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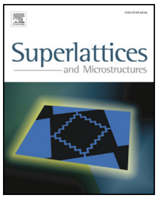

First-principles study of hydrogen retention and diffusion behaviors in 4H-SiC

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ABSTRACT

Here we explicitly present the stability, structure, energetics and diffusion processes of H atom in 4H-SiC with and without intrinsic defects by first-principles calculations. The formation energy and interaction energy of H interstitial at eleven potential interstitial sites are calculated and compared with previous results. Besides, the structure stability of 4H-SiC is evaluated by means of deformation energy. Additionally, the energies of H atom incorporation and solution within the defective 4H-SiC have been calculated and discussed. The minimum energy paths (MEPs) with migration barriers are also calculated for atomic H by interstitial and vacancy-mediated mechanisms. In the defect-free areas of 4H-SiC matrix, interstitial H tends to diffuse three-dimensionally, which is finally trapped into the stable positions of H_{Si}, H_C, or T_{Si} on row A. The migration barriers for vacancy-mediated migration display a rather diverse behavior. On the whole, the energy barrier by V_C-mediated diffusion is slightly smaller than that by V_{Si}-mediated diffusion, excluding the paths of $BC_2' \rightarrow V_C^A$ and $BC_2' \rightarrow V_{Si}^A$ which show a opposite manner.

1. Introduction

Silicon carbide (SiC) is currently intended to be used as structure and confinement material in some nuclear fusion and fission reactor projects due to its minimal activation, good thermal conductivity and thermal stability [1–5]. The key concern for the usage of SiC is that lots of hydrogen (H) isotopes including tritium (T) might be retained in a narrow surface layer of the injection range if a few keV H isotope ions are implanted into SiC. Moreover, the high energetic helium (He) produced by deuterium-tritium (D-T) reaction is thought to interact with the fusion materials and may lead to increase of H isotopes retention, which can degrade the physical and mechanical properties of fusion materials [6]. Therefore, it is important to detailedly elucidate the mechanism of H isotopes trapping and detrapping in SiC solid from the viewpoint of fusion safety and economic concern.

Many efforts have been devoted to understanding the interaction between H isotopes with SiC and their retention in SiC. On the one hand, different types of SiC in terms of radiation induced H isotopes absorption and displacement damage effects have been reported [7–9]. The results indicate that in the practical use of SiC within a fusion reactor blanket, independently of an initial low H isotopes absorption for a particular type of SiC material, the displacement damage produced by neutrons will increase the H isotopes retention in a similar way for any type of SiC. On the other hand, it is found D desorption consists of two states, scilicet the desorption

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of D bound to Si at low temperature and D bound to C at high temperature [10]. The H isotopes exchange behavior, the retention and re-emission behaviors in SiC have been also reported [11,12]. Knowledge for H diffusion and solubility in SiC have been given experimentally [13]. Despite the number of experimental studies on SiC materials in the fusion environment in the past decades, many fundamental issues underlying the interaction between H and SiC remain poorly being understood due to the very complicated nature of such interaction. Indeed, the monovacancies and antisites properties with its thermal stability for 4H-SiC has been investigated experimentally and theoretically [14–16]. The formation of H bubbles in 3C-SiC is previously studied by first-principles molecular cluster model (MCM) [17,18] and supercell model (SCM) [19–21]. It widely demonstrates H prefers to form a stronger bond with C rather than Si. Besides, the mechanism for hydrogen-promoted information of helium polymer in SiC material is studied [6]. However, there is still scope for further investigation the quantities of the location for interstitial H in the lattice, its formation energy and migration energy, the interaction of H impurity with vacancies, which are all essential quantities that must be known before building larger scale models of bubble formation and evolution, including atomic Monte-Carlo, object/event based Monte-Carlo, and rate theory based kinetic approaches (cluster dynamics).

SiC exists as several different polytypes according to the stacking sequence of SiC atomic double layers in the crystal lattice. The most research interests are focused on the following three types: 2H-, 4H-, 6H-SiC, among which 4H-SiC with space group C_{6v}^{4} is used in electronic devices most frequently. Besides, SiC films are grown on Si substrates. While H is always present in Si, hence it is also interest to determine whether H is more stable in SiC or in Si, and if so, by how much and at which site. For these purposes, in present work, we systematically investigate the interaction between H and host atoms in 4H-SiC solid in terms of structures, stabilities, energetics and kinetics to elucidate the complex physical origin of H bubble formation using first-principles calculations. The paper is organized as follows. The rest of the paper is divided in two sections. A brief overview of the employed theoretical methodology is given in Sec. II. In Sec. III, a detailed analysis of our results is presented. Finally, a summary is given in Sec. IV.

