

Defect energetics of β -SiC using a new tight-binding molecular dynamics model

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Abstract

We present the calibration of a semi-empirical and orthogonal tight-binding total energy model for defect energetics in β -SiC, as based on a state-of-the-art ab initio data base for the formation energies of carbon and silicon vacancies, antisites, and self-interstitials. The present total energy model is further applied within a molecular dynamics framework to investigate the silicon and carbon interstitial defect contribution to the self-diffusion in β -SiC. We provide a fully atomistic model for both migration path and diffusivity, giving also a quantitative estimation of energy migration barriers.

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1. Introduction

Silicon carbide has recently attracted a huge interest as a possible candidate to be the first wall of the reaction chamber in a fusion reactor. The same material is also quite promising as a wide-gap semiconductor, as well as a structural material for aerospace applications.

Although the above possible technological applications of SiC span a wide range, there is a common feature underlying (and, possibly, affecting) all of them, namely the defect-induced microstructure evolution. While damage accumulation – as a result of irradiation – could drive to embrittlement, the formation and the interaction among point defects (possibly charged) can modify the overall electric and electronic properties of SiC, and the competitive growth among extended defects – as due to point defects ripening – can in fact affect

its mechanical response. It is, therefore, crucially important to understand at the proper atomic-scale the energetics of formation and migration of point defects in SiC.

Being silicon carbide a binary compound, the full set of point defects to deal with contains a rich variety of structures, namely: silicon and carbon vacancies, antisites, and interstitials. Furthermore, a full atomic-scale approach either require a high accuracy (in order to provide reliable energetics), and reduced computational workload (in order to allow those large-scale simulations needed to investigate diffusion processes). These conflicting requirements prevent a straightforward application of model potentials (cheap, but not accurate enough) and of ab initio methods (superior and accurate, but so heavy that most of the dynamical defect features fall out-of-reach).

In this work we present an investigation based on tight-binding (TB) total energy methods and molecular dynamics (TBMD). The TB approach provides a bridge between accuracy and numerical efficiency or, in other words, between empirical and ab initio total energy

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functionals [1]. Furthermore, TB is based on a simplified, but quite effective description of interatomic bonding: this is an essential feature when dealing with a material characterized by directional and covalent bonding. As a matter of fact, any fundamental process involved in the physics of point defects can be traduced into a sequence of bond breaking and rebonding phenomena. TB is accurately designed to provide a sharp description of both.

The paper is organized as follows, in Section 2 we briefly describe the calibration of the present TB model and provide a thorough discussion on defect energetics in β -SiC. In Section 3 we investigate the self-interstitial diffusivity process by means of TBMD simulations at high temperature.

2. The tight-binding model and the energetics of point defects

Good and reliable TB models already exist for the pure elemental Si [2] and C [3] materials. Instead of attempting a completely new calibration of a TB we therefore decided to develop an ad hoc interpolation scheme between the above two representations, able to effectively describe the β -SiC structure. Before doing that, we needed a reliable data base onto which calibrate such an interpolation scheme.

The data base was generated computing total energies and bulk chemical potentials within the density functional theory (DFT) and local density approximation following the parametrization of Perdew and Zunger [4] to the exchange-correlation functional, using ultra-soft pseudopotentials [5] and the plane-waves code provided in the VASP package [6].

The formation energies of point defects have been then computed using the standard formalism by Zhang and Northrup [7]. As for the bulk chemical potential of Si and C we used their calculated value in the diamond

structure at their theoretical equilibrium lattice constant. Finally, we simulated an isolated defect in a system with $N (+1, -1)$ particles in a determinate volume V and we repeated in the space this finite system, establishing with the supercell approach the density constant (N/V). The present DFT calculations have been quite demanding since a very large $3 \times 3 \times 3$ supercell of cubic shape encompassing 216 atoms was adopted for all of the defects, with a very high plane-wave cutoff of 158 eV and a $k = 0$ point mesh as suggested in [8]. Our TB model was validated respect simulations realized exactly equal using the same defect configuration to those applied by DFT simulations, only neutral defects have been here considered because we used just the Γ point for Brillouin zone integration. The results are summarized in Table 1.

