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Empirical potential approach for defect properties in 3C-SiC

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Abstract

Defect energetics in silicon carbide (SiC) have been widely studied using Tersoff potentials, but these potentials do not provide a good description of interstitial properties. In the present work, an empirical many-body interatomic potential is developed by fitting to various equilibrium properties and stable defect configurations in bulk SiC, using a lattice relaxation fitting approach. This parameterized potential has been used to calculate defect formation energies and to determine the most stable configurations for interstitials using the molecular dynamics method. Although the formation energies of vacancies are smaller than those obtained by ab initio calculations, the properties of antisite defects and interstitials are in good agreement with the results calculated by ab initio methods. It is found that the most favorable configurations for C interstitials are $\langle 100 \rangle$ and $\langle 110 \rangle$ dumbbells on both Si and C sites, with formation energies from 3.04 to 3.95 eV. The most favorable Si interstitial is the tetrahedral interstitial site, surrounded by four C atoms, with a formation energy of 3.97 eV. The present results will be discussed and compared to those obtained by others using various empirical potentials in SiC. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Empirical potential; Defect properties; Silicon carbide; Computer simulation

1. Introduction

The high mechanical strength, good thermal conductivity and low activation of silicon carbide (SiC) provide a number of potential applications in advanced electronic devices and high neutron radiation environments [1]. In the processing of SiC for electronic devices, ion implantation is considered to be the best means to introduce dopants in a controlled manner, but the implantation processes introduces structural damage and defects. The defects created by energetic displacement cascades during ion implantation or neutron irradiation and their subsequent evolution give rise to important microstructural changes that affect many of the macroscopic properties of electronic devices and nuclear components. Therefore, the study of defect formation and properties is of scientific as well as technological interest, which is crucial for understanding the response of SiC to self-diffusion, diffusion of substitutional impurities, radiation damage and ion implantation.

In our previous papers [2,3], an ab initio method has been employed to calculate defect properties in SiC, and the results were compared with those calculated by molecular dynamics (MD) using Tersoff potentials [4]. Although there is a good agreement in the formation of vacancies and antisite defects, a large disparity appears in the formation of self-interstitials. Ab initio calculations show

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that the most favorable configurations for C interstitials are $\langle 100 \rangle$ and $\langle 110 \rangle$ dumbbells centered at both C and Si sites, with formation energies from 3.16 to 3.39 eV. Ab initio calculations can provide a set of accurate defect formation energies, but require large computational efforts compared to the large-scale computer simulations normally applied to ion-solid interactions. In addition, a preliminary study of defect diffusion [5] suggests that the original Tersoff potentials give a very high interstitial migration energy, in contrast to experimental results. Swelling experiments [6] show that interstitials loops are formed even at room temperature, which indicate that at least one type of interstitial is mobile at room temperature. The nature of the potential will have significant influence on the mobility of defects and their clusters. Therefore, the development of more accurate potentials that match to ab initio calculations would provide for more accurate MD simulations of defect migration and cascade annealing processes.

In present paper, an empirical many-body interatomic potential is developed by fitting to various equilibrium properties and stable defect configurations in bulk SiC, using a lattice relaxation fitting approach. The point defect properties in 3C-SiC have been calculated by MD methods, and the results are compared with those calculated using ab initio calculations and with those obtained by others.

2. Construction of potential

The potential used in this paper is based on the Brenner potential formalism [7]. The Brenner potential form is essentially the same as that of the Tersoff potential [8], and it takes into account the chemical environment of the atoms as well as their geometrical relationships with one another. Some important aspects, such as bond conjugation and bond order, are treated by considering the inclusion of specially fitted bond order correction terms. The Brenner potential has been successfully applied to many important problems in chemistry and surface physics involving C–H systems [9] and C–Si–H systems [10]. The potential form is described in greater detail elsewhere [7], so only the relevant features are summarized here.

