Charge state control of the silicon vacancy and divacancy in silicon carbide

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ABSTRACT

Color centers in silicon carbide (SiC), such as the negative silicon vacancy (V_{Si}^-) and neutral divacancy ($V_{Si}V_C^0$), have recently been shown to be promising quantum bits (qubits) for a variety of applications in quantum communications and sensing. Considerable effort has been spent on improving the performance of these optical spin qubits, and the instability of their charge state is an important issue to be solved. Using electron paramagnetic resonance to monitor the charge state of dominant intrinsic defects in n-type, high-purity semi-insulating and p-type 4H-SiC, we reveal carrier compensation processes and the windows of the Fermi level that allow us to obtain stable V_{Si}^- and $V_{Si}V_C^0$ in equilibrium. We show that stable V_{Si}^- and $V_{Si}V_C^0$ ensembles can be obtained in n-type (p-type) via controlling the concentration of the Si vacancy (the C vacancy and the C antisite–vacancy pairs). The charge-state control of single V_{Si}^- and $V_{Si}V_C^0$ emitters is expected to be possible in pure p-type layers by controlling the concentration of the C vacancy. In ultrapure materials, optical repumping is required for charge state control of single emitters.

I. INTRODUCTION

Point defects in wide-bandgap semiconductors can have both ground and excited states within the energy gap and, hence, are luminescent centers or often called color centers. With the ground state being deep in the bandgap, the luminescence is often stable even at room temperature. Many color centers also possess a non-zero electron spin and can be excellent candidates for optical spin quantum bits (qubits).[1] The internal optical transitions within a defect provide the possibility to use resonant excitation to activate a particular optical transition without activating other luminescent centers and electronic states of the host. This helps to reduce the competition with other radiative and non-radiative recombination channels, enhancing the brightness of emitters and reducing the disturbance from other ionized defects. For semiconductors with host elements having low natural abundance of non-zero nuclear-spin isotopes like diamond and silicon carbide (SiC) (^{13}C: 1.1% with nuclear spin $I = 1/2$; ^{29}Si: 4.7%, $I = 1/2$), electron spins can have long coherence times owing to the diluted nuclear spin bath. A recent simulation of the coherence time in more than 12 000 host compounds at natural isotopic abundance

shows that SiC possesses the longest coherence times among widegap nonchalcogenides.[2] These favorable optical and spin properties make color centers in diamond and SiC promising spin qubits for applications in quantum technologies.[3–6]

In the development of solid-state spin qubits, the nitrogen-vacancy (NV) center in diamond is the leading contender.[3,4] Recently, SiC has emerged as a promising platform hosting different color centers that emit light near the telecom wavelengths and have long spin coherence times, favoring applications in quantum communications.[6] Among these, the negative Si vacancy (V_{Si}^-)[7] with zero-phonon lines (ZPLs) at 861.6 nm (V1 center) and 916.5 nm (V2 center) in 4H-SiC[8] and the neutral divacancy ($V_{Si}V_C^0$),[9,10] i.e., an uncharged complex consisting of a C vacancy (V_C) and a nearest Si vacancy, with ZPLs in the region of 1078–1132 nm in 4H-SiC,[11] are the most studied centers. Single emitters of the Si vacancy[12] and divacancy centers[13] with long coherence times have been realized. Resonant excitation can increase the readout contrast of single emitters from a few percent to ~94% for $V_{Si}V_C^0$.[14] However, under resonant excitation or off-resonant excitation with photon energies below certain thresholds, the photoluminescence (PL) decays with

time as observed for divacancy[15–17] and Si vacancy centers.[18] This is a common problem for color centers in wide-bandgap semiconductors, including the NV center in diamond. A second repump laser at a shorter wavelength is used for activating the desired charge state,[15–18] but in some cases, the PL decay and optical bleaching still occur for single V_{Si}^- emitters.[18] Repumping excites electrons to the conduction band (CB) and activates other defects, which interfere with the recombination process. These ionized and de-ionized defects create a fluctuating electrical environment, which influences the optical fine structure of quantum emitters, causing random jumps in the wavelength of the ZPLs and, hence, enhancing inhomogeneous line broadening, also known as spectral diffusion. Combining repumping with the electrical charge control using p-i-n or Schottky diodes has been shown to be a very effective way for controlling the charge state of the divacancy[19,20] and the Si vacancy[21,22] in SiC, allowing for fast switching between the bright and dark states. However, this approach is difficult to be implemented, e.g., for quantum emitters embedded in photonic devices.

In this work, we use electron paramagnetic resonance (EPR) to monitor the charge state of dominant intrinsic defects in equilibrium in n-type, high-purity semi-insulating (HPSI) and p-type 4H-SiC. By varying the concentration of defects in a large range by electron irradiation, we reveal the carrier compensation processes and the conditions for obtaining stable V_{Si}^- and $V_{Si}V_C^0$ centers under equilibrium. We show the defect control for achieving photostable V_{Si}^- and $V_{Si}V_C^0$ ensembles in n-type, p-type, and HPSI materials without the need of optical and electrical charge control. The charge-state control of single V_{Si}^- and $V_{Si}V_C^0$ emitters in pure p-type SiC epilayers by controlling the concentration of the C vacancy and in ultrapure SiC materials by optical repumping is discussed.

