Available online at www.sciencedirect.com
SCIENCE DIRECT
Physica B 376–377 (2006) 350–353
PHYSICA B
www.elsevier.com/locate/physb

Positron study of electron irradiation-induced vacancy defects in SiC

A. Kawasuso[a,*], M. Yoshikawa[b], H. Itoh[b], R. Krause-Rehberg[c], F. Redmann[c], T. Higuchi[d], K. Betsuyaku[d]

[a]*Advanced Science Research Center, Japan Atomic Energy Research Institute, Gunma 370-1299, Japan*
[b]*Takasaki Establishment, Japan Atomic Energy Research Institute, Gunma 370-1299, Japan*
[c]*Martin-Luther University, Halle D-06108, Germany*
[d]*Mizuho Information and Research Institute, Tokyo 101-8843, Japan*

Abstract

Based on positron annihilation experiments, we have proposed that in 3C-SiC isolated silicon vacancies are responsible for positron trapping after electron irradiation. We have also proposed that in hexagonal SiC one type of vacancy defects survives after annealing at 1000 °C which is attributable to carbon–vacancy–carbon–antisite complexes or silicon–vacancy–nitrogen pairs, while carbon vacancies, silicon vacancies and divacancies are excluded. In this study, from the theoretical calculations of positron lifetime and Doppler broadening of annihilation radiation, the above proposals are confirmed.

PACS: 61.72.Ji; 61.72.Cc; 61.72.Bb; 61.80.Fe

Keywords: SiC; Positron annihilation

1. Introduction

To characterize defects in SiC induced by fast particle irradiation, we have been studying both cubic and hexagonal SiC irradiated with fast electrons using positron annihilation spectroscopy [1]. We showed that isolated silicon vacancies (V_{Si}) act as effective positron trapping centers in 3C-SiC irradiated with MeV electrons [1–3]. No carbon vacancies (V_C) are detected apparently. Also, no further vacancy clusters and vacancy-related complexes are found after the thermal annealing of isolated silicon vacancies at 1000 °C. On the other hand, we showed that in hexagonal SiC one type of vacancy defects survives even at 1000 °C where isolated silicon vacancies disappear [1,4–7]. We recently proposed that the above vacancy defects are attributable to carbon–vacancy carbon-antisite (V_CC_{Si}) complexes or silicon–vacancy nitrogen ($V_{Si}N_C$) pairs, while divacancies ($V_{Si}V_C$) are excluded [8]. In this paper, we review the above circumstances with theoretical data on positron lifetime and Doppler broadening.

2. Experiment and calculation

Samples used in this study were chemical-vapor-deposition-grown n-type 3C-SiC, 4H- and 6H-SiC and modified-Lely-grown n-type 6H-SiC. These were subjected to electron irradiation with energy of 2 MeV and fluence of $3 \times 10^{17}\,e^-/cm^2$ at room temperature. Positron lifetime and Doppler broadening measurements were performed. The details are described elsewhere [1–8].

Theoretical calculations were performed to obtain positron lifetimes and Doppler broadening spectra for small vacancies and vacancy clusters in the same manner that we reported elsewhere [3,8]. Briefly, we used super-cells composed of 128 Si atoms and 128 C atoms for the perfect 3C-SiC lattice and 48 Si atoms and 48 C atoms for the perfect 4H-SiC lattice. We also examined 6H-SiC, but the results are nearly the same as those obtained for 4H-SiC. Hence, we will not state the case of 6H-SiC here. Vacancy defects were generated by removing appropriate atoms.

*Corresponding author. Tel.: +81 27 346 9331; fax: +81 27 346 9432.
E-mail address: ak@taka.jaeri.go.jp (A. Kawasuso).

