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Polytype–dependent vacancy annealing studied by positron annihilation

A. Kawasuso[1], M. Yoshikawa[1], M. Maekawa[1], H. Itoh[1], T. Chiba[2], F. Redmann[3], R. Krause-Rehberg[3], M. Weidner[4], T. Frank[4], G. Pensl[4]

[1] Japan Atomic Energy Research Institute, Watanuki, 1233, Takasaki, Gunma, 370-1292, Japan
[2]National Institute for Materials Science, Namiki, 1-1, Tsukuba, 305-0044, Japan
[3] Martin-Luther-Universität, Friedemann-Bach-Platz 6, D-06108 Halle, Germany
[4] Universität Erlangen-Nürnberg, Staudtstrasse 7, D-91058 Erlangen, Germany

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Abstract. In this research we investigated the dependence of annealing behavior of vacancy defects on SiC polytype using positron annihilation spectroscopy. We found that vacancy defects in 3*C* SiC induced by electron irradiation and multiple-He implantation are annealed below 1100^{o}C while those in hexagonal SiC above 1200^{o}C. The amount of residual vacancy defects due to post-electron-irradiation annealing at 1000^{o}C increases as hexagonality. From two-dimensional angular correlation of annihilation radiation (2D-ACAR) measurements, it was confirmed that the positron annihilation center in electron-irradiated 3*C* SiC should be silicon vacancies with tetrahedral symmetry. Silicon vacancies should be constituents in vacancy defects responsible for positron trapping in electron-irradiated hexagonal SiC. However, 2D-ACAR experiment shows that the local symmetry is different from that for silicon vacancies in 3*C* SiC.

Introduction

We have so far been studying properties of vacancy defects in SiC induced by bombardment using positron annihilation spectroscopy [1-4]. It was confirmed that silicon vacancy related defects act as strong positron trapping centers in 3*C*, 4*H* and 6*H* SiC irradiated with electrons. Obtained displacement energy for Si site [4] was in good agreement with radiation damage theories [5]. By irradiation, silicon vacancies are created only in cubic sites in 3*C* SiC, while both in cubic and hexagonal sites in hexagonal SiC. In this research, we studied if properties of vacancy defects such as thermal stability and atomic structure are affected by the existence of inequivalent lattice sites.

Experiment

Specimens used in this study are chemical-vapor-deposition (CVD) grown *n*-type 3*C*, 4*H* and 6*H* SiC epilayers doped with nitrogen ([N]=5×10^{15}–1×10^{16} cm^{-3}). We also used modified-Lely-grown bulk *n*-type 6*H* SiC crystals doped with nitrogen ([N]=1×10^{17} cm^{-3}). These specimens were irradiated with 0.5-2 MeV electrons to various doses at room temperature. Multiple He-implantation was also conducted in a similar manner as ref. [3]. Isochronal annealing was done from 100 to 1700^{o}C for 30 min in vacuum or dry argon ambient. Positron annihilation (the Doppler broadening) measurements were performed using slow positron beams at room temperature. Positron annihilation measurements based on the angular correlation of annihilation radiation (ACAR) technique were carried out for 3*C* and bulk 6*H* samples using positrons directly emitted from a ^{22}Na source.

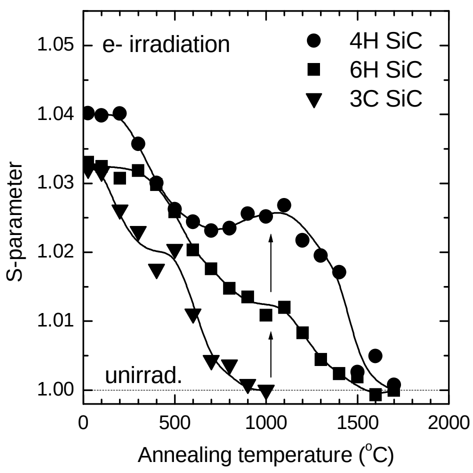

Fig. 1 Annealing behavior of normalized *S*-parameter for *n*-type 3*C*, 4*H* and 6*H* SiC epilayers after 2MeV electron irradiation to a dose of $3x10^{17}$ e^-/cm^2.

