Ab initio molecular dynamics calculations of threshold displacement energies in silicon carbide

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Using first-principles molecular dynamics simulations, we have determined the threshold displacement energies and the associated created defects in cubic silicon carbide. We found rather anisotropic values, with an average of 19 eV (38 eV) for the C sublattice (Si sublattice), respectively. Those are close to the experimental consensus, and relaxed configurations are in good agreement with recent works on the stability of point defects in silicon carbide. We carefully investigated the limits of our approach. Our paper shows that displacement energies and associated Frenkel pairs could be determined with first-principles accuracy in silicon carbide, and suggests that it may be also the case for other covalent materials.

Particle irradiation is a well known and extensively used technique, allowing for the modification of mechanical, magnetic, electrical, and optical properties of materials. For instance, a suitable ion irradiation may harden a material, lead to a local oxydation state, or activate a magnetic order. The utility of ion irradiation is also well known for electronics, with the doping or gettering processes, and for radiation therapy. Besides, damage accumulation due to irradiation is also an important research field, related to space and nuclear applications.

The interaction of an energetic ion with the matter is a complex phenomenon, especially at high energies. Impinging ions are simultaneously slowed down by inelastic collisions with electrons, and by elastic collisions with atoms. The displacement of lattice atoms leads to creation of defects and accumulation of damage. A key quantity, relevant to the process and different for each irradiated material, is the threshold displacement energy (E_d). E_d may be defined as the minimal kinetic energy that has to be transferred to a lattice atom in order to create a stable Frenkel pair that survives at least 10^{-12} s. For instance, E_d values are required as key input in large-scale irradiation simulation packages, such as SRIM/TRIM, extensively used for determining implantation profiles in doping processes, or for calculating damage accumulation in materials.

This quantity is rather difficult to measure, since single created defects have to be identified during experiments, and associated with a well-defined irradiation energy. Then, there has been an increasing number of works aiming at the E_d determination from molecular dynamics (MD) simulations. The procedure is simple: after a defined impulse given to an atom, which is usually called the primary knock-on atom (PKA), the evolution of the system is monitored. Once the transfered energy exceeds the E_d, there is formation of a Frenkel pair in the system. As far as we know, all simulations but one[1] have been done with molecular dynamics and classical empirical potentials. In fact, several reasons hinder *ab initio* molecular dynamics. First, determining an energy threshold from molecular dynamics requires many runs, since the kinetic impulsion is progressively increased to find the threshold, and the procedure is stochastic due to nonzero

temperature. Second, usually, large systems have to be employed. Finally, there is a value associated with each crystallographic direction and with each element in a multicomponent system, which considerably increases the number of runs.

The silicon carbide is a material for which potentials are known to give contrasted results. It has potential applications in electronics, as a replacement for silicon, and in nuclear technology. Silicon carbide is also very interesting from a fundamental point of view, since it can be considered as a model for zinc-blende two-component covalent materials. There have been several measurements of the E_d, with different techniques, but a large dispersion of values is obtained.[2] In the absence of precise data, it is usually assumed that average values for C and Si sublattices are 20 and 35 eV, respectively. However, subsequent molecular dynamics studies did not clearly confirm these values. Average values were found from 17 to 40 eV for the C sublattice and from 42 to 57 eV for the Si sublattice, with very different extreme values.[1,3–7] In addition, the nature of the created defects is different from one study to another. We have recently shown that these discrepancies are due to the use of different empirical potentials.[8] In fact, the kinetic energy required for the creation of a Frenkel pair is obviously related to the energy barrier that the lattice atom must overcome to reach an interstitial site. Empirical potentials usually give a poor description of these saddle states, especially for covalent materials. An *ab initio* molecular dynamics determination of E_d and the associated Frenkel pairs would then be very valuable. This knowledge would also be useful for identifying defects generated on C or Si sublattice.[9] Finally, the anisotropy of E_d has to be accurately determined, for it has consequences for ion implantation along different crystal directions.

