Photoluminescence lineshapes and charge state control of divacancy qubits in silicon carbide

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Abstract

Divacancy in its neutral charge state (\(V_CV_{Si}^0\)) in 4H silicon carbide (SiC) is a leading quantum bit (qubit) contender. Owing to the lattice structure of 4H SiC four different \(V_CV_{Si}\) configurations can be formed. Ground and optical excited states of \(V_CV_{Si}^0\) exhibit \(S=1\) spintriplet state and the corresponding transition energies are around \(\approx 1.1\, \text{eV}\) falling in the near-infrared wavelength region. Recently, photoluminescence (PL) quenching has been experimentally observed for all \(V_CV_{Si}\) configurations in 4H SiC, i.e. the corresponding zero-phonon lines (ZPLs) appear only at higher-than-ZPL photoexcitation energies (threshold energies). It has been shown that \(V_CV_{Si}^0\) is converted to \(V_CV_{Si}^-\) upon photoexcitation below the corresponding excitation threshold energies at cryogenic temperature, i.e. \(V_CV_{Si}^-\) is the so-called dark state. In this study we demonstrate that the threshold energy for reionization is temperature dependent. We further carry out density functional theory (DFT) calculations in order to investigate the temperature dependent reionization spectrum, i.e. the spectrum of the \(V_CV_{Si}^- \rightarrow V_CV_{Si}^0\) process and found that simultaneous reionization and qubit manipulation can be carried out at around room temperature (\(\approx 300\, \text{K}\)) by using the usually applied excitation wavelength. We also investigate the PL lineshape of \(V_CV_{Si}^0\) by using the Huang-Rhys theory.
I. INTRODUCTION

Spin active point defects in wide band gap semiconductors have proven to be promising candidates for numerous applications in the strongly emerging field of quantum technology. In particular, they are applicable as single-photon emitters being pivotal in quantum information processing\textsuperscript{1–5}, ultrasensitive nanosensors in magnetometry\textsuperscript{6–11} or thermometry\textsuperscript{7,12} and quantum bits (qubits)\textsuperscript{13}. Leading contender of this family is the single negatively charged nitrogen-vacancy defect, i.e. the so-called NV center in diamond exhibiting highly promising magneto-optical properties in this respect\textsuperscript{14–16}. Nevertheless, further alternatives have been searched for in the past few decades embedded in technologically more mature materials than diamond.

A suitable host candidate to this end is silicon carbide (SiC) introducing different crystal modifications called polytypes. The technologically most relevant polytype is the hexagonal 4H SiC consisting of Si-C bilayers exhibiting hexagonal (h) or quasicubic (k) symmetry (see in Fig. 1). Consequently, lattice structure of 4H SiC offers different lattice sites for point defects. In particular, for the carbon vacancy (V\textsubscript{C}) - silicon vacancy (V\textsubscript{Si}) defect complex, i.e. for the divacancy (V\textsubscript{C}V\textsubscript{Si}) in 4H SiC — which is one of the most scrutinized defects in SiC — four different defects configurations can be formed in the 4H lattice resulting from the two possible defect sites for both V\textsubscript{C} and V\textsubscript{Si}. Henceforward, we will denote the different configurations with the indication of the lattice sites of the C/Si vacancies, respectively, in brackets as V\textsubscript{C}V\textsubscript{Si}(hh), V\textsubscript{C}V\textsubscript{Si}(kk), V\textsubscript{C}V\textsubscript{Si}(hk) and V\textsubscript{C}V\textsubscript{Si}(kh). The hh and kk configurations are called axial or on-axis configurations exhibiting C\textsubscript{3v} symmetry, while the hk and kh configurations are basal or off-axis configurations with C\textsubscript{1h} symmetry. Lattice structure of 4H SiC and the V\textsubscript{C}V\textsubscript{Si} defect configurations are shown in Fig. 1.