II. EXPERIMENTAL

During the many years of work with the characterization of SiC, we have a large collection of materials including HPSI 4H-SiC substrates from different suppliers as well as n-type and p-type 4H-SiC irradiated by 2-, 2.5-, or 3-MeV electrons with the fluence covering a wide range of 10^{14}–10^{19} cm^{-2}. These samples have different initial doping levels and contain various dominant intrinsic defects, such as V_{Si}, V_C, $V_{Si}V_C$, and the C antisite–vacancy pair ($C_{Si}V_C$) (i.e., a complex between a C on a Si lattice site and a nearest C vacancy), with different concentrations. Annealing is performed in N_2 gas-flow ambient. Irradiated samples are annealed at temperatures in the range of 800–1050 °C for the creation of divacancy. The annealing time varies between 0.5 and 1 h.

EPR measurements are performed on a Bruker X-band (∼9.5 GHz) E500 spectrometer equipped with a continuous He-flowed cryostat allowing for the regulation of the sample temperature between 4 and 300 K.

The PL measurements are performed using a double monochromator (SPEX 1404) equipped with 600 grooves/mm gratings blazed at 1000 nm and an InGaAsP photomultiplier, which ensures optimum sensitivity in the emission region of divacancy.

III. RESULTS AND DISCUSSION

The primary defects induced by radiation in SiC are vacancies, interstitials, and antisites. Some dominant EPR defects, such as the

EI1 and EI3 centers,[23] have been attributed to C interstitial-related defects.[24] Interstitial defects in SiC are predicted to have low migration barriers and, hence, can be annealed out at low temperatures.[25,26] Various interstitial-related defects observed by deep level transient spectroscopy (DLTS) are found to be annealed out at temperatures below ∼500 °C.[27–29] The C antisite does not introduce any energy level within the bandgap and is electrically inactive. The Si antisite (Si_C) has a single donor level (+|0) at ∼0.35 eV above the valence band (VB)[30] and is not of importance for carrier compensation processes. In irradiated SiC after annealing at ∼400 °C, the main defects are vacancies (V_C and V_{Si}). The C vacancy is known to remain stable at very high annealing temperatures.[31,32] The Si vacancy becomes mobile at ∼700 °C, leading to the formation of divacancies and C antisite–vacancy pairs. However, it anneals out gradually in a wide temperature range and can still survive after annealing at ∼1000 °C as shown below. Thus, single vacancies (V_C and V_{Si}), the divacancy, and the C antisite–vacancy pairs are the dominant defects in annealed materials.

The energy levels (or more precisely the charge transition levels) of these vacancies and vacancy-associated defects given in Fig. 1 are determined by combining DLTS, EPR, and hybrid functional within density functional theory (DFT) calculations. For V_{Si}, the levels were reported by DFT calculations in combination with DLTS.[22,26,33,34] The levels of V_C were determined from DLTS, EPR, and calculations,[35–37] while for $V_{Si}V_C$, the energy levels were predicted from a recent calculation.[17] For the $C_{Si}V_C$ center, two donor levels and one acceptor level are predicted to be within the

FIG. 1. Energy-level diagram for different charge states of the dominant defects V_{Si}, V_C, $V_{Si}V_C$, and $C_{Si}V_C$ in 4H-SiC. The N_CV_{Si} pairs are expected in N-doped n-type materials after irradiation and annealing. The approximate levels are given in eV with respect to the valence band edge. The shallow N donor and B acceptor are two main residual impurities in undoped materials. In doped p-type materials, the main shallow acceptor is Al. The red and green levels refer to donor and acceptor states, respectively.

bandgap.[26,33] Its single donor level (+|0) at ~1.1 eV below the conduction band (CB) is supported by recent EPR work.[38] In N-doped n-type SiC, paired defects between a nitrogen donor and a nearest Si vacancy (termed the nitrogen-vacancy pair, $N_C V_{Si}$) are expected to form after irradiation and annealing. The acceptor levels of the $N_C V_{Si}$ pairs are predicted by DFT calculations.[39] In the following, we consider the carrier compensation between these dominant defects in n-type, p-type, and HPSI materials to find the conditions for achieving stable V_{Si}^- and $V_{Si}V_C^0$ in equilibrium.

A. N-type 4H-SiC

For the study of Si vacancy, it is desirable to anneal the sample at ~600 °C to remove interstitial-related defects without creating divacancies and C antisite–vacancy pairs. It can be judged from the diagram of energy levels in Fig. 1 that in irradiated n-type materials in the absence of the divacancy and C antisite–vacancy pair, V_{Si} can be stable in the negative charge state if the Fermi level is located at its (0|-) level at ~E_V + 1.25 eV. This means that the concentration of the N shallow donor should be lower than the total concentration of the B acceptor and V_{Si}. In commercial SiC grown by physical vapor transport (PVT), the concentration of residual B impurity is in the low 10^{15} cm^{-3} range. The contamination with B during the chemical vapor deposition (CVD) coming from the susceptor is less ([B] ~ $1–3 \times 10^{13}$ cm^{-3}). The concentration of the N shallow donor is [N] > 10^{17} cm^{-3} in commercial n-type SiC substrates grown by PVT and in the $10^{14}–10^{15}$ cm^{-3} range for commercial CVD layers.

