

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

Cite as: J. Appl. Phys. 129, 215702 (2021); doi: 10.1063/5.0052131

Submitted: 29 March 2021 · Accepted: 17 May 2021 ·

Published Online: 3 June 2021



Nguyen T. Son<sup>a)</sup> and Ivan G. Ivanov

## AFFILIATIONS

Department of Physics, Chemistry and Biology, Linköping University, SE-581 83 Linköping, Sweden

**Note:** This paper is part of the Special Topic on Materials, Methods, and Applications of Color Centers with Accessible Spin.

<sup>a)</sup>Author to whom correspondence should be addressed: [tien.son.nguyen@liu.se](mailto:tien.son.nguyen@liu.se)

## 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.

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## 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).<sup>1</sup> 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) (<sup>13</sup>C: 1.1% with nuclear spin  $I = 1/2$ ; <sup>29</sup>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.<sup>2</sup> These favorable optical and spin properties make color centers in diamond and SiC promising spin qubits for applications in quantum technologies.<sup>3–6</sup>

In the development of solid-state spin qubits, the nitrogen-vacancy (NV) center in diamond is the leading contender.<sup>3,4</sup> 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.<sup>6</sup> Among these, the negative Si vacancy ( $V_{Si}^-$ )<sup>7</sup> with zero-phonon lines (ZPLs) at 861.6 nm (V1 center) and 916.5 nm (V2 center) in 4H-SiC<sup>8</sup> and the neutral divacancy ( $V_{Si}V_C^0$ ),<sup>9,10</sup> 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,<sup>11</sup> are the most studied centers. Single emitters of the Si vacancy<sup>12</sup> and divacancy centers<sup>13</sup> with long coherence times have been realized. Resonant excitation can increase the readout contrast of single emitters from a few percent to ~94% for  $V_{Si}V_C^0$ .<sup>14</sup> However, under resonant excitation or off-resonant excitation with photon energies below certain thresholds, the photoluminescence (PL) decays with



bandgap.<sup>26,33</sup> Its single donor level (+|0) at  $\sim 1.1$  eV below the conduction band (CB) is supported by recent EPR work.<sup>38</sup> 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.<sup>39</sup> 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  $\sim 600^\circ\text{C}$  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  $\sim E_V + 1.25$  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  $10^{15}\text{ cm}^{-3}$  range. The contamination with B during the chemical vapor deposition (CVD) coming from the susceptor is less ( $[B] \sim 1\text{--}3 \times 10^{13}\text{ cm}^{-3}$ ). The concentration of the N shallow donor is  $[N] > 10^{17}\text{ cm}^{-3}$  in commercial n-type SiC substrates grown by PVT and in the  $10^{14}\text{--}10^{15}\text{ cm}^{-3}$  range for commercial CVD layers.

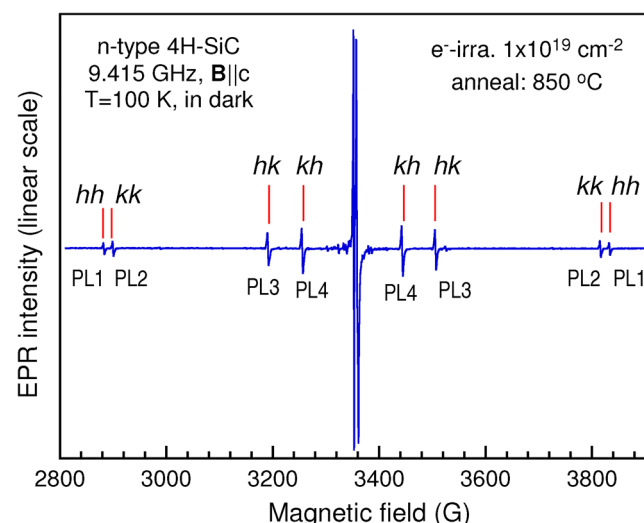
Thus, for ensemble studies in commercial CVD SiC layers, a concentration of  $V_{Si}$  in the  $10^{16}\text{ cm}^{-3}$  range or larger is required to compensate the N donor for achieving the stable  $V_{Si}^-$  center. In practice, electron irradiation with a fluence of  $\sim 1\text{--}5 \times 10^{17}\text{ cm}^{-2}$  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.<sup>8,40</sup>

