J Mater Sci (2009) 44:1828–1833
DOI 10.1007/s10853-008-3180-2

The energetics of helium and hydrogen atoms in β-SiC: an ab initio approach

Jong Hyun Kim · Yong Duk Kwon · Parlindungan Yonathan · Ikhwan Hidayat · June Gunn Lee · Jung-Hae Choi · Seung-Cheol Lee

Received: 3 September 2008 / Accepted: 10 December 2008 / Published online: 3 February 2009
© Springer Science+Business Media, LLC 2009

Abstract Silicon carbide is a prime candidate for plasma-facing materials in future fusion reactors. The formation energies of various interstitial configurations of helium and hydrogen atoms in β-SiC were estimated based on density functional theory. Special consideration was given to the helium and hydrogen interstitials as the bubble seeds in β-SiC. From an energetic point of view, only one helium atom could position itself into the tetrahedral sites. However, up to three hydrogen atoms could easily position themselves into the tetrahedral sites by forming a stable H_2 molecule or a 3H-trimer that was newly identified in this study. Based on the different behaviors of helium and hydrogen, an explanation is proposed for the experimental observations of bubble formation in irradiated β-SiC.

Introduction

Silicon carbide (SiC) is an excellent material for a number of applications. It is a remarkable structural material due to extraordinary properties at high temperatures and under high mechanical stresses.

J. H. Kim (✉) · Y. D. Kwon · P. Yonathan · I. Hidayat · J. G. Lee
School of Materials Science and Engineering, Yeungnam University, 214-1 Dae-dong, Gyeongsan-si 712-749, South Korea
e-mail: ttongkaji@ynu.ac.kr

J.-H. Choi · S.-C. Lee
Computational Science Center, Korea Institute of Science and Technology, Cheongryang, P.O. Box 131, Seoul 130-650, South Korea

SiC is also a wide band-gap semiconductor and is considered one of the best candidates for high-temperature and high-power electronic devices. Furthermore, SiC is a prime candidate for plasma-facing materials in future fusion reactors, due to its low induced radioactivity as well as excellent thermo-mechanical properties.

However, as a fusion-reactor material SiC has a critical issue with tolerance to radiation damages from high-energy particles of plasma. The interaction of high energetic particles with matters is a complex phenomenon. The impinging particles are normally slowed down by collisions with atoms. In the process, however, the displacement of lattice atoms leads to the creation and accumulation of various defects.

In a fusion process, besides the displacement damage, significant amounts of helium (He) and hydrogen (H) will be produced and will cause additional damage to materials. At the first wall, for example, the He and H production rates are approximately 1,500 appm (atomic parts per million)/MWa/m^2 and 500 appm/MWa/m^2, respectively. Therefore, the accumulation and retention of He and H in SiC is one of the main concerns in fusion materials research.

The effects of He and H on the structural and mechanical properties of metals and alloys are extensively reported and documented. Nevertheless, such information was relatively scarce for ceramic materials, especially for SiC. Recently, however, there has been a noticeable increase in the number of studies on SiC as a fusion material.

Various experiments were performed to investigate the microstructure changes of SiC by implantations of He ions [1, 2], by multi-ion beam implantation [3], and by neutron irradiation [4]. Point defects, line defects, and defect clusters were observed after implantation and irradiation, which led to amorphous structure even at a relatively low

level of 0.3 dpa (displacements per atom) and at temperatures even below room temperature [5].

At higher temperatures, in parallel with gas escape, the combination and accumulation of mobile defects create bigger defects, such as bubbles, voids and cavities [6–10]. He and H interstitials in the SiC structure were identified as one of the main causes for these defects. Consequently, swelling in SiC up to 10 volume percent has been reported due to the above mentioned types of damage [11–14]. Although recovery from swelling takes place with increasing temperature, complete recovery is not attained even after long annealing periods at 1000 K [15, 16], which implies the existence of trapped and relatively immobile He and H atoms in the SiC structure.

In addition, it was reported that the mechanical properties of SiC are reduced up to 20% by the deleterious effects of these He and H atoms together with the displacement damage [17]. It was also reported that an H atom could play a role in enhancing bubble nucleation and also in increasing the numbers of bubbles in SiC [3, 18].