Thus, for ensemble studies in commercial CVD SiC layers, a concentration of V_{Si} in the 10^{16} cm^{-3} range or larger is required to compensate the N donor for achieving the stable V_{Si}^- center. In practice, electron irradiation with a fluence of ~$1–5 \times 10^{17}$ cm^{-2} gives an optimum concentration of photostable V_{Si}^- centers for PL studies in CVD 4H-SiC layers. In such conditions, the emission is very stable and optically detected magnetic resonance (ODMR) of V_{Si}^- can be performed with resonant excitation without need for the use of a repump laser.[8,40]

It is more difficult to achieve V_{Si} stable in the negative charge state in equilibrium in PVT materials compared to CVD layers due to higher concentrations of the N donor. With irradiation fluences below 10^{18} cm^{-2}, the Fermi level is still at the N donor level, and typically, only the EPR spectrum of the shallow N donor is detected in darkness. It has been shown that in n-type 4H-SiC ([N] ~ 1×10^{17} cm^{-3}) heavily irradiated by electrons (a fluence of ~4×10^{18} cm^{-2}), the T_{V2a} signal [i.e., the signal of V_{Si}^- at the quasi-cubic lattice site, $V_{Si}^-(k)$] measured in darkness is very weak but increased drastically under illumination (λ = 808 nm).[7] This indicates that in equilibrium, only a small part of V_{Si} is in the single negative charge state and mostly the multiple charge states V_{Si}^{2-} and V_{Si}^{3-} are populated.

It is even more difficult to tune the Fermi level for achieving $V_{Si}V_C^0$ in equilibrium in n-type SiC. After annealing, the nitrogen-vacancy pairs ($N_C V_{Si}$) are expected to form in an n-type N-doped material. The $N_C V_{Si}$ defect has two acceptor levels (0|−) and (−|2−) at ~E_V + 1.5 eV and ~E_V + (2.5–2.6) eV, respectively[39] (Fig. 1). If the total concentration of the $N_C V_{Si}$ pair and V_{Si} is larger than the concentration of the N donor, the Fermi level can be at the (0|−) acceptor level of $N_C V_{Si}$, keeping $V_{Si}V_C$ in the neutral charge state.

We have noticed that $V_{Si}V_C$ can be stable in the neutral charge state in heavily irradiated n-type samples. As an example, Fig. 2 shows the EPR spectrum of $V_{Si}V_C^0$ in commercial n-type ([N] ~ 1×10^{17} cm^{-3}) 4H-SiC irradiated by electrons to a fluence of 1×10^{19} cm^{-2} and annealed at 850 °C measured in darkness for the magnetic field along the c-axis (**B**||**c**). In 6H-SiC, the observation of $V_{Si}V_C^0$ in darkness was reported in materials irradiated to a fluence of 10^{20} neutrons/cm^2.[10] The requirement of such a high fluence of radiation may explain why in most reported EPR studies of divacancy in n-type SiC, the $V_{Si}V_C^0$ spectrum can only be detected under illumination.

For studies of single emitters, the concentration of defects is usually in the ~$10^9–10^{10}$ cm^{-3} range, which is negligible compared to the N concentration in n-type CVD layers. Therefore, the Fermi level will remain at the N donor level after irradiation, keeping the Si vacancy in the (3−) charge state. The resonant excitation of 1.44 and 1.36 eV for the ZPLs V1 and V2 of V_{Si}^-, respectively, can excite electrons from the (2−) and (3−) charge states (at ~0.7 and ~0.4 eV below the CB, respectively) to activate the single negative charge state V_{Si}^-, but the alternation between the charge states, V_{Si}^{2-} and V_{Si}^-, causes bleaching of single emitters even under repumping.[18] The $V_{Si}V_C$ center is predominantly in the (2−) charge state, and it is not possible to activate the neutral charge state under excitation with photon energies lower than the threshold of ~1.3 eV as reported in previous studies.[15–17] It has been shown that in pure n-type layers with the nitrogen concentration of [N] ~ $5–6 \times 10^{13}$ cm^{-3}, repumping is required for
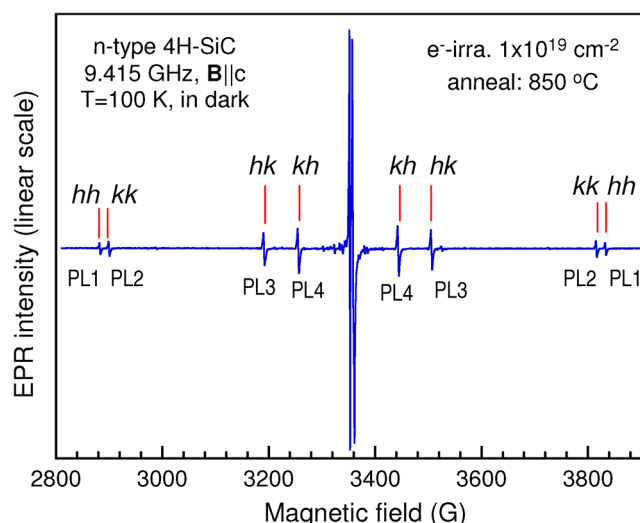
FIG. 2. EPR spectrum of heavily irradiated and annealed n-type 4H-SiC ([N] ~ 1×10^{17} cm^{-3}) measured in darkness at 100 K for **B**||**c** showing four configurations of the neutral divacancy $V_{Si}V_C^0$ with a spin S = 1 corresponding to four ZPLs PL1 and PL2 with C_{3v} symmetry and PL3 and PL4 with C_{1h} symmetry. PL1, PL2, PL3, and PL4 ZPLs correspond to four configurations of $V_{Si}V_C^0$ labeled as (hh), (kk), (hk), and (kh), where h and k refer to inequivalent lattice sites in 4H-SiC corresponding to a hexagonal (h) or quasi-cubic (k) local crystal structure.

