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Abstract. Electron paramagnetic resonance (EPR) was used to study high-purity semi-insulating 4H-SiC irradiated with 2 MeV electrons at room temperature. The EPR signal of the EI4 defect was found to be dominating in samples irradiated and annealed at ~750°C. Additional large-splitting ^{29}Si hyperfine (hf) lines and also other ^{13}C and ^{29}Si hf structures were observed. Based on the observed hf structures and annealing behaviour, the complex between a negative carbon vacancy-carbon antisite pair ($V_C C_{Si}^-$) and a distance positive carbon vacancy (V_C^+) is tentatively proposed as a possible model for the EI4 defect.

Introduction

The EI4 defect was previously observed by electron paramagnetic resonance (EPR) in p-type 4H- and 6H-SiC irradiated with electrons at 400°C [1]. The EI4 spectrum is similar to the P4 spectrum reported by Vainer and Ilin [2] in heat-treated n-type 6H SiC and might be related to the same defect. A difference is in the Si hf splitting (~0.64 mT for P4 [2] and 1.14 mT for EI4 [1]). Because of low signal intensities, the hf tensor was not determined. A model of a long-distant pair of carbon vacancies was proposed for the defect [1,2]. However, it seems that in previous studies some of the hf structure was not detected for the EI4 defect since the observed Si hf splittings were small and isotropic and can account for only a very low spin density. We have recently found that the EI4 defect is commonly detected in as-grown high-purity semi-insulating (HPSI) 4H- and 6H-SiC substrates grown by high-temperature chemical vapour deposition (HTCVD) [3].

In this work, using electron irradiation and annealing to enhance the EI4 signal in HPSI 4H-SiC, we were able to detect additional large-splitting hf lines which were shown to be related to the allowed and forbidden transitions of the interaction between an electron spin S=1 and a nuclear spin I = 1/2 of a ^{29}Si nucleus (~4.7% natural abundance). In the direction of the c axis when the EPR signal is strongest, two weak hf lines, which could be from the hf interaction between the electron spin of the defect and the nuclear spin of a ^{13}C nucleus (I = 1/2 and 1.1% natural abundance), were observed. Based on the observed additional hf structures and the annealing behaviour, a model of a complex involving two carbon vacancies and a C antisite is proposed for the EI4 defect.

Experiment

The starting materials used in our study are HPSI 4H-SiC substrates grown by HTCVD. The residual concentrations of the common impurities are in the range of mid 10^{15} cm^{-3} or less (mid 10^{15} cm^{-3} for the N donors ~1-3×10^{15} cm^{-3} for the B acceptors). The samples were irradiated at room temperature by 2-MeV electrons with a dose of 2×10^{18} cm^{-2}. The EPR measurements were

performed on an X-band (~9.5 GHz) Bruker E580 EPR spectrometer.

Results and discussion

In as-irradiated 4H-SiC samples, the EPR spectrum measured in darkness at 77 K shows a strong signal of the carbon vacancy in the single positive charge state (V_C^+) [4] and a very weak signal of the EI4 defect [Fig. 1(a)]. At room temperature, the EPR spectrum shows strong signal of the singly negatively charged silicon vacancy (V_{Si}^- and the T_{V2a} centre) [5,6] [Fig. 1(b)]. With increasing annealing temperature, the EI4 signal increased whereas the signals of V_C^+ and V_{Si}^- decreased. After annealing at ~750°C, the EI4 signal reached its maximum and became stronger than the V_C^+ signal [Fig. 2(a)]. Strong EPR signals of the negative carbon vacancy-carbon antisite pair, $V_CC_{Si}^-$ [7] and the neutral divacancy [8], were also observed under illumination. With a magnetic field **B** along the c axis (**B**||**c**), the EI4 spectrum consists of two lines separated by ~15.3 mT, corresponding to the low- and high-field lines of the spin S=1 centre. Each line is accompanied by two weak pairs of hf lines with large splittings (8.63 mT and 9.76 mT) and the structures of these hf lines can be seen in the inset of Fig. 2(a). The intensity ratio of each hf line and the main line is about 4%, which is approximate the natural abundance of the ^{29}Si isotope. However, one of the hf lines varies in intensity with the direction of **B** and even disappears at some directions as if it is from a forbidden transition. The angular dependence of the main lines and hf lines can be described by the spin-Hamiltionian

