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BEAM INTERACTIONS WITH MATERIALS AND ATOMS

Density functional study on helium and hydrogen interstitials in silicon carbide

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ABSTRACT

Silicon carbide with various defects such as carbon or silicon vacancies, anti-sites, and helium or hydrogen interstitials are studied in detail by ab initio calculations. The energy minimized structures of vacancies and helium or hydrogen interstitials are investigated. The calculated electronic spectra explain well some of the important features of silicon carbide observed in experiments. The phonon spectra of silicon carbide with hydrogen interstitials between silicon and carbon bond are calculated, and the frequency of the hydrogen–carbon stretching mode is consistent with experiments.

1. Introduction

Silicon carbide (SiC) is a wide band gap semiconductor with many practical applications, such as wireless temperature sensors [1] and neutron detectors [2–4]. It is also an advanced material candidate to be used in fusion [5–7 and references therein] and fission devices [8]. There are many types of silicon carbides, such as 6H-SiC, 4H-SiC, 2H-SiC, and 3C-SiC, etc. The degradation of SiC in the reactor is partly from helium (He) and hydrogen (H) injections.

He and H injections can cause various defects, including point defects, linear defects, planar defects, volume defects and mixed defects. When the impurity He or H atoms are injected into the SiC, there are many possibilities. First, high energy impurity atom may kick out a silicon (Si) or a carbon (C) atom from its original site to form a local vacancy, and the ejected C or Si atom may further interact with the host to form anti-sites defects. Second, low energy impurity He or H atoms may stay in SiC as the interstitials. In such cases, the impurity atoms are likely to be trapped to the center of the cage when the initial position of the impurity atom are not far from the center of a cage, and more complex defects can be formed when the initial position of the impurity atoms are located between a C–Si bond, depending on chemical properties of the interstitials. Because He atom is inert and H atom is reactive, the impacts of helium or hydrogen interstitials are significantly different. H tends to form bonds with neighboring C atom, and He tends to stay isolated in the cage. Furthermore, di-vacancies may form according to ab initio calculations [9]. Also, extended defects could be formed by thermal annealing [10].

It is well-known that many stable as well as pseudo-stable defects may form in the ion injection processes. After annealing at 623 K, some pseudo-stable defects may disappear [11], and some defects cannot be recovered [10]. It is important to know the pseudo-stable as well as the most stable structures for interstitials. Various defects can be studied experimentally by photoluminescence [12], electric measurement [13], and Raman scattering [14], etc. Theoretically, electronic spectrum has been calculated to study various defects. As far as we know, electronic structures of pure SiC have been studied [15–17], and nitrogen donors in SiC have been discussed [18]. It is found that the minimum band gap of 3C-SiC is 2.39 eV, and the maximum band gap of 2H-SiC is 3.33 eV [19]. The band gap of 6H-SiC is in the middle and can be modified by various defects. There exist other theoretical studies on SiC by molecular dynamic simulations on defects in SiC [20]. Defects can act as donors or acceptors, and their charge states can also be changed [21,22]. In the experiments, there are deep levels around the Fermi level [11,23,24]. There are also some ab initio calculations on vacancies and anti-sites in SiC [9,25].

In this paper, we focus on the ab initio studies of pseudo-stable and the most stable forms of He or H interstitial defects and their impacts on electronic structures. Three most common forms of SiC, i.e., 3C-SiC [26,27], 4H-SiC [12,19], and 6H-SiC [1,28] are studied by MedeA-VASP [29–33]. The band structures as well as the density of states (DOS) of various defects in 6H-SiC are compared. The optical spectra of four typical stable 6H-SiC with helium (He)

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and hydrogen (H) interstitials are studied in details by MedeA-VASP and OPTIC programs [34]. The highest phonon frequency of the most stable form of H interstitials is also calculated by MedeA [33]. The calculated spectra are consistent with experimental measurements [35].

2. Computational approach

The calculations are carried out using density functional theory (DFT). Geometrical optimization, band structures and density of states, as well as phonon calculations are carried out in the framework of the Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation (GGA) of the density functional method [36,37]. The default cut off energy is chosen to be 520 eV, and the default k-mesh is chosen to be $13 \times 13 \times 5$.

Because the VASP optic program only supports LDA [34,38], the optimized structures using GGA are optimized again using LDA in our calculations. Then single point energies and the optic matrix elements are obtained in the new structures. In all optical spectrum calculations, we used the dense k-points of $25 \times 25 \times 5$ to get more accurate results.

In our calculations, the unit cell of the perfect SiC contains 24 Si and 24 C atoms. When defects are considered, one defect is introduced in this unit cell. For example, one Si or C atom can be removed to form a vacancy, or one Si (C) atom can be replaced by one C (Si) atom to form an anti-site. Also, one H or He atom can be added to form an interstitial. Because only one defect is included in the unit cell with 48 atoms in these calculations, the defect ratio is about 2%. For the same reason, the atomic percent of H or He as interstitials in all of our calculations is also about 2%.The defect formation energy of V_C is defined as [39]:

$$E_f(V_C) = E(\mathrm{Si_{24}C_{23}}) + E(\mathrm{C_{gas}}) - E(\mathrm{Si_{24}C_{24}}) - [E(\mathrm{SiC}) - E(\mathrm{Si_{gas}}) - E(\mathrm{C_{gas}})] + (E^A_{coh}(\mathrm{C}) - E^A_{coh}(\mathrm{Si}))/2$$

where $E(\mathrm{Si_{24}C_{23}}), E(\mathrm{Si_{24}C_{24}}), E(\mathrm{SiC}), E(\mathrm{Si_{gas}}), E(\mathrm{C_{gas}})$ are calculated with VASP, and the last term of the above equation is set to 1.37 eV [39], which is half the difference of the Si and C experimental cohesive energy. The other defect formation equations are similar to the above equation.