0921-4526/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.physb.2005.12.090

Valence electron wavefunctions were computed using the abinit4.1.4 code [9] with the cut-off energy of 60 Ry. Lattice relaxations were taken into consideration for V_C [10], V_{Si} [10–12], V_CC_{Si} [10–12], $V_{Si}N_C$ [13] and $V_{Si}V_C$ [14] while not for vacancy clusters. We used the Slater-type core wavefunction parameterized by Clementi and Roetti [15] to mimic the results of the Hartree–Fock calculation. Self-consistent positron wavefunctions were obtained based on the two-component density-functional theory in order to minimize the energy functional. The Boronski–Nieminen enhancement factor was used with the semiconductor model proposed by Puska [16]. Using the conventional scheme, electron–positron momentum distributions and positron lifetimes were computed.

3. Results and discussion

3.1. 3C-SiC

After electron irradiation of 3C-SiC with energies greater than 0.5 MeV, prolonged positron lifetimes and enhanced (reduced) $S(W)$ parameters have been observed. The annealing behavior of the observed positron lifetime and S parameter well coincides with that of electron spin resonance (ESR) T_1 signal intensity attributed to single negative silicon vacancies (V_{Si}) [1,2]. Therefore, it is proposed that positrons are mainly trapped at V_{Si} in electron-irradiated 3C-SiC. Below we explain this fact with theoretical supports.

Table 1 lists the calculated positron lifetime and Doppler broadening parameters for various vacancy defects in 3C-SiC with the published experimental lifetime and $S(W)$ parameters [1–3,17]. Fig. 1 shows the ratio curves of coincidence Doppler broadening (CDB) spectra, i.e., $N(p)/N_{bulk}(p)$, where $N(p)$ denotes the original CDB spectrum. The experimental CDB ratio curve for isolated silicon vacancies is also shown together. The calculation shows that positron lifetime and $S(W)$ parameter for V_C increase (decrease) only slightly from the bulk values. The CDB ratio curve for a carbon vacancy is also very similar to that for the bulk. These are due to the weak localization of positrons at carbon vacancies because of the strong Coulomb repulsion from the nearest neighbor Si atoms. The binding energy of a positron to a carbon vacancy is also estimated to be rather small (less than 50 meV). Thus, the detection of carbon vacancies may be problematic when they coexist with the other types of vacancy defects and/or at high temperatures where de-trapping effect becomes sufficient. Contrarily, for silicon vacancies, both positron lifetime and $S(W)$ parameters increase (decrease) sufficiently from the bulk values. The binding energy is also high enough to localize positrons at V_{Si}. These are the reasons why silicon vacancies are preferentially detected in positron annihilation experiments.

Positron lifetime and $S(W)$ parameters obtained with the relaxed geometry of V_{Si} given by Zywietz et al. [10] are in good agreement with the experiment, but the values with the ideal geometry are not. Therefore, the amount of lattice

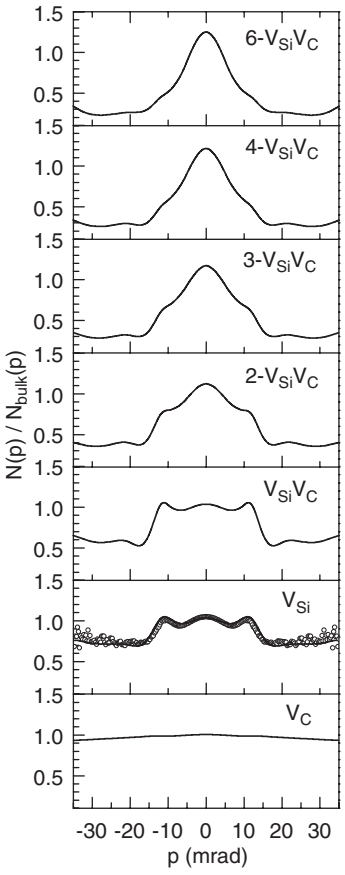

Fig. 1. Calculated CDB ratio curves for various vacancy type defects in 3C-SiC. Experimental data for V_{Si} obtained for 3C-SiC after irradiation with 2 MeV electrons with the fluence of 3×10^{17} e^-/cm^2 (open circles) are also plotted together.