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  $10^{18}\text{ cm}^{-2}$ , 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 ( $[N] \sim 1 \times 10^{17}\text{ cm}^{-3}$ ) heavily irradiated by electrons (a fluence of  $\sim 4 \times 10^{18}\text{ cm}^{-2}$ ), 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 ( $\lambda = 808\text{ nm}$ ).<sup>7</sup> 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  $\sim E_V + 1.5$  eV and  $\sim E_V + (2.5\text{--}2.6)$  eV, respectively<sup>39</sup> (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 ( $[N] \sim 1 \times 10^{17}\text{ cm}^{-3}$ ) 4H-SiC irradiated by electrons to a fluence of  $1 \times 10^{19}\text{ cm}^{-2}$  and annealed at  $850^\circ\text{C}$  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  $10^{20}\text{ neutrons/cm}^2$ .<sup>10</sup> 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  $\sim 10^9\text{--}10^{10}\text{ cm}^{-3}$  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  $\sim 0.7$  and  $\sim 0.4$  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.<sup>18</sup> 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  $\sim 1.3$  eV as reported in previous studies.<sup>15–17</sup> It has been shown that in pure n-type layers with the nitrogen concentration of  $[N] \sim 5\text{--}6 \times 10^{13}\text{ cm}^{-3}$ , repumping is required for



**FIG. 2.** EPR spectrum of heavily irradiated and annealed n-type 4H-SiC ( $[N] \sim 1 \times 10^{17}\text{ cm}^{-3}$ ) 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<sup>41</sup> and divacancy centers.<sup>42</sup>

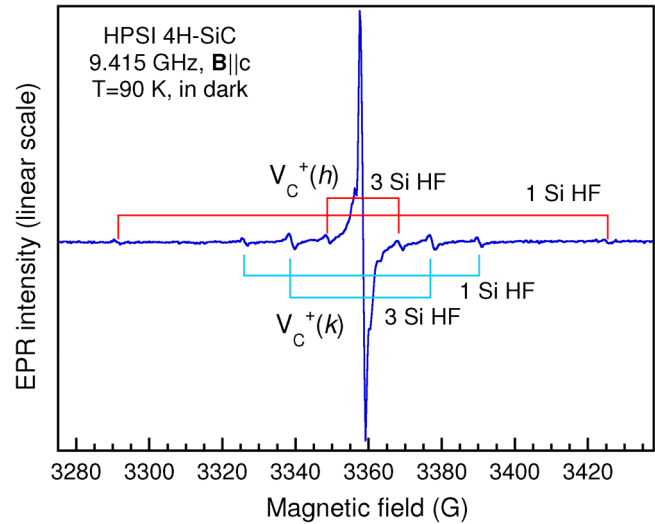
## B. HPSI 4H-SiC

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  $10^{15} \text{ cm}^{-3}$  range).<sup>43,44</sup> 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  $\sim 3\text{--}6 \times 10^{15} \text{ cm}^{-3}$ ), while in others,  $V_{Si}$ ,  $V_C$ , and  $C_{Si}V_C$  are dominant with the concentration of  $\sim 1\text{--}4 \times 10^{15} \text{ cm}^{-3}$  ( $[V_{Si}V_C] \sim 5 \times 10^{14} \text{ cm}^{-3}$ ).<sup>45</sup>

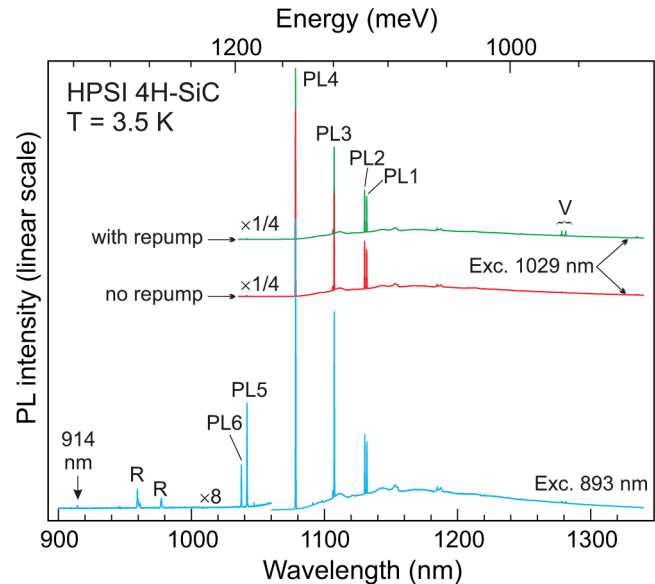
In HPSI wafers with  $[N] > [B]$ , the Fermi level can be at the acceptor levels of  $V_{Si}V_C$  at  $\sim E_C - 1.3$  eV, and  $V_{Si}^-$  will be stable in equilibrium but not  $V_{Si}V_C^0$ . We have noticed that in most of the cases, the acceptor levels of  $V_{Si}V_C$  are not enough to compensate 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  $E_a \sim 0.8\text{--}0.9$  eV.<sup>43,45</sup>

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.<sup>44,45</sup> 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<sup>35</sup> 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,<sup>11</sup> which are assigned to the neutral divacancies at stacking faults.<sup>46</sup> 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.<sup>15–17</sup> 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  $^{29}\text{Si}$  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.<sup>17</sup> 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.

