



Nucleation and growth of vacancy clusters in β -SiC during irradiation

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A B S T R A C T

Molecular dynamics and molecular static calculations have been performed using the empirical many-body interatomic potential to obtain the formation and binding energies of relaxed configuration of vacancy clusters in β -SiC, which are necessary when the nucleation and growth process of clusters is investigated. The formation energy of vacancy clusters in β -SiC depends on the size, vacancy composition, and vacancy configuration of clusters. When the size and vacancy composition of clusters are given, the vacancy configuration of clusters with the lowest formation energy is primarily given so as to take the smallest number of dangling bonds. Especially when the fraction of the number of silicon vacancies to the number of carbon vacancies in a cluster is quite high or quite low, the formation property of antisite defects in clusters becomes a key factor to determine the stable configuration of clusters.

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1. Introduction

SiC/SiC composites are one of the promising candidates for the blanket structural material of fusion reactors, because of high stability at high temperature. Microstructural changes in the material during irradiation have been reported in literatures [1], where voids are observed by the transmission electron microscopy (TEM) when irradiation temperature is greater than about 1273 K. This temperature range for void formation in β -SiC is much greater than those in other materials proposed as the blanket structural material.

As a first step towards constructing a model for simulating microstructural evolution in β -SiC during irradiation, the formation and binding energies of vacancy clusters in β -SiC were evaluated as a function of the size, vacancy composition, and vacancy configuration of clusters.

2. Procedure

The formation energy of vacancy clusters in β -SiC was calculated using molecular dynamics (MD) and molecular static (MS) calculations. Interatomic potential employed here was the Gao-Weber potential [2], which was obtained by modifying the Tersoff potential [3] to improve the description of the property of self-interstitial atoms (SIAs) in β -SiC. This is the Brenner-type bond-order potential [4], where the potential energy of an atom in a crystal can primarily be determined by the number and type of atoms within the first nearest neighbor distance.

Firstly, a vacancy cluster was introduced into an otherwise perfect β -SiC crystal with the constant volume under 3-D periodic boundary condition. The crystal size was $10a_0 \times 10a_0 \times 10a_0$, where $a_0 = 0.436$ nm is the lattice constant. This crystal contains 4000 silicon lattice sites and 4000 carbon lattice sites. In the present calculations, all possible configurations of vacancies in a cluster were considered and employed as the initial positions of vacancies. The system was then kept at the finite temperature for 50–80 ps, during which atomic configuration around the cluster was fully relaxed by the effect of the finite temperature, although the positions of vacancies did not change at all during the relaxation, without the exceptional cases for clusters with very high fraction ($n_V^{\text{Si}}/n_V^{\text{C}}$) or for those with very low fraction, where n_V^{Si} and n_V^{C} denote the numbers of silicon- and carbon-vacancies in a cluster, respectively. Temperatures used here for relaxation were 100, 300, 600, 800, 1000 and 1300 K. Finally, the system was quenched to 0 K to obtain the converged value of total potential energy. The simulated quenching continued for 5–20 ps. Note that, this combined method with MD and MS techniques [5] can provide more relaxed configuration of defect clusters than a simple static relaxation method [6]. Actually, lower activation energy for vacancy migration in β -SiC was obtained by this combined method [7]. In the present calculations, the lowest formation energy of vacancy clusters was chosen among the energies obtained using several temperatures employed for the relaxation, and listed as a function of the size, vacancy composition, and vacancy configuration of clusters.

