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Section 2. Radiation effects in monolithic SiC-based ceramics

Displacement threshold energies in β-SiC

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Abstract

We have calculated the displacement threshold energies (E_d) for C and Si primary knock-on atoms (PKA) in β-SiC using molecular dynamic simulations. The interactions between atoms were modeled using a modified form of the Tersoff potential in combination with a realistic repulsive potential obtained from density-functional theory calculations. The simulation cell was cubic, contained 8000 atoms and had periodic boundaries. The temperature of the simulation was about 150 K. Our results indicate strong anisotropy in the E_d values for both Si and C PKA. The displacement threshold for Si varies from about 36 eV along [001] to 113 eV along [111], while E_d for C varies from 28 eV along [111] to 71 eV along [111]. These results are in good agreement with experimental observations. © 1998 Elsevier Science B.V.

1. Introduction

Silicon carbide (SiC) is a wide band gap (~2.4–3.3 eV) semiconductor with high-power and high-frequency electronic device applications in radiation and high-temperature environments. It has potential uses in space stations, advanced fighter aircraft, proposed fusion reactors and the petroleum and automotive industries [1–3]. In addition, SiC-based composite materials are candidates for use as low-activation structural materials in fusion reactors because they possess desirable physical, mechanical and thermal properties [4]. SiC is known to exist in the form of more than a 100 polytypes, of which β- or 3C-SiC is cubic and the rest are hexagonal and referred to collectively as α-SiC. The polytypes are all made of corner-sharing SiC_4 and CSi_4 tetrahedra but differ in the planar stacking sequence along a principal crystallographic axis [3]. For the applications discussed above, β-SiC is of considerable interest in addition to the 6H and 4H forms of α-SiC. The cubic polytype has the zinc blende structure with a lattice constant a_0 of about 4.35 Å and a band gap of about 2.4 eV.

Both semiconductor doping by ion-implantation and long-term operation in a radiation environment result in the production of atomic-scale defects by the displacement mechanism. The evolution of these non-equilibrium defects determines the ultimate performance of the material. In spite of the technological importance of SiC, the production and evolution of displacement damage in this material is not well understood. One of the principal material parameters that determines the extent of this damage is the displacement threshold energy (E_d). This is defined as the minimum energy needed to displace an atom from its lattice site. Experimental estimates of E_d in SiC differ by nearly an order of magnitude and the reasons for these differences are unclear [5–12].

Electron irradiation in a high-voltage electron microscope (HVEM) is one of the commonly used experimental techniques to determine E_d. This method provides a discrete value along a particular direction. Hudson and Sheldon [5] determined E_d for Si atoms along [111] in β-SiC to be 106 eV from the minimum electron energy to form defects visible in the HVEM. A subsequent study [6], using the same technique, reported values of 90, 54 and 54 eV along [111], [110] and [100], respectively in β-SiC. The authors ascribed these energies to the displacement of carbon atoms. The ⟨0001⟩ direction in α-SiC is similar to the ⟨111⟩ in β-SiC in that it is perpendicular to the

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Table 1
Summary of electron irradiation experiments leading to amorphization in < 0001 > α-SiC

	Ref.		
	[8]	[7]	[9]
Flux (m^{-2} s^{-1})	1.5×10^{23}	$0.5–1.1\times10^{24}$	$2.5–4.3\times10^{24}$
Temperature (K)	20	163	140
Critical voltage (kV)	650	725	180
Highest fluence (m^{-2})	3.6×10^{27}	1.8×10^{27}	8.85×10^{27}

close-packed plane. Inui et al. [7] determined the threshold energy for Si in 6H α-SiC to be 97 eV along ⟨0001⟩ from the minimum electron energy needed for amorphization at 163 K.

