Comparison of threshold displacement energies in β-SiC determined by classical potentials and ab initio calculations

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Abstract

Using classical molecular dynamics and ab initio calculations, we have determined threshold displacement energies in cubic silicon carbide, in order to understand the large disparity of values available in literature. First, we checked the influence of simulation parameters such as the box size and the temperature control. Then, we compared empirical potentials and ab initio methods, within the sudden approximation (SA). Our results clearly show that the use of available empirical potentials is the largest source of errors, and call for the improvement of existing potentials or the determination of threshold displacement energies by ab initio molecular dynamics.
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1. Introduction

Due to promising perspectives in both electronics and nuclear applications, the properties of silicon carbide under irradiation have been largely studied over the last decade [1–3]. During the irradiation process, the energy of the impinging particles is transferred to the lattice, leading to defect creation and damage accumulation. One important quantity for characterizing this process is the threshold displacement energy E_d, that is the minimum energy required for the formation of a stable Frenkel pair. Experimentally the determination of E_d is tricky, since it requires the study of the formation of isolated point defects. Moreover this data depends on the crystallographic

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orientation. Several techniques have been used for investigating radiation effects in SiC. Those techniques include transmission electron microscopy (TEM), electron paramagnetic resonance (EPR) and luminescence analysis [4]. For silicon carbide a large disparity in the different measurements exists and no value of the threshold displacement energy can be given with certainty for both Si and C sublattices. For this reason, several previous studies were focussed on the determination of E_d by computational means, almost all of them employing molecular dynamics with empirical potentials [5–11]. Unfortunately the calculated E_d and the identified defects strongly diverged between all studies. For example, E_d on the C sublattice was determined to range from 16.0 to 38.0 eV along the [1 1 0] crystallographic direction. Three main reasons may explain such a disagreement. First, different empirical potentials were used to describe SiC. Though they were all closely related to the original Tersoff potential [12], some of them were subsequently modified to improve the description of repulsive interactions. Ab initio calculations were also performed [11] by Windl et al. More accurate results should be expected, compared to empirical potentials. But as a matter of fact, certainly in order to reduce the computation time, the basis set which has been used was too limited to correctly describe the charge transfers present in SiC defects. Second, the way calculations are performed could be different from one study to another. This concerns important parameters such as the size of the simulation box, integration algorithm, and how temperature is controlled during the simulation. Third, in a recent study, Malerba and Perlado proposed that there is an intrinsic uncertainty range for the determination of E_d, due to the occurrence of metastable defects [10]. Therefore, the use of different methods for describing silicon carbide, the ways simulations are performed, and this intrinsic uncertainty, are possible causes for the observed discrepancy in the threshold displacement energy calculations. The way a displacement event is defined is also a possible cause for discrepancy in the value of E_d. It remains to be determined which one is the most important. In this paper, we checked the influence of simulation parameters such as the box size and

the temperature control, by first calculating E_d using classical molecular dynamics. Then, we compared empirical potential methods with a more precise ab initio method, by performing static calculations. Our results clearly show that the use of empirical potentials is the largest source of errors, and call for the improvement of existing potentials or the determination of threshold displacement energies by ab initio molecular dynamics.

2. Computational method

The threshold displacement energy is determined by examining the response of a perfect crystal, when an initial kinetic energy is given to an atom located in the center of the simulation cell. Consequently this atom, which is usually called the primary knock-on atom (PKA), recoils in the direction of the initial impulsion. The relaxation of the system is monitored and the amount of initial energy transferred to the atom is gradually increased (0.1 eV increment) until a stable Frenkel pair is formed, involving or not the PKA.

Classical molecular dynamics (MD) simulations were carried out with the XMD code [13], the interatomic interactions being described by the semi-empirical many-body potential from Tersoff [12]. All simulations were performed with a constant number of particles, ranging from 64 ($2a_0 \times 2a_0 \times 2a_0$ cell) to 8000 ($10a_0 \times 10a_0 \times 10a_0$ cell) atoms, and at constant volume. A time step of 0.5 fs was used. During the simulation, the temperature was kept at 300 K using different methods as explained further. In order to insure that created defects are stable, simulations were performed up to 20 ps.