Various efforts have been undertaken to minimize swelling in SiC under irradiation by improving the manufacturing process of SiC, which was demonstrated by the team at Kyoto University [19, 20]. Another focus is the identification of the mechanism on bubble formation in SiC. Chen and Jung [2] observed higher bubble formation along grain boundaries of β-SiC with a clear dependence of bubble appearance on the type of boundary. Taguchi et al. [21] also reported similar observations, that He bubbles mainly formed at SiC grain boundaries at an irradiation temperature of 1000 °C. On the other hand, He bubbles formed both at SiC grain boundaries and within grains at an irradiation temperature of 1300 °C.

The role of H atoms on bubble formation in SiC is not clear. It is believed that, relatively speaking, an H atom is less able to accumulate into bubbles. Miwa et al. [3] reported a strong effect of He on cavity swelling up to 10 dpa, while notable effects of H on cavity swelling only occurred under heavy irradiation by H ions above 10 dpa. Hojou et al. [22] reported bubble formation under very heavy irradiation by H ions (above 4.8×10^{18} H/cm^2) followed by electron irradiation. They believed that implanted H atoms trapped in the dangling bonds of amorphous SiC were knocked out by electron irradiation and coagulated with each other to form bubbles.

Other researchers [23–26] have focused on calculations based on density functional theory (DFT) for the various defect-related systems of SiC in relation not only to fusion materials but also to H-passivation as a semiconductor. Van Ginhoven et al. [23] calculated the formation energies of He insertions and their activation energies for diffusion in cubic silicon carbide at the presence of point defects. Aradi et al. [24] identified the stable configurations of hydrogen and dihydrogen defects in SiC.

Eberlein et al. [25] presented the structure, diffusion and rotational energies, and the vibrational modes of the hydrogen molecule in the hexagonal part of 4H–SiC and in 2H–GaN. They reported that, in both materials, the hydrogen molecule is stable and aligned along the c-axis. Calculation by Kaukonen et al. [26] found that only singly positive or negative charge states of H were thermodynamically stable in SiC. They identified various stable H_2 molecules in the tetrahedral site surrounded by silicon atoms in SiC. Furthermore, they suggested that charged H ions may diffuse to form an electrically inactive H_2 molecule, which may in turn cluster to bigger H complexes.

In spite of all these experiments and computations, the picture of bubble formation by He and H atoms in SiC is far from clear, mainly because of the complexities involved, ranging from the atomic scale to the macro scale. In computational studies, only one He or up to two H atoms in the interstitial sites of SiC were considered, although the interstitial sites might trap more atoms, especially in the case of H atoms.

In this study, β-SiC was investigated by ab initio simulation to identify the atomic scale behaviors of He and H in relation to the bubble formation that is frequently observed in most SiC materials under irradiation. Special consideration was given to the tetrahedral sites in β-SiC that can provide proper space for several foreign atoms. Up to four He or four H atoms were introduced into these sites to evaluate the possibility of stable complex formations with He or H atoms that have never been reported before. In addition, the differences in behavior of He and H atoms were identified in terms of bubble nucleation in β-SiC.

Computational method

A $2 \times 2 \times 2$ supercell of β-SiC containing 64 atoms (32 silicon atoms and 32 carbon atoms) was generated as the base structure for the simulations to minimize the defect–defect interactions and electrostatic effects within a moderate computing capability. All calculations were carried out based on DFT using the Vienna ab initio simulation package (VASP) [27, 28].

The interactions between electrons and ions were described by projector augmented wave (PAW) potentials [29, 30]. The exchange-correlation energy of electrons was calculated by the Perdew–Burke–Ernzerhof (PBE) parameterization [31] within generalized-gradient approximation (GGA) with spin polarization considered. An energy cutoff of 400 eV and the k-point mesh of $4 \times 4 \times 4$ by the Monkhorst-Pack scheme [32] were used. Brillouin-zone

integration was performed by using the tetrahedron method with Bloch corrections [33].

