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Silicon vacancies in 3*C*-SiC observed by positron lifetime and electron spin resonance

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Abstract. Positron lifetime and electron spin resonance (ESR) measurements were performed for 1-MeV electron-irradiated cubic silicon carbide (3*C*-SiC). From a comparison of the annealing behaviors of positron lifetime and ESR signal, we identified the annihilation of positrons localized at single-negative silicon vacancies. The positron lifetime at silicon vacancies was first determined experimentally to be 188 ± 4 ps. This value agrees well with the theoretical positron lifetime for silicon vacancies [G. Brauer et al. Phys. Rev. B **54**, 2512 (1996)]. The trapping coefficient of single-negative silicon vacancies was also derived.

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Silicon carbide (SiC) is a promising semiconductor material for high-power and high-frequency devices. In device fabrication using ion implantation, various kinds of point defects are unintentionally introduced. Radiation-induced defects frequently act as deep recombination centers and hence degrade the performance of devices. It is therefore necessary to establish the technique to control them. On the other hand, point defects have an important role when they assist impurity diffusion. In SiC, vacancies and interstitials in carbon and silicon sublattices and antisite defects can exist. Moreover, defects may have different properties in the cubic and hexagonal sites, which have different local atomic arrangements. Single-vacancies and interstitials and also Frenkel pairs in SiC are thought to be stable even at room temperature. The variety of defect species and their high thermal stability are quite different from the same group-IV semiconductor, Si.

In the last ten years, positron annihilation spectroscopy (PAS) has been extensively applied to the studies of vacancy defects in various semiconductors [1, 2]. Although this technique is also applied to SiC [3, 4], fundamental positron annihilation parameters, such as positron lifetime and trapping coefficient, even for simple vacancies in SiC have not yet been adequately determined. To improve the defect analysis using PAS, the determination of such fundamental parameters is indispensable. In this work, we performed positron lifetime measurements for 1-MeV electron-irradiated 3*C*-SiC. To enhance the reliability of experiment, we also employed electron spin resonance (ESR) measurement and compared annealing behaviors of positron lifetimes and ESR signals. From the correlation between observed lifetimes and ESR signals, we could identify the positron annihilation due to silicon vacancies in 3*C*-SiC.

1 Experiment

Specimens used in this work were cut from an undoped single-crystalline 3*C*-SiC film with a thickness of 30 μm, which was grown epitaxially on a Si(100) substrate at 1410 °C by chemical vapor deposition. The as-grown film was n-type and the residual carrier density was $1 \times 10^{16}\ \mathrm{cm}^{-3}$ at room temperature. The specimens were irradiated with 1-MeV electrons up to a fluence of $1.1 \times 10^{18}\ \mathrm{e}^{-}/\mathrm{cm}^{2}$ at room temperature using a Cockcroft–Walton type accelerator. Isochronal annealing was performed in the temperature range from 100 to 1000 °C with a temperature step of 50 °C for 5 min in a dry argon atmosphere.

The positron source was prepared by depositing ^{22}NaCl ($\approx 6 \times 10^{4}$ Bq) onto a titanium film of thickness 3 μm. It was sandwiched by two specimens and then positron lifetime measurements were performed at room temperature using a conventional spectrometer with a time resolution of about 230 ps (full width at half maximum, FWHM). About 5×10^{6} counts were accumulated in each spectrum. In our measurement, two source annihilation components were determined to be about 128 ps and 540 ps with the respective intensities of 10.4% and 0.5% using high-purity Si crystals [4]. About 60% of positrons from the source was expected to transmit the specimens [5]. Therefore, the rear of each specimen was supported by unirradiated p-type 6*H*-SiC (300 μm thick) which gave a single positron lifetime of 139 ± 2 ps related to the annihilation in the bulk state (bulk lifetime). After subtracting the source and background components, lifetime spectra were decomposed with two exponential terms (bulk and defects) using a computer program of PATFIT-88 [6]:

$$L(t) = (I_1/\tau_1)\exp(-t/\tau_1) + (I_2/\tau_2)\exp(-t/\tau_2)\,, \qquad (1)$$

where $\tau_i (i = 1, 2)$ are the lifetimes and I_i the intensities $(I_1 + I_2 = 1)$. If the two-state trapping model, where positrons are assumed to annihilate through the bulk state and the trapped state at vacancies, is valid, the lifetimes are given by

$$\tau_1 = 1/(1/\tau_B + \kappa)\,, \qquad (2)$$

$$\tau_2 = \tau_V\,, \qquad (3)$$

where τ_B is the bulk lifetime, τ_V the lifetime of positrons at vacancies and κ the net positron trapping rate of vacancies:

$$\kappa = (I_2/I_1)(1/\tau_B - 1/\tau_2)\,. \qquad (4)$$

The trapping rate is proportional to the trapping coefficient and the concentration of defect ($\kappa = \mu C$). Referring to defect concentration, we use the trapping rate rather than the intensity I_2 since I_2 is not proportional to the defect concentration. The validity of analysis based on the two-state trapping model can be checked from the difference between the lifetimes τ_1 determined by (1) and the right-hand side of (2).