The formation energy of vacancy clusters is defined as energy required for introducing a vacancy cluster into an otherwise perfect β -SiC crystal, which is given by

$$E_F(n_V^{\text{Si}}, n_V^{\text{C}}) = E^{\text{tot}} - N_{\text{Si}}\varepsilon_{\text{Si}} - N_{\text{C}}\varepsilon_{\text{C}}, \quad (1)$$

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where N_{Si} and N_{C} are the numbers of silicon atoms and carbon atoms in the system, respectively, with the relation of $N_{\text{Si}} = 4000 - n_{\text{V}}^{\text{Si}}$ and $N_{\text{C}} = 4000 - n_{\text{V}}^{\text{C}}$. E^{tot} is the total potential energy of a relaxed system containing the cluster. $\varepsilon_{\text{Si}} = -6.21$ eV and $\varepsilon_{\text{C}} = -6.61$ eV are the calculated cohesive energies of a silicon atom and a carbon atom in a perfect β -SiC crystal, respectively. Using the formation energy thus evaluated, the binding energy of silicon vacancies to a cluster is given by

$$E_{\text{B}}^{\text{Si-V}}(n_{\text{V}}^{\text{Si}}, n_{\text{V}}^{\text{C}}) = E_{\text{F}}(1, 0) + E_{\text{F}}(n_{\text{V}}^{\text{Si}} - 1, n_{\text{V}}^{\text{C}}) - E_{\text{F}}(n_{\text{V}}^{\text{Si}}, n_{\text{V}}^{\text{C}}), \quad (2)$$

and the binding energy of carbon vacancies to a cluster is given by

$$E_{\text{B}}^{\text{C-V}}(n_{\text{V}}^{\text{Si}}, n_{\text{V}}^{\text{C}}) = E_{\text{F}}(0, 1) + E_{\text{F}}(n_{\text{V}}^{\text{Si}}, n_{\text{V}}^{\text{C}} - 1) - E_{\text{F}}(n_{\text{V}}^{\text{Si}}, n_{\text{V}}^{\text{C}}), \quad (3)$$

where $E_{\text{F}}(1, 0)$ and $E_{\text{F}}(0, 1)$ are the formation energies of an isolated silicon vacancy and an isolated carbon vacancy, respectively.

3. Results and discussion

The formation energies of an isolated silicon-vacancy and an isolated carbon-vacancy in β -SiC were calculated to be $E_{\text{F}}(1, 0) = 3.49$ eV and $E_{\text{F}}(0, 1) = 2.56$ eV, respectively. A carbon vacancy has the dilatational displacement field, where 1st nearest neighbor (1NN) silicon atoms are displaced by $0.09a_0$ away from the vacancy and 2nd nearest neighbor (2NN) carbon atoms are displaced by $0.01a_0$ away from 1NN atoms. A silicon vacancy has also the dilatational displacement field with the same amount of atomic displacements as above.

The formation energy of vacancy clusters in β -SiC depends, not only on the numbers ($n_{\text{V}}^{\text{Si}}, n_{\text{V}}^{\text{C}}$), but also on the vacancy configuration of clusters, which is, as a first approximation, represented by the number of dangling bonds in the cluster. It was, in many cases, observed that a vacancy cluster with the fixed numbers ($n_{\text{V}}^{\text{Si}}, n_{\text{V}}^{\text{C}}$) takes the lowest formation energy when the number of dangling bonds in the cluster is the smallest. Besides, vacancy absorption process by a vacancy cluster is considered to occur so as to reduce the total number of dangling bonds in the system. This suggests that the number of dangling bonds is a good indicator for providing the lowest formation energy of clusters. Table 1 is a list of the calculated formation energy of a cluster with ($n_{\text{V}}^{\text{Si}}, n_{\text{V}}^{\text{C}}$), which is the lowest among the calculated energies depending on the vacancy configuration of the cluster.

Fig. 1 shows the size dependence of the lowest formation energy of clusters listed in Table 1, where cluster size is defined by $n = n_{\text{V}}^{\text{Si}} + n_{\text{V}}^{\text{C}}$. As shown in the figure, the lowest formation energy is an increasing function of n . Consider an empirical relationship for void formation energy as described by $E_{\text{F}} = 4\pi R^2 \gamma (1 - \delta/R)$ [5,8], where γ is the surface energy for flat surface, δ is a constant, and R is void radius having a relationship with n as $4\pi R^3/3 = n\Omega$. Here, Ω is the atomic volume, and the second term in this equation represents a correction term due to the curvature of void surface. When the calculated formation energies of vacancy clusters with $n_{\text{V}}^{\text{Si}}/n_{\text{V}}^{\text{C}} = 1$ were used to fit to the empirical expression,

