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Identification of the negative carbon vacancy at quasi-cubic site in 4H-SiC by EPR and theoretical calculations

X. T. Trinh^{1,a*}, K. Szász^{2,b}, T. Hornos^{2,c}, K. Kawahara^{3,d}, J. Suda^{3,e},
T. Kimoto^{3,f}, Á. Gali^{2,4,g}, E. Janzén^{1,h} and N. T. Son^{1,i}

¹Department of Physics, Chemistry and Biology, Linköping University, Sweden

²Institute for Solid State Physics and Optics, Wigner Research Centre for Physics, Hungarian Academy of Sciences, Hungary

³Institute of Physics, Loránd Eötvös University, Hungary

⁴Department of Electronic Science and Engineering, Kyoto University, Japan

⁵Department of Atomic Physics, Budapest University of Technology and Economics, Hungary

^axuatr@ifm.liu.se, ^bszasz.krisztian@wigner.mta.hu, ^ctom.hornos@gmail.com,

^dkawahara@semicon.kuee.kyoto-u.ac.jp, ^esuda@kuee.kyoto-u.ac.jp,

^fkimoto@kuee.kyoto-u.ac.jp, ^gagali@szfki.hu, ^herija@ifm.liu.se, ⁱson@ifm.liu.se

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Abstract. In freestanding *n*-type 4H-SiC epilayers irradiated with low-energy (250 keV) electrons at room temperature, the electron paramagnetic resonance (EPR) spectrum of the negative carbon vacancy at the hexagonal site, $V_C^-(h)$, and a new signal were observed. From the similarity in defect formation and the spin-Hamiltonian parameters of the two defects, the new center is suggested to be the negative C vacancy at the quasi-cubic site, $V_C^-(k)$. The identification is further supported by hyperfine calculations.

Introduction

The carbon vacancies in 4H-SiC were predicted to have low formation energies and their different charge states from double positive charge to double negative charge states are within the band gap [1-3]. In a previous electron paramagnetic resonance (EPR) study of *n*-type 4H-SiC substrates irradiated by high-energy (2 MeV) electrons, only the negative carbon vacancy at the hexagonal site, $V_C^-(h)$, was identified [4]. In a recent study of high-doped *n*-type 4H-SiC freestanding layers irradiated by low-energy (250 keV) electrons, which create defects mainly in the C sublattice such as C vacancies, C interstitials and their associated complexes, two dominant EPR signals, $V_C^-(h)$ and a new center, have been observed [5]. However, due to the interference of strong EPR signals of the N shallow donor in the unirradiated side of the layer, the study of these two centers could only be done at elevated temperatures (>100 K) when the N signals disappeared. In the present study, using layers with both sides irradiated to avoid the interference of the signals of the N donors, EPR studies can be performed also at low temperatures. Combining EPR results obtained in a wide temperature range and theoretical calculations of the ligand hyperfine constants of V_C^- at two equivalent lattice sites, we identify the new EPR signal as the negative C vacancy at the quasi-cubic site, $V_C^-(k)$, and consolidate the previous assignment of V_C^{2-} as the origin of the Z_1/Z_2 negative-U defect [5,6].

Result and discussion

Freestanding *n*-type 4H-SiC layers (~100 μm thick) with the N concentrations of $[N] \sim 1.6 \times 10^{17} \text{ cm}^{-3}$ were irradiated by 250 keV electrons at room temperature to a fluence of $\sim 7.5 \times 10^{18} \text{ cm}^{-2}$ on