Electron spin resonance measurements were performed with an X-band (9 GHz) microwave incident on a TE_{110} cylindrical cavity using a JEOL JES-TE300 spectrometer.

2 Results and discussion

Figure 1 shows the positron lifetime spectra for the unirradiated and the irradiated specimens. A single lifetime of 140 ± 2 ps was obtained for the unirradiated specimen. This value coincides with the bulk lifetime for the virgin p-type 6*H*-SiC within the experimental error. In addition, the obtained lifetime is in good agreement with the theoretical bulk lifetime for 3*C*-SiC [3, 7]. Thus, we conclude that the obtained lifetime is the bulk lifetime.

An apparent increase in the lifetime was observed after irradiation. This shows the introduction of vacancy defects by irradiation. From the analysis using (1), two lifetime components were obtained; $\tau_1 = 76 \pm 4$ ps and $\tau_2 = 189 \pm 3$ ps with $I_2 = 72.3\%$. The positron trapping rate κ is estimated to be $4.97\,\mathrm{ns}^{-1}$. The lifetime τ_1 is in agreement with that expected from the two-state trapping model ($\tau_1^{TM} = 82$ ps), assuring the validity of the analysis based on this model. That is, the lifetime τ_2 represents the lifetime of positrons trapped at vacancy defects. The lifetime τ_2 is close to the positron lifetime at silicon vacancies theoretically calculated using the local-density approximation [3, 7]. It was also found that the lifetime τ_2 was independent of the electron fluence [8]. These results indicate that positrons are trapped by defects related to silicon vacancies.

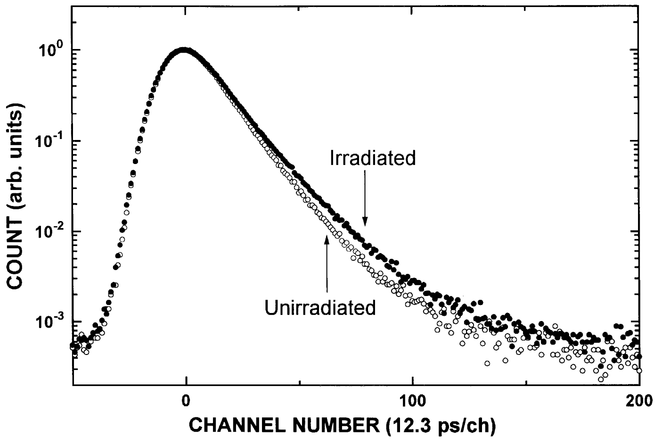

Fig. 1. Positron lifetime spectra for the unirradiated specimen (*open circle*) and the specimen irradiated with 1-MeV electrons at a fluence of 1.1×10^{18} e^-/cm^2 (*filled circle*)

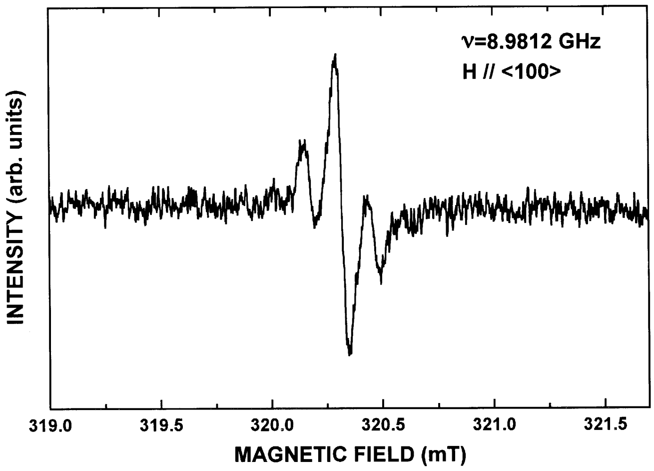

Fig. 2. ESR spectrum recorded at 296 K for the specimen irradiated with 1-MeV electrons at a fluence of 1.1×10^{18} e^-/cm^2. The magnetic field was applied parallel to the $\langle 100 \rangle$ axis

After irradiation, we also found an ESR signal as shown in Fig. 2. From the *g*-value (2.003), this signal is assigned to the $T1$ center [9, 10]. The $T1$ center has the T_d symmetry and $S = 3/2$ and is inferred to arise from single-negative silicon vacancies (V_{Si}^-). As described below, the results of the annealing experiment strongly indicate that the $T1$ signal and the lifetime τ_2 have the same origin.