The phonons are calculated by MedeA [33]. In phonon calculations, in addition to the default setting mentioned above, the interaction range between atoms is chosen to be 1 nm and the displacements of atoms are chosen to be ±0.002 nm. An atomic frozen technique is employed in our phonon calculations. Such atomic frozen technique has been tested in the study of highly localized phonon modes of oxygen molecule in CdTe system [40] and proved to be effective. In this paper only H and its nearest neighbor C were allowed to vibrate in phonon calculation.

3. Results and discussion

3.1. Perfect silicon carbide

The unit cell of 6H-SiC ($\mathrm{Si_{24}C_{24}}$) is shown in Fig. 1a. The symmetry of $\mathrm{Si_{24}C_{24}}$ is P-3m1. The optimized lattice constants and other important calculated results are listed in Table 1. The calculated free energy is −361.55526 eV for the 6H-SiC structure, −361.55368 eV for corresponding 4H-SiC structure, and −361.54250 eV for the corresponding 3C-SiC structure. Because these calculated VASP free energies are very close, these calculated results explain well why silicon carbide forms many stable and long-range ordered modifications, the so-called polytypes [41]. However, although the free energies are close, the band gaps of various structures vary in a wide range from 2.39 to 3.33 eV [19]. Since 6H-SiC structure is one of the most common polytypes of appropriate band gap [1,41], the electronic structures of the perfect 6H-SiC and defects in the 6H-SiC are investigated. The band structure and density of states of 6H-SiC are shown in Fig. 1b. The calculated band gap is 2.03 eV, that is lower than the experimental band gap of around 3 eV [1,19,42]. As is well known, even though the density functional theory underestimates the band gap [43,38], the relative band gaps of different structures are still accurate in VASP, and the underestimated part can be adjusted by incorporating a self energy correction [43,38]. In our calculations, a self energy correction of about 1 eV is included. With this correction, the calculated band gaps of both 6H-SiC and 4H-SiC are very close to the experimental band gaps [1,19,42].

3.2. Vacancies and anti-sites in silicon carbide

Carbon vacancy (V_C): A carbon atom closest to the center of the unit cell in Fig. 1a is removed to form a carbon vacancy (V_C). The defect formation energy of the optimized structure with V_C is very high, up to 7.04 eV as shown in Table 1. The ionization potential of C is only 11.26 eV [44]. This indicates that the binding of C atom in SiC is very strong that explains why melting point of SiC is high. The corresponding band structure is shown in Fig. 2a. By adding 1.0 eV of self energy correction, our calculated band gaps of 6H-SiC with and without V_C are 3.30 eV and 3.03 eV, respectively. This suggests defect can significantly modify the perfect 6H-SiC band gap by about 0.27 eV. It seems that the band gap of V_C in 6H-SiC (3.30 eV) can comparable with the top experimental band gap of the pure 2H-SiC (3.33 eV) [19,45,46]. Carbon vacancy produces two shallow donor levels near the conduction band and one deep level in the gap. The V_C acts like a hole. Fermi level is close to the conduction band. This is consistent with the calculations by Li [22].

Silicon vacancy (V_{Si}): A silicon atom closest to the center of the unit cell in Fig. 1a is removed to form a silicon vacancy (V_{Si}). The calculated band structure is shown in Fig. 2b. As shown in Fig. 2b, there are also three impurity bands: two above and one below the Fermi level. The band gap of SiC with V_{Si} is less than that with V_C. The Si vacancy is almost neutral. The Fermi level is almost in the middle of the band gap. The atom locations do not change much after relaxation. From Table 1, we can see that both types of vacancies, V_C and V_{Si}, raise the band gap, and both types of vacancies produce three impurity levels. The formation energies of both are very high, and the impurity levels are from dangling bonds near the vacancy.

Anti-site ($\mathrm{Si_C}$): A carbon atom closest to the center of the unit cell in Fig. 1a is replaced by a silicon atom to form an anti-site ($\mathrm{Si_C}$). The band structure is shown in Fig. 2c. There is one shallow band above Fermi level and there are two bands below Fermi level.

Anti-site ($\mathrm{C_{Si}}$): A silicon atom closest to the center of the unit cell in Fig. 1a is replaced by a carbon atom to form an anti-site ($\mathrm{C_{Si}}$). The band structures are shown in Fig. 2d. There are two impurity bands. There does not appear to be any impurity bands near Fermi level for this type of anti-site.

From above results, we can see that the formation energies of both vacancies are high, that is consistent with the results of others that the displacement of an atom from its lattice site requires very high energy [4]. Both types of anti-sites reduce the band gap. The anti-site $\mathrm{C_{Si}}$ is much more stable than vacancies. That is because the formation of tetrahedral bonds is energetically favorable for both C and Si atoms. Since C is more electronically negative than Si, and the bonding of C–C is relatively stronger than the bonding of C–Si, the formation energy of $\mathrm{C_{Si}}$ is much less than $\mathrm{Si_C}$ and the two vacancies. This explains why the stability of $\mathrm{C_{Si}}$ in SiC after annealing is found in electron paramagnetic resonance experiment [17].