$$H = \mu_B \mathbf{B}.\mathbf{g}.\mathbf{S} + D[S_{zz}^2 - S(S+1)/3] + E(S_{xx}^2 - S_{yy}^2) + \mathbf{S}.\mathbf{A}.\mathbf{I},$$

here μ_B is the Bohr magneton, S = 1, and D and E are the fine-structure parameters representing the zero-field splitting due to the axial and orthorhombic fields, respectively. We found that the angular dependence can also be fitted with an isotropic g value of 2.004 instead of the anisotropic g tensor as determined in Ref. [1]. The fine-structure parameters were determined as $D = 3D_{zz}/2 = 343.7 \times 10^{-4}$ cm^{-1}, $E = (D_{xx}-D_{yy})/2 = 64.8 \times 10^{-4}$ cm^{-1} and the angle between the principal D_{zz} and the c-axis is 53.6°. It is also confirmed that the large-splitting hf lines are related to the allowed and forbidden transitions from the hf interaction of the electron spin and the nuclear spin of one ^{29}Si neighbour [transitions are indicated in the inset of Fig. 2(a)]. (Some forbidden hf transitions with $\Delta m_I = \pm 1$ can become allowed due to second-order admixtures arising from cross products of the terms D and A [9].) The principal hf values are determined as $A_{xx} = 62.9 \times 10^{-4}$ cm^{-1}, $A_{yy} = 57.8 \times 10^{-4}$ cm^{-1}, $A_{zz} = 86.4 \times 10^{-4}$ cm^{-1} and the angle between the principal z axis of the A tensor and the c
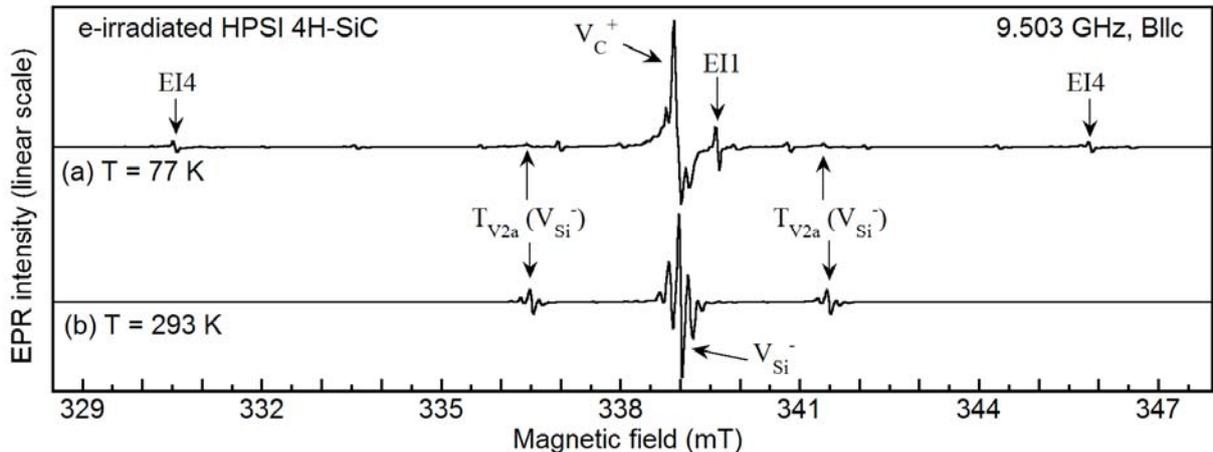

