



First principles calculations for iodine atom diffusion in SiC with point defects



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ABSTRACT

The formation energies, diffusion barriers, vibration frequencies of complex iodine defects in 3C-SiC are calculated. The effective diffusion rates of these complex defects are evaluated in the temperature range from 300 K to 2000 K. The iodine interstitial diffusion is the dominant diffusion mechanism in bulk SiC since its diffusion energy barriers is the lowest. On the contrary, if the iodine atom substitutes a Si or a C atom, the diffusion rate is the lowest. The diffusion rates of other iodine point defects coupled with vacancies are between the rates of these two cases. The vacancies near the iodine atoms are traps for the iodine and they can slow down the diffusion rate of iodine atoms. The experimental diffusion rate of iodine in SiC is between that of calculated interstitial and substitutional iodine. It may result that the experimental data is from the combination of all the point defect diffusion mechanisms.

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1. Introduction

Silicon carbide (SiC) is widely used in industry as ceramic brake disc [1], light emitting diodes (LEDs) [2,3], and semiconductor electronics devices that operate at high temperatures or high voltages [4,5]. Silicon carbide composite material is a promising candidate for replacement of Zircaloy cladding in light water reactors because of its high chemical and thermal stability and its low neutron absorption cross section [6–10]. The fuel cladding material in nuclear reactor is an important safety barrier which is used to prevent the radioactive fuel products from releasing to the cooling water [11]. How radioactive fuel products release from the cladding materials is of great interests to engineers and researchers to develop high quality cladding materials [12].

One of the important fission products which is harmful to human and causes damages to the reactors is radioactive iodine. For example, iodine isotopes ¹²⁹I ($T_{1/2} = 15.7 \times 10^6$ years) and ¹³¹I ($T_{1/2} = 8$ days) in the thyroid gland is harmful to human body [13]. In light water reactors, iodine induced stress corrosion cracking (ISCC) occurs on the inner side of the Zr fuel cladding [14–16].

Experimental research works have been carried out to study the iodine inside cladding materials. For example, ion implantation are used to generate iodine doped samples of cladding materials, and following high temperature annealing are used to activate the diffusion process, then, Rutherford backscattering spectrometry (RBS) are used to detect the concentration and analyze the diffusion parameters for the iodine diffusion in Zr [17] and SiC [13,18,19]. Specifically, Friedland and his co-authors systematically studied the iodine diffusion in single crystal and poly-crystal SiC by experimental methods [13,19,20], which can be used as references for our calculations.

Computational simulations are also used to study the iodine inside cladding materials [21–23]. They provide insights for material design and overcome the limitation of the experimental research. For example, irradiation facility, detection limitation, and expensive cost are obstacles for experimental research. Diffusion of Cs, Ag, and B in silicon carbide has been studied by Morgan et al. [24–26]. Interstitial iodine diffusion in a stoichiometric SiC sample is calculated and compared with the diffusion of iodine interstitial in Zr by first principles calculation and nudged elastic band methods [27]. Since neutron irradiation will generate high concentration point defects in the cladding material, defect effects on iodine diffusion should be considered [28,29]. As Friedland et al. claimed, iodine transport is influenced by lattice defects in SiC. As a result, point defect effect on iodine diffusion is interesting and it is studied in our work.

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In this paper, first-principles calculations and nudged elastic band method are used to study the formation energies, migration energy barriers, and attempt-to-diffuse rates of various iodine defects in bulk 3C-SiC material. The interstitial diffusion is the dominant bulk diffusion mechanism since its diffusion energy barriers is the lowest. On the contrary, if the iodine atom substitutes a Si or a C atom, the diffusion rate is the lowest one. The diffusion rates of other complex iodine coupled point defects are between these two cases.

2. Calculation methods

2.1. Density functional theory calculations

The ground state energies of the systems are evaluated through density functional theory (DFT) calculations [21,30] by Vienna *ab initio* Simulation Package (VASP) code [7,31,32]. Projected augmented wave (PAW) method [33,34] is used to deal with the wave functions near the core region of atoms and the exchange correlation within the generalized gradient approximation (GGA) parameterized by Perdew, Burke, and Enzerof (PBE) [35,36] is used in the calculations. The cutoff of the plane-wave kinetic energy is 400 eV. The summations over the Brillouin zone are performed with a $2 \times 2 \times 2$ Monkhorst-Pack k -point mesh and spin polarization is used in all calculations. The residual minimization method with direct inversion in the iterative subspace (RMM-DIIS) [37,38] is used in the electronic relaxation with an energy convergence criterion of 10^{-4} eV. Conjugate gradient method is used to minimize the Hellmann-Feynman forces in the ionic relaxations and the force stopping criterion is 0.05 eV/Å. A $2 \times 2 \times 2$ 3C-SiC supercell with 64 atoms is used in the calculations. Various defects may be generated in the super cell to study the iodine diffusion properties in SiC.