Regarding its impact in quantum technology, V\textsubscript{C}V\textsubscript{Si} in 4H SiC exhibits several desirable properties making it a promising qubit candidate. In particular, electronic structure of the neutral V\textsubscript{C}V\textsubscript{Si} center (V\textsubscript{C}V\textsubscript{Si}\textsubscript{0}) introduces spintriplet (S=1) ground and optical excited states\textsuperscript{13,17,18}. The corresponding optical transitions, i.e. the zero-phonon lines (ZPL) are around 1100 nm falling into the near-infrared (NIR) region where optical fibers have low absorption window\textsuperscript{13}. This property makes the divacancy desirable candidate as single photon emitter in quantum communication and as an ultrasensitive biomarker\textsuperscript{19–21}. Indeed, recently a V\textsubscript{C}V\textsubscript{Si}-based high-fidelity infrared spin-photon interface\textsuperscript{22} and entanglement and
Figure 1. (a) Lattice structure of the perfect 4H SiC. The crystal axis (c-axis) being perpendicular to the h/k bilayers is also indicated. (b) Microscopic structure of the divacancy defect. (c) The four possible V_CV_Si configurations embedded to the 4H SiC lattice. Color code of atoms is indicated.

control of single nuclear spins\textsuperscript{23} have been demonstrated. The corresponding ZPLs are denoted and identified as PL1 - V_CV_Si(hh), PL2 - V_CV_Si(kk), PL3 - V_CV_Si(hk) and PL4 - V_CV_Si(kh)\textsuperscript{13}.

Recently, photoluminescence (PL) quenching of divacancy defects in 4H SiC has been observed, i.e. PL signals of V_CV_Si\textsuperscript{0} defects do not appear upon certain excitation energies\textsuperscript{24–27}. On the other hand, it has been demonstrated that applying a second laser (repump laser) with a higher photon energy completely recovers the PL intensity of the V_CV_Si\textsuperscript{0} centers\textsuperscript{24–27}. Here, we note that the PL quenching phenomenon is not unique for V_CV_Si\textsuperscript{0} in 4H SiC, but it has already been observed for several other defects as for NV center in diamond\textsuperscript{28}. The physical mechanism behind the quenching phenomenon may be the charge state switching of the corresponding defect upon illumination as already demonstrated by previous experimental and theoretical works\textsuperscript{24–28}. In this way, the role of the repump laser is to reionize the defect, i.e. to control the charge state being investigated. In particular, for divacancy defects the 'dark' charge state has been attributed to either the single positive\textsuperscript{26} or the single negative charge state\textsuperscript{25} by earlier experimental works. In order to unveil this issue, we reported a combined experimental and density functional theory (DFT) study\textsuperscript{27} where we addressed the single negative charge state [V_CV_Si\textsuperscript{-}] as the so-called dark state by comparing the photoexcitation threshold energies at cryogenic temperatures (above which the V_CV_Si\textsuperscript{0}-related PL signals recover) with the calculated ionization energies.
In this work, we investigate the PL lineshape and the temperature dependent charge state control of the $V_{\text{C}V_{\text{Si}}^0}$ defect configurations in 4H SiC by means of Kohn-Sham DFT calculations. To this end we calculated the $V_{\text{C}V_{\text{Si}}^0}$-related PL and the $V_{\text{C}V_{\text{Si}}^-} \rightarrow V_{\text{C}V_{\text{Si}}^0}$ reionization spectra based on the Huang-Rhys (HR) theory. Based on our results, we suggest an excitation scheme aiming to achieve the charge state control of $V_{\text{C}V_{\text{Si}}^0}$ and its simultaneous qubit manipulation by a single color laser beam. Our paper is organized as follows: we describe the computational methodology in Sec. II, where we briefly describe the HR theory in Subsec. IIA and the methodology of the $ab$ initio DFT calculations in Sec. IIB. We report and discuss our results in Sec. III. In particular, PL spectra of the $V_{\text{C}V_{\text{Si}}^0}$ defect configurations are discussed in Sec. IIIA, the $V_{\text{C}V_{\text{Si}}^-} \rightarrow V_{\text{C}V_{\text{Si}}^0}$ reionization spectra are reported in Sec. IIIB and we discuss the possibilities of the charge state control of the neutral charge state in Sec. IIIC. We conclude our work in Sec. IV.

II. METHODOLOGY

A. Huang-Rhys theory

At $T = 0$ K the PL spectrum $[I^{\text{EM}}(\hbar\omega)]$ can be expressed as

$$I^{\text{EM}}(\hbar\omega) = C^{\text{EM}} \omega^3 \mu_{\text{EG}}^2 \sum_{n,m} \left| \langle \Theta_{\text{ES}}^m(Q) | \Theta_{\text{GS}}^n(Q) \rangle \right|^2 \delta(E_{\text{ES}}^m - E_{\text{GS}}^n - \hbar\omega),$$

