Electron spin resonance identification di-carbon-related centers in irradiated silicon

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A previously unreported electron spin resonance (ESR) spectrum was found in γ-ray irradiated silicon by the detection of the change in microwave photoconductivity arising from spin-dependent recombination (SDR). In the specially prepared silicon crystals doped by ^{13}C isotope, a well resolved hyperfine structure of SDR-ESR lines due to the interaction between electrons and two equivalent carbon atoms having nuclear spin $I = 1/2$ was observed. The Si-KU4 spectrum is described by spin Hamiltonian for spin $S = 1$ and of $\boldsymbol{g}$ and $\boldsymbol{D}$ tensors of orthorhombic symmetry with principal values $g_1 = 2.008$, $g_2 = 2.002$, and $g_3 = 2.007$; and $D_1 = \pm 103$ MHz, $D_2 = \mp 170$ MHz, and $D_3 = \pm 67$ MHz where axes 1, 2, and 3 are parallel to the $[1\bar{1}0]$, [110], and [001] crystal axes, respectively. The hyperfine splitting arising from ^{13}C nuclei is about 0.35 mT. A possible microstructure of the detect leading to the Si-KU4 spectrum is discussed. *Published by AIP Publishing.*
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I. INTRODUCTION

Substitutional carbon (C_s) is one of the most common impurities in silicon. C_s plays an important role in the formation of point defects under irradiation. Carbon atoms and their complexes are isoelectronic to silicon. Thus, they are important in the investigations of the fundamental mechanisms of defect creation and the electronic structures of interstitial and self-interstitial atoms produced in primary radiation events.[1,2] Interstitial carbon (C_i) atoms created by irradiation are mobile at room temperature. When captured by C_s, they form C_iC_s pairs, which are the dominating radiation defects arising under room temperature irradiation of silicon crystals. The microscopic structure of radiation defects containing carbon atoms has been intensively studied by electron spin resonance (ESR). This has led to the finding of several ESR spin S = 1/2 spectra originating from the C_i atoms[1,2] and the C_iC_s pairs.[3] These spectra have been observed in the naturally abounded irradiated silicon as well as in the silicon doped with the carbon-13 isotope.[1–3] It was found that C_iC_s pairs exist in two configurations: A and B for positive and negative charge states, respectively.[3] Applying the high sensitive methods of optical detection of magnetic resonance (ODMR)[4] and spin-dependent recombination (SDR)-ESR,[5–7] the spectra of the excited spin $S = 1$ states of $(C_iC_s)^0$ centers in B configuration were found and investigated. In the B configuration, two carbon atoms occupy the nearest substitution positions along the $\langle 111 \rangle$ crystal axis. They also contain interstitial silicon (Si_i) atom on the bond between them (C_s-Si_i-C_s). The excited triplet state of this center gives the dominant SDR-ESR spectrum Si-PT1 of trigonal symmetry detected after the irradiation of float-zone (FZ) silicon crystals.[5–7]

The C_iC_s pairs act as trapping centers of vacancies transforming the C_sC_s configuration studied by ESR and infrared absorption.[8,9] In this center, the C_s atoms occupy the nearest substitution positions along the $\langle 111 \rangle$ axis without the Si_i atoms. The ESR spin $S = 1/2$ Si-GGA2 spectrum of $(C_sC_s)^-$ has been described by Spin-Hamiltonian parameters of trigonal symmetry.[9]

In the present work, we report the SDR-ESR investigations of a previously unreported ESR spectrum. We use FZ silicon single crystals irradiated at room temperature with γ-rays at doses of about 5×10^{17} cm^{-2} when the crystals had 1) no intentional carbon doping and 2) doping of carbon with isotopic enrichment ^{13}C:$^{12}C = 60\%$:40%.

II. EXPERIMENTAL

The SDR-ESR spectra were recorded using an X-band (9.05 GHz) EPR spectrometer monitoring magnetic resonance change in microwave field absorption caused by photo excited carriers created by band-gap illumination. 100-kHz modulation of the magnetic field and detection of the second derivative of the absorption signal were employed. Detailed descriptions of the SDR mechanisms and the SDR-ESR detections are provided in Refs. 5–7.