In this paper, we report an *ab initio* molecular dynamics determination of E_d. On the one hand, we show that such calculations are feasible, at least for covalent materials for which the vacancy-interstitial separation of the Frenkel pair is very small. On the other hand, E_d values have been obtained in β-SiC for all high symmetry directions shown in Fig. 1, for both Si and C lattices, with the first-principles accuracy. Our results show that our calculated average values
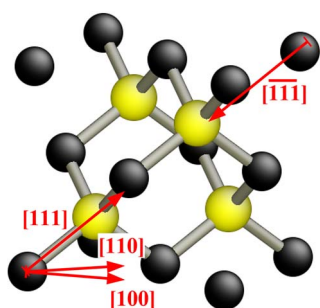
FIG. 1. (Color online) Representation of the main crystallographic directions in β-SiC. Carbon atoms are drawn in black, and silicon atoms in light gray (yellow in the electronic version).
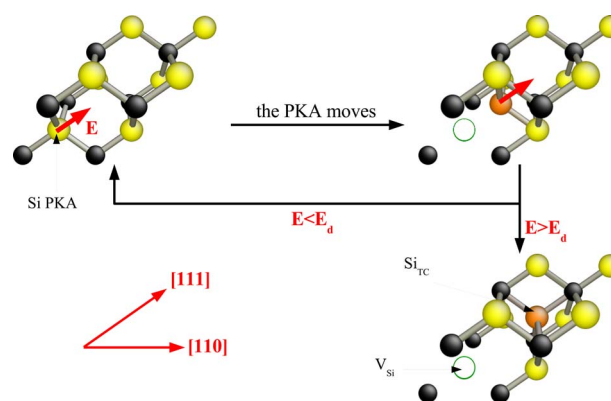

FIG. 2. (Color online) A Si PKA along the $\langle 111 \rangle$ direction. Carbon atoms are drawn in black, and silicon atoms in light gray (yellow in the electronic version). The silicon PKA is drawn in gray (orange in the electronic version), and the vacancy is represented by an open circle. A kinetic energy E is given to a Si atom, which is subsequently displaced. If $E < E_d$, the PKA returns to its original location. If $E > E_d$, there is formation of a silicon vacancy V_{Si} and a silicon tetrahedral interstitial surrounded by four carbon atoms Si_{TC}.

are close to the experimental consensus. They, also, point out which Frenkel pairs are to be expected in irradiated SiC. Investigation of the Frenkel pairs recombination is beyond the scope of this work, but our results may be used as a starting point, in particular for the determination of recombination paths.

The *ab initio* molecular dynamics calculations were performed using the plane-wave pseudopotential code GP,[10] based on the density functional theory (DFT).[11,12] The exchange-correlation potential proposed by Ceperley and Alder, and parametrized by Perdew and Zunger was used.[13] We considered a Γ sampling of the Brillouin zone, and a 35-Ry kinetic cutoff. With those parameters, the calculated lattice parameter $a_0 = 4.34$ Å and the bulk modulus $B = 221$ GPa were found to reproduce rather good experimental values, 4.36 Å and 224 GPa, respectively.[14] We also checked that pseudopotential cores did not overlap during simulations. All calculations were performed with a constant number of particles, with a 64-atom cell ($2a_0 \times 2a_0 \times 2a_0$), except for the Si PKA in the $\langle 100 \rangle$ direction where a 96-atom cell ($3a_0 \times 2a_0 \times 2a_0$) was required to keep the PKA in the cell. Such conditions are known to be not sufficient for an accurate determination of defect formation energies and migration barriers. In fact, while defect structures and migration paths are in qualitative agreement, errors up to 1 eV are to be expected. However, much larger energies are involved in the calculation of E_d. A time step $dt = 1$ a.u. was used during the ballistic phase of the simulation, then increased to 2 a.u. during the relaxation phase. A thermostat with $T = 300$ K was used to provide realistic initial conditions for the MD runs and to simulate the energy dissipation of a large system as demonstrated in Ref. 8. The maximum duration of each run was 2.8 ps. If a stable Frenkel pair occurred, the system was then completely relaxed to obtain the stable configuration. At most 10 runs were done to roughly determine E_d for each case. Then five runs were performed to improve the precision to 1 eV. Finally, because of the intrinsic stochasticity of the process, three additional runs were made to confirm the determined E_d and the associated Frenkel pair.

As an example, Fig. 2 shows two possible cases in a typical threshold displacement energy determination, after a kinetic energy E is transferred to a silicon atom along the $\langle 111 \rangle$ direction. The PKA first moves from its equilibrium position along the $\langle 111 \rangle$ direction. If E is below the threshold displacement energy E_d, in this case 22 eV, it returns to this

location and no Frenkel pair is created. On the contrary, if E is above E_d, the PKA reaches an interstitial location in the lattice, leaving its original site free. Thus there will be formation of a Frenkel pair, i.e, an interstitial and a vacancy, separated by a distance d_{FP}. In this example, a vacancy and a silicon in a carbon tetrahedral site ($V_{Si} + Si_{TC}$), separated by a distance $d_{FP} = 0.87a_0$, are produced above the E_d.