where the transitions from the corresponding vibronic substates of the excited state (ES), indexed by $m$, to those of the ground state (GS) with the index $n$ are also considered establishing the phonon sideband (PSB) besides the ZPL. If $m = n = 0$, $I^{\text{EM}}(\hbar\omega)$ denotes the lineshape of the ZPL. In Eq. 1 $\mu_{\text{EG}}$ is the corresponding matrix element (which is now a three component vector with the length of $\mu_{\text{EG}}$) of the transition dipole moment operator, $\hat{\mu}_{\text{EG}} = q \sum_j \hat{r}_j$ defined as

$$\mu_{\text{EG}} = \left\langle \Psi_{\text{ES}}(r_i) | \hat{\mu}_{\text{EG}} | \Psi_{\text{GS}}(r_i) \right\rangle,$$

and $\hbar\omega$ is the photon energy. The prefactor $\omega^3$ in Eq. 1 consists of the photon density of states (DOS) causing spontaneous emission ($\sim \omega^2$) and the perturbing field of those photons ($\sim \omega$). In contrast, the absorption spectrum is a linear function of $\omega$ since no spontaneous
emission is involved in this case. Thus the absorption spectrum can be expressed as
\[ I_{\text{ABS}}(\hbar \omega) = C_{\text{ABS}}^2 \mu_{\text{EG}}^2 \sum_{n=0,m} \left| \left\langle \Theta_{n=0}^m(Q) \right| \Theta_{m=0}^n(Q) \right\rangle^2 \delta(E_m^\text{ES} - E_n^\text{GS} - \hbar \omega), \]  
(3)

where, however, \( n = 0 \) owing to the no-phonon modes in the ground state at \( T = 0 \) K. In Eqs. 1 and 3 \( C_{\text{EM}} \) and \( C_{\text{ABS}} \) are the corresponding constants of the emission and absorption, respectively. Since \( C_{\text{EM/ABS}} \) and \( \mu_{\text{EG}} \) are constants across the spectrum, we used Eqs. 4 and 5 as the luminescence and absorption lineshapes \([L_{\text{EM/ABS}}(\hbar \omega)]\), respectively, defined as

\[ L_{\text{EM}}(\hbar \omega) = \omega^3 \sum_{0,m} \left| \left\langle \Theta_{n=0}^m(Q) \right| \Theta_{m=0}^n(Q) \right\rangle^2 \delta(E_m^\text{ES} - E_n^\text{GS} - \hbar \omega), \]  
(4)

\[ L_{\text{ABS}}(\hbar \omega) = \omega \sum_{n=0,m} \left| \left\langle \Theta_{n=0}^m(Q) \right| \Theta_{m=0}^n(Q) \right\rangle^2 \delta(E_m^\text{ES} - E_n^\text{GS} - \hbar \omega) \]  
(5)

In Eqs. 1, 3 - 5 the overlapping integral of the GS and ES vibrational states denoted by \( \Theta_{\text{ES}}^m(Q) \) and \( \Theta_{\text{GS}}^n(Q) \), respectively.

PL and reionization spectra including phonon-assisted electronic transitions were obtained by applying the Huang-Rhys (HR)\(^{29}\) theory as implemented by Gali et al.\(^{31}\). In the HR framework three basic assumptions are established as: (i) normal modes and (ii) vibrational frequencies are identical in the initial and final states, and (iii) the equilibrium configuration is shifted by \( \Delta Y \) in the final state with respect to the initial nuclear configuration. Generalized nuclear configuration weighted by the nuclear masses \( (Y) \) can be defined as \( Y = M^{1/2}X \), where \( X = (R_1, ..., R_2) = (X_1, Y_1, Z_1, ..., X_N, Y_N, Z_N) \) is a vector constructed by the nuclear coordinates and

\[
M = \begin{bmatrix}
M_1 & & \\
& M_1 & \\
& & M_1 \\
& & & M_2 \\
& & & & \ddots \\
& & & & & M_N
\end{bmatrix}
\]  
(6)

is the mass tensor. The partial HR factor \( (S_k) \) can be calculated as the scalar product of
the normal vectors of mode $k$ ($Y_k^0$) and the displacement vector of $\Delta Y$ as

$$S_k = (\Delta Y^T Y_k^0)^2.$$  \hspace{1cm} (7)

By Eq. 7 the (total) HR factor ($S$) can be defined as

$$S = \sum_k S_k.$$  \hspace{1cm} (8)