Ab initio calculations were performed using the plane-wave pseudopotential code JEEP [14] based on density functional theory (DFT) [15,16]. The exchange–correlation potential proposed by Ceperley and Alder and parameterized by Perdew and Zunger was used [17]. We considered a Γ-point sampling of the Brillouin zone, a 64-atoms cell ($2a_0 \times 2a_0 \times 2a_0$), and a 35 Ry kinetic energy cut-off. Those parameters have been optimized to insure accuracy of the calculation and to keep reasonable computational times. Hence, the theoreti-

cal lattice parameter and bulk modulus were found to reproduce rather well experimental values, respectively 4.34 Å and 221 GPa against 4.36 Å and 224 GPa [18].

3. Threshold displacement energy results

E_d has been already calculated using several potentials, most of them related to the original Tersoff potential. Hence, Hensel et al. [5] used a Tersoff potential with a short-range repulsion modeled by a two-body term close to the Ziegler–Biersack–Littmark potential [6]; this study is noted TZBL later on. Two previous studies considered modified Tersoff potentials with a repulsive part derived from an ab initio calculation. Since they differ by a different set of cut-off parameters, those studies are respectively called TA1 [7,8] and TA2 [9,10]. Perlado used the original Tersoff potential [3], this study being noted T1. Windl et al. [11] employed the original Tersoff potential (T2), and also made first-principle calculations using a minimal basis set with the "Fireball96" method (FB) [19]. In Table 1, the threshold displacement energies, calculated for the low-index directions as shown in Fig. 1, are reported. Only the main crystallographic directions are discussed as some calculations have shown that the PKA tends to follow low-index directions [7–10]. To complete this comparison, our results, obtained with the original Tersoff potential (T3) in a 512-atoms box, are included in the table.
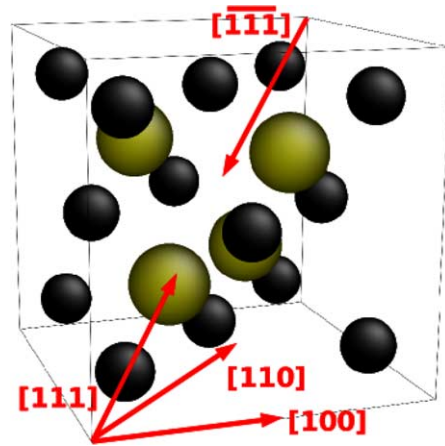

Fig. 1. Representation of the main crystallographic directions in the cubic cell of β-SiC. Carbon atoms are drawn in black, and silicon atoms lighter.

First we consider a C atom and the [1 0 0] crystallographic direction (noted in this work C[1 0 0]). In TZBL, T2 and T3, the C atom recoils consecutively to the initial kinetic impulsion towards the nearest tetrahedral interstitial C_{TSi} ($E_d \sim 13.5$ eV), with a Frenkel pair distance d_{FP} between the interstitial and the vacancy equal to $0.5a_0$ (Fig. 2). In the other studies, i.e. TA1, TA2, T1 and FB, authors report a much larger E_d, around 30 eV, and a C atom recoiling further to form a CC dumbbell oriented along [1 0 0], with $d_{FP} > 0.5a_0$, as shown in Fig. 2. So already for this first case, it is clear that the nature of the defect and the associated E_d can be very different in previous works.

