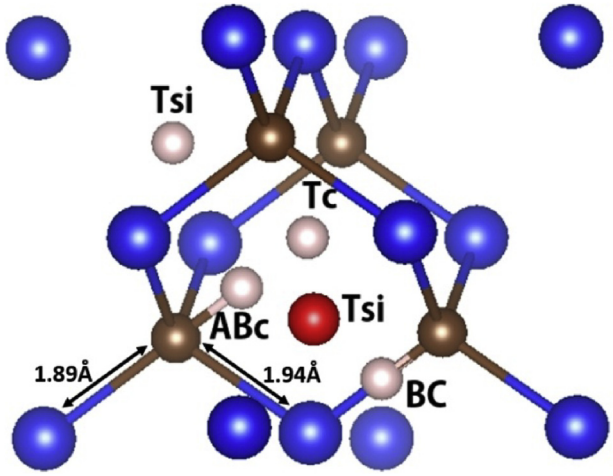

Fig. 1. Local geometric structures for H at the sites of ABc, BC, Tsi and Tc in SiC. Blue, brown, red, pink balls represent Si, C, He, H atoms, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)