The potential energy, E, is given as a sum over individual bonds according to the following expression:

$$E = \sum_i \sum_{j(>i)} f_{ij}(r_{ij}) \left[V^{\mathrm{R}}(r_{ij}) - \overline{B}_{ij} V^{\mathrm{A}}(r_{ij}) \right], \tag{1}$$

The repulsive, V^{R}, and attractive, V^{A}, pair energies are given by the following Morse-type formulation:

$$V^{\mathrm{R}} = [D^e/(S-1)] \exp\left[-\beta\sqrt{2S}(r - R^{\mathrm{e}}) \right] \tag{2}$$

and

$$V^{\mathrm{A}} = [D^{\mathrm{e}} S/(S-1)] \exp\left[-\beta\sqrt{2/S}(r - R^{\mathrm{e}}) \right], \tag{3}$$

where D^{e} and R^{e} are the dimer bond energy and distances, and β and S are adjustable parameters. The cut-off function, $f_{\mathrm{ij}}(r_{\mathrm{ij}})$, is used to restrict the pair interaction to nearest neighbors and is defined as:

$$f(r) = \begin{cases} 1, & r \leqslant R^1, \\ 0.5\left\{1 + \cos\left[\frac{\pi(r-R^1)}{R^2-R^1}\right]\right\} & R^1 < r \leqslant R^2, \\ 0, & r > R^2, \end{cases} \tag{4}$$

where R^1 and R^2 are adjustable parameters. It should be pointed out that the second derivative of the cut-off function is discontinuous, and thus, the low-order algorithms should be used in the dynamical simulations. The many-body interaction, which is adopted from Brenner, is formulated as:

$$\overline{B}_{ij} = 0.5[B_{ij}^{-\delta_i} + B_{ji}^{-\delta_j}]$$

$$B_{ij} = 1 + \sum_{k \neq i,j} f_{ik}(r_{ik}) g_i(\theta_{ijk}), \tag{5}$$

where the angular function $g(\theta)$ is given by

$$g(\theta) = \alpha\left\{ 1 + c^2/d^2 - c^2 \Big/ \left[d^2 + (1+\cos\theta)^2 \right] \right\}. \tag{6}$$

The values for the various parameters in Eqs. (1)–(6) were chosen by fitting to a number of properties of crystalline silicon carbide and some

interstitial properties in SiC. The physical properties include the cohesive energy, lattice constant and bulk modulus. For the C–C and Si–Si interactions, the potential derived by Dyson and Smith [11] is used, where the parameters were fitted to bulk elastic constants, lattice constants, equilibrium diatomic bond energy and phonon mode frequencies. It was also fitted to reproduce several highly coordinated polytypes of bulk carbon and silicon. Instead of fitting to the equilibrium diatomic bond energy, D^e and R^e for the C–C and Si–Si interactions are selected to give correct order of the formation energies of several interstitial configurations obtained previously by ab initio calculations [2,3]. Four configurations of C interstitials used here are C^+–C⟨1 0 0⟩, C^+–Si⟨1 0 0⟩, C^+–C⟨1 1 0⟩ and C^+–Si⟨1 1 0⟩ dumbbells, with formation energies of 3.16, 3.59, 3.32 and 3.28 eV, respectively.

The physical properties of crystalline SiC were fitted first. The potential parameters were then used to calculate the formation energies of interstitials using a static relaxation method and D^e and R^e were adjusted to converge the formation energies to those obtained by ab initio calculations. The entire process proceeded in iterative steps, with each change in D^e and R^e requiring a refit of all the other parameters of the C–Si interaction. The cut-off distances were chosen to be as large as possible, while still excluding the second shell of neighbors in 3C-SiC structure. Another important consideration when selecting cut-off distances was that the C dumbbells form more stable configurations than C tetrahedral interstitials. The model parameters fitted in this way for SiC are listed in Table 1.