both sides. After irradiation, the layers become semi-insulating with the Fermi level located at ~ 0.53 eV below the conduction band [6]. The EPR spectrum measured at 6 K in darkness shows only the SI-1 signal [7] [Fig. 1(a)]. When the temperature reaches ~ 85 K, two EPR lines appear. Fig. 1(b) shows the EPR spectrum measured at 100 K in darkness for the magnetic field $\mathbf{B}$ along the c-axis ($\mathbf{B} \parallel \mathbf{c}$). Both lines are dramatically enhanced by illumination with energies $h\nu \sim 1.3$ eV. The higher field line is from $V_C^-(h)$ [4] and the new line at a slightly lower field was previously assumed to be related to $V_C^-(k)$ based on the similarity in the observed spin-Hamiltonian parameters of the two centers and their formation [5]. The temperature dependence of the signals in darkness is typical for a negative-U system. In equilibrium, V_C is in the EPR inactive 2- charge state, which lies deeper than the $(-|0)$ state. The activation of $V_C^-(k)$ requires either thermal energies (i.e., high temperatures) or illumination. The $V_C^-(k)$ line disappears when the temperature is ≥ 250 K, whereas the $V_C^-(h)$ signal can be detected at 295 K [Fig. 1(c)]. This indicates that the $(-|0)$ is deeper for $V_C^-(h)$ than for $V_C^-(k)$, supporting the previous assignment of the levels of V_C [5]. The spin-Hamiltonian parameters of $V_C^-(h)$ and $V_C^-(k)$ at 140-150 K were previously determined [4,5]. Below we show our study of $V_C^-(k)$ at low temperature.

The activation of the negative charge state by light is much less efficient for $V_C^-(h)$ than for $V_C^-(k)$ at low temperatures. At ~ 30 K and under weak illumination with light of photon energy $h\nu \sim 1.3$ eV, the $V_C^-(h)$ signal is almost in the noise level and only the $V_C^-(k)$ spectrum consisting of a strong main line accompanied by three pairs of satellites was observed [Fig. 2(a)]. The intensity ratios between the largest and smallest splitting hf lines and the main lines are $\sim 10\%$, which is approximately the natural abundance of two ^{29}Si atom ($I=1/2$ and 4.67% natural abundance), and are therefore assigned to the hf structures due to the hf interactions between the electron spin and the nuclear spin of one ^{29}Si atom occupying one of two Si sites (denoted as $\text{Si}_{3,4}(k)$ and $\text{Si}_{5,6}(k)$, respectively). From the intensity ratio of $\sim 2.5\%$ of the main line, the weakest hf lines are assigned to the hf structure due to the hf interaction between the electron spin and the nuclear spin of one ^{13}C atom ($I=1/2$, 1.1%) occupying one of two C sites, denoted as $\text{C}_{1,2}(k)$.

The angular dependence of the line positions of $V_C^-(k)$ with $\mathbf{B}$ rotating in the $(1\bar{1}00)$ plane is shown in Fig. 2(b). The splitting of the main line into three lines at arbitrary directions indicates the C_{1h} symmetry of the center. This angular dependence can be described by the spin-Hamiltonian

$$\mathcal{H} = \mu_B \mathbf{g} \cdot \mathbf{B} \cdot \mathbf{S} + \sum_i \mathbf{S} \cdot \mathbf{A}_i \cdot \mathbf{I}_i \quad (1)$$

Here μ_B is the Bohr magneton with $S=1/2$ and $I=1/2$. The first term describes the electron Zeeman interaction and the second term represents the hf interactions between the electron spin

Fig. 1. EPR spectra in a high-doped n-type 4H-SiC layer irradiated with 250 keV electrons measured in darkness for $\mathbf{B} \parallel \mathbf{c}$ at different temperatures. (a) At 6 K, only the SI-1 signal [7] can be observed; (b) at 100 K, weak $V_C^-(k)$ and $V_C^-(h)$ signals could be detected while (c) at 295 K, only $V_C^-(h)$ spectrum could be observed.

Fig. 2. EPR spectra of $V_C^-(k)$ measured at 30 K under illumination with light of photon energies $h\nu \sim 1.3$ eV for magnetic field parallel to c -axis (a) and the angular dependence of EPR signal positions of $V_C^-(k)$ (open circles) with magnetic field rotating in the $(1\ 0\ 0)$ plane (b). The solid curves represent the simulated angular dependence using parameters in Table 1 and Eq. (1). The inset shows the calculated spin densities for stable configuration, which predominantly occurs at low temperatures, giving rise to the observed hf structures due to hf interaction with two nearest Si neighbors in the basal plane [$Si_{3,4}(k)$] and with C and Si atoms in the second and third nearest neighbors [$C_{1,2}(k)$, $Si_{5,6}(k)$, respectively].

and the nuclear spin of ^{29}Si and ^{13}C neighboring atoms. The principal values of the g - and A -tensors for $V_C^-(k)$ at 30 K obtained from the best fits are given in Table 1. The simulated angular dependences of line positions for $V_C^-(k)$ using obtained parameters and Eq (1) are also plotted as solid curves in Fig. 2(b).