β-SiC in our simulation model was assumed to be stoichiometric, and the charge states of defects were not considered, because our focus was on the small clusters of He or H in relation to the formation of bubbles. The formation energy of various defect systems with interstitials, E^f_{system}, were defined at the identified ground states as

$$E^f_{\text{system}} = E_{\text{system}} - E^{\text{bulk}}_{\text{SiC}} - nE^{\text{atom}}_{\text{He,H}} \quad (1)$$

where E_{system} is total energy of system with defects, $E^{\text{bulk}}_{\text{SiC}}$ is total energy of perfect supercell of β-SiC, $E^{\text{atom}}_{\text{He,H}}$ is energy of single He or H atom, respectively, and n is number of He or H atoms added to the supercell of β-SiC.

The lattice constant and cohesive energy of the bulk β-SiC were estimated to be 4.39 Å and 12.97 eV/SiC, respectively. These values are in accordance with the values reported from experiments [34, 35] and from calculations [36]. We used this lattice constant as the reference, and in all of our calculations, the atomic positions of each configuration with He or H atoms up to four were fully relaxed in a strain-free condition by appropriate adjustments of the cell volume.

Results and discussion

He atoms in β-SiC

SiC is a typical covalent-bond solid that leads to a relatively lower packing of atoms and, hence, has rather larger sites for interstitials: tetrahedral sites with C (carbon) atoms as the first neighbors and with Si (silicon) atoms as the first neighbors. In this study, He and H impurities were only considered to fill these tetrahedral sites of β-SiC, as schematically shown in Fig. 1. This is because they are the most probable sites for the foreign atoms, such as He and H atoms, which can lead to the nucleation and growth of bubbles in β-SiC.

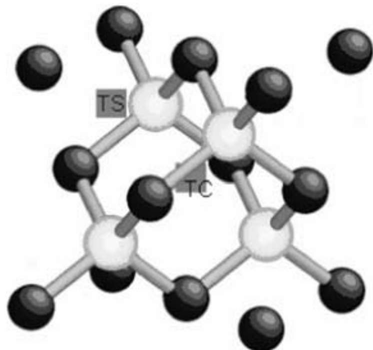

Fig. 1 Schematics of interstitial sites in β-SiC: TC site at the center of tetrahedron made of four C atoms (grey) and TS site at the center of tetrahedron made of four Si atoms (black)

Table 1 Formation energies (eV/defects) of He interstitials in β-SiC

No. of He atoms	in TC site (eV/defects)	in TS site (eV/defects)
1	3.31	2.87
2	6.10 (1 He-in-TC + 1He-in-TS)	9.42
4	11.47 (4 He-in-TS)	12.35 (3 He-in-TC + 1 He-in-TS)

The formation energies of He interstitials in β-SiC were calculated by taking He as an isolated atom as the reference state and are summarized in Table 1. The formation energies for a single He interstitial in the TC site (tetrahedral site surrounded by four C atoms) and the TS site (tetrahedral site surrounded by four Si atoms) were 3.31 eV and 2.87 eV, respectively. The centers of each tetrahedral site were identified as the most stable positions for the He atom.

Locating two He atoms in the TC site spontaneously stabilized into one He-in-TC plus one He-in-TS. Hence, its formation energy, 6.10 eV, is very close to the sum of one He-in-TC plus one He-in-TS in their isolated states. Locating two He atoms in the TS site, however, simply increased the formation energy to 9.42 eV with a volume expansion of 0.7%.

Locating four He atoms in the TC site spontaneously stabilized into four He-in-TS, while locating four He atoms in the TS site led to three He-in-TC plus one He-in-TS. Figure 2 shows one example of the simulation results that initially started as β-SiC with four He atoms in the TS site. In this case, the volume expansion was 2.8%. Owing to the inert nature of He atoms, no significant bonding between He atoms and the host atoms was observed in all the cases.

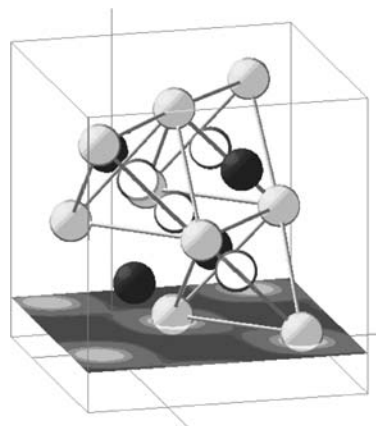

Fig. 2 Schematics of the relaxed β-SiC–4He system showing three He-in-TC (white) surrounded by four C atoms (grey) and one He-in-TS (white) surrounded by four Si atoms (black)

In summary, the results indicate that the number of He atoms that can be stabilized into β-SiC is limited to only one, preferably in a TS site. However, it still requires a relatively high formation energy of 2.87 eV. This clearly implies the limited role of He interstitials in the process of bubble nucleation. This further implies that for bubble formation, it is necessary for He atoms to associate with other space-providing defects, such as vacancies or grain boundaries.