studies of single emitters of the Si vacancy[41] and divacancy centers.[42]
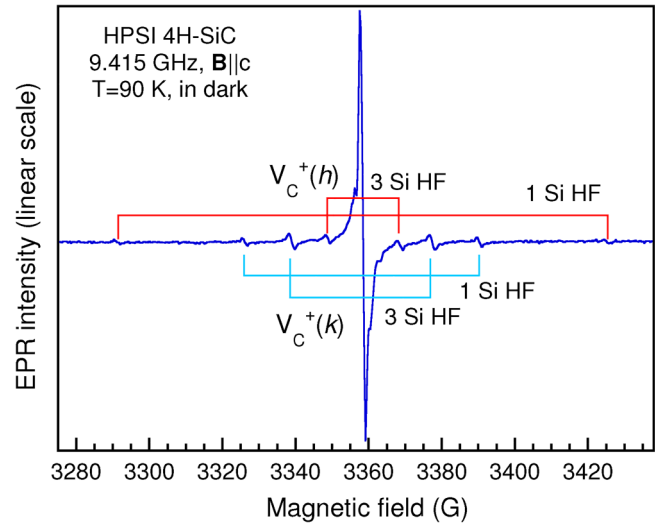
B. HPSI 4H-SiC

In HPSI SiC, intrinsic defects formed during the growth are used for the compensation of residual shallow dopants (the N donor and B acceptor with comparable concentrations in the low-to-mid 10^{15} cm^{-3} range).[43,44] The location of the Fermi level in HPSI materials varies from $\sim$0.8 to $\sim$1.5 eV below the CB depending on the relative concentrations between these dominant intrinsic defects and shallow dopants. In some HPSI types, only V_C and $V_{Si}V_C$ are present (with the concentration of $\sim$3–6 × 10^{15} cm^{-3}), while in others, V_{Si}, V_C, and $C_{Si}V_C$ are dominant with the concentration of $\sim$1–4 × 10^{15} cm^{-3} ([$V_{Si}V_C$] $\sim$ 5 × 10^{14} cm^{-3}).[45]

In HPSI wafers with [N] > [B], the Fermi level can be at the acceptor levels of $V_{Si}V_C$ at $\sim E_C$–1.3 eV, and V_{Si}^- will be stable in equilibrium but not $V_{Si}V_C{}^0$. We have noticed that in most of the cases, the acceptor levels of $V_{Si}V_C$ are not enough to compensate N and the (2−) acceptor levels of V_{Si} and V_C at $\sim E_C$–0.7 eV can be partially populated. The Fermi level will then locate in between the (2−) acceptor levels of vacancies and the divacancy. This is the case of HPSI materials with the activation energy of $E_a \sim$ 0.8–09 eV.[43,45]

It can be seen from Fig. 1 that the window for observing V_C in the single positive charge state in equilibrium is very narrow: the Fermi level should be at its (2+|+) level or between its (2+|+) and (+|0) levels [i.e., when the (+|0) level is not fully populated]. Such conditions were found to be satisfied in a certain HPSI 4H-SiC material grown by PVT, which has an activation energy of $E_a \sim$ 1.5 eV.[44,45] In PVT growth, the concentration of residual acceptors is set by the contamination of B in the SiC powder, while the concentration of the N donor can be reduced. Therefore, in some HPSI wafers, [B] > [N] and the B acceptor can compensate the N donor. With V_C and $V_{Si}V_C$ being the dominant defects while V_{Si} and $C_{Si}V_C$ are absent, the (+|0) and (2+|+) levels of V_C become the highest-lying donor levels, which then compensate the rest of B acceptors and pin the Fermi level there. The energy of the (+|0) level of V_C at $\sim E_C$–1.5 eV[35] explains the activation energy of $E_a \sim$ 1.5 eV in this "p-type like" HPSI material. Figure 3 shows the EPR spectrum of V_C^+ in such an HPSI 4H-SiC sample measured in darkness, confirming that V_C is stable in the single positive charge state in equilibrium. Such location of the Fermi level also ensures that the divacancy is in the neutral charge state and should have stable PL as shown below.

