Negative-U System of Carbon Vacancy in 4H-SiC


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(Received 23 August 2012; published 31 October 2012)

Using electron paramagnetic resonance (EPR), energy levels of the carbon vacancy ($V_C$) in 4H-SiC and its negative-U properties have been determined. Combining EPR and deep-level transient spectroscopy we show that the two most common defects in as-grown 4H-SiC—the $Z_{1/2}$ lifetime-limiting defect and the $EH_7$ deep defect—are related to the double acceptor (2−0) and single donor (0+) levels of $V_C$, respectively.

DOI: 10.1103/PhysRevLett.109.187603 PACS numbers: 76.30.Mi, 61.72.jd, 61.82.Fk, 71.55.Ht

It has been suggested by Anderson [1] that the energy gain associated with electron pairing in the dangling bonds of a defect and coupled with a large lattice relaxation might overcome the Coulomb repulsion of the two electrons, resulting in a net effective attractive interaction between the electrons at the site (a negative correlation energy $U$ or negative $U$). For a vacancy with spread dangling bonds, reconstructed bonds can be formed leading to symmetry lowering of the defect. This splits up the degenerate state, facilitating the electron pairing and the capture of a second electron may lead to lowering of the energy. Such a defect is called a negative-U center. A typical example of a negative-U defect is the monovacancy in Si [2].

In 4H-SiC, calculations without charge correction [3] suggested that $V_C$ is a negative-U center for negative and positive charge states. With including charge correction, the negative-U behavior is not found in some calculations [4] while it remains in another [5] for $V_C$ in the negative charge state. A recent calculation using hybrid density functionals [6] found the negative-U behavior of $V_C$ at the quasicubic k site, $V_C(k)$, with the double negative (2−0) charge states lying slightly (< 0.1 eV) lower than the single negative (−0) charge state. The symmetry lowering (to $C_{1h}$) of $V_C$ was confirmed by electron paramagnetic resonance (EPR) in 4H- and 6H-SiC [7–9]. The EPR signal of the positive vacancy ($V_C^+(h)$ and $V_C^+(k)$) [7,9] and $V_C^-(h)$ (Ref. [8]) have been observed and no clear data indicating the negative-U behavior of $V_C$ have so far been reported.

$V_C$ is predicted to have low formation energies in both Si- and C-rich conditions [3,4,6]. $V_C$ is frequently detected by EPR in high-purity semi-insulating substrates and is believed to play an important role in carrier compensation [10]. It has been shown from deep-level transient spectroscopy (DLTS) that the two most common and unavoidable defect levels in as-grown 4H-SiC layers grown by chemical vapor deposition (CVD) are the $Z_{1/2}$ level [11] at ~0.56–0.71 eV below the conduction band minimum $E_C$ and the $EH_7$ level at ~$E_C – (1.55–1.65)$ eV [12,13]. The $Z_{1/2}$ level in 4H-SiC is known to be a negative-U center associated with two higher-lying levels, $Z_1$ at ~0.52 eV and $Z_2$ at ~0.45 eV below $E_C$ [14]. Different defect models such as the divacancy [15], nitrogen-related defect [16] or N-dicarbon interstitial complex [17] were suggested for $Z_{1/2}$. The $Z_{1/2}$ center was found to appear always together with the $EH_7$ defect with the same depth profile in 4H-SiC CVD layers and to act as dominant carrier-lifetime-limiting defect in the material [18]. The concentrations of these two levels in CVD layers were found to be (i) significantly increased after irradiation even with low-energy (116–210 keV) electrons which displace C atoms only, creating defects in the C sublattice [13,19] and (ii) very close to each other in all kind of samples regardless of growth, irradiation, or annealing conditions used [13]. The $Z_{1/2}$ and $EH_7$ levels were, therefore, suggested to belong to the same defect such as $V_C$ or a $V_C$-related complex [20]. It has been shown that the concentrations of the $Z_{1/2}$ and $EH_7$ levels can be efficiently reduced by C implantation and annealing [20] or by thermal oxidation [21,22], supporting the $V_C$-related defect model. However, due to the lack of experimental evidence indicating the negative-U behavior of $V_C$, the origin of the $Z_{1/2}$ defect remains to be identified. Concurrent with the reduction of the $Z_{1/2}$ concentration, a significant increase of the carrier lifetime was observed [21–23], confirming that $Z_{1/2}$ is the dominant lifetime-limiting defect in the material and, hence, technologically important for device applications.
In this Letter, we report the result of our EPR study of $n$-type 4H-SiC epitaxial layers irradiated with low-energy electrons (250 keV) which generate mainly $V_C$, $C$ interstitials and their associated defects. (The Si vacancy can be created by 250 keV electrons but its concentration is below the detection limit of EPR.) With the presence of only $V_C$ in absence of other EPR signals, which are dominant in samples irradiated by high-energy electrons, we could detect both the signals of $V_C(h)$ and $V_C(k)$. Using EPR and photoeitxation EPR (photo-EPR) we could determine the ionization energy of the single and double acceptor states of $V_C$ and to reveal its negative-$U$ properties. 