2.2. Formation energy of a point defect

Since point defect may affect the diffusion of iodine atom in bulk SiC, various point defects are generated in the SiC super cell. The formation energy (F) of certain point defect in a SiC super cell is defined as the following equation [39],

$$F = E^f - E_{\text{pure}} + \sum dn_s E_s = E^f - E_{\text{pure}} + dn_C E_C + dn_{\text{Si}} E_{\text{Si}} - E_I \quad (1)$$

Here, F represents the formation energy of certain point defect; E^f represents the energy of a structure which contains certain defect; E_{pure} is the system energy of the SiC super cell without any defect; E_s represents for the energy of certain single atom or the cohesive energy of certain bulk material, for example, E_I is the energy of a single I atom in gas phase computed in the same super-cell box as SiC. E_C and E_{Si} are the cohesive energies per atom of bulk diamond and Si; dn_s is the corresponding atom number difference for species s inside the super cell.

In order to verify the accuracy of our calculations, formation energies of six types of intrinsic defects in bulk SiC are calculated

Table 1
Formation energy (eV) of six intrinsic defects in bulk SiC calculated with Eq. 1. The formation energies are compared with the data in Ref. [39,40].

| Defects | Formation energy (eV) | Ref. [39] | Ref. [40] |
|----------------------|-----------------------|-----------|-----------|
| ν_C | 4.67 | 4.41 | 3.73 |
| ν_{Si} | 7.73 | 7.41 | 8.33 |
| C_{Si} | 3.46 | 3.59 | |
| Si_C | 4.18 | 4.01 | |
| $S_{\text{Si}(110)}$ | 8.69 | 8.97 | 8.56 |
| $S_{C(100)}$ | 6.47 | 6.73 | 6.71 |

and listed in Table 1. These defects are carbon vacancy (ν_C), Si vacancy (ν_{Si}), Carbon anti-site defect (C_{Si}), Si anti-site defect (Si_C), Si split self interstitial along $\langle 110 \rangle$ direction ($S_{\text{Si}(110)}$), and carbon split interstitial along $\langle 100 \rangle$ direction ($S_{C(100)}$). Anti-site C_{Si} means a carbon atom is on a Si sub-lattice and Si_C means a Si atom is on a carbon sub-lattice. Self split interstitial means an intrinsic interstitial atom shares the lattice site with the original site atom. Compared with Ref. [39,40], our calculation data is reasonably accurate. The point defect formation energies are calculated in both a $2 \times 2 \times 2$ box with 64 atoms and a $3 \times 3 \times 3$ box with 216 atoms. Most of the formation energy differences are lower than 0.6 eV. Balancing the computing time, the super cell with 64 atoms are used in our calculations.

2.3. Diffusion energy barrier and attempt-to-diffuse frequency calculations

Climb image nudged elastic band (CI-NEB) method [41–43] is used to calculate the diffusion energy barriers and search the minimal energy paths and the saddle points of an iodine diffusion inside SiC. The transition state tool–VTST code [44] coupled with VASP package are employed to perform the NEB calculations. There are 4 images in the cases of single barrier calculations or 9 images for the more complex movements between the initial and the final configurations for the NEB calculations. For the iodine diffusion via I_{SiC} , increasing the number of images from 4 to 9 results in the barrier energy change less than 0.1 meV. The fictitious spring constant is 5.0 eV/Å² and the force convergence criteria is 0.05 eV/Å. The volume is fixed in NEB calculation since the volume change can be ignored during diffusion process.

The frequency of diffusion follows the Arrhenius law [45],

$$\Gamma = \Gamma_0 \exp\left(-\frac{\Delta E}{k_B T}\right), \quad (2)$$

where ΔE represents the diffusion energy barrier and Γ_0 is the attempt-to-diffuse frequency. Considering the transition state theory (TST) [46,47] and the classical harmonic approximation, the frequency of a diffusion event is $\Gamma_0 = n\nu$, where n is the number of equivalent diffusion paths and ν is,

$$\nu = \frac{\prod_{i=1}^{3N} \nu_i}{\prod_{i=1}^{3N-1} \nu'_i}, \quad (3)$$

ν_i and ν'_i represent the normal vibration models of initial state and transition state. There are $3N - 1$ normal vibration models of transition state because one of the frequencies is imaginary.

2.4. Effective diffusion coefficient

In order to compare the diffusion rates among different diffusion mechanisms via various point defects, effective diffusion coefficients of iodine in SiC via different diffusion mechanisms are calculated. The concentrations of point defects are used to tune the diffusion coefficient in the effective diffusion coefficient and it can be written as [39,48],

$$D_i^{\text{eff}} = D_i^{\text{int}} \frac{C_i}{\sum C_i} \quad (4)$$

The D_i^{eff} and D_i^{int} in Eq. (4) represent the effective and intrinsic diffusivity of certain diffusion mechanism via specified defect. The diffusion coefficient follows the Arrhenius law,

$$D = D_0 \exp\left(-\frac{\Delta E}{k_B T}\right) \quad (5)$$

the diffusivity D_0 obey the equation [39],

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