In many of these HVEM studies, it is not clear whether the observed effect should be attributed to the Si or C sublattice. This can lead to more than a factor of 2 uncertainty in the value of E_d estimated from the threshold energy of the incident electron. In addition, the lowest voltage at which amorphization occurs in HVEM experiments may depend on the electron flux. This is demonstrated in Table 1 which shows the flux, temperature, critical voltage for amorphization and the highest fluence used in three electron irradiation experiments of ⟨0001⟩ α-SiC [7–9]. For irradiation at the highest flux, the lowest voltage at which amorphization was observed was 180 kV in contrast to about 700 kV for the two lower flux irradiations. In addition to HVEM experiments, minority carrier lifetime measurement [10], electron spin resonance [11] and Rutherford back scattering [12] have been used to determine E_d in SiC. Unlike the HVEM irradiations, these techniques provide values averaged over various crystal orientations. The values range from about 20 to 60 eV with the lower end corresponding to C displacement.

In an effort to understand the differences in the available experimental data, several molecular dynamics simulations of displacement production in SiC have been performed. In such simulations using realistic potentials, the displacement energy for each species can be determined along various crystallographic directions. El-Azab and Ghoniem [13] calculated the average E_d to be 16.3 and 92.6 eV, respectively, for C and Si in β-SiC using the Pearson potential [14]. E_d for Si is considerably higher than the average value of about 30 eV recommended by Zinkle and Kinoshita [15] based on experimental evidence. Huang et al. [16] have pointed out that the Pearson potential is unsuitable for studying defects in SiC as it fails to reproduce equilibrium properties. Instead, they recommend the Tersoff potential [17] for these calculations. Wong et al. [18] have calculated E_d for Si and C along various low-index directions in β-SiC using the Tersoff potential. Their results indicate that E_d for Si is less than that for C along [001]. Moreover, along [111], the thresholds are more than a factor of two less than those measured from HVEM experiments [5,7].

Recently, the C parameters in the Tersoff potential were modified to provide a better fit to diamond than to graphite [19,20]. The new parameters constitute an improvement for simulations of β-SiC. In addition Tang and Yip [21] have recommended modifications to the cutoff distance, the distance at which the interatomic potential goes to zero. In the new scheme, the cutoff distances are scaled with the system volume to avoid certain unphysical effects associated with the original Tersoff potential. In an effort to obtain a better understanding of the displacement process, we have performed a molecular dynamics simulation of displacement events in β-SiC using the Tersoff potential with the modifications discussed above. In addition, we have used a realistic repulsive potential [22] from ab initio calculations, instead of the ZBL universal repulsive potential [23], to describe the short-range atomic interactions.

2. Details of the simulation

The molecular dynamic simulations in the present study were performed using the computer code MDCASK [24]. The code was run on the T3D massively parallel computer at Lawrence Livermore National Laboratory. The simulation cell consisted of 8000 atoms (10 × 10 × 10 unit cells) and had periodic boundaries. The energy, volume and number of particles were kept constant during the simulation (microcanonical ensemble). Since experimental studies have shown that reproducible values of E_d are obtained at temperatures below 300 K [6], the initial temperature of the simulation was set to 150 K.

The interactions between the atoms were modeled using the Tersoff potential [17,19,20] with cutoff distances scaled with the cell volume [21]. The energy E as a function of distance r_{ij} between atoms i and j, and the angle θ_{ijk} between the ij and ik bonds is given by

$$E = \tfrac{1}{2}\sum_{i\neq j} V_{ij} = \tfrac{1}{2}\sum_{i\neq j} f_c(r_{ij})\left[A_{ij}\exp(-\lambda_{ij}r_{ij}) - b_{ij}B_{ij}\exp(-\mu_{ij}r_{ij})\right]. \tag{1}$$