Table 1
Full parameter set is shown for three types of interactions of SiC

Parameter	C	Si	Si–C
R^e (Å)	1.515	2.197	1.7631
D^e (eV)	4.265	2.887	4.682
β (Å^{-1})	1.50	1.469	1.728
S	1.44	1.32	1.541
δ	0.80469	0.78	–
R^1 (Å)	2.2	2.2	2.2
R^2 (Å)	2.5	2.5	2.5
α	0.011304	0.013318	–
c	19	14	–
d	2.5	2.1	–

3. Results and discussion

In this paper, the parameterized potentials are used to determine the energetics and nature of defect formation in 3C-SiC. It is known that there are two types of vacancies, namely the C and Si vacancies, and two types of antisite defects. These defects are shown in Fig. 1(a), where Si_C represents a silicon atom on a carbon site and C_{Si} a carbon atom on a silicon site. For self-interstitial defects, there are ten possible structures, two carbon and two silicon tetrahedral interstitials, depending on

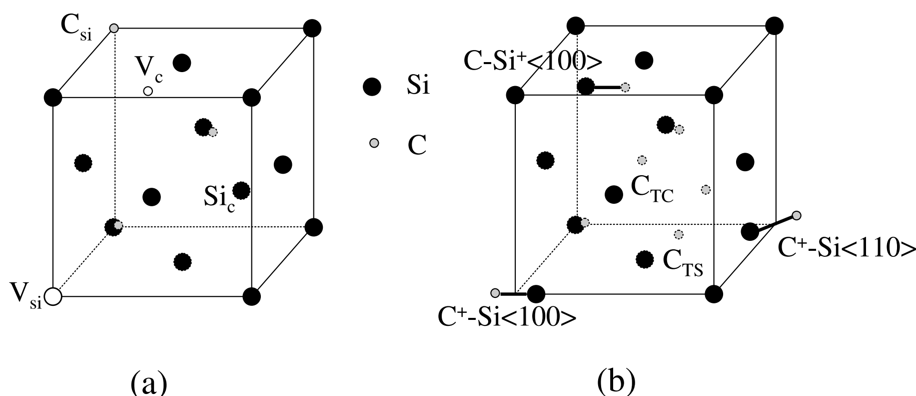

Fig. 1. Schematic illustration of (a) vacancies and antisite defects and (b) the possible interstitials that may exist in 3C-SiC, where the symbol (+) indicates the interstitial atom.

the arrangement of neighbor atoms, and four possible ⟨1 0 0⟩ dumbbell configurations centered on Si sites or C sites. Besides these tetrahedral and ⟨1 0 0⟩ dumbbell configurations, it is also possible to have two ⟨1 1 0⟩ dumbbell configurations. The representative configurations of self-interstitials are indicated in Fig. 1(b). The formation energies for the various defects are defined as follows [2]:

$$E_f^v = \Delta E^v(X) + \varepsilon \tag{7}$$

for a vacancy;

$$E_f^a(X_Y) = \Delta E^a(X_Y) \tag{8}$$

for an antisite defect; and

$$E_f^i(X) = \Delta E^i(X) - \varepsilon \tag{9}$$

for an interstitial, where X and Y represent the C or Si species, and ε is the negative cohesive energy in a perfect crystal of 3C-SiC in the ground state. ΔE denotes the total energy difference between the crystal containing a defect and the perfect crystal with the same number of lattice sites.