The energy levels of $V_C$ obtained by EPR correlate well with those determined by DLTS for the negative-$U$ $Z_{1/2}$ center [14], allowing an unambiguous identification of the $Z_{1/2}$ center as the doubly negatively charged ($2–0$) state of $V_C$. Our study of the depth profile of the carrier concentration by capacitance-voltage ($C-V$) measurements and DLTS also shows that the $Z_{1/2}$ and $E_{H_0/7}$ centers in implanted and annealed samples are of double acceptor and single donor type, respectively, supporting the identification of these deep levels to different charge states of $V_C$.

The starting material is $n$-type 4H-SiC layers grown on 4H-SiC substrates. The layers are 100 μm thick with the N concentration of $\sim 1.6 \times 10^{17}$ cm$^{-3}$. Two sets of samples, each consisting of five samples, labeled A–E, were prepared for EPR (with substrate removed) and DLTS measurements. The layers were irradiated by 250 keV electrons at room temperature with different fluences (sample A: 7.5, B: 7.2, C: 5.7, D: 4.3, and E: 3.1, in $10^{18}$ cm$^{-2}$). EPR measurements were performed on a X-band ($\sim 9.4$ GHz) Bruker E500 spectrometer equipped with a He-flow cryostat allowing the regulation of the sample temperature in the range 4–295 K. For illumination, a halogen lamp (200 W) and a 0.25 m single grating Jobin-Yvon monochromator were used as a light source. In photo-EPR experiments, we used the second order of a 600 g/mm grating which gives a dispersion of 3.2 nm/mm. With a fully open slit (3 mm), the band width of the excitation is 9.6 nm (or $\sim 4$–6 meV in the spectral region 1700–1500 nm). With the error of $\sim 6$ meV in the photon energy, the error in determination of the energy threshold is expected to be within ±10 meV. For DLTS and $C-V$ measurements, we also used $n$-type epitaxial layers ($\sim 10$ μm thick) with a net doping concentration of $\sim 2.5 \times 10^{15}$ cm$^{-3}$ and implanted with 4.3 MeV $^{28}$Si ions at room temperature to doses of $1–4 \times 10^8$ cm$^{-2}$ which result in a nonuniform defect distribution with a peak at $\sim 1.8$ μm. The implanted samples were then annealed at 1150 °C in N$_2$ flow for 3.5 h followed by thermal evaporation of Ni to form Schottky barrier contacts. $C-V$ (using 1 MHz probe and 1 Hz sweep frequency) and DLTS measurements were performed in the temperature range 150–700 K.

We found from $C-V$ measurements that there is a compensated region (CR) in highly irradiated samples (A–D) where the N donors were completely compensated by deep levels. The thickness of the CR varies with the electron fluence (from $\sim 25$ μm for sample D to $\sim 45$ μm for sample A). In the CR, the Fermi level is located at $\sim E_F = 0.53$ eV as estimated from the series resistance of the Schottky barrier diodes. No EPR signal of $V_C$ could be detected in darkness at low temperatures ($T < 80$–85 K for samples A–D and at above 100 K for sample E) [Fig. 1(a)]. A weak signal of $V_C(h)$ could be detected in darkness at $T > 90$ K in the samples A–D. In the heavily irradiated sample A, a new line was detected in addition to the $V_C(h)$ signal [Fig. 1(b)]. Under illumination, the signals of $V_C(h)$ and the new line increase substantially [Fig. 1(c)]. After illumination, the signals are persistent in darkness. The principal values of the $g$ tensor and the Si hyperfine (hf) $A$ tensor determined at 140 K for $V_C(h)$ are $g_\| = 2.0040$, $g_\perp = 2.0038$, and the $A$ values (in unit of mT) $A_g = 9.92$, $A_\perp = 7.72$ (for Si atom along the $c$ axis) and $A_{105} = 4.11$, $A_{104} = 4.05$, $A_{103} = 5.21$ (for three Si$_{1–4}$ atoms in the basal plane). For the new spectrum, the corresponding parameters are $g_\| = 2.0046$,