Table 1
Calculated positron lifetime (τ), Doppler broadening parameters (S and W) and binding energy (E_B) for various vacancy defects in 3C-SiC

State	τ (ps)	S	W	E_B (eV)
Calculation				
Bulk	143	1.000	1.000	
V_C[a]	145	1.005	0.975	−0.01
V_{Si}[a]	190	1.031	0.715	1.7
$V_{Si}V_C$[b]	208	1.057	0.590	2.6
2-$V_{Si}V_C$	240	1.122	0.436	3.3
3-$V_{Si}V_C$	282	1.160	0.346	4.1
4-$V_{Si}V_C$	299	1.198	0.312	4.7
6-$V_{Si}V_C$	329	1.227	0.297	5.8
Experiment[c]				
V_{Si}	~190	1.028–1.039	0.805–0.834	

Values in bracket are the results calculated considering lattice relaxation. The windows for S and W parameters are 0–3 mrad and 15–30 mrad, respectively. The full-width at half-maximum of the resolution function is assumed to be 3.92 mrad (1 keV). In the last line, experimental values for isolated silicon vacancies are also presented.

[a]Calculated using relaxed geometry given by Zywietz et al. [10].

[b]Calculated using relaxed geometry given by Torppo et al. [15].

[c][1–3,17].

relaxation evaluated by Zywietz et al. is reasonable to explain the experiment. Furthermore, from Fig. 1, the overall shape of calculated CDB ratio curve agrees well with the experiment shown together. It is also reported that two-dimensional angular correlation of annihilation radiation (2D-ACAR) spectra for isolated silicon vacancies clearly exhibit the tetrahedral geometry of silicon vacancies [3]. Thus, the above discussion supports the previous identification of silicon vacancies as positron trapping centers.

Here, we also would like to demonstrate that positron lifetime and $S(W)$ parameters systematically increases (decreases) with the size of vacancy cluster. The positron lifetimes are in good agreement with those calculated by Brauer et al. [18] based on the linear muffin-tin orbital method. Present S parameters are calculated with the full-width at half-maximum (FWHM) of resolution function to be 3.92 mrad (1 keV in energy), which is common in CDB measurements. Assuming FWHM = 5.49 mrad (1.4 keV) which is common in single detector measurements, S parameter is reduced by approximately 17% in all the cases. S-parameter for 6-$V_{Si}V_C$ reported by Anwand et al. [19] is smaller than that calculated here. This discrepancy is probably due to resolution influence. Since the CDB ratio curve also systematically changes with the size of vacancy cluster as shown in Fig. 1, it can be used for estimating the size of vacancy cluster in addition to positron lifetime.

3.2. Hexagonal SiC

In the case of electron-irradiated hexagonal SiC, it should be noted that vacancy defects still survive after annealing at 1000 °C [1,4–7]. The observed positron lifetime is close to that for silicon vacancies (~190 ps). However, the above vacancy defects might be vacancy complexes but not be isolated silicon vacancies since isolated silicon vacancies already disappear below 1000 °C. Proposed candidates are V_CC_{Si}, $V_{Si}N_C$ and $V_{Si}V_C$ [8].

Table 2 lists the positron lifetimes and $S(W)$ parameters and binding energies calculated for various vacancy defects in 4H-SiC. The polytype dependences of these parameters are rather small and hence these results are basically applicable for 6H-SiC as well. Carbon vacancies act as very weak positron trapping centers similar to the case of 3C-SiC. Calculated positron lifetime for $V_{Si}V_C$ is longer than that observed in the experiments, while those for V_CC_{Si} and $V_{Si}N_C$ are comparable to the experiment. Fig. 2 shows the CDB ratio curves calculated for V_CC_{Si} and $V_{Si}N_C$ with the experimental curves for 6H- and 4H-SiC after 2 MeV electron irradiation and annealing at 1000 °C. (By the way, the CDB ratio curves for V_{Si}, $V_{Si}V_C$ and $V_{Si}N_C$ are rather similar to each other.) It is found that the shape of these curves are similar to each other at $|p|<20$ mrad. Only a difference appears at $|p|>20$ mrad, where the ratio curve for V_CC_{Si} increases with p while that for $V_{Si}N_C$ moderately increases. The increasing behavior of the ratio curve at $|p|>20$ mrad is due basically to the enhanced annihilation probability of positrons with carbon 1 s electrons but also