Figure 3 shows the annealing behaviors of the lifetimes (τ_1 and τ_2) and the intensity (I_2). The lifetime τ_1 agrees with that expected from the two-state trapping model (τ_1^{TM}) up to 1000 °C. This again suggests the validity of the analysis based on the two-state trapping model. The lifetime τ_2 exhibits a nearly constant value (188 ± 4 ps) during the course of annealing up to 850 °C whereas the intensity I_2 decreases at 100–200 °C and 800–900 °C. This result shows that the type of defects responsible for the second lifetime component does not change and that the concentration decreases by annealing. Figure 4 shows the annealing behaviors of the positron trapping rate and the $T1$-signal intensity. The positron trapping rate and $T1$-signal intensity show quite similar behavior; they first decrease at 100–200 °C and finally diminish at 800–900 °C. The above result just shows that the positron annihilation center and the $T1$ center are originating from the same defect species, i.e., V_{Si}^-. Thus, the obtained lifetime 188 ± 4 ps is related to the annihilation of positrons localized at V_{Si}^-. As proposed in the previous work [9], the annealing at 100–200 °C is attributed to the partial disappearance of silicon vacancies through the recombination with interstitials. The annealing at 800–900 °C may be caused by the migration of silicon vacancies to their sinks [9]. The annealing tempera-

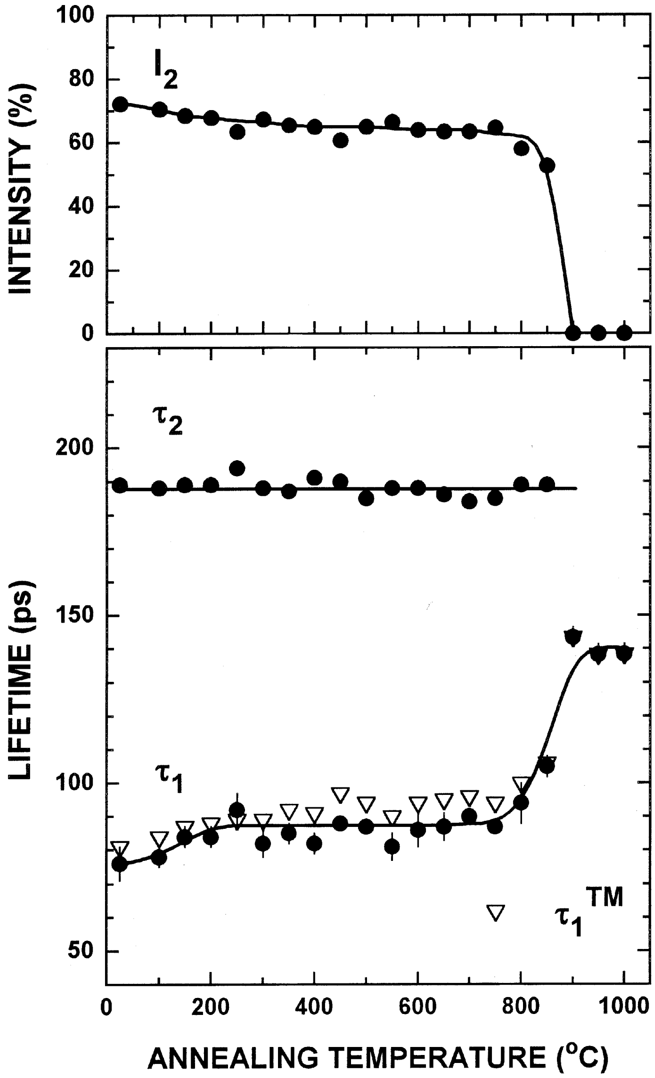

Fig. 3. Positron lifetimes (τ_1 and τ_2) and intensity I_2 as a function of annealing temperature for the specimen irradiated with 1-MeV electrons at a fluence of 1.1×10^{18} e^-/cm^2. The lifetime τ_1^{TM} denotes the lifetime τ_1 expected from the two-state trapping model