The samples of $3.5 \times 10 \times 0.3$ mm^3, with the long edge oriented along the $\langle 110 \rangle$ axis of the crystal, were placed in the cylindrical TE011-mode cavity. The temperature of the sample was controlled by Oxford-Instruments He-gas flow cryostat and kept in the range 20–30 K. The magnetic field was calibrated by isotropic ESR Mn^{2+} spectra in the MnO powder.

III. RESULTS AND DISCUSSIONS

Strong SDR-ESR spectra Si-PT1 arising from the (C_s-Si_i-C_s) center including interstitial Si atom[5–7] were observed in all FZ silicon samples after irradiation. The spectrum detected in the sample doped with enriched ^{13}C isotope is shown in Fig. 1. The new low-intensity Si-KU4 spectrum, originating from the excited triplet (spin $S = 1$) state of

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defects, was found in all the investigated FZ silicon samples. In the enriched ^{13}C isotope doped silicon, the hyperfine splitting due to ^{13}C nuclear spins is observed. The Si-KU4 spectrum is shown in Fig. 1 for B $||\langle 111\rangle$.

The fine structure of the Si-KU4 spectrum is well described by Hamiltonian for spin $S = 1$ and $\boldsymbol{g}$ and $\boldsymbol{D}$ tensors of orthorhombic (C_{2v}) symmetry

$$H = \boldsymbol{g}\beta\boldsymbol{B}\,\boldsymbol{S} + \boldsymbol{S}\,\boldsymbol{D}\,\boldsymbol{S}, \tag{1}$$

where β is the Bohr magneton, $\boldsymbol{g}$ is the electron g-tensor, $\boldsymbol{B}$ is the magnetic field, $\boldsymbol{S}$ is the spin operator, and $\boldsymbol{D}$ is the traceless tensor describing the dipole–dipole interaction between a pair of electrons forming spin $S = 1$. The first term is electron-Zeeman splitting and the second describes the fine structure. The principal values of $\boldsymbol{g}$- and $\boldsymbol{D}$- tensors are as follows: $g_1 = 2.0080$, $g_2 = 2.0020$, and $g_3 = 2.0070$; and $D_1 = \pm 103$ MHz, $D_2 = \mp 170$ MHz, $D_3 = \pm 67$ MHz where axes 1, 2, and 3 are parallel to the $[1\bar{1}0]$, [110], and [001] crystal axes, respectively. The accuracy for g values is about ± 0.0002 and for D ± 1 MHz. The angular dependence of Zeeman line positions for the Si-KU4 spectrum is shown in Fig. 2. In the ^{13}C isotope (nuclear spin $I = 1/2$) enriched silicon, each Zeeman line of the Si-PT1 and Si-KU4 spectra splits into five hyperfine components. The hyperfine structures of these spectra are shown in Fig. 3. The figure unambiguously shows that both centers contain two equivalent carbon atoms. The hyperfine ^{13}C splitting of the Si-KU4 spectrum is approximately 0.35 mT, which is about half of that of the Si-PT1 spectrum. Two electrons forming the total spin $S = 1$ in (C_s-Si_i-C_s) center are localized at the interstitial Si atom situating between two carbon atoms.[3] This center has a trigonal (C_{3v}) symmetry with the fine structure splitting of 86 mT and ^{13}C hyperfine splitting is about 0.6 mT. The fine structure splitting of the Si-KU4 spectrum determined by $\boldsymbol{D}$-tensor is 18.5 mT, which is 4.6 times lower than that for the Si-PT1 spectrum. It shows that the magnetic dipole interaction between two electrons and the density of electron wave functions on ^{13}C nuclei is smaller for the Si-KU4 center than those for the Si-PT1 center.