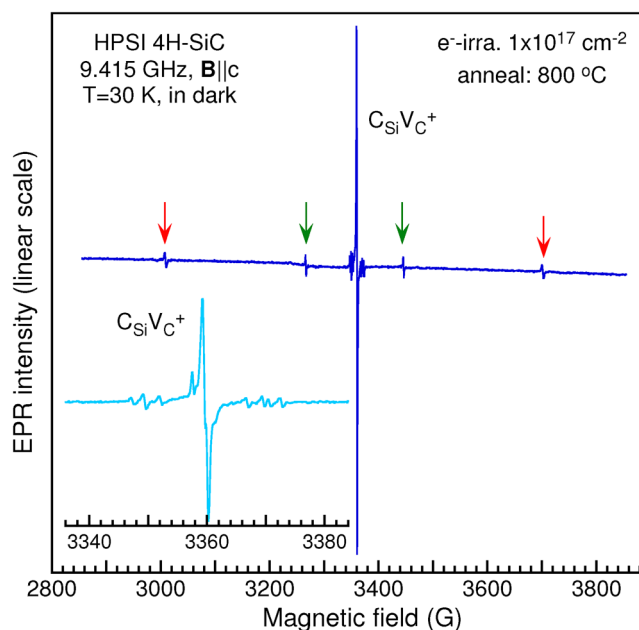
The absence of Si vacancy, as confirmed in the PL in Fig. 4, allows us to create a low density of Si vacancy in the material by irradiation for studies of single  $V_{Si}^-$  emitters. Indeed, stable single emitters of  $V_{Si}^-$  in this HPSI 4H-SiC material have been reported.<sup>12,47</sup> However, with the concentration of residual impurities (N and B) and intrinsic defects being in the  $10^{15} \text{ cm}^{-3}$  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,<sup>44</sup> 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  $E_a \sim 1.3 \text{ eV}$ . 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.<sup>45</sup> 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  $\sim 1.1$  or  $\sim 1.3 \text{ eV}$  as previously reported.<sup>45</sup> Thus, in the case of HPSI 4H-SiC having activation energy of  $\sim 1.3$  or  $\sim 1.1 \text{ eV}$ , the divacancy will be in the ( $1-$ ) or ( $2-$ ) charge state, respectively. Optical excitation with photon energies above  $\sim 1.3 \text{ eV}$  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  $\sim 1.3 \text{ eV}$ , the electron photoionization from these acceptor levels becomes less efficient (and even ceases 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<sup>16</sup> and others.<sup>15,17</sup> Thus, the PL quenching of divacancy is not due to losing 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  $\sim 1.3 \text{ eV}$  and converts to the negative charge state giving rise to PL quenching of the neutral charge state.<sup>15,17</sup>