H atoms in β-SiC

The formation energies of H interstitials in β-SiC were calculated by taking H as an isolated atom as the reference state and are summarized in Table 2.

In general, the TS site seems be more likely to receive H atoms. The formation energies for single H interstitials in TC and TS sites were 0.78 eV and 0.48 eV, respectively. However, the most stable H was identified as the H–C complex between Si and C in the carbon-filled TS site with a formation energy of 0.36 eV. The bonding was mostly formed with C with distances of 1.10 Å.

Placing two H atoms in the TC and TS sites markedly decreased the formation energy to 0.21 eV and −1.10 eV, respectively. The distances between H atoms were 0.77 Å in the TC site and 0.72 Å in the TS site, which are close to the bonding distance of H_2 molecules in the gas phase by our calculation (0.74 Å) and another calculation (0.73 Å) [37]. All these results strongly suggest the formation of stable H_2 molecules in β-SiC in agreement with other calculations [25, 26]. Similar behaviors of H atoms in Si have also been reported [38, 39].

Placing three H atoms in the TC site, as shown in Fig. 3a, increased the formation energy only slightly, to 0.29 eV, by forming a 3H-trimer with a volume expansion of 0.7%. The existence of this relatively stable complex has never been reported. It was noted that three H atoms in the tetrahedron formed significant bonds with each other.

Placing three H atoms in the TS site further decreased the formation energy to −1.29 eV by forming a stable H_2 molecule plus a H–C complex at the bond-center between Si and C. As shown in Fig. 3b, one H atom spontaneously moved to a neighboring C atom.

Table 2 Formation energies (eV/defects) of H interstitials in β-SiC

No. of H atoms	in TC site (eV/defects)	in TS site (eV/defects)
1	0.78	0.48 (0.36[a])
2	0.21 (H_2)	−1.10 (H_2)
3	0.29 (3H Trimer)	−1.29 (H_2 + H–C)
4	−0.27 (H_2 + two H–C)	−1.49 (H_2 + two H–C)

[a] At the bond-center between Si and C in the carbon-filled TS

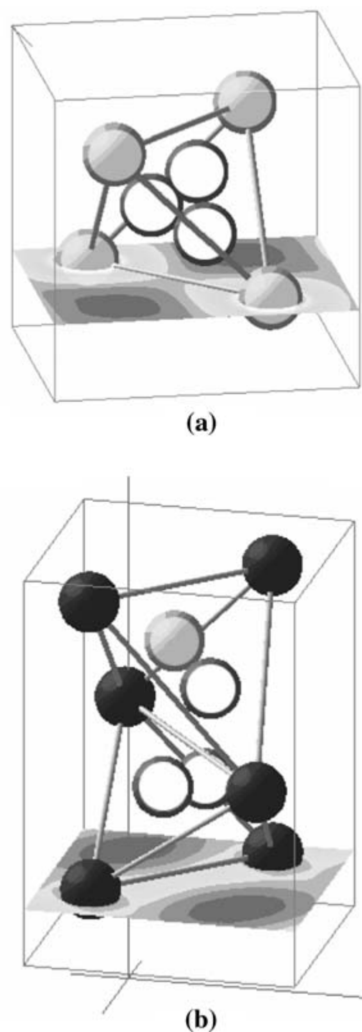

Fig. 3 Schematics of the β-SiC system with three H atoms (white) **a** in the TC site, showing a 3H-trimer, and **b** in the TS site showing an H_2 molecule plus an H–C complex (C atoms: grey, Si atoms: black)

Placing four H atoms in TC and TS interstitial sites was found to be only an extension of the SiC–3H cases. Four H atoms in the TC site stabilized into an H_2 molecule plus two H–C complexes, as shown in Fig. 4a, while four H atoms in the TS site stabilized into an H_2 molecule plus two H–C complexes, as shown in Fig. 4b. Considering their formation energies, we note that the H–C complexes formed together with an H_2 molecule have a lower formation energy by 0.55 $\sim$ 0.60 eV than that of the H–C complex alone, presumably due to the distorted structures around them because of the presence of the nearby H_2 molecule.