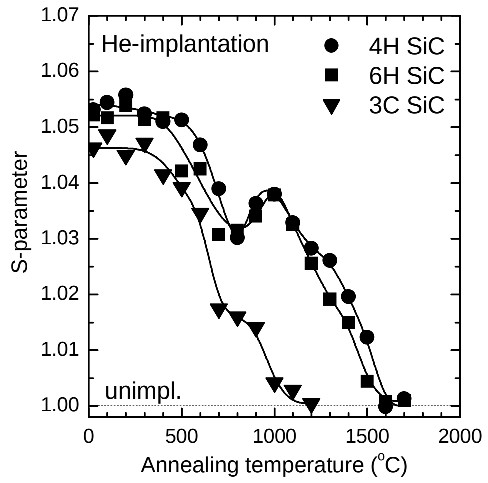

Fig. 2 Annealing behavior of normalized *S*-parameter for *n*-type 3*C*, 4*H* and 6*H* SiC epilayers after multiple He-implantation.

Results and Discussion

Figure 1 shows the annealing behavior of normalized *S*-parameters (peak intensities in the Doppler broadening spectra) for 3*C*, 4*H* and 6*H* SiC irradiated with 2MeV electrons to a dose of $3x10^{17}$ e^-/cm^2. Increased *S*-parameters after irradiation are clearly seen suggesting the generation of vacancy defects. In 3*C* SiC, *S*-parameter recovers to bulk values (*S*=1.00) in two steps first at around 200°C and then at 600-700°C. Above 1000°C, no other vacancy defects are detected. Since the above two-step annealing is typically seen for isolated silicon vacancies in positron lifetime and electron spin resonance measurements [6,7], we conclude that isolated silicon vacancies are responsible for positron trapping. The first annealing step was attributed to vacancy-interstitial mutual recombination and the second to migration of silicon vacancies themselves [7]. It is found that vacancy defects in both 4*H* and 6*H* SiC also exhibits two-step annealing. In the previous studies, we reported that vacancy defects in electron irradiated 4*H* and 6*H* SiC are originating from silicon vacancy related defects [1,2]. However, each annealing step for hexagonal SiC shifts to relatively higher temperature than that for 3*C* SiC. That is, the first annealing step for hexagonal SiC approximately overlaps with the second annealing for 3*C* SiC (600-700°C), and the second annealing steps appear far above that for 3*C* SiC (>1200°C). In contrast to the annealing of vacancy defects in 3*C* SiC below 1000°C, vacancy defects in hexagonal SiC have much higher thermal stabilities.

It is interesting to note that *S*-parameter after annealing at 1000°C increases in the order of 3*C* → 6*H* → 4*H* as indicated by arrows in Fig. 1. Considering that their hexagonalities are 0%, 33% and 50%, respectively, the concentration of residual vacancies after 1000°C annealing turns out to increase with hexagonality of SiC. Similar trends could be seen even when electron energies are varied below 2MeV. Although silicon vacancies are responsible for positron trapping in hexagonal SiC, the nature differs from isolated silicon vacancies in the case of 3*C* SiC.