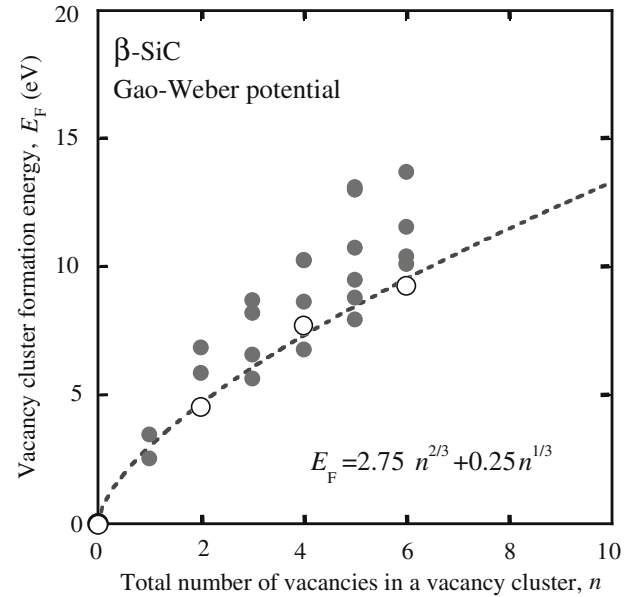


Fig. 1. The lowest formation energy of vacancy clusters in β -SiC as a function of cluster size, $n = n_{\text{V}}^{\text{Si}} + n_{\text{V}}^{\text{C}}$, where n_{V}^{Si} and n_{V}^{C} are the numbers of silicon- and carbon-vacancies in a cluster. The open and closed circles indicate clusters with $n_{\text{V}}^{\text{Si}}/n_{\text{V}}^{\text{C}} = 1$ and with $n_{\text{V}}^{\text{Si}}/n_{\text{V}}^{\text{C}} \neq 1$, respectively.

$\gamma = 11.98$ eV/nm² was obtained. Surprisingly, this value is in good agreement with the calculated surface energies of $\gamma = 10.25, 13.50, 17.25, 21.88$ and 25.60 eV/nm² for (111), (110), (211), (100)Si and (100)C flat surfaces, respectively. It indicates that the classical expression of spherical void energy agrees well with the formation energy of nanovoids as small as one vacancy. Note that, calculated formation energies obtained here for vacancy clusters in β -SiC are much higher than those in bcc Fe [5], and are comparable to those for SIA clusters in β -SiC [9].

Tables 2 and 3 represent the binding energy of vacancies to a vacancy cluster in β -SiC. Roughly speaking, the binding energy of carbon vacancies to a silicon-vacancy rich cluster is relatively high, while the binding energy of carbon vacancies to a carbon-vacancy rich cluster is low and, in some cases, it is negative. Similarly, the binding energy of silicon vacancies to a silicon-vacancy rich cluster is relatively low, while the binding energy of silicon vacancies to a carbon-vacancy rich cluster is very high.

Especially when the fraction $n_{\text{V}}^{\text{Si}}/n_{\text{V}}^{\text{C}}$ is quite high or quite low, the binding energy of vacancies to a cluster shows that the cluster is thermally unstable. For example, consider the process: $\text{V}_1^{\text{Si}}\text{V}_4^{\text{C}} + \text{V}_1^{\text{C}} \rightarrow \text{V}_1^{\text{Si}}\text{V}_5^{\text{C}}$. During the process, two silicon atoms individually having two dangling bonds are newly created, as schematically shown in Fig. 2(a). Because of the presence of the two silicon atoms with very high potential energy, the cluster is unstable with very low binding energy. It indicates that, not only the to-

Table 1

Calculated formation energy of the most stable vacancy clusters in β -SiC as a function of the numbers of silicon vacancies and carbon vacancies in the cluster in the unit of eV. The superscript (a) indicates the spontaneous creation of antisite defects.