The cutoff function is

$$f_c(r_{ij}) = \begin{cases} 1, & r_{ij} \leq R_{ij}, \\ 0.5 + 0.5\cos\left[\pi\dfrac{r_{ij}-R_{ij}}{S_{ij}-R_{ij}}\right], & R_{ij} < r_{ij} \leq S_{ij}, \\ 0, & r_{ij} > S_{ij}, \end{cases} \tag{2}$$

and the bond-order parameter is given by

$$b_{ij} = \chi_{ij}\left(1 + \zeta_{ij}^{n_i}\right)^{-1/2n_i}, \tag{3}$$

where

$$\zeta_{ij} = \sum_{k \neq i,j} f_c(r_{ik}) \beta_i g(\theta_{ijk}), \tag{4}$$

and

$$g(\theta_{ijk}) = 1 + \frac{c_i^2}{d_i^2} - \frac{c_i^2}{d_i^2 + (h_i - \cos\theta_{ijk})^2}. \tag{5}$$

λ_{ij} and μ_{ij} are arithmetic averages and A_{ij}, B_{ij}, R_{ij}, and S_{ij} are geometric averages of the corresponding i and j values. Since there are several versions of the Tersoff potential, the parameters and cutoffs used in this study are shown in Table 2. This potential provides a good description of the equilibrium properties of β-SiC such as the lattice constant, elastic constants and cohesive energy. However, it does not provide a satisfactory description of the short-range interactions which are important from the point of view of atomic displacement and defect creation. To overcome this deficiency, the Tersoff potential has to be used in conjunction with a repulsive potential, usually the ZBL universal potential [23], at close separations. The ZBL potential, which is fit using eight free parameters, can lead to errors in the potential energy of the order of 10% in some parts of the fitting regime [22].

Table 2
Parameters of the Tersoff potential used in the present work. See the text for a description of the parameters

	C	Si
A (eV)	1544.8	1830.8
B (eV)	389.63	471.18
λ (Å^{-1})	3.4653	2.4799
μ (Å^{-1})	2.3064	1.7322
β	4.1612×10^{-6}	1.1×10^{-6}
n	0.99054	0.78734
c	19981	100390
d	7.034	16.217
h	-0.33953	-0.59825
R (Å)	1.8	2.7
S (Å)	2.1	3.0
$\chi_{\mathrm{Si-C}} = 1.0086$		

Table 3
The repulsive potential $V_{\mathrm{R}}(r)$ and its derivative $\mathrm{d}V_{\mathrm{R}}(r)/\mathrm{d}r$

r (Å)	$V_{\mathrm{R}}(r)$ (eV)	$\mathrm{d}V_{\mathrm{R}}(r)/\mathrm{d}r$ (eV/Å)
0.004	2.93×10^5	-8.04×10^7
0.010	1.12×10^5	-1.22×10^7
0.040	2.27×10^4	-9.59×10^5
0.100	6.49×10^3	-1.04×10^5
0.200	2.04×10^3	-1.83×10^4
0.300	9.18×10^2	-6.82×10^3
0.400	4.53×10^2	-3.04×10^3
0.500	2.40×10^2	-1.43×10^3
0.600	1.37×10^2	-7.19×10^2
0.700	8.37×10^1	-3.92×10^2
0.800	5.31×10^1	-2.40×10^2
0.900	3.32×10^1	-1.65×10^2
1.000	1.93×10^1	-1.17×10^2
1.200	3.15	-5.05×10^1

In the present work, we have used an ab initio repulsive potential obtained from a cubic spline interpolation of data points at intervals varying from 0.001 to 0.1 Å. The data points were calculated using the DMol [25,26] software package which is based on density functional theory. This method has been found reliable by comparison to fully numerical Hartree–Fock calculations [22]. The repulsive potential $V_{\mathrm{R}}(r)$ was connected smoothly to the Tersoff potential $V_{\mathrm{T}}(r)$ using the Fermi function $F(r)$ [27]. The combined potential and the Fermi function are given, respectively, by

$$V(r) = [1 - F(r)]V_{\mathrm{R}}(r) + F(r)V_{\mathrm{T}}(r) \tag{6}$$

and

$$F(r) = [1 + \mathrm{e}^{-14(r-0.95)}]^{-1}, \tag{7}$$

where r is in Å. Table 3 lists the repulsive potential and its derivative for interatomic distances less than 1 Å, and Fig. 1 shows the graphical form of the combined potential $V(r)$ for distances greater than 1 Å.