Figure 4 shows the PL spectra of this HPSI 4H-SiC sample measured at 3.5 K. The bottom spectrum is obtained with an off-resonant excitation at 893 nm showing the four ZPLs of $V_{Si}V_C{}^0$ and the PL5 and PL6 lines,[11] which are assigned to the neutral divacancies at stacking faults.[46] This spectrum also illustrates the absence of V_{Si}^- emission, the ZPL of which should appear at $\sim$916 nm. The two spectra at the top are measured with 1029-nm excitation without and with 514-nm repump laser. The 1029-nm ($\sim$1.205 eV) excitation is known to cause quenching of PL1–PL4 ZPLs in n-type and HPSI materials.[15–17] However, in this sample, the $V_{Si}V_C{}^0$ PL is stable under 1029-nm excitation without repump. The only effect of the repump laser is to bring up the contribution from the PL lines of the neutral vanadium (V^0). The divacancy

FIG. 3. EPR spectrum of an HPSI 4H-SiC sample with an activation energy of $E_a \sim$ 1.5 eV containing dominant V_C and $V_{Si}V_C$ and no V_{Si} and $C_{Si}V_C$ with [B] > [N], measured in darkness at 90 K showing the signals of V_C^+ at the hexagonal $V_C^+(h)$ and quasi-cubic $V_C^+(k)$ lattice sites. The hyperfine structures due to the interaction with nearest ^{29}Si neighbors are indicated.
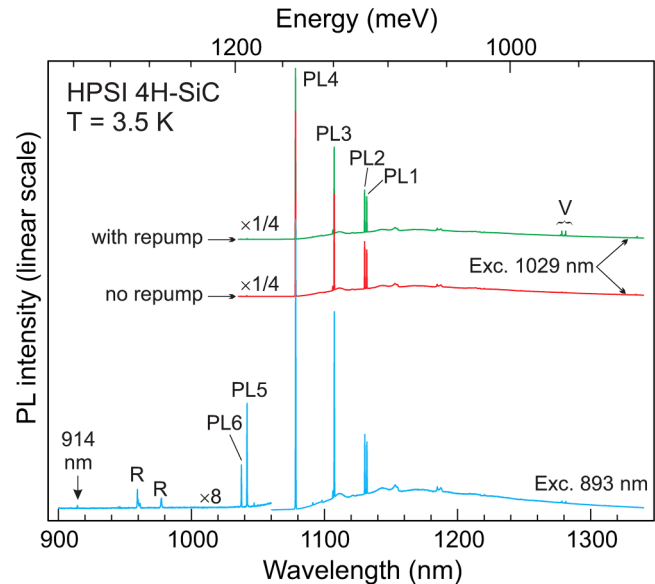
FIG. 4. Low-temperature PL spectra of the HPSI 4H-SiC sample used to detect the EPR spectrum of V_C^+ shown in Fig. 3. The bottom spectrum obtained with 893 nm excitation displays no contribution from V_{Si}^-. The line denoted "914 nm" is most likely due to tantalum impurity.[17] The two upper spectra are obtained with 1029-nm excitation without and with a 514-nm repump laser. The lines labeled V appearing under repumping are from the neutral vanadium center.

luminescence is essentially unaffected except for a minute decrease in intensity (by a few percent) when the repump laser is applied.

The absence of Si vacancy, as confirmed in the PL in Fig. 4, allows us to create a low density of Si vacancy in the material by irradiation for studies of single V_{Si}^- emitters. Indeed, stable single emitters of V_{Si}^- in this HPSI 4H-SiC material have been reported.[12,47] However, with the concentration of residual impurities (N and B) and intrinsic defects being in the 10^{15} cm^{-3} range, long coherence times and narrow optical linewidths may not be expected for the Si vacancy qubits.

It is known that different parts of the same HPSI wafer can have different activation energies, e.g., between 1.3 and 1.5 eV,[44] since the incorporation of N during the growth is not homogeneous on the wafer. In the part that has N concentration higher than that of B ([N] > [B]), the acceptor levels (0|−) and (−|2−) of the divacancy can be populated, resulting in an activation energy of $E_a \sim 1.3$ eV. In this case, V_{Si}^- is stable, but the divacancy will be in the single or double negative charge state.

HPSI materials grown by PVT also contain the Si vacancy and the C antisite–vacancy pairs as shown by EPR.[45] The presence of $C_{Si}V_C$ will make it difficult to obtain $V_{Si}V_C^0$ in equilibrium even in the case of [B] > [N]. If the concentration of $C_{Si}V_C$ is higher than that of the B acceptor, electrons from its (+|0) level can fill up the acceptor levels of $V_{Si}V_C$ lying just below and the divacancy will be in (1−) or (2−) charge state. The Fermi level will move up to the (+|0) level of $C_{Si}V_C$ or in between the acceptor levels of divacancy. In this case, the HPSI material has an activation energy of ~1.1 or ~1.3 eV as previously reported.[45] Thus, in the case of HPSI 4H-SiC having activation energy of ~1.3 or ~1.1 eV, the divacancy will be in the (1−) or (2−) charge state, respectively. Optical excitation with photon energies above ~1.3 eV is therefore required to pump electrons from these acceptor states to the CB for activating the neutral charge state and stabilizing the $V_{Si}V_C^0$ emission. When the excitation energy is reduced below ~1.3 eV, the electron photoionization from these acceptor levels becomes less efficient (and even seizes at liquid helium temperatures) compared to the recapturing process, leading to PL quenching. This explains the PL quenching of divacancies in as-grown HPSI 4H-SiC observed by Golter and Lai[16] and others.[15,17] Thus, the PL quenching of divacancy is not due to loosing electrons to the CB and electron traps that convert $V_{Si}V_C^0$ to $V_{Si}V_C^+$ as suggested in Ref. 16. Instead, the divacancy captures electrons emitted from other centers under excitation with energies below ~1.3 eV and converts to the negative charge state giving rise to PL quenching of the neutral charge state.[15,17]