![FIG. 1 (color online). EPR spectra in $n$-type 4H-SiC CVD layers irradiated by 250 keV electrons with different fluences (sample E: $3.1 \times 10^{18}$ cm$^{-2}$, C: $5.7 \times 10^{18}$ cm$^{-2}$ and A: $7.5 \times 10^{18}$ cm$^{-2}$) measured at 100 K (a)–(b) in darkness and (c) under illumination. The dependence of the EPR intensity of $V_C(h)$ and $V_C(k)$ on the photon energy in (d) sample E and (e) sample C. The error in determination of the energy threshold in the spectral region is within ±0.01 eV.](http://example.com/fig1.png)
g_\perp = 2.0035, A_{||} = 3.69, A_{\perp} = 2.96 \text{ (for Si)}_1, A_{xx} = 6.05, A_{yy} = 5.94, A_{zz} = 7.49 \text{ (for Si}_2\text{–}_4). \text{ The angle } \theta \text{ between the principal } A_{zz} \text{ and the } c \text{ axis is } 75.9^\circ \text{ for } V_C^-(h) \text{ and } 69.2^\circ \text{ for the new center. The experimental errors are } \pm 0.0001 \text{ for the } g \text{ values and } \pm 0.08 \text{ mT for the } A \text{ values. For the new spectrum, the } \text{hf constants of } \text{Si}_2\text{–}_4 \text{ are larger than that of Si}_1. \text{ From the obtained } g \text{ tensor and the Si hf tensors, this new spectrum is identified to be related to } V_C^-(h) \text{ [24].}

Photo-EPR experiments were performed on samples } E \text{ and } C. \text{ The dependence of the EPR intensity of } V_C^-(h) \text{ and } V_C^-(k) \text{ on the photon energy is shown in Fig. 1(d) for sample } E \text{ and in Fig. 1(e) for sample } C. \text{ The temperature dependence of the } V_C^- \text{ signal in darkness and the photo-EPR data can be explained by the scheme of energy levels of a negative- } U \text{ center in Fig. 2 with the } (2\text{-}0) \text{ level lying lower than the } (1\text{-}0) \text{ level. In the single negative charge state, } V_C^- \text{ prefers to capture another electron to become doubly negatively charged and lowers its energy. Thus, at low temperatures, } V_C^- \text{ is in the } 2^- \text{ charge state } (S = 0) \text{ and no EPR signal can be observed. At elevated temperatures (} > 90 \text{ K}), \text{ the higher-lying } (1\text{-}0) \text{ state can be partly populated due to internal thermal excitation of electrons from the } (2\text{-}0) \text{ level and, hence, a weak signal of } V_C^- \text{ could be detected in darkness [Fig. 1(b)]. We assign the energy threshold of } \sim 0.74 \text{ eV for observing the } V_C^-(k) \text{ signal in sample } E \text{ [see Fig. 1(d)] to the optical transition from the } (2\text{-}0) \text{ level to } E_C^- \text{. The corresponding transition for } V_C^-(h) \text{ is } \sim 0.78 \text{ eV [Fig. 1(d)]. In sample } C, \text{ the } V_C^- \text{ signal already weakly appears in darkness (at 100 K). When the photon energy reaches } h\nu \sim 0.74 \text{ eV, the } V_C^- \text{ signal appears as expected [Fig. 1(e)]. The } V_C^- \text{ signal starts decreasing at } h\nu \sim 0.74 \text{ eV. We attributed this threshold } (\sim 0.74 \text{ eV}) \text{ to the transition from the } (1\text{-}0) \text{ level of } V_C^-(h) \text{ to } E_C^- \text{ which reduces the population of the } (1\text{-}0) \text{ level and, hence, the } V_C^- \text{ signal.}

In agreement with previous studies [25], we also found that in } n\text{-type } 4H\text{-SiC irradiated with } 250 \text{ keV electrons } V_C^- \text{ is the dominant EPR defect and } Z_{1/2} \text{ and } E_{H_7} \text{ are the dominant DLTS centers. The obtained energy transitions from the } (2\text{-}0) \text{ level of } V_C^- \text{ to } E_C^- \text{ (} \sim 0.74 \text{ eV for } V_C^-(k) \text{ and } \sim 0.78 \text{ eV for } V_C^-(h) \text{) are very close to the ionization energy of the } Z_{1/2} \text{ level } (E_C^- \sim 0.56\text{–}0.71 \text{ eV}) \text{ [14,15]. The transition from the } (1\text{-}0) \text{ level of } V_C^- \text{ to } E_C^- \text{ (} \sim 0.74 \text{ eV}) \text{ is also close to the ionization energy of the higher-lying states } Z_1 \text{ (} \sim E_C^- - 0.52 \text{ eV) and } Z_2 \text{ (} \sim E_C^- - 0.45 \text{ eV}) \text{ [14]. (The optical transitions involve a Franck-Condon shift in the range } \sim 0.03\text{–}0.3 \text{ eV, which is also in good agreement with the recent calculated values [5].)