The atoms in the simulation cell were allowed to attain equilibrium for 2.1 ps (2100 time steps) and then an atom near the center of the cell was given a kinetic energy of 20 to 120 eV with the velocity set along a certain direction. The atoms were allowed to relax for 3.9 ps following this recoil event and their positions, velocities and energies were recorded as a function of time and subsequently analyzed. The calculations were performed for several

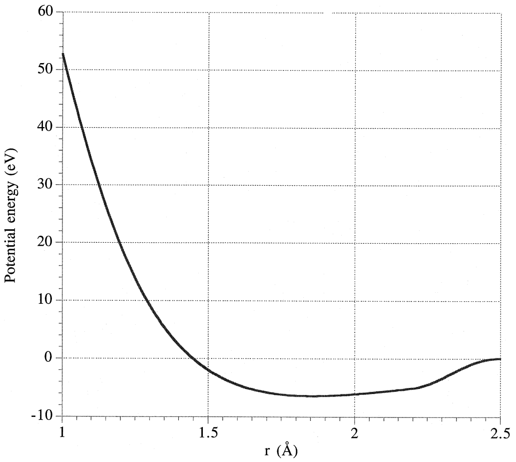

Fig. 1. Potential energy curve for β-SiC obtained by joining the ab initio repulsive and Tersoff potentials.

different energies along each recoil direction and the displacement energies were determined to an accuracy of 1 eV.

3. Results and discussion

Fig. 2 shows the potential energy and displacement of 25 and 30 eV C recoils along [111] as a function of time. Within 0.5 ps after the recoil event, the system relaxes to the final configuration and the kinetic energy of the recoil decays to nearly zero. This energy is absorbed by the other atoms in the cell. The resulting increase in the temperature of the cell was found to be less than 100 K for all the recoils examined in this study. When a C atom is given a kinetic energy of 25 eV, its potential energy increases by about 4 eV as the kinetic energy decays. However, within 0.5 ps, the potential energy returns to the original value which corresponds to a maximum displacement of $0.8a_0$ followed by the return of the PKA to its original position. This indicates that 25 eV is insufficient to displace C along [111].

For a 30 eV C recoil along [111], the potential energy at the final position increases by about 2.5 eV compared to the initial lattice site. The recoil comes to rest at a distance of $0.7a_0$ away from the starting position, which indicates the occurrence of atomic displacement. This suggests that the displacement threshold energy for C recoils along [111] in β-SiC is between 25 and 30 eV. By performing simulations at intermediate energies, we have determined the threshold energy to an accuracy of 1 eV. For instance, E_d for C along [111] is 28 ± 1 eV, which means that 27 eV is insufficient while 29 eV is enough to produce a displacement. The simulations were performed along several other low-index directions and a high-index direction $[77\bar{1}\bar{0}]$.

Table 4 lists the values of E_d for C and Si sublattices in β-SiC. The displacement threshold for C is less than that for Si in all directions examined except $[\bar{1}\bar{1}\bar{1}]$. E_d for C varies from a low of 28 eV along [111] to a high of 71 eV