As for our interpolation scheme, we recall that the TB total energy functional E_{tot} can be cast [1] in the form

$$E_{\text{tot}} = E_{\text{bs}} + E_{\text{rep}}, \quad (1)$$

where E_{bs} is the band structure term given by the sum of one electron TB energies and E_{rep} is an affective repulsive potential (in charge of describing ion–ion interactions, as well as of correcting the double counting of electron–electron interactions contained in the first term). In this work we assumed that the Si–C two-center, orthogonal TB hopping integrals are simply given as an average between the Si–Si [2] and the C–C [3] ones. On the other hand, the effective repulsive potential for Si–C pairs E_{rep} (Si–C) is put in the form of a weighted average

$$E_{\text{rep}}(\text{Si–C}) = \alpha_{\text{Si}} E_{\text{rep}}(\text{Si–Si}) + \alpha_{\text{C}} E_{\text{rep}}(\text{C–C}) \quad (2)$$

with unconstrained α_{Si} and α_{C} parameters to be fitted.

The calibration of α_{Si} and α_{C} is a twofold process. At first, we determined the optimal range of variation for the two parameters by fitting the experimental values of β -SiC equilibrium lattice constant ($a_{\text{SiC}} = 4.31 \text{ \AA}$) and formation enthalpy ($\Delta H = -0.63 \text{ eV}$) [9]. It is worth remarking that the such experimental values are in excellent agreement with present DFT results. Within

Table 1

Formation energies of point defects in β -SiC as computed by DFT, TB and Tersoff model potential, both Si-rich and C-rich conditions were applied

	Ab inito data		Present TB data		Tersoff data	
	C rich	Si rich	C rich	Si rich	C rich	Si rich
Carbon antisite	2.65	3.91	2.15	3.19	1.88	2.52
Silicon antisite	5.06	3.79	4.55	3.51	4.83	4.19
Carbon vacancy	4.06	3.42	5.23	4.71	4.04	3.72
Silicon vacancy	8.06	8.70	5.30	5.82	3.13	3.46
Carbon interstitial (carbon coordinated)	9.90	10.53	4.97	5.48	7.05	7.37
Carbon interstitial (silicon coordinated)	9.50	10.13	3.95	4.47	4.23	4.56
Silicon interstitial (carbon coordinated)	7.34	6.70	6.84	6.32	17.84	17.52
Silicon interstitial (silicon coordinated)	9.45	8.81	7.54	7.02	16.06	15.74

All energies are expressed in eV.

such a range of variation for α_{Si} and α_{C} , both quantities are reasonably well reproduced. For each pair (α_{Si} , α_{C}) there selected, we then computed the formation energy of eight point defects and compared the TB results to ab initio ones. The actual definition of formation energy $E_f(X)$ for the defect X is

$$E_f(X) = E^X - \mu_{\text{Si}}N_{\text{Si}} - \mu_{\text{C}}N_{\text{C}}, \quad (3)$$

where E^X is the total energy of the simulation cell containing the X defect, while N_{Si} and N_{C} represent the number of silicon and carbon atoms in the defect cell. The silicon and carbon chemical potential μ_{Si} and μ_{C} obey the following general constrains:

$$\mu_{\text{Si}} \leq \mu_{\text{Si}}(\text{bulk}), \quad (4)$$

$$\mu_{\text{C}} \leq \mu_{\text{C}}(\text{bulk}), \quad (5)$$

$$\mu_{\text{Si}} + \mu_{\text{C}} = \mu_{\text{SiC}}(\text{bulk}), \quad (6)$$

where $\mu_{\text{Si}}(\text{bulk})$ and $\mu_{\text{C}}(\text{bulk})$ are, respectively, the chemical potential of bulk silicon and diamond, while $\mu_{\text{SiC}}(\text{bulk})$ is the SiC cohesive energy divided by the number of Si–C pairs in the simulation cell.

Eight different defects were considered, including both silicon and carbon vacancies and antisites, and four kinds of self-interstitials (each one with tetrahedral symmetry): a Si (or C) interstitial coordinated to other four Si (or C) atoms. Defects energetics have to be evaluated in both the carbon rich [i.e. $\mu_{\text{C}} = \mu_{\text{C}}(\text{bulk})$ and $\mu_{\text{Si}} = \mu_{\text{SiC}}(\text{bulk}) - \mu_{\text{C}}(\text{bulk})$] condition and the silicon rich [i.e. $\mu_{\text{Si}} = \mu_{\text{Si}}(\text{bulk})$ and $\mu_{\text{C}} = \mu_{\text{SiC}}(\text{bulk}) - \mu_{\text{Si}}(\text{bulk})$] condition. The best agreement between present TB model and DFT results was obtained for the pair ($\alpha_{\text{Si}} = 0.28$, $\alpha_{\text{C}} = 0.50$), corresponding to an equilibrium lattice constant of 4.295 Å and a formation enthalpy of -0.46 eV. In Table 1 we present a detailed comparison between the two sets of data, where TB calculations have been performed on 216-atom periodically-repeated cubic cell. For sake of completeness, we also include the results obtained by the Tersoff empirical potential, using similarly large simulations cells.