Figure 2 shows the annealing behavior of normalized *S*-parameters for 3*C*, 4*H* and 6*H* SiC after multiple He-implantation. Doses of implanted He ions were well below amorphous generation level. It is found that *S*-parameter for 3*C* SiC decreases first at around 600°C and then at around 1000°C. The annealing step at 200°C as observed for electron-irradiated 3*C* SiC is not

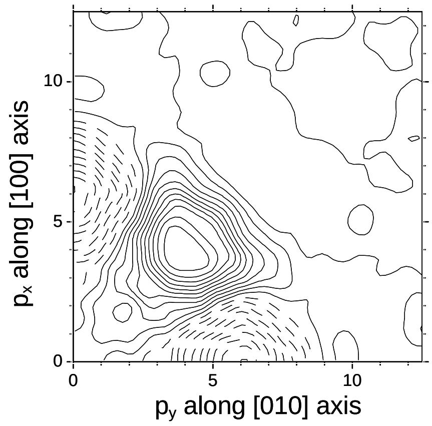

Fig. 3 ACAR spectrum from silicon vacancies in 3*C* SiC after 1MeV electron irradiation to a dose of 6x10^{17} e^{-}/cm^{2}. Solid and broken lines represent positive and negative values, respectively. Counter spacing is 10% to the maximum.

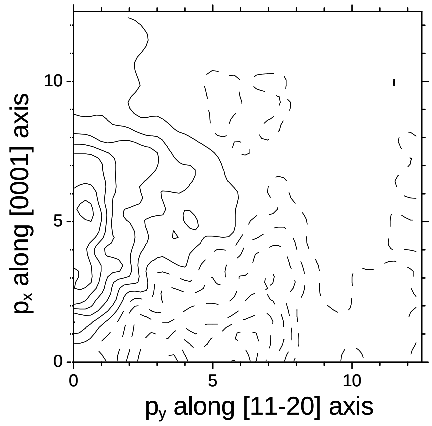

Fig. 4 ACAR spectrum from silicon vacancy related defects in 6*H* SiC after 2MeV electron irradiation to a dose of 3x10^{17} e^{-}/cm^{2}. Solid and broken lines represent positive and negative values, respectively. Counter spacing is 5% to the maximum.

observed here. Probably, after He-implantation the amount of defects responsible for the first annealing step is much higher than in the case of electron irradiation. Hence, such a broad annealing step appeared because of overlapping of the first and second annealing steps observed in electron irradiation. At round 1000^{o}C, one more annealing step is seen. This may be explained as the disappearance of residual vacancy defects, which could not be annealed at 600^{o}C. Above 1100^{o}C, no more vacancy defects are detected similarly to the case of electron irradiation.

The first annealing step for He-implanted 4*H* and 6*H* SiC at around 600^{o}C coincides with that for He-implanted 3*C* SiC. Therefore, probably similar kinds of vacancy defects are generated irrespective to polytype. It is seen that *S*-parameters for 4*H* and 6*H* SiC show prominent peaks after annealing at 1100^{o}C. It is inferred that during annealing defects become mobile and new complex defects are generated resulting the peaks in *S*-parameters. Such peaks are not seen in electron-irradiated 6*H* SiC and also in 3*C* SiC but a little increase appeared in electron-irradiated 4*H* SiC. Therefore, it is possible to say that such peaks, i.e., generation of complex defects, are enhanced in ion implanted hexagonal SiC. We reported that the peaks could be correlated with the generation of $Z_{1/2}$ and $RD_{1/2}$ levels in He-implanted 6*H* and 4*H* SiC, respectively [3]. After these peaks, *S*-parameters in both 4*H* and 6*H* SiC monotonically decrease and almost completely recover to the unimplanted level at 1700^{o}C. Carefully to see, *S*-parameter for 4*H* SiC is even higher than that for 6*H* SiC in between 1300^{o}C and 1600^{o}C. In this temperature range, no vacancy defects are detected for He-implanted 3*C* SiC. Thus, again we found that *S*-parameter increases in the order of 3C → 6H → 4H.