Since the } V_C^- \text{ signal can be detected in darkness in samples } A\text{–}D \text{ at } T > 90 \text{ K, whereas } V_C^-(k) \text{ can only be weakly seen in sample } A \text{ at } T \sim 100\text{–}130 \text{ K, it is likely that the energy separation between the } (2\text{-}0) \text{ and } (1\text{-}0) \text{ levels is smaller for } V_C^- \text{ and larger for } V_C^-(k). \text{ Therefore, we assign } V_C^- \text{ to } Z_1 \text{ and } V_C^-(k) \text{ to } Z_2. \text{ The optical transitions from the acceptor states of } V_C^- \text{ to } E_C \text{ are shown in Fig. 2. For comparison, the ionization energies of } Z_{1/2} \text{ center determined by DLTS [14,15] are also shown in Fig. 2. The same DLTS defect in } 6H\text{-SiC (the } E_1 \text{ and } E_2 \text{ centers) also shows a similar order of the energy levels of } E_1 \text{ (} V_C^- \text{ at } h\text{–}site \text{) and } E_2 \text{ (} V_C^- \text{ at two cubic } k_1 \text{ and } k_2 \text{ sites with double intensity) [26]. Here we reassign the charge states proposed in Ref. [14] from } (0\text{+}) \text{ to } (1\text{-}0) \text{ for } Z_1 \text{ and } Z_2 \text{ and from } (1\text{–}+) \text{ to } (2\text{-}0) \text{ for } Z_{1/2}. \text{ The energy transitions observed in our photo-EPR experiments are smaller than those obtained before in Ref. [25]. In those photo-EPR experiments on low-doped } (\sim 7 \times 10^{14} \text{ cm}^{-3}) \text{ samples [25], the concentration of } V_C^- \text{ is limited by the N concentration (more than 2 orders of magnitude less compared to the doping level in our samples } A\text{–}E \text{) and, therefore, the } V_C^- \text{ signal was much weaker and could only be detected with excitation energies above } \sim 1.0 \text{ eV [25]. The obtained energies of acceptor levels of } V_C^- \text{ are rather close to those reported in recent hybrid functional calculations [6]. However, after charge correction, the negative- } U \text{ behavior of } V_C^- \text{ disappeared [6]. It is clear that the methods used for charge correction in conventional [4] or hybrid functional calculations [6] result in an overcorrection.}

The threshold } \sim 1.8\text{–}1.9 \text{ eV present in previous photo-EPR experiments [27,28] has recently been reassigned to the transition from the valence band } E_V \text{ to the } (2\text{+1}+) \text{ level of } V_C \text{ [5]. However, the reassignment was made by considering only the photo-EPR data for irradiated } p\text{-type [27] and as-grown semi-insulating [28] materials. Such an excitation is clearly not possible in irradiated } n\text{-type material [8,25] with the Fermi level located close to the } (2\text{-}0) \text{ state of } V_C^- \text{ and neither } V_C^- \text{ nor } V_C^+ \text{ signals could be

FIG. 2 (color online). Scheme of energy levels of } V_C \text{, determined by photo-EPR. The } Z_{1/2} \text{ and } E_{H_7} \text{ levels determined by DLTS [11,14,15] are given for comparison. Here the optical transitions obtained by photo-EPR involve a Franck-Condon shift in the range } \sim 0.03\text{–}0.3 \text{ eV. For clarity, the location of the states in the scheme does not follow the relative scale and the levels determined by photo-EPR are aligned to the corresponding levels determined by DLTS the optical transitions from the } (1\text{-}0) \text{ and } (2\text{-}0) \text{ states to the conduction band involve different Franck-Condon shifts for } V_C^- \text{ and } V_C^-(k). \text{ The photo-EPR data for the } (0\text{+}) \text{ level are from Ref. [25].}
of a nonuniform distribution of deep acceptorlike traps which excites electrons from the (0|+) level to \( E_C \) as illustrated in Fig. 2. The threshold correlates well with the DLTS \( E_{H6/7} \) level, or more precisely, the \( E_{H7} \) level in material irradiated with low-energy electrons \([13,19,25]\) where the \( V_C \) EPR center and the \( Z_{1/2} \) and \( E_{H7} \) DLTS centers are the clearly dominant defects \([25]\). The Franck-Condon shift involved in the \( \sim 1.8 \) eV optical excitation is in the range of \( \sim 0.25 \) eV, corroborating the association with the \( E_{H7} \) level at \( \sim 1.55 \) eV below \( E_C \).