Table 1

Calculated threshold displacement energies (in eV) and associated defects in β-SiC, when available, along the main crystallographic directions, from different studies

	TZBL		TA1		TA2		T1		T2		T3		FB	
C[1 0 0]	13.5	C_{TSi}	31.0	CC	30.0	CC	35–40	CC	13.5	C_{TSi}	13.5	C_{TSi}	28.5	CC
C[1 1 0]	17.5		38.0		26.0	CSi	30	CC	30.5		16.0	C_{TSi}	38.5	
C[1 1 1]			71.0		41.0	CSi					37.0	C_{TSi}		
C[$\bar{1}\bar{1}\bar{1}$]	21.5		28.0		20.0	CSi	20–25	C_{TSi}	22.0		21.0	C_{TSi}	27.5	
Si[1 0 0]	42.5		36.0	SiSi	35.0	SiSi	30–35	SiSi	45.5	SiSi	42.0	SiSi		
Si[1 1 0]	65.5		71.0		73.0	SiSi	80–85		56.5		50.0	Various		
Si[1 1 1]	46.5		39.0		38.0	SiSi	35–40		46.5		42.0	Si_{TC}		
Si[$\bar{1}\bar{1}\bar{1}$]			113.0		27.0	C_{TSi}	35–40	CC			20.5	C_{TSi}		

C_{TSi}, CC, SiSi, CSi and Si_{TC} correspond respectively to a carbon in a silicon tetrahedral site, a carbon–carbon dumbbell, a silicon–silicon dumbbell, a carbon–silicon dumbbell and a silicon in a carbon tetrahedral site.
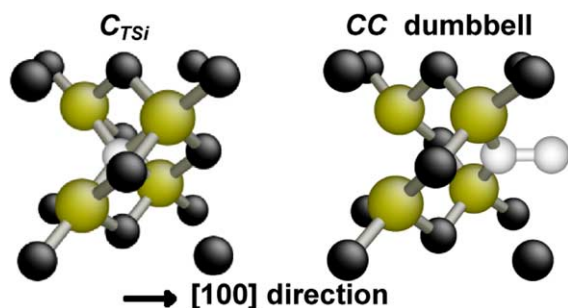
Fig. 2. Ball-and-stick representations of C_{TSi} interstitial and CC dumbbell along the [1 0 0] direction. Carbon atoms are drawn in black, silicon atoms lighter and the defects in white.

Along the C[1 1 0] direction, the C atom hits its C first neighbour and thus is strongly deviated from its initial trajectory: towards $\langle 0\,0\,\bar{1}\rangle$ or any equivalent direction to form a C_{TSi} interstitial in our work (T3), or towards $\langle \bar{1}\,\bar{1}\,\bar{1}\rangle$ to form a CSi dumbbell in TA2. E_d ranges from 16.0 to 38.5 eV depending on the study. Considering now the C[1 1 1] case, the C atom encounters directly a Si atom, and bounces backward. Our calculations showed that a stable C_{TSi} interstitial is created with $E_d = 37$ eV. A close E_d value (41 eV) is obtained with TA2, but with a different stable defect, i.e. a CSi dumbbell with one of the closest Si atoms delimiting the nearby empty tetrahedral interstitial [10]. However, as in TA2, there is no systematic creation of stable defects for higher values. Indeed even for kinetic impulsions above E_d, a Frenkel pair is not always created; this behaviour was explained by Malerba and Perlado by proposing an uncertainty band in which the atomic displacement may or may not be produced [9,10]. The value obtained with TA1, 71 eV, is noticeably higher. Finally, for the C[$\bar{1}\,\bar{1}\,\bar{1}$] case, the PKA heads for the tetrahedron defined by four Si atoms. A C_{TSi} interstitial is formed in our work, whereas a CSi dumbbell is obtained with TA2. E_d ranged between 20.0 and 28.0 eV depending on the study.