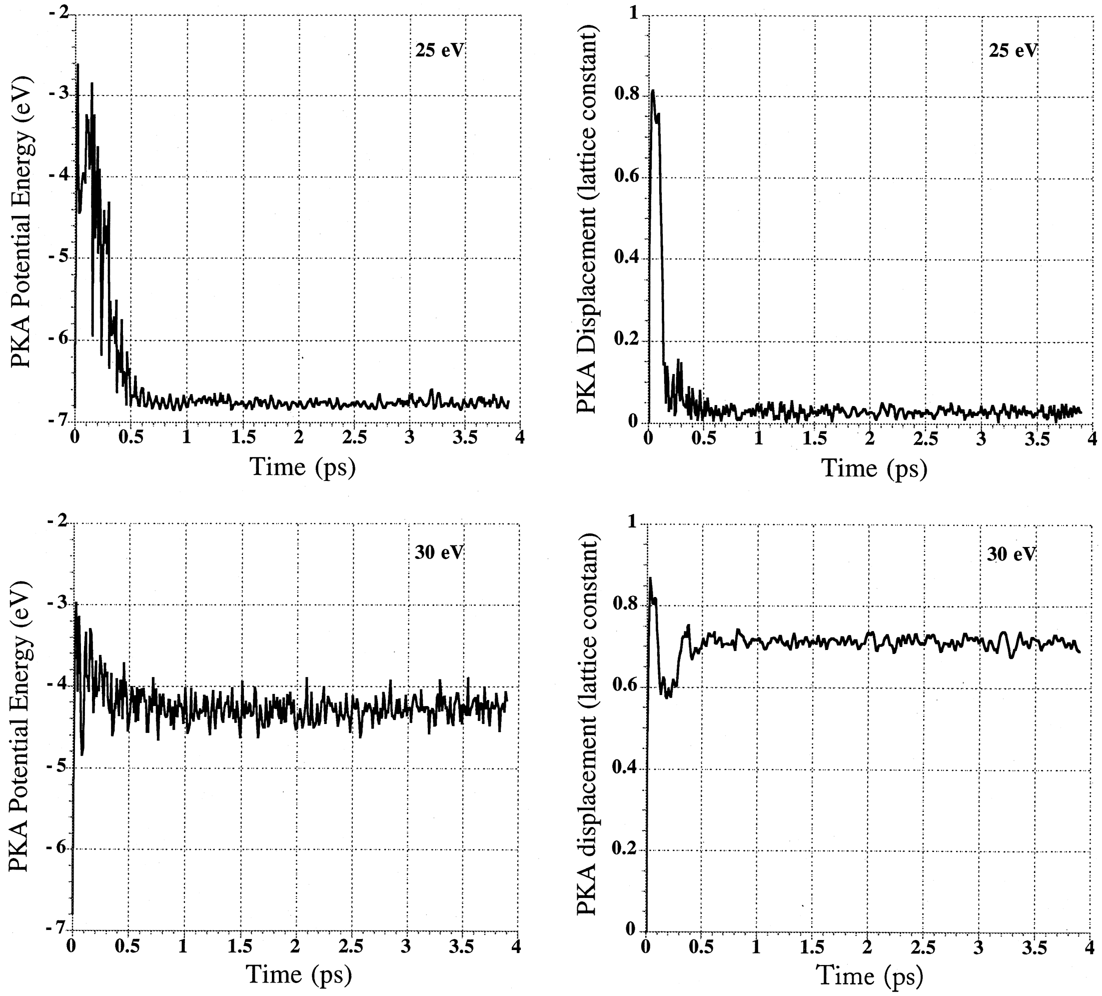

Fig. 2. The evolution of the potential energy and displacement of 25 and 30 eV C recoils along [111] in β-SiC.

Table 4
Displacement threshold energies (eV) for the C and Si sublattices in β-SiC

Direction	C	Si
[001]	31 ± 1	36 ± 1
[110]	38 ± 1	71 ± 1
[111]	28 ± 1	113 ± 1
[$\bar{1}\bar{1}\bar{1}$]	71 ± 1	39 ± 1
[$77\bar{1}0$]	36 ± 1	39 ± 1

along [$\bar{1}\bar{1}\bar{1}$]. For Si, the values range from 36 eV along [001] to 113 eV along [111]. The results indicate a large anisotropy in the displacement threshold in β-SiC. In addition, the [111] direction is not symmetric from the point of view of displacement events.