No. of carbon vacancies in a cluster, n_{V}^{C}	No. of silicon vacancies in a cluster, n_{V}^{Si}					
	0	1	2	3	4	5
0	0.00	3.49	6.87	8.22 ^a	10.27 ^a	13.12 ^a
1	2.56	4.56	6.60	8.67	10.76	13.73 ^a
2	5.89	5.66	7.70	9.51	11.58	
3	8.72	6.80	8.81	9.29		
4	10.28 ^a	7.97	10.13			
5	13.03 ^a	10.42				

Table 2

Calculated binding energy of carbon vacancies to a vacancy cluster in β -SiC as a function of the numbers of silicon vacancies and carbon vacancies in the cluster in the unit of eV.

No. of carbon vacancies in a cluster, n_{V}^{C}	No. of silicon vacancies in a cluster, n_{V}^{Si}					
	0	1	2	3	4	5
0						
1		1.49	2.83	2.11	2.07	1.95
2		-0.77	1.46	1.46	1.72	1.74
3		-0.27	1.42	1.45	2.78	
4		1.00	1.39	1.24		
5		-0.19	0.11			

Table 3

Calculated binding energy of silicon vacancies to a vacancy cluster in β -SiC as a function of the numbers of silicon vacancies and carbon vacancies in the cluster in the unit of eV.

No. of carbon vacancies in a cluster, n_V^C	No. of silicon vacancies in a cluster, n_V^{Si}					
	0	1	2	3	4	5
0			0.11	2.14	1.44	0.64
1	1.49	1.45	1.42	1.40	1.40	0.52
2	3.72	1.45	1.68	1.42		
3	5.41	1.48	3.01			
4	5.80	1.33				
5	6.10					

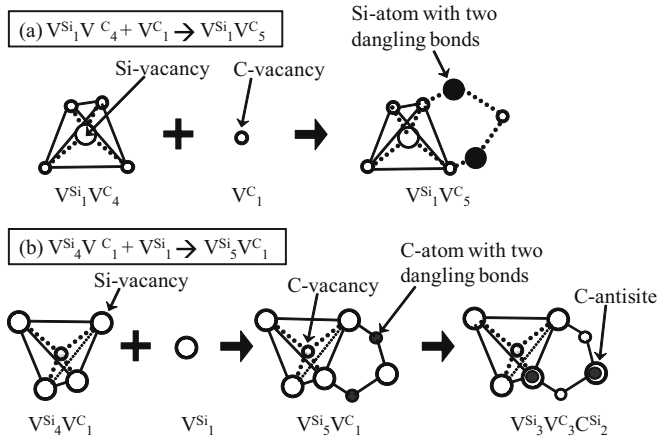


Fig. 2. Schematic representation of vacancy absorption process by (a) a carbon-vacancy rich cluster ($V_1^{Si} V_4^C$) cluster and (b) a silicon-vacancy rich cluster ($V_4^{Si} V_1^C$) cluster. Carbon antisite defects are spontaneously created in a $V_4^{Si} V_1^C$ cluster.

tal number of dangling bonds in the system, but also the number of dangling bonds per an atom is an important factor for evaluating the formation energy of clusters. Furthermore, when the reaction process: $V_4^{Si} V_1^C + V_1^{Si} \rightarrow V_5^{Si} V_1^C$ is considered, additional reaction occurs during the process, as shown in Fig. 2(b), where two carbon atoms with two dangling bonds are firstly produced as is similar to the above, and then such atoms spontaneously move and occupy vacant silicon sites to be carbon antisite defects. These spontaneous structural changes in a $V_5^{Si} V_1^C$ cluster were not observed in a $V_1^{Si} V_5^C$ cluster. This asymmetric behavior between silicon-vacancy rich clusters and carbon-vacancy rich clusters is probably caused by the difference of formation properties between silicon antisites and carbon antisites in clusters, as discussed below.