Different results are expected for the Si sublattice as Si is heavier than C. Indeed, higher energies are needed to create a stable Frenkel pair, which can be obtained with a secondary knock-on C atom in some cases. Along the Si[1 0 0] direction, all studies agree about a Si PKA recoiling until a SiSi dumbbell, orientated along the [1 0 0] direc-

tion, is formed. But there is still a large E_d range, from 30.0 to 45.5 eV. The Si[1 1 0] case is certainly the most complicated one due to the high kinetic energy transferred to the PKA. For example, in TA2, authors report that Si PKA can form SiSi dumbells with different Si atoms for $E_d = 73$ eV. However, in our work, as soon as the energy exceeded 50 eV, we found that the Si PKA bounces backwards and a lot of different stable defects were identified: SiSi and CC dumbbells of various orientations, C_{TSi} interstitial, C_{Si} and Si_C antisites. Along the Si[1 1 1] direction, we observed the creation of a distorted Si_{TC}, although with TA2, the formation of SiSi dumbbells oriented along $\langle 1\,0\,0\rangle$ or any equivalent direction is reported. E_d is found to range from 35.0 to 46.5 eV, depending on the calculations. Last, for the Si[$\bar{1}\,\bar{1}\,\bar{1}$] case, we found that the Si PKA hits its C first neighbor, displaces it and then returns to its initial location. The displaced C atom moves towards the closest tetrahedron defined by four Si atoms and forms an C_{TSi} interstitial, which is found stable in our work but not in TA2. Here, E_d is found to be 20.5 eV, against 27.0 eV with TA2. In TA1, the very high value of E_d (113 eV) can be explained by the definition the authors used for the threshold displacement energy [7,8]. Indeed, the reported value corresponds to the energy needed to form a Frenkel pair involving the PKA and not a secondary knocked C atom. This brief comparison of our work with the other studies illustrates the large variety of possible created defects, and the associated discrepancy in the determination of the threshold displacement energy. In the following, we investigate and discuss possible explanations.

4. Influence of box size and temperature control

There are parameters in simulations that may significantly influence the outcome. In previous studies, the box size ranged from 64 to 8000 atoms and the way the temperature was controlled during simulation, was also different. Because both could be possible reasons of the uncertainty in the determination of E_d, we have investigated their influence. Box size effects were studied by performing several simulations from 64 to 8000 atoms. Con-

cerning temperature control, most of the studies used a thermostat, that is a velocity rescaling method applied on one or several boundary layers of the simulation box. Here, different tests have been performed: without thermostat, or with a rescaling of the velocities applied on one or several boundary layers, or applied on atoms out of a sphere centered on the PKA ($r_{sphere} = a_0$), or also on all atoms. We found that rescaling velocities on some outer boundary layers of the box (each side or only two opposite sides) does not give significative differences compared to a sphere rescaling. On the contrary, rescaling the velocity on all atoms should be avoided since it has a spurious effect on the E_d calculation: in the very first steps of the simulation, the PKA velocity will be artificially modified by the thermostat and, consequently, a larger initial impulsion will be required to create a Frenkel pair, with a too large E_d. In the following, we have considered two cases: one with a PKA-centered thermostat, and the other without thermostat. Table 2 describes how the threshold displacement energies, obtained along two equivalent directions in C and Si sublattices i.e. C[$\bar{1}\bar{1}\bar{1}$] and Si[1 1 1], depend on box sizes and temperature control. Here, the 8000-atoms box can be considered as the reference simulation box in which the temperature variations are the more realistic. It is clear from Table 2 that (i) E_d does not depend on the presence or not of thermostat and (ii) that the difference between the minimal case (64-atoms cell) and the reference case (8000-atoms cell) is always less than 5% of the E_d value. Therefore, the
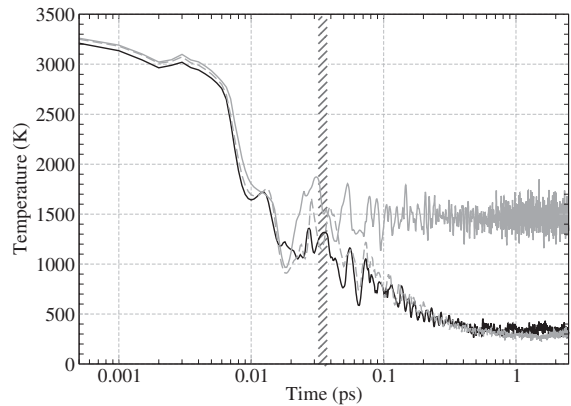