Fig. 3 shows a perspective view of the β-SiC crystal structure with an arrow indicating the [111] direction. A Si atom (black circle) moving along this direction encounters a C atom (white circle) at a distance of about 1.89 Å. However, in the opposite direction it does not directly encounter a C atom until a distance of about 5.66 Å. This should make the displacement of Si atoms difficult along [111] and much easier along [$\bar{1}\bar{1}\bar{1}$]. Our results show that E_d for Si is 113 eV along [111] but only 39 eV along [$\bar{1}\bar{1}\bar{1}$]. The E_d for C should follow the opposite trend which is also demonstrated by our results. Our calculated values for C are 28 eV along [111] and 71 eV along [$\bar{1}\bar{1}\bar{1}$]. The existence of this asymmetry was observed for the C sublattice in a previous work [18] but not for the Si sublattice. The high value of 113 eV calculated in this work for E_d of Si along [111] is consistent with the results of high-energy electron irradiation experiments [5–8].

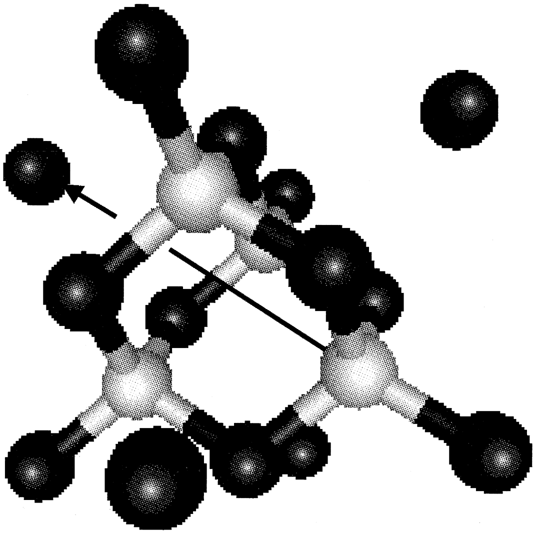

Fig. 3. The [111] direction in β-SiC in perspective view. The darker circles are Si atoms.

Along [001], the calculated thresholds are low (~ 35 eV) and the difference between the Si and C values is small. This is not surprising, because [001] in β-SiC is not a close-packed direction which should make displacements easy for both species. The E_d for C and Si along an arbitrarily chosen high-index direction, [$77\bar{1}0$], are similar to the values along [001]. Along [110], which is a close-packed direction, the calculated threshold energies are high, especially for Si which has a threshold of 71 eV. This direction is known to have a high displacement threshold energy [18].

The present calculations provide some insights into the large differences in the displacement threshold energy values of β-SiC estimated from experiments. Since the threshold energy varies significantly with crystallographic orientation, data obtained from electron irradiation experiments along discrete directions will show considerable scatter. In addition, the asymmetry in the atomic arrangement along [111] can lead to different results for irradiations along [111] and [$\bar{1}\bar{1}\bar{1}$]. For the five crystallographic directions examined, the average E_d values are about 40 eV for C and 60 eV for Si. This is in reasonable agreement with the value of 60 eV from the electron spin resonance technique [11]. Along several of the directions examined, the threshold energies were found to be about 30 eV for C and 40 eV for Si. We recommend these values for use in TRIM calculations [23]. Further work is currently under way to study the properties of point defects in β-SiC.

4. Summary

We have used a combination of ab initio repulsive and Tersoff potentials to perform molecular dynamics simulations of displacement events in β-SiC at about 150 K. Our results show that the displacement threshold energy can vary strongly with crystallographic direction from 28 to 71 eV for C and from 36 to 113 eV for Si. There is a large difference between the [111] and [$\bar{1}\bar{1}\bar{1}$] directions for both species due to the asymmetry in the atomic arrangement along this direction. In general, E_d is lower for C than for Si. Our results are in reasonable agreement with experimental findings.

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