Table 1. Spin-Hamiltonian parameters of $V_C^-(k)$ in 4H-SiC at 30 K determined by EPR. The principal A -values are given in the unit of mT (1 mT=28.025 MHz). The polar angle θ and azimuthal angle ϕ of the principal Z axis of the g - and A -tensors are given in degrees. The angles $\phi=0$ and $\phi=90$ correspond to the $[1\ 1\ \bar{2}\ 0]$ and $[1\ \bar{1}\ 0\ 0]$ directions, respectively. The corresponding calculated values for the stable configuration of $V_C^-(k)$ are given in parentheses. The parameters of the $V_C^-(h)$ at 60 K [4] were also given for comparison.

Center	Parameters	X($\perp$)	Y($\perp$)	Z($\parallel$)	θ	ϕ
$V_C^-(k)$ at 30 K	g	2.0027	2.0038	2.0054	9.9	90
	$A(Si_{3,4})$	10.04 (9.38)	10.15 (9.61)	12.99 (12.71)	68.9 (69.9)	39.0 (41.0)
	$A(C_{1,2})$	1.33 (1.27)	1.31 (1.26)	1.85 (1.86)	62.7 (63.6)	51.8 (47.2)
	$A(Si_{5,6})$	0.87 (0.78)	0.85 (0.74)	1.12 (1.03)	82.3 (82.4)	6.4 (5.6)
$V_C^-(h)$ at 60 K [4]	g	2.00407	2.00287	2.00459	38	
	$A(Si_1)$	7.76	7.76	10.07	7	
	$A(Si_2)$	11.67	11.78	15.19	101	

Supercell (576 atoms) calculations of $V_C^-(k)$ in 4H-SiC using HSE06 hybrid density functional [9] found two C_{1h} configurations with one stable at low temperatures. Combining HSE06 hybrid

density functional with the contribution of the core spin-polarization [10], we calculate the ligand hf constants for $V_C^-(k)$. The spin density for the stable configuration of $V_C^-(k)$, which is expected to occur predominantly at low temperature and correspond with observed EPR hf lines at 30 K, is shown in the inset in Fig. 2(b). The obtained principal values of the hf tensors for the hf interaction between the electron spin and the nuclear spins of neighboring ^{29}Si and ^{13}C atoms, $\text{Si}_{3,4}(k)$, $\text{C}_{1,2}(k)$, $\text{Si}_{5,6}(k)$, are given in Table 1. As can be seen in Table 1, the ligand hf constants of $V_C^-(k)$ obtained by calculations are in good agreement with that determined by EPR, supporting the identification of $V_C^-(k)$.

For $V_C^-(h)$ at low temperatures, only the hf interactions with the Si_1 along the c-axis and one of three Si atoms in the basal plane (Si_2) were observed [4]. It can be seen from the hf constants (Table 1) that the spin density is distributed more in $(11\bar{2}0)$ or equivalent planes (in the c-direction) for $V_C^-(h)$ and mainly in the basal plane for $V_C^-(k)$.

Summary

Using high-doped *n*-type 4H-SiC freestanding layers irradiated with 250 keV electrons, we were able to study the EPR signals of V_C^- at low temperatures. The ligand hf constants determined by EPR and by supercell calculations are in good agreement with each other, supporting the identification of V_C^- at the quasi-cubic site. The temperature dependence of the EPR signal of V_C^- reveals the negative-U behavior of V_C^- and supports previous identification of the origin of the Z_1/Z_2 center and its higher-lying Z_1 and Z_2 levels to be related to the double and single acceptor levels of V_C at the hexagonal and quasi-cubic sites, respectively.

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