In summary, it is quite clear that the H atom always prefer to bond either with other H atoms if they are available or with C atoms, which have higher electronegativity. Contrary to the case of He atoms, the TC site in β-SiC could hold up to three H atoms with formation

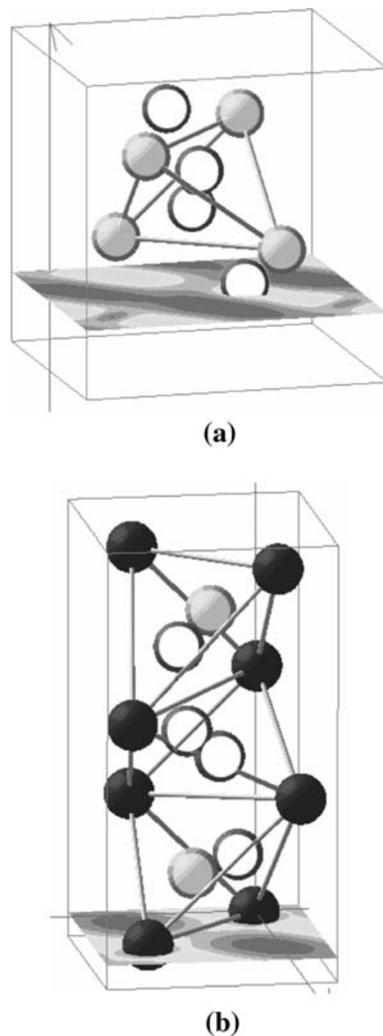

Fig. 4 Schematics of the β-SiC system with four H atoms (white) **a** in TC site **b** in TS site (C atoms: grey, Si atoms: black)

energy of 0.29 eV, while the TS site could hold two H atoms with formation energy of −1.10 eV.

This implies that, unlike the He atoms, H atoms may not need to find other spacious positions other than the TC or TS sites in β-SiC. The relatively high stability of these trapped H atoms can limit their mobility to assemble into bubbles. This leads to the conclusion that not H atoms but He atoms could be the leading cause of bubble formations in β-SiC, although H atoms can cause swelling by volume expansion. Further study is underway on the behaviors of He and H atoms in β-SiC with the presence of vacancies.

Conclusions

The energetics of various interstitial configurations in the β-SiC with He and H atoms were calculated using DFT.

Only a single He interstitial is energetically feasible in β-SiC. Therefore, He atoms have to associate with other space-providing defects, such as vacancies or grain boundaries, to nucleate and form bubbles.

H atom always prefer to bond either with other H atoms or with C atoms in β-SiC. When two H atoms are available, they always formed a stable H_2 molecule.

Up to three H atoms could easily be positioned into the TC sites in β-SiC by forming a newly identified 3H-trimer with a formation energy of 0.29 eV. Two H atoms could easily be positioned into the TS sites in β-SiC by forming an H_2 molecule with a negative formation energy of −1.10 eV.

In contrast to He atoms, H atoms may not need to find other spacious positions other than the TC or TS sites in β-SiC. The relatively high stability of these trapped H atoms can limit their mobility to assemble into bubbles. This leads to the conclusion that not H atoms but He atoms could be the leading cause of bubble formations in β-SiC.

Acknowledgements The authors wish to acknowledge partial support for this research by the NURI (New University Regional Innovation) Project (04-A-A-08) of the Korean Government. The authors also wish to acknowledge partial support for this research by the Korea Science and Engineering Foundation (KOSEF) Grant (R11-2008-072-01003-0/S.C.L/J.H.C) of the Korea Government.