For quantum memory or sensing using spin ensembles, a higher concentration of the Si vacancy or divacancy is desired. However, increasing further the concentration of intrinsic defects in this HPSI material by irradiation and annealing introduces also the $C_{Si}V_C$ defect. As discussed above, the presence of $C_{Si}V_C$ defect will shift the Fermi level from the donor levels of V_C up that changes the charge state of the divacancy to (1−) or (2−).

The change of the Fermi level induced by the presence of $C_{Si}V_C$ defect will not influence the charge state of V_{Si}^-. We have noticed that after electron irradiation with any fluences and with or without annealing, the EPR signal of V_{Si}^- is still detected in darkness. However, this location of the Fermi level leads to the transformation of V_C^+ to V_C^0. As a result, the signal of V_C^+ disappears while
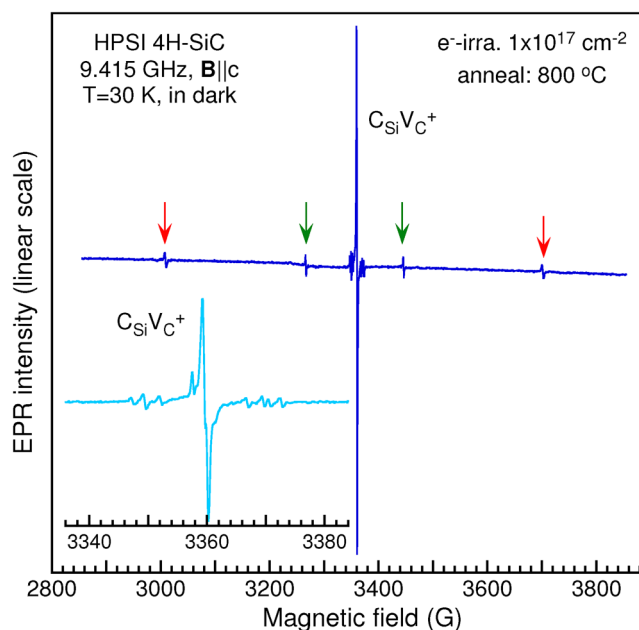

FIG. 5. EPR spectrum of the HPSI 4H-SiC sample, that gives rise to the EPR signal in Fig. 3, after electron irradiation (fluence: 1×10^{17} cm^{-2}) and annealing at 800 °C measured at 30 K in darkness for **B**||**c** showing the strong signal of the $C_{Si}V_C^+$ center,[48] while the signal of V_C^+ is not detectable. Two pairs of weak lines with the splitting of ~175 and ~695 G (indicated by green and red arrows, respectively) are from two unidentified defects with spin S = 1. The inset shows the central part of the spectrum measured with a higher magnetic-field resolution (1024 data points/100 G) showing overlapping lines with ^{29}Si hyperfine structures from $C_{Si}V_C^+$.

the $C_{Si}V_C^+$ signal[48] is dominating in the EPR spectrum measured in darkness as can be seen in Fig. 5.

For obtaining the divacancy stable in the neutral charge state in irradiated HPSI materials, the Fermi level should be pulled down to the donor levels of V_C or the acceptor (0|−) level of V_{Si}. (Due to the low doping level of N in HPSI materials, the N_CV_{Si} pair has low concentration and, hence, a negligible role in the carrier compensation process.) This requires reducing the concentration of the C antisite–vacancy pairs and/or increasing the concentration of V_{Si}.