To extract information on local atomic arrangements concerning vacancy defects, we carried out two-dimensional angular correlation of annihilation radiation (2D-ACAR) measurements. Figures 3 and 4 shows the anisotropy plots of momentum densities associated with vacancy defects in electron-irradiated 3*C* and 6*H* SiC at [100]-[010] and [0001]-[11-20] projections, respectively. (Bulk components were already subtracted using intensities obtained from positron lifetime measurements.) The spectrum for 6*H* SiC was obtained after annealing at 1000^{o}C. It is found that momenta of electrons at vacancy defects in 3*C* SiC have a pronounced anisotropy along the [111] direction and a four-fold symmetry around the [001] axis. This directly shows that defects have a tetrahedral symmetry. Actually, the obtained ACAR spectrum can be well reproduced using linear combination of atomic orbital (LCAO) calculation taking into account of carbon 2*sp*^{3} electrons [4]. We also accomplished coincidence Doppler broadening measurements before [1,2]. Core electron momentum distribution obtained from this measurement exhibited the character for carbon 1*s* electrons suggesting that surrounding atoms around vacancies should be carbon atoms. This further indicates that observed defects are related to silicon vacancies and not to carbon vacancies.

On the other hand, the electron momentum distribution for vacancy defects in 6*H* SiC shows an anisotropy along the [0001] axis. This two-fold symmetry around the [1-100] direction means that the dangling bonds along the [0001] axis exist. If the vacancy defects are simple silicon vacancies, then the momentum distribution can be reproduced with a tetrahedral configuration of dangling bonds as well as the case of 3*C* SiC described above. However, the obtained momentum distribution could not be reproduced by this way suggesting that the symmetry around vacancy defects is lowered from tetrahedral by some reasons. It was found that by rotating the crystal orientation around the [0001], the two-fold symmetry was still observable. This allows us to conclude that the vacancy defects have a rotational symmetry around the *c*-axis. As a trial we may suppose that silicon vacancies on hexagonal sites in hexagonal SiC have a C_{3V} symmetry. Then, the LCAO calculation showed a momentum distribution, which matches the experimental results, better than that extracted from tetrahedral symmetry.

Summary

In summary, we have studied the annealing behavior of irradiation-induced vacancy defects in SiC depending on polytype. We found that silicon vacancy related defects are responsible for positron trapping in 3*C*, 4*H* and 6*H* SiC after electron irradiation. In 3*C* SiC, isolated silicon vacancies are the major positron trapping centers and they disappear below 1000^{o}C. In hexagonal SiC, observed silicon vacancy related defects exhibited higher thermal stability than isolated silicon vacancies in 3*C* SiC. The anisotropies of momentum distributions obtained from 2D-ACAR measurements suggest that isolated silicon vacancies with a tetrahedral symmetry are important in 3*C* SiC, while silicon vacancy related defects in 6*H* SiC should have a reduced symmetry from tetrahedral.

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References

[1] A. Kawasuso, F. Redmann, R. Krause-Rehberg,T. Frank, M. Weidner, G. Pensl,P. Sperr,H. Itoh: J. Appl. Phys. **90** (2001) 3377.

[2] A. Kawasuso, F. Redmann, R. Krause-Rehberg, M. Weidner, T. Frank, G. Pensl, P. Sperr, W. Triftshauser and H. Itoh, Appl. Phys. Lett., **79** (2001)3950.

[3] A. Kawasuso, M. Weidner, F. Redmann, T. Frank, P. Sperr, R. Krause-Rehberg and G. Pensl, Physica B: Condensed Matter, **308-310** (2001) 660.

[4] A. Kawasuso *et al*, to be published in Phys. Rev. B.

[5] R. Devanathan, W. J. Weber and F. Gao, J. Appl. Phys. **90** (2001)2303**.**

[6] A. Kawasuso, H. Itoh, M. Morishita, M. Yoshikawa, T. Ohshima, I. Nashiyama, S. Okada, H. Okumura and S. Yoshida, Appl. Phys. A**67** (1998) 209.

[7] H. Itoh, A. Kawasuso, T. Ohshima, M. Yoshikawa, I. Nashiyama, S. Tanigawa, S. Misawa, H. Okumura and S. Yoshida, Phys. Stat. Sol. (a)**162** (1997) 173.

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