2. Computational method

The DFT calculations are performed in the framework of the projector-augmented-wave (PAW) method [22] and the Perdew-Burke-Ernzerhof (PBE) generalized-gradient approximation [23], as implemented in the Vienna *ab initio* simulations package (VASP) [24]. The Si ($3s^2 3p^2$), C ($2s^2 2p^2$) and H ($1s^1$) electrons are treated as valence electrons. The Brillouin zone is sampled with a 3×3×3 *k*-points mesh for the 64-atom supercell, generated by the Monkhorst-Pack method [25]. A plane-wave energy cutoff of 500 eV is used for structure optimization to ensure a good convergence of the total energy. The conventional cell is considered relaxed with a force threshold of 0.01 eV/Å using the conjugate algorithm. During calculation of the total energy of a defected structure, the shape and size of the supercell are fixed while the fractional atomic coordinates are relaxed until the Hellmann-Feynman forces are less than 0.02 eV/Å. In order to calculate the migration energies of H impurities in 4H-SiC, each saddle-point structure and associated minimum energy pathway (MEP) are calculated by employing the image nudged elastic band (CINEB) method [26]. Three images are then linearly interpolated between the initial and end positions per each hydrogen migration pathway to calculate the minimum energy barrier.

3. Results and discussion

3.1. Interstitial atomic hydrogen in bulk 4H-SiC

3.1.1. Geometries and energetics

Due to the stacking sequence of layers of tetrahedra along the *c* axis, there are two different rows in crystal 4H-SiC, namely rows A and B, which possess a greater variety of non-equivalent sites to occupy for the potential impurities. Firstly, two types of CSi_4 and SiC_4 tetrahedra sites are considered due to the different second nearest neighbor (2NN) environment, namely, T_{Si}, T_C, T'_{Si}, and T'_C, as shown in Fig. 1(a) and (d). Secondly, two types of hexagonal interstitials on row A are situated inside the hexagonal Si_3C_3 ring close to Si (H_{Si}) or close to C (H_C) atoms, as depicted in Fig. 1(b). Thirdly, there are two highly symmetric interstitial sites in 4H-SiC. The first one is located at the center between two hexagonal Si_3C_3 rings (H_R), and the second is an interstitial on row B between a trigonal Si_3 and a trigonal C_3 ring (T_R), as indicated in Fig. 1(c) and (d), respectively. In addition, there are three types of bridge sites, BC, BC'_1, and BC'_2, as shown in Fig. 1(a) and (d), respectively.

The formation energy of an interstitial H atom in 4H-SiC is generally given as

$$E^{for}(\mathrm{H}) = E(\mathrm{SiC,\ H}) - E(\mathrm{SiC}) - E(\mathrm{H}), \tag{1}$$

where $E(\mathrm{SiC,\ H})$ is the total energy for the supercell containing a H atom, E(SiC) is the total energy of the original perfect supercell, and $E(\mathrm{H})$ is half the energy of a H_2 molecule in vacuum, calculated as −3.38 eV. With such a scheme, a system with positive formation energy means its formation process is endothermic, while negative one means exothermic.

The corresponding formation energies after relaxation are compiled in Table 1 for a single H atom inserted in each of above eleven potential interstitial sites. As it is highlighted in Table 1, the interstitial H atom preferentially occupies the H_{Si} and BC'_2 sites with the lowest energy of 2.62 eV. H_C, T_{Si}, and T'_{Si}, in that order, follow H_{Si} in possible candidates to form disks or bubbles, which is quite differently from that for interstitial He defects in 4H-SiC [27]. The previous calculations demonstrate He prefers to occupy the H_R site with 2.385 eV in that the H_R possess the biggest space. This is all because the He element is filled-shell electronic configuration which tends to occupy the position with large space or low charge density. However, the H atom only has one electron in its outmost shell which is likely to obtain or share the outmost electron with the neighboring ions. On the other hand, the interstitial H is instability at