Increasing the concentration of the Si vacancy helps to pull down the Fermi level. This is possible since the formation energy of $C_{Si}V_C$, i.e., the barrier for trapping a nearby C atom by V_{Si}, and the dissociation energy required to release V_{Si} from the pair are comparable,[26,49] and the Si vacancy is annealed out gradually in a wide temperature range of 700–1200 °C.[50] Therefore, both defects can be present in a wide range of annealing temperatures and the Si vacancy does not really anneal out entirely. Moreover, a significant fraction of the dissociation process of $C_{Si}V_C$ also leaves C_{Si}–Si_C–C_{Si} clusters behind,[49] making it possible to have the total concentration of V_{Si} and the rest of B acceptors larger than the concentration of $C_{Si}V_C$. We check this possibility by increasing the radiation fluence and find that it is not possible to obtain $V_{Si}V_C^0$ in equilibrium if the electron fluence is ~2×10^{18} cm^{-2} or less. However, increasing
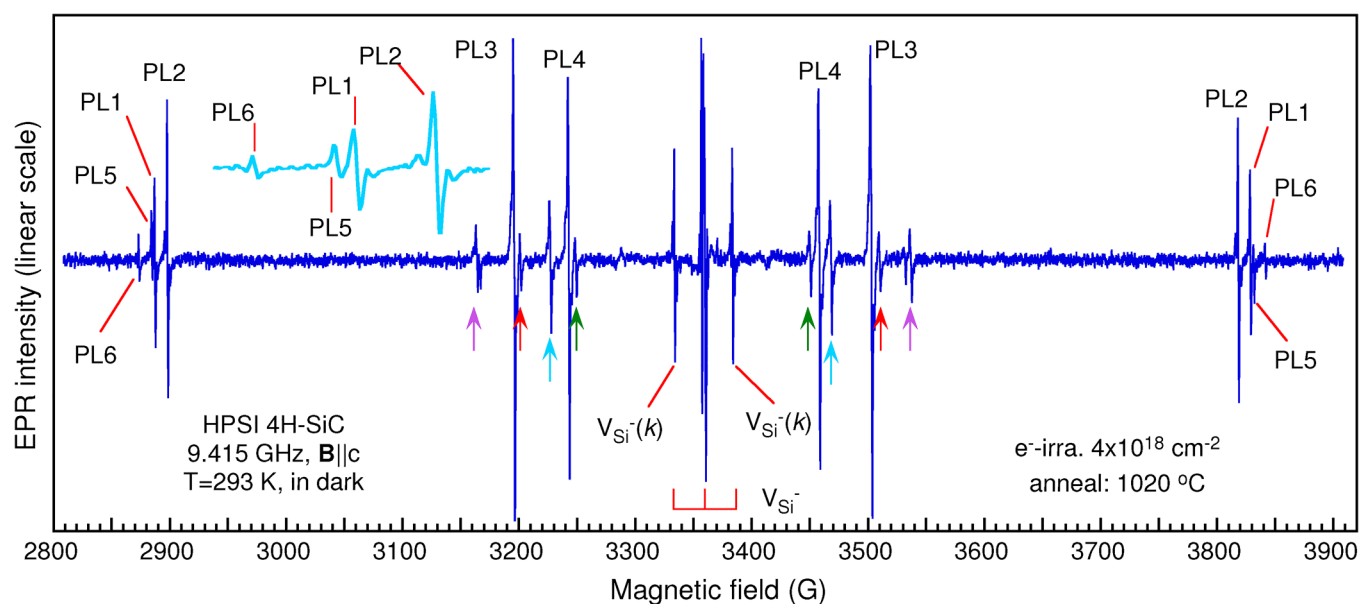
FIG. 6. EPR spectrum of irradiated HPSI 4H-SiC measured in darkness for **B||c** at 293 K showing four configurations of $V_{Si}V_C^0$ and configurations of $V_{Si}V_C^0$ at stacking faults: PL5 and PL6 with C_{3v} symmetry and other four pairs of weak lines (indicated by arrows with different colors) belong to four configurations with C_{1h} symmetry. These lines are not labeled since the PL spectra related to these configurations have not been observed. Three lines in the central spectrum are from the S = 3/2 V_{Si}^- center. The inset shows a part of the spectrum between 2868–2905 G in an extended magnetic field scale with lines from axial configurations PL1 and PL2 of $V_{Si}V_C^0$ and PL5 and PL6[11] of $V_{Si}V_C^0$ at stacking faults[46] indicated.

the electron fluence to $4 \times 10^{18}\,cm^{-2}$ combined with appropriate annealing can increase the concentration of the vacancies and divacancy and, at the same time, move the Fermi level down to return $V_{Si}V_C$ back to the neutral charge state.

Figure 6 shows the EPR spectrum of HPSI 4H-SiC irradiated by electrons to a fluence of $4 \times 10^{18}\,cm^{-2}$ and annealed at ~1020 °C measured in darkness at room temperature for the magnetic field along the c-axis (**B||c**). In addition to strong signals from four configurations PL1–PL4 of the divacancy, weaker signals from $V_{Si}V_C^0$ at stacking faults[46] including two axial PL5-PL6 centers[11] and basal configurations with C_{1h} symmetry are observed. The PL5 and PL6 lines are indicated in the inset. The weak pairs of lines from the corresponding basal configurations of these centers are indicated by arrows with different colors. The three strong lines at the centrum of the spectrum are from the S = 3/2 negative Si vacancy V_{Si}^-. Here, the low- and high-field lines with a splitting of 50 G are from V_{Si}^- at the quasi-cubic site (the lines from V_{Si}^- at the hexagonal site overlap with the ^{29}Si hyperfine structure and are too close to the central line to be seen with this magnetic field scale).