While the partial HR factor indicates the weight of phonon mode $k$ in the corresponding electronic transition, total HR factor gives a measure for the strength of the overall electron-phonon coupling. Accordingly, in case of $S = 0$ no phonon sideband appears in the PL spectrum, only the zero-phonon line (ZPL) representing the electronic transition with no phonon assistance. By using the HR factors overlapping integral of the initial and final vibrational wavefunctions describing the lineshape of the spectrum can be written as

$$\langle \Theta_m(Q)|\Theta_n^R(Q)\rangle = \prod_k \langle m_k|n_k \rangle,$$  \hspace{1cm} (9)

where $\Theta_m^R(Q)$ and $\Theta_n^R(Q)$ stand for the vibrational wavefunctions of the initial and final states, respectively $m_k$ and $n_k$ stand for the phonon occupation of mode $k$ in the final and initial states with the corresponding $n$ and $m$ quantum numbers, respectively, and

$$|\langle m_k|n_k \rangle| = e^{-S_k} \frac{S_k^{m-n}}{(m-n)!}.$$  \hspace{1cm} (10)

Experimental determination of the $S$ factor can be carried out via the so-called Debye-Waller (DW) factor ($w$)$^{32,33}$ which can be directly read out from the corresponding spectra. DW factor represents the ratio of the ZPL and total intensity in the corresponding spectrum and can be expressed using $S$ as $w = \exp(-S)$. If the spectrum is normalized obtaining the probability density function (PDF) of the corresponding electronic transition, i.e. the total area under the curve is 1, DW factor is the magnitude of the area locked in by the ZPL. We note that all HR spectra presented in this work are normalized.

Temperature dependence of the HR spectrum is also of high importance. Temperature dependent HR spectra are generated by multiplying the HR spectra obtained at $T = 0$ K by the Boltzmann distribution as the high temperature and low concentration limit of the
Bose-Einstein distribution describing the occupation of a certain phonon mode.

B. Computational methodology

In order to obtain the neutral PL spectra for all defect configurations we calculated the neutral ground and optical excited states by DFT. Excited state calculations were carried out by applying the $\Delta$SCF method$^{34}$. In addition, for the the $V_CV_{Si}^- \rightarrow V_CV_{Si}^0$ reionization spectra we calculated the ground state of $V_CV_{Si}^-$. Nuclear coordinates in the initial and final states, i.e. the fully relaxed geometries were obtained by minimizing the forces between the ions falling below the threshold of 0.01 eV/Å. The corresponding electronic structure for all $V_CV_{Si}^0$ defect configurations in the neutral ground/excited state and that for $V_CV_{Si}^-$ in the ground state is shown in Fig. 2. Here we note that both excited state of $V_CV_{Si}^0$ and ground state of $V_CV_{Si}^-$ introduce a degenerate $e$ KS state to the band gap occupied by three electrons giving rise to the so-called dynamical Jahn-Teller (JT) effect$^{35}$. Accordingly, the symmetry will be reduced from $C_{3v}$ to $C_{1h}$ (even for axial configurations) by coupling to phonons in order to split the corresponding $e$ level removing the degeneracy in total energy. In calculation of the corresponding spectra we use static JT distorted geometries exhibiting the lowest total energy.

Figure 2. Electronic structure of the [(a), (d)] ground and [(b), (e)] excited state of $V_CV_{Si}^0$ defects and [(c), (f)] ground state of $V_CV_{Si}^-$ defects. Figures (a)-(c) corresponds to the axial defects exhibiting $C_{3v}$ symmetry and those of (d)-(f) show the electronic structures of the basal defect configurations possessing $C_{1h}$ symmetry. Black arrows represent electrons while gray arrows stand for the reminiscent holes after optical excitation. Valence band (VB) and conduction band (CB) of 4H SiC are also indicated along with the characters of the corresponding Kohn-Sham states.
All investigated $V_C V_Si$ defect configurations were modelled in a 576-atom 4H supercell. In order to reach sufficient accuracy in the total energies, we employed $\Gamma$ – point centered $2 \times 2 \times 2 k$-point mesh for all ground and excited state calculations. Here we note that, applying only $\Gamma$-point sampling of the Brillouin-zone the accuracy is not sufficient to distinguish the correct order in the total energies of the different $V_C V_Si$ configurations as pointed out in Ref. 27. For the electronic structure calculations we employed the HSE06 range-separated hybrid functional\textsuperscript{36}. Kohn-Sham (KS) wavefunctions were expanded in plane wave basis set with the cutoff energy of 420 eV. In the calculations only valence electrons were treated explicitly, core-electrons were considered in the framework of projector augmented wave (PAW) method\textsuperscript{37} as implemented in the Vienna Ab-Initio Simulation Package (VASP)\textsuperscript{38}. For charge correction in total energies of the $V_C V^-_{Si}$ defect configurations we employed the Freysoldt charge correction scheme\textsuperscript{39}.