The properties of various defects in 3C-SiC are studied using MD simulations in a cubic box of 1000 unit cells consisting of 8000 atoms with periodic boundary conditions and constant pressure relaxations at a temperature of 0 K. The formation energies of interstitials, antisite defects and vacancies are listed in Table 2, together with those obtained previously by ab initio calculations. For the interstitial defects, there is a good agreement between ab initio calculations and the present results, particularly for the C interstitials. It is of interest to note that both methods give a lower formation energy for C interstitials than Si interstitials, and the most stable configuration is the C^+–C⟨1 0 0⟩ dumbbell (The symbol '+' indicates the interstitial atom), with formation energy of 3.16 and 3.04 eV for ab initio and MD calculation, respectively. Both models predict that the most favorable configurations for C interstitials are ⟨1 0 0⟩ and ⟨1 1 0⟩ dumbbells, rather than tetrahedral interstitials. Any configuration of the C interstitials that are in tetrahedral positions appears energetically unfavorable and may be unstable with respective to conversion back to the ⟨1 0 0⟩ or ⟨1 1 0⟩ dumbbells of C interstitials at higher temperatures. Although the formation energy of Si interstitials is lower than that calculated by ab initio methods, the relative stability of the Si interstitials is very similar to ab initio calculations. The results indicate that the Si tetrahedral surrounded by four C atoms is the most favorable Si interstitial. The present results suggest generally higher formation energies for Si interstitials, with the most unfavorable configurations being Si^+–C⟨1 0 0⟩ and Si_{TS} interstitials, which is consistent with ab initio results. This is expected because of the size difference between Si and C atoms.

Table 2
The formation energies of interstitials, antisite defects and vacancies in 3C-SiC, together with those calculated by ab initio method [2,3]

Defects	Formation energy (eV)	
	Ab initio	Present work
C^+–C⟨1 0 0⟩	3.16	3.04
C^+–Si⟨1 0 0⟩	3.59	3.43
C^+–C⟨1 1 0⟩	3.32	3.30
C^+–Si⟨1 1 0⟩	3.28	3.95
Si^+–C⟨1 0 0⟩	10.05	7.54
Si^+–Si⟨1 0 0⟩	9.32	5.53
C_{TC}	6.41	4.65
C_{TS}	5.84	4.32
Si_{TC}	6.17	3.97
Si_{TS}	8.71	6.77
Csi	1.32	1.69
Si_C	7.20	7.79
V_C	5.48	2.76
Vsi	6.64	3.30

For the antisite defects, Si_C and C_{Si}, the formation energies of 7.79 and 1.69 eV are in reasonable agreement with those calculated by ab initio methods. The larger value given by both the MD and ab initio calculations for the Si_C antisite defect has a simple physical interpretation in that a small C atom is replaced by a large Si atom. This may suggest that the defect properties in SiC are strongly influenced by the relative sizes of the atomic species. Nevertheless, the large energy increase in forming an antisite defect pair, predicted by both ab initio DFT calculations and MD simulations, implies that the 3C-SiC structure may be thermally stable against the formation of highly disordered structures.

In the case of vacancies, the present calculations with the new potential give lower formation

energies than those determined by ab initio methods, but both models predict that the formation energy of the C vacancy is lower than that of the Si vacancy. Using the Tersoff potential, it was previously shown that, despite a large disparity in the formation energies for interstitials [3], the formation energies for C and Si vacancies are 5.15 and 6.31, respectively, which are in good agreement with those determined by the ab initio method. These results suggest that the Tersoff potentials may be more reasonable to describe vacancy properties in 3C-SiC than the potential derived for interstitials.

4. Summary

In this paper, an empirical many-body interatomic potential based on Brenner formalism is constructed for SiC. The potential is fitted to the cohesive energy, lattice constant and bulk modulus, as well as some interstitial properties using a lattice relaxation fitting approach. The defect formation and properties have been calculated using the parameterized potential with MD methods, and the results are compared with previous ab initio calculations. In general, C interstitials have lower formation energies than Si interstitials, and the most favorable configurations for C interstitials are $\langle 1\,0\,0 \rangle$ and $\langle 1\,1\,0 \rangle$ dumbbells, with formation energies from 3.04 to 3.95 eV, but the most favorable Si interstitial is as a tetrahedral interstitial, surrounded by four C atoms. These results are in good agreement with those obtained by ab initio calculations. The larger size of the Si atom may give rise to higher formation energies of Si interstitials. Although the formation energies of vacancies are smaller than those calculated by ab initio method, the properties of antisite defects are in reasonable agreement with ab initio results.

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