Fig. 1. EPR spectra in HPSI 4H-SiC irradiated with 2-MeV electrons at room temperature measured for **B**||**c** at (a) 77 K and (b) 293 K showing the dominating signals from the V_C^+ and V_{Si}^- defects and weak lines of the EI4 centre.
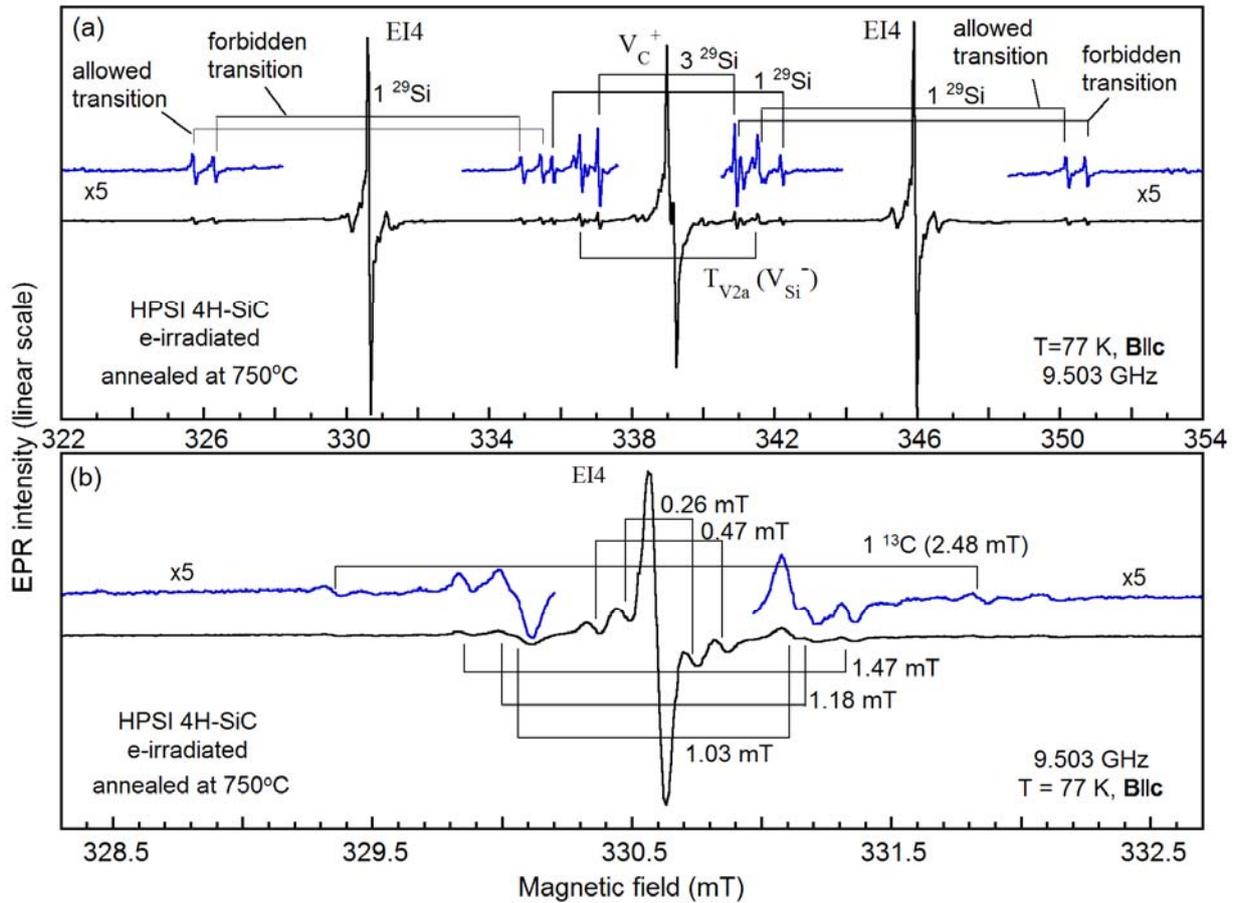
Fig. 2. (a) EPR spectrum observed for **B∥c** at 77 K in HPSI 4H-SiC sample after electron irradiation and annealing at 750°C. The inset shows large-splitting hf lines corresponding to allowed and forbidden transitions of the hf interaction between the electron spin S = 1 of the defect and the nuclear spin of a ^{29}Si neighbour. The Si hf structure of V_C^+ is also indicated. (b) The low-field line of the EI4 spectrum in (a) measured with a field modulation of 0.03 mT, showing six different pairs of hf lines.

axis is 5.3°.