For the vibrational modes, we calculated the corresponding dynamical matrix containing the second order derivatives of the total energy by means of the Perdew-Burke-Ernzerhof (PBE)\textsuperscript{40} functional. We also determined the corresponding eigenvectors. Here we note that the calculated dynamical matrix and hence the HR and DW factors depend on the supercell size. However, based on preliminary studies\textsuperscript{30} the 576-atom supercell applied in this work may be sufficiently big to reach convergent results.

Localization of the phonon modes can be addressed by the inverse participation ratio (IPR)\textsuperscript{30,41} defined as

$$\text{IPR}_k = \frac{N \sum_i u_i^4}{\left(\sum u_i^2\right)^2},$$

where $u_i$ is the vector displacement amplitude of the $i$th atom in the $k$th phonon mode and $N$ is the number of atoms in the supercell that is $N=576$ in our case. Consequently, the IPR fall in the region of $[1, N]$. When all atoms participating in a phonon mode possess equal amplitudes in their motion, the IPR is equal to the number of atoms vibrating in the certain phonon mode.
III. RESULTS AND DISCUSSION

In Secs. IIIA - IIIC we provide our numerical results for the V\textsubscript{C}V\textsubscript{0}\textsubscript{Si} PL spectra and the reionization spectra for the V\textsubscript{C}V\textsubscript{0}\textsubscript{Si} → V\textsubscript{C}V\textsubscript{0}\textsubscript{Si} transition for all V\textsubscript{C}V\textsubscript{0}\textsubscript{Si} defect configurations. We also discuss the charge state control and simultaneous qubit manipulation of V\textsubscript{C}V\textsubscript{0}\textsubscript{Si} in 4H SiC.

A. PL spectra of V\textsubscript{C}V\textsubscript{0}\textsubscript{Si} configurations

In order to verify the methodology\textsuperscript{34} for calculating the PL spectra, first we compare the total PL spectrum (i.e. including all contributions from the individual V\textsubscript{C}V\textsubscript{0}\textsubscript{Si} configurations) obtained from theory with the non-quenched V\textsubscript{C}V\textsubscript{0}\textsubscript{Si} spectrum reported in Sec. IIID. Accordingly, the non-quenched PL spectra were recorded at T = 3.5 K with using two different excitation wavelengths, 976 nm and 1053 nm (cf. Fig. 10) along with a 532 nm repump laser in order to maintain the neutral charge state (i.e. to avoid quenching). Excitation energies can be taken into account in the calculations by multiplying the obtained numerical spectra with the cross-sections (\(\sigma\)) of the individual V\textsubscript{C}V\textsubscript{0}\textsubscript{Si} configurations, respectively, as 

\[
L_{EM}(E_{ex}, \hbar \omega) = \sigma(E_{ex}) L_{EM}(\hbar \omega),
\]

where \(L_{EM}(E_{ex}, \hbar \omega)\) denotes the PL lineshape upon the excitation energy of \(E_{ex}\). In our calculations, we identified \(\sigma(E_{ex})\) as the transition probability at \(E_{ex}\), i.e. \(\sigma(E_{ex}) = PDF(E_{ex})\). We report the corresponding values in Table I.

The total numerical PL emission spectra (cf. Fig. 3) upon 976 nm and 1053 nm excitation are then obtained by summarizing the lineshape spectra obtained for the individual V\textsubscript{C}V\textsubscript{0}\textsubscript{Si} configurations. Numerical and experimental emission spectra can be well-compared via the ZPL intensities. To this end, we listed the the ratio of the numerical and experimental ZPL

| Config. | \(\sigma_{th}\) 976 nm | \(\sigma_{th}\) 1053 nm | \(R_{th}\) 976 nm | \(R_{th}\) 1053 nm | \(R_{exp}\) 976 nm | \(R_{exp}\) 1053 nm |
|---------|----------------|----------------|--------------|--------------|--------------|--------------|
| hh      | 0.0015         | 0.0013         | 1            | 1            | 1            | 1            |
| kk      | 0.0018         | 0.0017         | 1.26         | 1.33         | 1.16         | 1.33         |
| hk      | 0.0021         | 0.0019         | 1.42         | 1.42         | 2.62         | 2.55         |
| kh      | 0.0022         | 0.0015         | 1.53         | 1.18         | 3.90         | 1.75         |
Figure 3. Calculated PL emission lineshapes for (a) 976 nm and (b) 1053 nm excitation wavelengths.