Although there are single TB values displaying sizeable differences with respect to DFT data, it is apparent that we improved qualitatively with respect to model potential predictions. In particular, this is the case of Si-related defects which are very badly accounted for by the Tersoff potential [10]. Overall the results of Table 1 make us confident about the reliability of the here fitted TB model.

We like to conclude this section by pointing out that the present results have been obtained by adding only two new adjustable parameters to the previous TB representations for Si and C. This is, in our opinion, an important point, whether it is intended to keep as clean

as possible the underlying physico-chemical picture typical of the tight-binding model. It is nevertheless expected that even a better agreement would be possible, provided that a more sophisticated interpolation scheme is adopted or a totally new TB model for SiC is developed.

3. Diffusivity of carbon and silicon self-interstitial

We have used the above TB total energy functional to power a molecular dynamics simulation of silicon and carbon interstitial diffusion in β -SiC.

In this case we made use of a smaller cell, containing 64 atoms plus the defect one. The equations of motion have been integrated by means of the velocity-Verlet algorithm with a time-step as short as 0.7×10^{-15} s. The system was at first equilibrated during a constant-temperature, constant-volume run at the desired temperature, thus loosing memory of the initial placement of the interstitial defect. Then the atomic trajectories have been aged for 3×10^5 time-steps during a microcanonical run and collected to compute the diffusivity according to the Einstein random-walk formula.

The results are reported in Fig. 1 as open triangles for C interstitial and a star symbols for Si interstitial. In both cases it is easily possible to interpolate the scattered data by an Arrhenius-like plot (full and dot-dashed lines) which provide a direct numerical estimation for the migration energy of self-interstitials: $E_m(\text{C}) = 0.51$ eV and $E_m(\text{Si}) = 0.55$ eV. Although these values look quite similar, it is hard to draw a general conclusion, valid even at low temperatures. As a matter of fact, more extensive simulations are needed below 1500 K in order to check whether a possible non-Arrhenius behaviour (i.e. a change in the slope of the diffusivity) is indeed

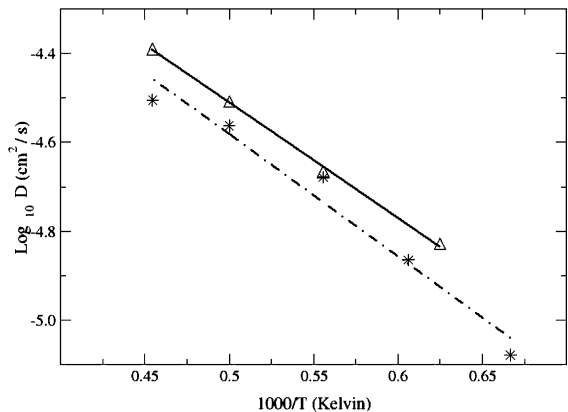


Fig. 1. Diffusivity plot for the diffusivity of carbon (open triangles) and silicon (star symbols) interstitials in the range 1500–2200 K. The full and dot-dashed lines represent the best Arrhenius-like linear interpolation.

observed in one or both cases. Work is in progress along this path.

A careful inspection on the atomic trajectories gives valuable information about the actual migration path and mechanism. In both cases, the interstitial defect diffuses through a concerted mechanism involving similar (i.e. with the same chemical nature) lattice atoms. In other words, a Si (or C) interstitial forms metastable configurations bonding itself to another Si (or C) lattice atom and creating a complex which is actually hard to classify (the temperature simulation is so high that the bound pair continuously vibrates among many different isomeric structures). Occasionally, the pair is broken by thermal vibrations and one of the two Si (or C) atoms is recovered into a lattice position. The second one makes jumps through interstitial channels, getting finally bound to another Si (or C) atom lying at a different position. It is worth noticing that, once that the pair is formed, it is no longer possible to determine which is the 'interstitial' atom and which is the 'lattice' one: the actual identity of the diffusing particles is continuously varied. According to this discussion, we can classify the diffusion mechanism as a 'lattice assisted'.

Such a 'lattice assisted' diffusion actually involves only the silicon (carbon) sublattice when the diffusing interstitial is Si (C). This is not surprising, given the hierarchy of formation energies provided in Table 1. In order to have, say, a Si interstitial to kick-out a carbon atom from its lattice position, we need to create a Si antisite and a C interstitial.

The formation energy for such a defect pair is too high to have such a process occurring. The same argument holds for a C interstitial to kicking-out a Si lattice atom.

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