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

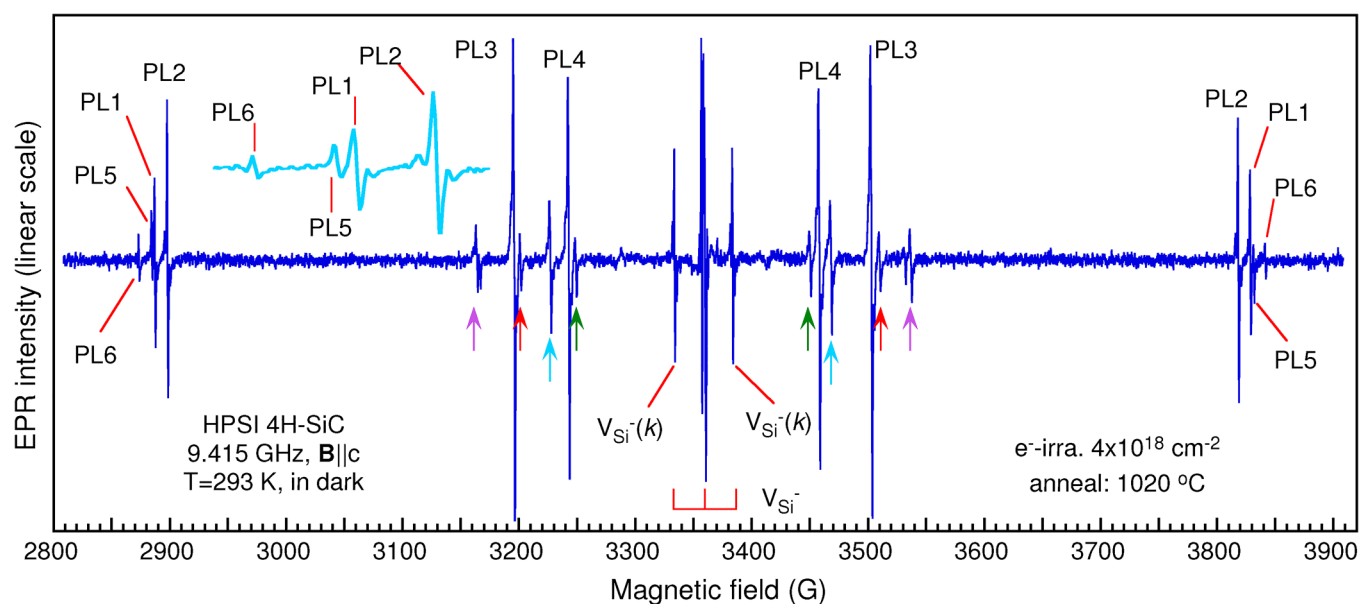


**FIG. 5.** EPR spectrum of the HPSI 4H-SiC sample, that gives rise to the EPR signal in Fig. 3, after electron irradiation (fluence:  $1 \times 10^{17} \text{ cm}^{-2}$ ) and annealing at  $800^\circ\text{C}$  measured at  $30 \text{ K}$  in darkness for  $B||c$  showing the strong signal of the  $C_{Si}V_C^+$  center,<sup>48</sup> while the signal of  $V_C^+$  is not detectable. Two pairs of weak lines with the splitting of  $\sim 175$  and  $\sim 695 \text{ G}$  (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  $^{29}\text{Si}$  hyperfine structures from  $C_{Si}V_C^+$ .

the  $C_{Si}V_C^+$  signal<sup>48</sup> 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,<sup>26,49</sup> and the Si vacancy is annealed out gradually in a wide temperature range of  $700\text{--}1200^\circ\text{C}$ .<sup>50</sup> 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  $C_{Si}\text{--}Si\text{--}C_{Si}$  clusters behind,<sup>49</sup> 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  $\sim 2 \times 10^{18} \text{ cm}^{-2}$  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 2888–2905 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<sup>11</sup> of  $V_{Si}V_C^0$  at stacking faults<sup>46</sup> indicated.

the electron fluence to  $4 \times 10^{18} \text{ cm}^{-2}$  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  $4 \times 10^{18} \text{ cm}^{-2}$  and annealed at  $\sim 1020^\circ\text{C}$  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<sup>46</sup> including two axial PL5–PL6 centers<sup>11</sup> 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 center 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  $^{29}\text{Si}$  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  $\sim 1020^\circ\text{C}$  supports the suggestion on the annealing behavior of Si vacancy from theoretical calculations.<sup>26,49</sup> It is likely that the disappearance of the Si vacancy signal in EPR and optically detected magnetic resonance (ODMR) after annealing at  $\sim 700$ – $750^\circ\text{C}$  as reported in previous studies<sup>8,51</sup> 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,<sup>50</sup> the

concentration of  $V_{Si}^-$  is reduced by  $\sim 25\%$  and  $\sim 85\%$  after annealing at  $\sim 700$  and  $\sim 820^\circ\text{C}$ , respectively. In the previous studies of  $n$ -type 3C-SiC with the N concentration in the mid-to-high  $10^{16} \text{ cm}^{-3}$  ranges and the Si vacancy concentration of  $\sim 1 \times 10^{17} \text{ cm}^{-3}$  in as-irradiated materials,<sup>51</sup> the  $V_{Si}$  concentration can be reduced by a factor of two after annealing at  $\sim 750^\circ\text{C}$  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,<sup>51</sup> 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 ( $[Al] \sim 10^{17} \text{ cm}^{-3}$ ), 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.<sup>52</sup> The  $V_C^+$  center can still be detected in darkness even after annealing at  $950^\circ\text{C}$ <sup>31</sup> 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  $5 \times 10^{12}$ – $5 \times 10^{13}$  cm $^{-3}$ . Reducing the N concentration to make pure p-type layers with the concentration of the residual B acceptor of  $\sim 1$ – $3 \times 10^{13}$  cm $^{-3}$  is possible.<sup>21</sup> 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 ( $\sim 1.15$  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  $N_C V_{Si}$  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.

#### ACKNOWLEDGMENTS

Financial support by the Swedish Research Council (Grant Nos. VR 2016-04068 and VR 2016-05362), the EU H2020 project QuanTELCO (Grant No. 862721), and the Knut and Alice Wallenberg Foundation (Grant No. KAW 2018.0071) is acknowledged.

#### DATA AVAILABILITY

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

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