References

1. Hojou K, Furuno S, Kushita KN, Otsu H, Izui K (1992) J Nucl Mater 583:191
2. Chen J, Jung P (2000) Ceram Int 26:513
3. Miwa S, Hasegawa A, Taguchi T, Igawa N, Abe K (2005) Mater Trans 46(3):536
4. Suzuki T, Yano T, Mori T, Miyazaki H, Iseki T (1995) Fusion Technol 27:314
5. Katoh Y, Kishimoto H, Kohyama A (2002) Mater Trans 43(4):612
6. Kishimoto H, Katoh Y, Kohyama A, Ando M (2002) In: Proceeding of the 20th international symposium: effects of radiation on materials, ASTM STP 1405, vol 345, West Conshohocken, PA, 2002
7. Nogami S, Hasegawa A, Abe K, Taguchi T, Yamada R (2000) J Nucl Mater 283(87):268
8. Jung P, Klein H, Chen J (2000) J Nucl Mater 283(87):806
9. Katoh Y, Kishimoto H, Kohyama A (2002) J Nucl Mater 307(11):1221
10. Ryazanov AI, Klaptsov AV, Kohyama A, Katoh Y, Kishimoto H (2004) Phys Scrip T111:195
11. Snead LL (1998) J Nucl Mater 253:20
12. Hollenberg GW (1995) J Nucl Mater 219:70
13. Senor DJ, Youngblood GE, Brimhall JL, Trimble DJ, Newsome GA, Woods JJ (1996) Fusion Technol 30:956
14. Huang H, Ghoniem NM (1997) J Nucl Mater 250:192
15. Kishimoto H, Katoh Y, Kohyama A, Ando M (2000) In: Proceedings of the second Asian–Australasian conference on composite materials, ACCM-2000, vol 2, pp 733–738
16. Pramono Y, Imai M, Yano T (2003) J Nucl Sci Technol 40(7): 531
17. Hasegawa A, Nogami S, Aizawa T, Katou K, Abe K (2002) J Nucl Mater 307–311(2):1152

18. Kai JJ, Chen FR, Keng HT, Tseng TH (2005) Cavity formation in SiC/SiC composites during Multi-ion beam irradiation at elevated temperatures, Presented at EUROMAT, Prague, Czech 2005
19. Hinoki T, Ozawa K, Kishimotoand H, Kohyama A (2006) In: Proceeding of 7th IEA WS on SiC/SiC composites, Petten, The Netherlands, 2006
20. Nozawa T, Ozawa K, Kondo S, Hinoki T, Katoh Y, Snead LL, Kohyama A (2006) In: Proceeding of the 22nd symposium STP1475 ASTM International, USA
21. Taguchi T, Igawa N, Miwa S, Wakai E, Jitsukawa S, Snead LL, Hasegawa A (2004) J Nucl Mater 335(3):508
22. Hojou K, Furuno S, Izui K (2006) J Electron Microscopy 40(3):157
23. Van Ginhoven RM, Chartier A, Meis C, Weber WJ, Corrales LR (2006) J Nucl Mater 348:1–2, 51–59
24. Aradi B, Gali A, Deák P, Lowther JE, Son NT, Janzen E, Choyke WJ (2001) Phys Rev B 63:245202
25. Eberlein TAG, Huggett L, Jones R, Briddon PR (2003) Physica B Condensed Matter 340:171
26. Kaukonen M, Fall CJ, Lento J (2003) Appl Phys Lett 83:923
27. Kresse G, Joubert D (1999) Phys Rev B 59:1758
28. http://cms.mpi.univie.ac.at/vasp, Vienna ab initio simulation package (VASP) 2008
29. Kresse G, Furthmüller J (1996) Comp Mater Sci 6:15
30. Blöchl PE (1994) Phys Rev B 50:17953
31. Perdew JP, Burke K, Ernzerhof M (1996) Phys Rev Lett 77:3865
32. Monkhorst HJ, Pack JD (1976) Phys Rev B 13:5188
33. Blöchl PE, Jepsen O, Andersen OK (1994) Phys Rev B 49:16223
34. Heyd J, Scuseria GE (2004) J Chem Phys 121:1187
35. Deák P, Buruzs A, Gali A, Frauenheim T (2006) Phys Rev Lett 96:236803
36. Tongay S, Durgun E, Ciraci S (2004) Appl Phys Lett 85(25):6179
37. Kolandaivel P, Suba N, Senthilkumar K (2000) Int J Quantum Chem 76:662
38. Gharaibeh M, Estreicher SK, Fedders PA, Ordejón P (2001) Phys Rev B 64:235211
39. Estreicher SK, Wells K, Fedders A, Ordejón P (2001) J Phys Cond Matt 13:6271