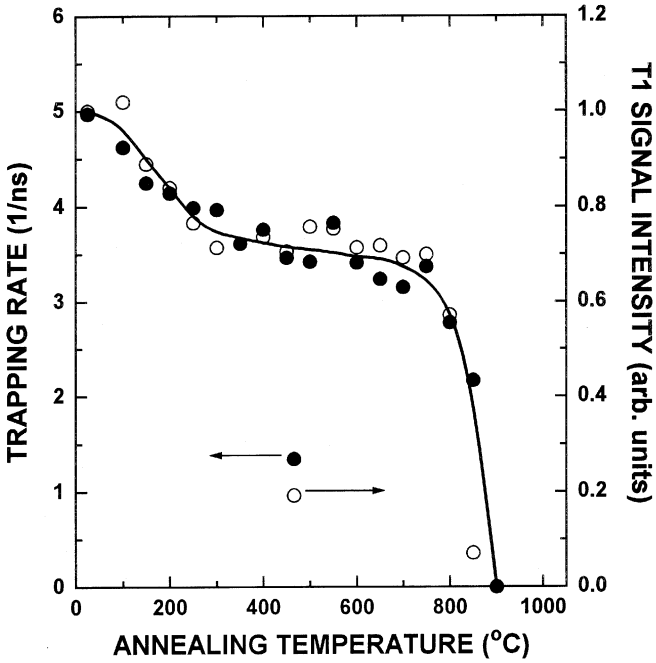

Fig. 4. Positron trapping rate responsible for the second lifetime component in Fig. 2 (*filled circle*) and $T1$-signal intensity (*open circle*) as a function of annealing temperature

ture is a little bit higher than that observed in the previous work (750 °C). It is explained as the difference in the sink concentration depending on the crystal quality of individual specimens.

The concentration of silicon vacancies after irradiation is calculated to be $1.9 \times 10^{16}\,\mathrm{cm}^{-3}$ ($= 1.97 \times 10^{-7}$ in atomic fraction) from the $T1$-signal intensity. Since the positron trapping rate is $4.97 \times 10^9\,\mathrm{s}^{-1}$ after irradiation, the trapping coefficient of V_{Si}^- is estimated to be $\approx 2.5 \times 10^{16}\,\mathrm{s}^{-1}$. Considering the fact that about 40% of positrons annihilate in the specimens, however, the net trapping coefficient should be about 2.5 times larger, i.e., $\approx 6 \times 10^{16}\,\mathrm{s}^{-1}$. This value is about three times as great as that of single-negative vacancies in Si at room temperature [11]. In the case that positron trapping is dominated by the Coulomb attraction between positrons and negatively charged defects, the trapping radius (r) may be simply given by $Ze^2/4\pi\varepsilon r = 3k_BT/2$, where Z is the charge number of the defect and ε is the dielectric constant [12]. The dielectric constant of SiC is 6.7 and it is smaller than that of Si (11.9). This implies that trapping radius in SiC is larger than that in Si even if Z is the same. Thus, the trapping coefficient of V_{Si}^- in SiC reflects the enhanced Coulomb attraction due to its small dielectric constant.

It is known that carbon vacancies may also be produced by 1-MeV electron irradiation [4, 13]. However, neither the positron lifetime nor ESR signal related to carbon vacancies was observed. The absence of ESR signal arising from carbon vacancies is explained by the fact that carbon vacancies are electrically neutral (V_C^0) and hence nonparamagnetic in n-type 3C-SiC [7, 8, 13]. The positron trapping rate of single-negative vacancies is expected to be at least ten times as great as that of neutral vacancies due to the Coulomb attraction [11]. Thus, neutral carbon vacancies are presumably ineffective trapping centers in the competition with single-negative silicon vacancies. Hence, no lifetime component related to carbon vacancies may be observed in the present experimental conditions.

3 Summary

In this research, we found a positron lifetime of 188 ± 4 ps and the ESR signals termed $T1$ in 1-MeV electron-irradiated 3C-SiC. The lifetime is in good agreement with the theoretical value for silicon vacancies. The annealing behaviors of the positron trapping rate and the $T1$-signal intensity were quite similar to each other. We therefore conclude that the observed positron trapping center is V_{Si}^-. The trapping coefficient of V_{Si}^- is derived to be $\approx 6 \times 10^{16}\,\mathrm{s}^{-1}$. The obtained positron annihilation parameters will be helpful for the defect analysis in SiC using PAS.

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