Fig. 3. Temperature as a function of simulation time for a 25 eV C PKA along the [$\bar{1}\bar{1}\bar{1}$] direction. Temperature in a 64-atoms cell is plotted in grey, with thermostat (dashed line) or without thermostat (straight line). Temperature corresponding to a embedded 64-atoms box in a 8000-atoms cell without thermostat, is plotted in black. The hatched band indicates approximately when the defect is created.

variation of both parameters does not explain the disparity of E_d values in the literature. Another important point about temperature control concerns the high temperature reached in a small cell in the beginning of the simulation when a large kinetic energy is partially converted to heat. Fig. 3 compares temperatures in a 64-atoms cell and inside an equivalent 64-atoms box, including the PKA, embedded into a 8000-atoms cell, with and without thermostat, after a 25 eV C PKA along the [$\bar{1}\bar{1}\bar{1}$] direction. During the first steps of the simulation, the temperature is very high, around 3250 K. However, no melting of the crystal occurred even if the experimental melting temperature is about 3100 K [20]. One possible explanation is the use of the Tersoff potential, for which calculated melting temperature is even much higher, about 4900 K [8]. More relevant is the fact that these high temperatures are present only during few simulation steps, a too short time to observe melting. The temperatures substantially decrease after creation of the defect. Nevertheless, the final temperature of the 64-atoms cell without thermostat is obviously important (about 1500 K), which stresses the need of a thermostat for controlling temperature. When comparing the evolution of the temperature between a 64-atoms cell (with

Table 2
Box size and thermostat effects on threshold displacement energies along two equivalent directions in C and Si sublattices

Box size	No thermostat	Thermostat
C[$\bar{1}\bar{1}\bar{1}$]		
64	20.0	21.0
216	20.0	20.5
512	21.5	21.0
8000	21.0	21.0
Si[1 1 1]		
64	40.5	40.5
216	42.0	42.0
512	42.0	42.0
8000	42.5	42.5

thermostat) and an embedded 64-atoms box (without thermostat), no significant differences can be observed. So, the behaviour of the atoms in the 64-atoms cell is comparable to the one in the big simulation cell. Therefore such a small simulation cell, together with a thermostat, could be used for the determination of E_d. Finally, neither the size of the cell nor the temperature control seem to explain the dispersion in calculated E_d.

5. Comparison between semi-empirical potential and ab initio

Now we focus on the comparison between empirical potentials and more precise ab initio calculations for selected directions, in order to check if the use of different potentials may be the main cause for the observed dispersion. As ab initio molecular dynamics simulations of E_d in SiC are a tremendous task, E_d values were determined using the sudden approximation (SA). SA supposes that the PKA is moved along a selected direction, from its initial site to the defect position, while all the other atoms are kept fixed. The total energy is calculated during the path and E_d is defined as the difference between the highest energy reached and the energy of the perfect crystal. This method allows a fast estimation of E_d, because using only static calculations, but is limited to the most simple cases, i.e. when the path to create a defect is straight. Results obtained with SA and the Tersoff potential are close from MD calculations, with differences always lower than 10%, except for Si[1 0 0] where the first encountered defect (Si$_{TC}$) is found stable. However this location is found unstable using ab initio calculations such as "Fireball96" and DFT-LDA.