There are several computational issues that are supposed to prevent the determination of E_d with first-principles methods. Hence, the cell must be big enough to contain the PKA during all the simulation. Here we have mainly used a 64-atom cell, which may be viewed as very small. However, in our simulations, the PKA does not move far away from its initial location before it is trapped in an interstitial site. Indeed in covalent materials, and especially in ceramics, the vacancy-interstitial separation d_{FP} is very short, often lower than a_0. This is clearly in contrast to metals, for which d_{FP} is several times a_0. Also, the cell should be large enough to prevent cumbersome interactions between the PKA and the thermostat during the simulation. Hence, in silicon, it has been suggested that a 64-atom cell is too small with respect to this issue.[15] However, we have recently shown that, in silicon carbide, the error due to the cell size problem is small compared to the discrepancy found between different calculation methods.[8] This is an important point, and we have performed an additional test with a larger cell (216 atoms) and C$\langle 100 \rangle$ to check the validity of this assumption. We found no difference with the 64-atom cell, with a similar E_d value. Another issue is related to the time step. It must be small enough to insure the accuracy of atomic trajectories, especially during the ballistic phase of the simulation. Hence, we have used a time step of 1 a.u., so that the maximum displacement during one time step for a C PKA of 50 eV is less than 0.007 Å, which is much lower than the upper threshold of 0.1 Å recommended by Corrales *et al.* for low energy cascade events.[16] Regarding all these points, we assert that the determination of E_d by *ab initio* methods is

TABLE I. Threshold displacement energies in β-SiC, calculated by DFT-local-density approximation molecular dynamics, along the main crystallographic directions. The associated defects and resulting Frenkel pair separations d_{FP} are also added. V_C, V_{Si}, CC, CSi, and Si_{TC} correspond, respectively, to a carbon vacancy, a silicon vacancy, a carbon-carbon dumbbell, a carbon-silicon dumbbell, and a silicon in a carbon tetrahedral site. The average values are weighted for equivalent directions. For the C[111] case, several defects were observed.

Direction	E_d (eV)	Defect	d_{FP} (a_0)
C[100]	18	V_C+tilted CC$_{\langle 100 \rangle}$	0.87
C[110]	14	V_C+CSi$_{\langle 0\bar{1}0 \rangle}$	0.48
C[111]	38		
C[$\bar{1}\bar{1}\bar{1}$]	16	V_C+CSi$_{\langle 010 \rangle}$	0.95
		C sublattice, weighted average: 19 eV	
Si[100]	46	V_{Si}+Si$_{TC}$	1.52
Si[110]	45	V_C+CSi$_{\langle 0\bar{1}0 \rangle}$	0.48
Si[111]	22	V_{Si}+Si$_{TC}$	0.87
Si[$\bar{1}\bar{1}\bar{1}$]	21	V_C+CSi$_{\langle 0\bar{1}0 \rangle}$	1.24
		Si sublattice, weighted average: 38 eV	

feasible at least in ceramics, and, as it will be shown further, these calculations are required for determining accurately the threshold displacement energies and the created defects.

We now describe and discuss our results. Table I reports the calculated E_d values and the associated Frenkel pairs, obtained for PKAs on both C and Si sublattices in the main crystallographic directions. The corresponding defect configurations are reproduced in Fig. 3. Globally, our results show various dumbbells and Si interstitials in tetrahedral site Si_{TC}. For C[100] and an energy above 18 eV, the PKA recoils toward the nearest tetrahedral interstitial site and moves further until it forms a tilted CC$_{\langle 100 \rangle}$ dumbbell interstitial with d_{FP} equal to $0.87a_0$. This configuration was previously described as the most stable CC dumbbell.[17] Several CSi dumbbells were also identified. For C[110] and E_d equal to 14 eV, the C atom replaces its C first neighbor, which is subsequently displaced to create a CSi$_{\langle 0\bar{1}0 \rangle}$ with $d_{FP}=0.47a_0$. This configuration is also found in the case of a Si PKA along the $\langle 110 \rangle$ direction, and an energy above 45 eV, with a different collision sequence. Considering now the C[$\bar{1}\bar{1}\bar{1}$] direction, above 16 eV, the C atom heads for the tetrahedron defined by four Si atoms, and does not form a C$_{TSi}$ tetrahedral interstitial as it could be primarily expected, but a slightly tilted CSi$_{\langle 010 \rangle}$ dumbbell with a Si atom. The Frenkel pair separation d_{FP} is $0.95a_0$. This is consistent with previous *ab initio* calculations from Lento *et al.*, predicting the conversion of the C$_{TSi}$ tetrahedral interstitial to the CSi$_{\langle 010 \rangle}$ dumbbell interstitial.[18] The last case for which a CSi dumbbell is obtained is the Si[$\bar{1}\bar{1}\bar{1}$] with E_d equal to 21 eV. Here the Si atom collides with its C first neighbor, displaces it, and returns to its original location. The resulting CSi$_{\langle 0\bar{1}0 \rangle}$ interstitial is separated from the vacancy by $1.24a_0$. Silicon
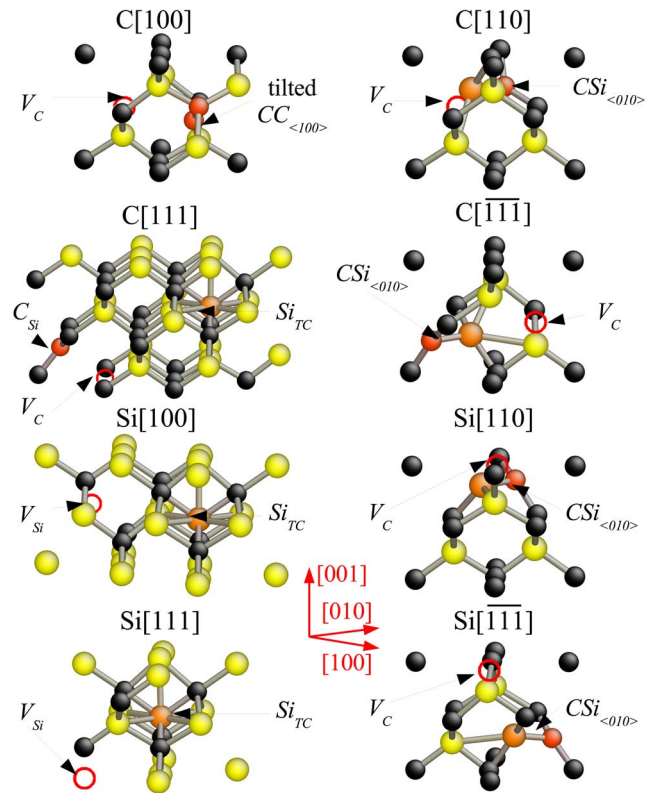