The observation of a strong signal of V_{Si}^- in an irradiated sample after annealing at ~1020 °C supports the suggestion on the annealing behavior of Si vacancy from theoretical calculations.[26,49] It is likely that the disappearance of the Si vacancy signal in EPR and optically detected magnetic resonance (ODMR) after annealing at ~700–750 °C as reported in previous studies[8,51] is due to the change of the Fermi level that transforms V_{Si}^- to the EPR-inactive V_{Si}^{2-} center. As shown in a recent annealing study of Si vacancy,[50] the

concentration of V_{Si}^- is reduced by ~25% and ~85% after annealing at ~700 and ~820 °C, respectively. In the previous studies of n-type 3C-SiC with the N concentration in the mid-to-high $10^{16}\,cm^{-3}$ ranges and the Si vacancy concentration of ~$1 \times 10^{17}\,cm^{-3}$ in as-irradiated materials,[51] the V_{Si} concentration can be reduced by a factor of two after annealing at ~750 °C and can no longer compensate the N donor. As a result, electrons will populate the (2−) charge state of V_{Si}. Since the EPR measurements were performed in darkness,[51] the V_{Si}^- signal will not be detectable.

C. P-type 4H-SiC

As shown above, the EPR observation of the V_C^+ center in darkness is an indication that the Fermi level is located at its (2+|+) or (+|0) donor levels and V_{Si}^- and $V_{Si}V_C^0$ should be stable in equilibrium. It has been shown in previous studies that in irradiated commercial p-type 4H-SiC ([Al] ~ $10^{17}\,cm^{-3}$), the EPR signal of V_C^+ can always be detected in darkness if the concentration of V_C is enough to compensate Al shallow acceptors and pins the Fermi level at its donor levels.[52] The V_C^+ center can still be detected in darkness even after annealing at 950 °C[31] well above the temperatures needed to form the divacancy and C antisite–vacancy pairs. This indicates that the concentration of $C_{Si}V_C$ is not enough to compensate the Al shallow acceptors and V_C is involved in the compensation process, pinning the Fermi level at its donor levels. This makes it possible to obtain stable V_{Si}^- and $V_{Si}V_C^0$ for spin ensembles in p-type materials.

For studies on single emitters, the concentration of V_{Si} and $V_{Si}V_C$ should be low ($\sim 10^9$–10^{10} cm^{-3}) for the observation of individual emitters. The V_C center can be introduced during the growth of pure CVD layers with a concentration varying in the range of 5×10^{12}–5×10^{13} cm^{-3}. Reducing the N concentration to make pure p-type layers with the concentration of the residual B acceptor of ~ 1–3×10^{13} cm^{-3} is possible.[21] Pure semi-insulating materials then can be grown by tuning the concentration of V_C to the mid-10^{13} cm^{-3} range to compensate the B acceptor. Such materials with the Fermi level located at the donor levels of V_C are ideal for achieving stable V_{Si}^- and $V_{Si}V_C^0$ single emitters. However, keeping the concentration of the C vacancy in the mid-10^{13} cm^{-3} ranges is not desirable for reducing optical linewidths. Reducing the concentration of the C vacancy further and using a repump laser for the charge-state control may be a better approach for obtaining long spin coherence times and narrow optical linewidths. For the Si vacancy, n-type layers are preferable since the activation of V_{Si}^- from V_{Si}^{2-} or V_{Si}^{3-} requires repumping with lower photon energies compared to the activation of V_{Si}^- from V_{Si}^0 in p-type materials.

In p-type materials, the divacancy will be in the positive charge state and the conversion from $V_{Si}V_C^+$ to $V_{Si}V_C^0$ can be done by exciting electrons from the VB directly to its positive charge state at $\sim E_V + 1.1$ eV. With the energies of ZPLs PL1–PL4 in the range of 1.095–1.150 eV, resonant excitation for PL4 (~ 1.15 eV) may be sufficient for activating and stabilizing the neutral charge state of the divacancy.

IV. SUMMARY

Monitoring the charge state of dominant intrinsic defects in equilibrium using EPR helps to determine the location of the Fermi level and reveals the conditions for achieving photostable V_{Si}^- and $V_{Si}V_C^0$ PL emissions in n-type, HPSI and p-type 4H-SiC materials with different doping levels and defect concentrations. The results show that in n-type materials, V_{Si} can be stable in the negative charge state when its concentration is larger than that of the N donor, while the divacancy can be stable in the neutral charge state if the total concentration of V_{Si} and the N_CV_{Si} pair exceeds the concentration of the N donor.

In HPSI 4H-SiC with the activation energy of $E_a \sim 1.1$–1.5 eV, either as-grown or irradiated material, V_{Si} can be stable in the negative charge state. For the divacancy, the neutral charge state is stable in the as-grown HPSI material with the activation energy of $E_a \sim 1.5$ eV, in which the EPR of V_C^+ can be detected in darkness. Irradiation and annealing will move the Fermi level up and convert $V_{Si}V_C^0$ to $V_{Si}V_C^-$. In such materials, stable $V_{Si}V_C^0$ emissions can be achieved by reducing the $C_{Si}V_C$ defect and/or increasing the concentration of V_{Si}.

In the p-type material, photostable V_{Si}^- and $V_{Si}V_C^0$ ensembles can be obtained by controlling the concentration of the C vacancy and the C antisite–vacancy pair.

Due to the low concentration required for observation of individual emitters, optical repumping is required for the charge state control of single V_{Si}^- and $V_{Si}V_C^0$ emitters in n- and p-type materials. Pure p-type materials are preferable for neutral divacancy since excitation with low energies (>1.15 eV) may be sufficient for activating and stabilizing the $V_{Si}V_C^0$ emission.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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