Table 2
Calculated positron lifetime (τ), Doppler broadening parameters (S and W) and binding energy (E_B) for various vacancy defects in 4H-SiC

State	τ (ps)	S	W	E_B (eV)
Bulk	142	1.000	1.000	
V_C[a]	145	1.006	0.977	0.016
V_{Si}[a]	196	1.037	0.651	1.6
V_CC_{Si}[a]	184(168)	1.034(1.018)	0.658(0.747)	1.9(1.2)
$V_{Si}N$[b]	193(184)	1.027(1.021)	0.645(0.692)	1.5(1.5)
$V_{Si}V_C$[c]	215	1.054	0.575	2.0

Values in the bracket are the results for the cubic site, otherwise for the hexagonal site. For V_C, V_{Si} and $V_{Si}V_C$, site dependence was very small.
[a]Calculated using relaxed geometry given by Bockstedte et al. [12,13].
[b]Calculated using relaxed geometry given by Gerstmann et al. [14].
[c]Calculated using relaxed geometry given by Torppo et al. [15].

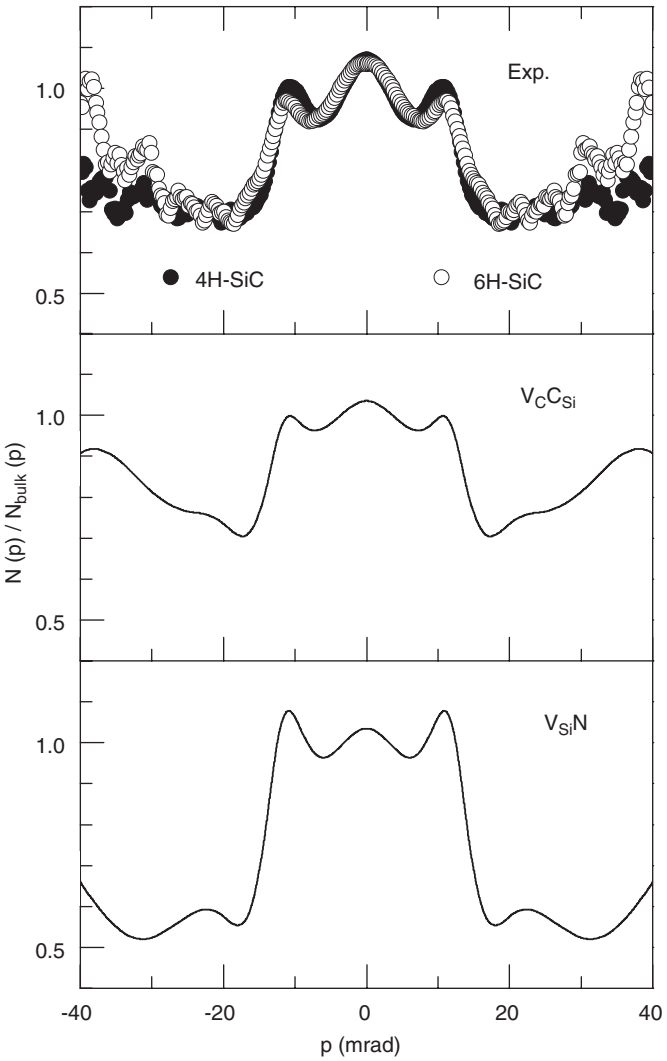

Fig. 2. Calculated CDB ratio curves for V_CC_{Si} and $V_{Si}N_C$ in 4H-SiC. Experimental CDB ratio curves for 6H- and 4H-SiC after irradiation with 2 MeV electrons with the fluence of 3×10^{17} e$^-$/cm^2 and subsequent annealing at 1000 °C for 30 min are also shown.

to the spatial distribution of positron wavefunction. If we consider the higher momentum regions, the calculation for V_CC_{Si} agrees with the experiment better than $V_{Si}N_C$. Although, in the previous 2D-ACAR study [8], the observed anisotropies of annihilation radiation are not distinguished for V_CC_{Si} and $V_{Si}N_C$, in the view point of CDB ratio curve, the V_CC_{Si} model is more preferred.