The double acceptor nature of \( Z_{1/2} \) and donor behavior of \( E_{H6/7} \), inferred from the EPR data, are unambiguously confirmed by C-V measurements performed on Si-implanted and annealed high-purity (epitaxial) \( n \)-type samples where the concentration of other deep-level defects is more than 1 order of magnitude lower than that of \( Z_{1/2} \) and \( E_{H6/7} \). At a sample temperature of 190 K, the thermal emission rate of electrons from the \( Z_{1/2} \) level (and the \( E_{H6/7} \) level) to \( E_C \) is negligible compared to both the probe (1 MHz) and sweep (1 Hz) rates used and the recorded data yield the true profile of responding electrons, i.e., the difference between the profile of shallow nitrogen donors and that of electrons trapped by \( Z_{1/2} \), Fig. 3(a). At 300 K, \( Z_{1/2} \) responds to the sweep voltage but not to the probe one, and an anomalous peak occurs at \( \sim 2.4 \) \( \mu \)m in Fig. 3(a). The occurrence of such a peak is a unique feature of a nonuniform distribution of deep acceptorlike traps \([29]\), and no evidence is found for a donorlike behavior of \( Z_{1/2} \), arising from the \( \sim E_C - 0.5 \) eV levels. Indeed, the data measured at 700 K, where \( Z_{1/2} \) responds to both the probe and sweep voltages, unambiguously rule out any donor activity of \( Z_{1/2} \) since the electron concentration at the maximum position of the defect profile ( \( \sim 1.8 \) \( \mu \)m) is essentially equal to the shallow nitrogen donor concentration. Moreover, at 700 K an intermediate case occurs for the \( E_{H6/7} \) center, responding to the sweep voltage but not the probe one, and as shown in Fig. 3(b), excellent agreement is obtained between the measurements and simulations assuming \( E_{H6/7} \) to be a donor. The simulations are based on a refined version of the model originally developed by Kimerling \([29]\) and as illustrated in Fig. 3(a), also the data at 190 and 300 K are closely reproduced by the simulations regarding \( Z_{1/2} \) as a double acceptor. In fact, \( Z_{1/2} \) and \( E_{H6/7} \) are found to exhibit identical concentration-versus-depth profiles except for a two-to-one ratio between the absolute values, showing the double acceptor and single donor behavior of \( Z_{1/2} \) and \( E_{H6/7} \), respectively, and fully supporting the conclusion from the EPR data that they originate from the same defect, \( V_C \).

In summary, using N-doped \( n \)-type 4H-SiC epitaxial layers irradiated with low-energy electrons (250 keV), we were able to detect the \( V_C \) signal at both the \( h \) and \( k \) site and to obtain more accurate energies of the single and double negative charge states of \( V_C \), showing its negative-\( U \) system. The direct correlation between EPR and DLTS data enables an unambiguous identification of the DLTS \( Z_{1/2} \) center \([\sim E_C - (0.56-0.71) \) eV\]) to the (2|0) of \( V_C \) and its higher-lying \( Z_1 \) \((\sim E_C - 0.52 \) eV\)) and \( Z_2 \) \((\sim E_C - 0.45 \) eV\)) states to the (0|0) states of \( V_C(h) \) and \( V_C(k) \), respectively. The carrier concentration-versus-depth profiles, obtained at different temperatures and with \( Z_{1/2} \) and \( E_{H6/7} \) as the decisive centers, fully support the conclusion from EPR that they are related to the double acceptor (2|0) and single donor (0|+) states of \( V_C \), respectively.

Support from the Swedish Energy Agency, the Swedish Research Council VR/Linné Environment LiLI-NFM, the Knut and Alice Wallenberg Foundation, the Norwegian Research Council (FRINAT program, CAPSiC and WEDD projects), and the Grant-in-Aid for Scientific Research (21226008) from JSPS is gratefully acknowledged.