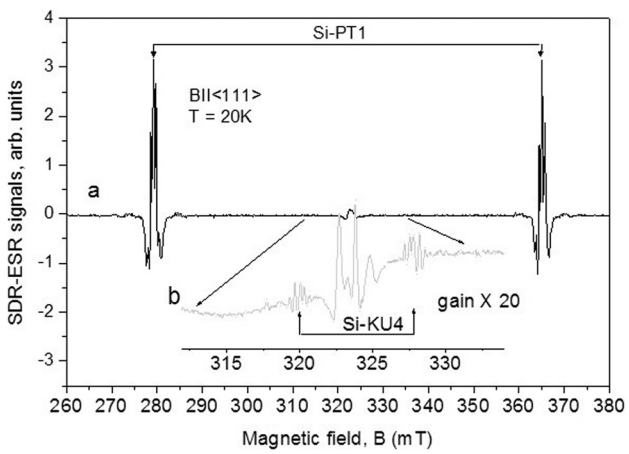

FIG. 1. SDR-ESR detected (a) Si-PT1 and (b) Si-KU4 spectra with B $||\langle 111\rangle$ of irradiated FZ Si sample doped with enriched ^{13}C isotopes. The group of lines between KU4, i.e., 322–325 mT, originates from other surface recombination centers and radiation defects.

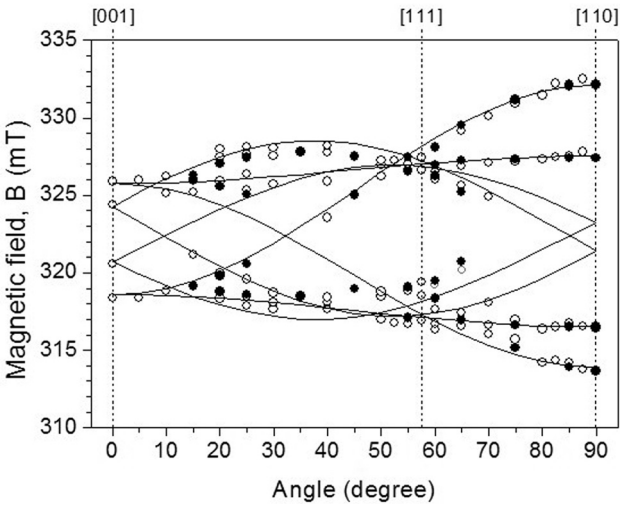

FIG. 2. Angular dependence of the line positions of the Si-KU4 spectrum. Experimentally determined points for irradiated FZ silicon (open circles) and irradiated FZ silicon doped with enriched ^{13}C isotopes (filled circles) are compared with calculated angular dependence using Eq. (1).

The observed intensities of the Si-KU4 spectrum are 50–100 times lower than those of the Si-PT1 spectrum in all our samples. It shows that the number of defects responsible for the Si-KU4 spectrum is significantly lower than that for the Si-PT1 spectrum, suggesting that the Si-KU4 center