FIG. 3. (Color online) Defect configurations for each considered crystallographic directions. Carbon atoms are drawn in black, and silicon atoms in light gray (yellow in the electronic version). Defects are drawn in two different shades of gray (orange and red for C and Si atoms, respectively, in the electronic version), and the vacancies are represented by an open circle.

tetrahedral interstitials surrounded by carbon atoms Si_{TC}, which were determined as the most stable tetrahedral interstitial,[17–19] were also created. The most simple case is Si[111] described in Fig. 2. Above 22 eV, the Si PKA directly moves toward the tetrahedral site and forms a Si_{TC}, $0.87a_0$ away from the vacancy. A Si PKA along the $\langle 100 \rangle$ direction, with an energy higher than 46 eV, leads to the formation of a Si_{TC} interstitial separated from the Si vacancy by $1.52a_0$, after a short collision sequence during which the Si PKA replaces another Si atom, this one moving in the following tetrahedral site. For the C[111] case and an energy higher than 38 eV, several mechanisms, occuring for similar energies, were observed depending on the way the C PKA rebounded on its closest silicon neighbor. In the first mechanism, the C PKA rebounds without displacing the Si atom and forms CSi$_{\langle \bar{1}00 \rangle}$, identical to C[110] and Si[110] cases. In the others, the C PKA encounters its Si first neighbor at short distance with enough energy to displace it to the next Si_{TC} interstitial site. Afterwards, the C PKA sometimes returns to its original location, leading to a final configuration similar to the Si [111] case, or it bounces backward, and after few recombinations forms additional defects such as C$_{Si}$ antisite and carbon vacancy V_C, as shown in Fig. 3. In this peculiar case, there is an uncertainty regarding the created defects,

but for a similar E_d, a somewhat different result than in previous works.[7] Finally, regarding all the different PKAs that have been studied, the created defects are always in fair agreement with the relative stability of defects found with static *ab initio* calculations. For instance, the formation of Frenkel pairs with a Si_{TC} interstitial directly next to the vacancy has not been observed in our work, whereas Frenkel pairs involving a carbon vacancy and a carbon interstitial have been found stable with close separations, in agreement with results from Bockstedte *et al.*[20]

Due to the high anisotropy of the E_d values, we have determined the average E_d on both C and Si sublattices, by weighting each values of E_d by the number of equivalent directions.[21] Our average E_d are in very good agreement with the values usually considered by the fusion community:

19 eV against 20 eV for the C sublattice, and 38 eV against 35 eV for the Si sublattice.

In conclusion, we have determined E_d in silicon carbide using *ab initio* molecular dynamics. We found that the threshold displacement energy is a strongly anisotropic quantity. Average calculated values of E_d were found in very close agreement to the experimental consensus for both C and Si sublattices, and created defects compare fairly well with previous theoretical investigations of defect formation energies in SiC. Such an agreement has never been obtained with semiempirical potentials or tight-binding methods. Our results suggest that a first-principles determination could also be performed for silicon and other covalent materials.

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