4. Summary

Positron lifetime and Doppler broadening of positron-electron annihilation radiation for various kinds of vacancy defects were theoretically calculated and compared with our previous data on electron-irradiated SiC. Theoretical calculation justifies the previous assignment of positron lifetime and Doppler broadening spectrum observed for electron-irradiated 3C-SiC to isolated silicon vacancies. It was shown that lattice relaxation is important to reproduce the observed positron lifetime. Also, the residual vacancy defects in hexagonal SiC after high temperature annealing ($>1000\,^{\circ}C$) can be attributed to V_CC_{Si}.

Acknowledgements

M. Bockstedte of Erlangen University is acknowledged for providing optimized atomic configurations of V_C and V_CC_{Si} obtained in their ab initio studies. This work was partly supported by the Alexander von Humboldt Foundation, the Nuclear Energy Fundamentals Crossover Research and Embedded High-Performance Computing (EHPC) Project of the Ministry of Education, Culture, Sports, Science and Technology, Japan.

References

[1] A. Kawasuso, et al., in: W.J. Choyke, H. Matsunami, G. Pensl (Eds.), Silicon Carbide—Recent Major Advances, Springer, Berlin, Heidelberg, NY, 2004, p. 563.
[2] A. Kawasuso, et al., Appl. Phys. A 67 (1997) 209.
[3] A. Kawasuso, et al., Phys. Rev. B 72 (2005) 45204.
[4] A. Kawasuso, H. Itoh, S. Okada, H. Okumura, J. Appl. Phys. 80 (1996) 5639.
[5] A. Kawasuso, et al., J. Appl. Phys. 82 (1997) 3232.
[6] A. Kawasuso, et al., J. Appl. Phys. 90 (2001) 3377.
[7] A. Kawasuso, et al., Appl. Phys. Lett. 79 (2001) 3950.
[8] A. Kawasuso, T. Chiba, T. Highchi, Phys. Rev. B 79 (2005) 193204.
[9] X. Gonze, et al., Comput. Mater. Sci. 25 (2002) 478.
[10] A. Zywietz, J. Furthmüller, F. Bechstedt, Phys. Rev. B 61 (2000) 13655;
A. Zywietz, J. Furthmüller, F. Bechstedt, Phys. Rev. B 59 (1999) 15166.
[11] M. Bockstedte, A. Mattausch, O. Pankratov, Phys. Rev. B 68 (2003) 205201.
[12] M. Bockstedte, A. Mattausch, O. Pankratov, Phys. Rev. B 69 (2003) 235202.
[13] U. Gerstmann, E. Rauls, T. Frauenheim, H. Overhof, Phys. Rev. B 67 (2003) 205202.
[14] L. Torpo, T.E.M. Staab, R.M. Nieminen, Phys. Rev. B 65 (2002) 85202.
[15] E. Clementi, C. Roetti, Atom. Data Nucl. Data 14 (1974) 177.
[16] M.J. Puska, R.M. Nieminen, Rev. Mod. Phys. 66 (1994) 841.
[17] A. Kawasuso, F. Redmann, R. Krause-Rehberg, M. Yoshikawa, K. Kojima, H. Itoh, Phys. Stat. Sol. (B) 223 (2001) R8.
[18] G. Brauer, W. Anward, E.-M. Nicht, J. Kuriplach, M. Šob, N. Wagner, P.G. Coleman, M.J. Puska, T. Korhonen, Phys. Rev. B 54 (1996) 2512.
[19] W. Anwand, G. Brauer, W. Skorupa, Appl. Surf. Sci. 194 (2002) 131.