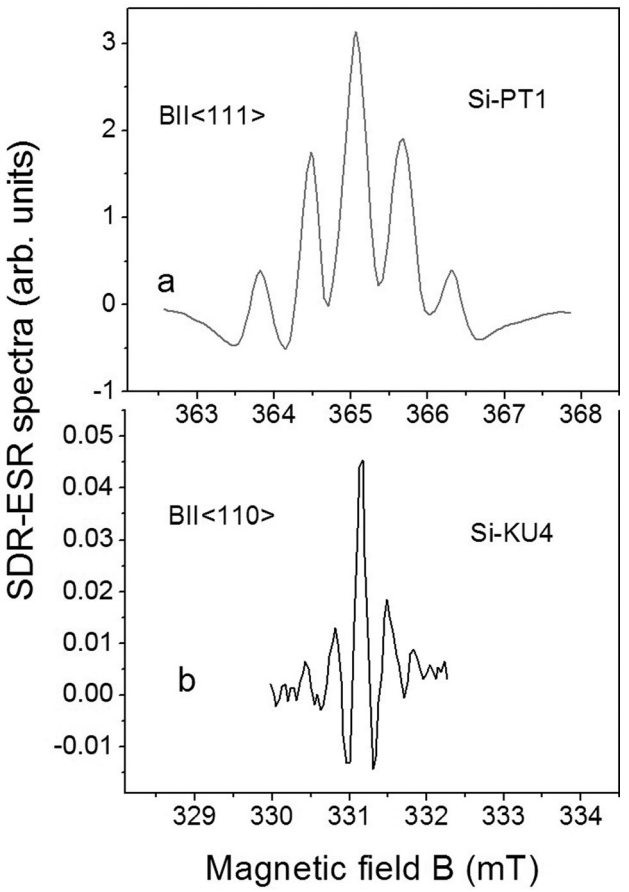

FIG. 3. ^{13}C hyperfine structure of (a) Si-PT1 and (b) Si-KU4 high field lines at the magnetic field orientations corresponding to maximal fine structure splitting.

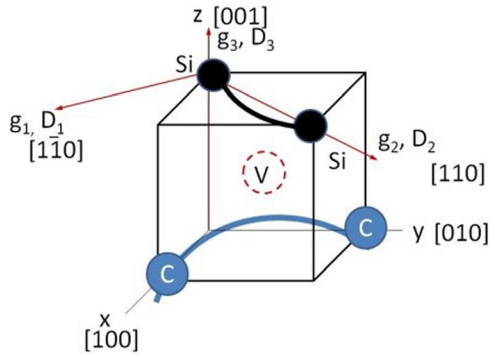

FIG. 4. One possible microstructure of the Si-KU4 center.

originates from the pairs of two C_s atoms which trap the vacancy created by irradiation.

The formation of the center responsible for the Si-KU4 spectrum under irradiation can be presented as successive capture of two vacancies by the (C_s-C_i) center

$$C_s - C_i + V \rightarrow C_s - C_s, \text{ and} \quad (2)$$

$$C_s - C_s + V \rightarrow C_s - V - C_s. \quad (3)$$

The first process was suggested and investigated in Ref. 9. The creation rate of the (C_s-V-C_s) centers is proportional to the products P_1 and P_2, where P_1 and P_2 are the probabilities of processes in Eqs. (2) and (3), respectively. This explains the low intensity of the Si-KU4 spectrum.

The capture of the vacancy by the C_s-C_s center may shift one C_s atom to the nearest substitution position and change the symmetry of the defect from trigonal (C_{3v}) to orthorhombic (C_{2v}). While our data are not enough to draw a definite conclusion on the microstructures of this defect center, one possible model is shown in Fig. 4. Two electrons forming the total spin $S = 1$ can be localized on bonding and antibonding orbitals between the Si atoms. This model is in agreement with the orthorhombic symmetry of center and consistent with the small fine structure and ^{13}C hyperfine splitting in the Si-KU4 spectrum.

Alternatively, two electrons can be localized on the orbitals connecting two C_s atoms. In this case, the orbitals are more extended than those in the C_s-C_s or C_s-C_i configurations, and hyperfine interaction with the ^{13}C nuclei is expected to be lower. Distinction between these possibilities can be made by the analysis of the ^{13}C and ^{29}Si hyperfine structures. Unfortunately, because of the low intensity of the Si-KU4 spectrum, it was difficult to measure full angular dependence of hyperfine ^{13}C satellites and to determine the tensor $A(^{13}C)$ of the hyperfine interaction. Furthermore, it was impossible to do this for the hyperfine interaction with the ^{29}Si nuclei having low (4.7%) abundance. Once can increase the ^{29}Si concentration through isotope engineering[10–12] to make the hyperfine ^{13}C satellites. However, too much abundance of ^{29}Si may lead to broadening of the main peak which can overlap with the hyperfine ^{13}C satellites. Fine tuning of ^{29}Si abundance is needed in the future studies.

IV. CONCLUSION

A new ESR spectrum (Si-KU4) of the excited triplet states of radiation defects having orthorhombic (C_{2v}) symmetry was found in γ-rays irradiated silicon by SDR-ESR spectroscopy. A tentative model of Si-KU4 composed of two equivalent C_s atoms having a vacancy between them (C_s–V–C_s) was suggested. A possible mechanism of the (C_s–V–C_s) formation as successive capture of two vacancies by (C_s-C_i) center was considered.

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