Figure 2(b) shows the low-field line of the EI4 spectrum for **B∥c** measured with a low magnetic field modulation (0.03 mT). In the *c* direction, the signal is strong and two weak satellites with a splitting of ~2.48 mT were observed [see the inset of Fig. 2(b)]. The intensity ratio between the hf lines and the main line is about 1% which is approximately the natural abundance of the ^{13}C isotope. This hf structure is therefore assigned to the hf interaction with one ^{13}C nucleus. When **B** is off the *c* axis, these ^{13}C hf lines split off and become too weak to be detected and hence the hf tensor has not been determined. Two strong inner hf lines of the EI4 spectrum [Fig. 2(a)] have been observed before and appear to be from the hf interaction with four Si in low resolution spectra [1]. In higher-resolution spectra, this hf structure is shown to be more complicated with three pairs of hf lines with the splitting of ~1.03 mT, ~1.18 mT and ~1.47 mT [see the inset of Fig. 2(b)]. These hf lines are slightly anisotropic and due to overlapping we have not been able to determine their angular dependence. Their intensity ratio corresponds approximately to the hf interaction with four Si atoms. Another pair of hf lines has a smaller splitting of ~0.47 mT, which is slightly anisotropic (~0.47 mT at **B∥c** and ~0.42 mT at **B⊥c**). Their intensity ratio is ~10% which corresponds to the hf interaction with two Si atoms. The smallest hf splitting of ~0.26 mT is isotropic.

We found that the EI4 signal rapidly increases with annealing temperature between 600°C and 750°C. In the temperature range 750-1000°C, it rapidly decreases and disappears after annealing at ~1000°C, while the signal of the divacancy increases at about the same rate and reaches its maximum. The annealing behaviour suggests that EI4 is a complex defect, but is not a very stable

one. It seems that the EI4 defect is transformed to the divacancy at temperatures above ~800°C. The observation of different Si hf structures also indicates that the centre may consist of more than one carbon vacancy and possibly also a C antisite. The distant V_C-V_C pair model proposed before [1,2] can not explain the formation of the EI4 defect since V_C is known to become mobile at temperatures higher than 750°C [10]. The migration of V_{Si} seems to play an important role in the formation of the EI4 defect. When a V_{Si}^- defect becomes mobile, it is attracted by Coulomb interaction and migrates close to a V_C^+ centre and can capture a nearest neighbour C to form a $V_C C_{Si}^-$ complex next to a V_C^+ defect. As a result, a neutral $V_C V_C C_{Si}^0$ complex can be formed. The defect is somewhat similar to a biradical system with two unpaired electrons, each locating on a dangling bond of two separated V_C. The coupling between two unpaired spins can give rise to a spin S = 1. In such a defect, forbidden transitions can be expected as often seen in irradiated quartz [11,12]. The formation energy of the $V_C V_C C_{Si}$ defect in 3C SiC [13] is found to be comparable or lower than that of the divacancy (depending on the position of the Fermi level). The transformation from the $V_C V_C C_{Si}$ defect to the divacancy has also been predicted to occur with an energy barrier of ~1.6 eV [13] which is in agreement with our annealing result.

Summary

In summary, we have observed additional ^{29}Si and ^{13}C hf structures of the EI4 EPR defect in HPSI 4H SiC irradiated with 2MeV electrons and annealed. Based on the observed hf structures and the annealing behaviour, the complex between a negative carbon vacancy-carbon antisite pair and a distance positive carbon vacancy is tentatively proposed as a possible model for the EI4 defect. The formation of the $V_C V_C C_{Si}$ complex is explained by the migration of the Si vacancy and the formation of the $V_C C_{Si}$ pair close to a C vacancy.

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