Table 3 reports results obtained with Tersoff potential and DFT-LDA in SA. They are also compared to values calculated by Windl et al. with the "Fireball96" method and DFT-LDA [11]. It is clear that values determined by DFT-LDA calculations are much more lower than the ones computed with Tersoff or "Fireball96". For example, along C[$\bar{1}\,\bar{1}\,\bar{1}$] direction, E_d is found to be 13.0 eV or 14.5 eV with DFT-LDA, to compare to 20.5 eV (Tersoff) and 25.5 eV ("Fireball96"). This

Table 3
Computed E_d (eV) in sudden approximation (classical and first-principle calculations)

Direction	Tersoff[a]	DFT-LDA[a]	Fireball96[b]	DFT-LDA[b]
C[1 0 0]	12.5	10.5	14.5	
C[$\bar{1}\,\bar{1}\,\bar{1}$]	20.5	13.0	25.5	14.5
Si[1 0 0]	27.5	Unstable	Unstable	
Si[1 1 1]	42.0	22.5	37.0	

[a] This work.
[b] [11].

points to the fact that the use of semi-empirical potentials for determining threshold displacement energies may introduce large errors.

6. Discussion

Considering the previous published works, calculated threshold displacement energies and nature of the created defects differ substantially from one study to the other. Our investigations have shown that the way to perform the simulations (box size, temperature control) is of less importance than the used potential, which is the preponderant factor in the determination of E_d. As a matter of fact, under the same conditions, calculations using the same potential are expected to give similar results. Indeed, considering the Tersoff potential used by Windl et al. and in this work (respectively T2 and T3), calculated E_d along each directions are comparable except in C[1 1 0] direction. In this case, the value given by Windl et al. corresponds to the energy found here to obtain the second type of defect. However, Perlado, who also used the original Tersoff potential, reported in some cases different results in term of E_d and defects, which is rather difficult to explain.

Using different potentials, a large range of E_d as well as various kinds of formed defects are obtained. Even if two studies found approximately the same E_d in a particular direction, the associated defect is not necessarily the same. Thus, along the C[$\bar{1}\,\bar{1}\,\bar{1}$] direction, in TA2 and in this work, E_d is determined to be about 20 eV, but the related defects are different, i.e. respectively CSi dumbbell and C$_{TSi}$ interstitial. This can be explained by the

fact that the relative formation energies of defects are very different between potentials [21–23]. Indeed, on the one hand the original Tersoff potential highly favored the formation of C_{TSi} interstitials, and on the other hand the modified Tersoff potential, used for example by Malerba and Perlado, favored the formation of dumbbells.

This difference between potentials also appears in the average values of displacement energies, weighted for equivalent directions. Using the original Tersoff potential T3, we found about 19 eV for C and 42 eV for Si, close to the values commonly accepted in the fusion community (20 eV for C and 35 eV for Si). However, they mainly correspond to tetrahedral interstitials, which, in the case of Si[1 0 0], have been shown to be unstable with static ab initio calculations. With TA1 and TA2, more stable dumbbells are obtained, but with average values 10–20 eV greater than the experimental suggestions. These results stress the need to refine displacement energy simulations.

It has been recently proposed that the uncertainty in the determination of E_d is intrinsically related to the material, with an energy range where defects may or may not be produced [10]. However, some defects can be found stable with one particular potential, but metastable with another one. Indeed using the original Tersoff potential, we have not been able to identify such metastable Frenkel pairs, even by monitoring the simulations over 20 ps. This underlines that the actual uncertainty in the determination of E_d is not intrinsic to SiC but is due to the use of the available semi-empirical potentials.

Several things could be done to get more precise values of E_d. First, one could improve existing potentials or develop new ones. This have been tried in several studies (TA1, TA2, TZBL), where the repulsive part of the potential have been modified, which is important to model energy transfer during cascade simulations. But, it is difficult to conclude that it improved the determination of threshold displacement energies. Actually the calculated stability of the different defects has also to be improved. Then regarding SA results, DFT-LDA calculations have highlighted that E_d is systematically lower than the ones given by empirical potentials or by "Fireball96". As the SA technique is limited, this calls for a complete and accurate determination of E_d by ab initio molecular dynamics. This is a difficult task because this method is really time expensive, and the determination of E_d requires a lot of different runs in term of PKA energy and crystallographic direction. The use of a small simulation cell would then be mandatory. On the basis of our calculations, such a small cell should be sufficient to determine the threshold displacement energies.

Acknowledgements

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