In a perfect β -SiC crystal with the zincblende-type structure of the equilibrium lattice constant $a_0^{\text{equil}} = 0.436$ nm, there are only Si–C bonds with an equilibrium separation distance of 0.189 nm. In a pure silicon crystal of the diamond-structure with $a_0^{\text{equil}} = 0.543$ nm, the equilibrium Si–Si bond length is 0.235 nm. Moreover, in a pure carbon crystal of the diamond-structure with $a_0^{\text{equil}} = 0.356$ nm, the equilibrium C–C bond length is 0.154 nm. When a silicon antisite is created in a β -SiC crystal with the zincblende-type structure, a silicon atom at an antisite position is surrounded by four silicon atoms, as is similar to the environment of a silicon atom in a perfect silicon crystal with the diamond-structure. The only difference between the environments is the bond length: the length of Si–Si bond associated with a silicon antisite in β -SiC is 0.189 nm, which is smaller than the equilibrium Si–Si bond length of 0.235 nm. It indicates that the Si–Si bond in β -SiC is in the compressive field. On the other hand, the C–C bond length associated with a carbon antisite in β -SiC is 0.189 nm that is larger than the equilibrium C–C bond length (0.154 nm). It indicates that

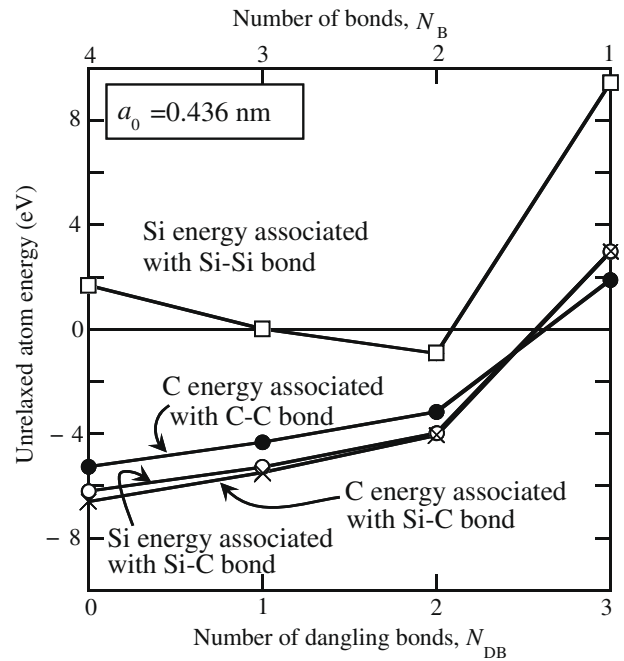


Fig. 3. Energy of an atom in an unrelaxed β -SiC crystal with the lattice constant of $a_0 = 0.436$ nm, as a function of the number of dangling bonds. Energy of a carbon atom of the C–C bond associated with a carbon antisite in β -SiC is an increasing function of the number of dangling bonds, similar to the case of the energy of silicon and carbon atoms individually located at regular sites in β -SiC crystal. On the other hand, energy of a silicon atom associated with the Si–Si bond in β -SiC shows very high and partly a decreasing function of N_{DB} .

the C–C bond of carbon antisite in β -SiC is in the tensile field. As shown in Fig. 3, this difference of the state of bonds associated with antisite defects created in a β -SiC crystal of $a_0 = 0.436$ nm produces the differences of atom potential energy. Namely, the compressive Si–Si bond has high potential energy and is very difficult to be produced in β -SiC, while the tensile C–C bond has relatively low potential energy and is easily created in β -SiC. The former property determines the behavior of carbon-vacancy rich clusters ($V_1^{Si} V_5^C$), and the latter property determines the behavior of silicon-vacancy rich clusters ($V_5^{Si} V_1^C$).

4. Summary

MD and MS calculations have been performed to evaluate the formation energy of vacancy clusters in β -SiC. The formation energy of vacancy clusters in β -SiC depends on the size, vacancy composition, and vacancy configuration of clusters. The vacancy configuration of clusters with the lowest formation energy is determined by the number of dangling bonds in the cluster and by the property of antisite defect formation in the cluster.

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