Figure 4. Calculated HR emission spectra for the optical transition of $V_{\text{Si}}^{r}V_{C}^{0}$ for all defect configurations. All spectra are normalized, i.e. the area under the curve is 1 and hence the $y$-axis represents the electronic transition probability from the ground to the optical excited state.

Intensities in Table I. Accordingly, trend in the ZPL intensity ratios agree well, however there are differences between the absolute values. This discrepancy may arise from the fact that, while polarization properties manifest in the experimental spectrum (i.e. the experimental spectrum is the sum of the individual polarization contributions parallel and perpendicular to the $c$-axis), in the theoretical spectrum all the emitted photons are considered. This implies that optical alignment of the PL measurement plays a key role in the obtained lineshape. In order to allow detection of both polarizations simultaneously, the experimental PL spectrum was registered through the edge of the sample.
Table II. Calculated and experimental\textsuperscript{42} ZPLs for all $V_C V^0_{Si}$ defect configurations in 4H SiC. In brackets we denoted the corresponding PL signals. HR ($S$) and DW ($w$) factors are also listed.

| Config (Signal) | $E_{ZPL}^{\text{exp}}$ (eV) | $E_{ZPL}^{\text{calc}}$ (eV) | $S$   | $w$  |
|-----------------|------------------------------|------------------------------|-------|------|
| $hh$ (PL1)      | 1.095                        | 1.142                        | 2.856 | 0.057|
| $kk$ (PL2)      | 1.096                        | 1.151                        | 3.380 | 0.034|
| $hk$ (PL3)      | 1.119                        | 1.167                        | 3.428 | 0.032|
| $kh$ (PL4)      | 1.150                        | 1.187                        | 3.540 | 0.029|

The calculated HR emission PDF for the $V_C V^0_{Si}$ optical transition are shown in Fig. 4. We note that, luminescence lineshape of $hh$ and $hk$ $V_C V^0_{Si}$ have recently been investigated in Ref. 43 reporting similar results to those shown in this paper, however here we provide higher-resolution spectra in Fig. 4 exhibiting more refined details. The spectra consist of a sharp ZPL and a PSB at lower energies. ZPLs in all spectra are shifted to the experimental ZPL positions as reported in Table II. The ZPL and the PSB is separated by a $\approx$ 20-30 meV gap and the broadening of the PSB is $\approx$ 400 meV. The total $V_C V^0_{Si}$-related PL spectrum obtained by adding up the PL spectra for the individual $V_C V^0_{Si}$ configurations is shown in Fig. 5 (a).

In order to describe the origin of the features in the PSB, we carried out IPR analysis. Accordingly, for all $V_C V^0_{Si}$ configurations, we found that in the phonon energy region of $\approx 17 - 35$ meV the phonon modes are mostly localized on the $3 \times Si$ atom neighboring the $V_C$ with the IPR of $\approx 1 - 5$ while those fall in the $\approx 35 - 115$ meV region are mostly localized on the $3 \times C$ atoms around the $V_{Si}$ with similar IPR [Fig. 5 (b)].

The corresponding HR and DW factors along with the experimental and calculated ZPLs are listed in Table II. Accordingly, the smallest ZPL corresponds to $V_C V^0_{Si}(hh)$ along with the smallest $S$ and thus the largest DW factor. Here we note that the exceptionally large value for the $V_C V^0_{Si}(hh)$ DW factor with respect to that of the other $V_C V^0_{Si}$ configurations is obtained also in Ref. 43. ZPL of $V_C V^0_{Si}(kk)$ is extremely close to the of $V_C V^0_{Si}(hh)$, i.e. the difference between the experimental value are only 1 meV ($\approx 0.1 \%$). On the other hand, $V_C V^0_{Si}(kk)$ exhibits by about $\approx 19 \%$ larger HR factor and $\approx 40 \%$ lower DW factor than that of $V_C V^0_{Si}(hh)$. The largest ZPL and HR factor along with the lowest DW factor is exhibited by $V_C V^0_{Si}(kh)$. 11
Figure 5. (a) Numerical transition probability density function of the $V_{C}V_{0}^{0}_{Si}$ related (a) total and (b) individual PL spectra. The total spectrum is generated by summing the individual $V_{C}V_{Si}^{0}$-related transition probability spectra shown in Fig 4. In the individual spectrum all corresponding ZPLs are shifted to 0 meV in order to illustrate the phonon energy. Phonon modes mostly localized on the $3 \times Si$ atoms around the $V_{C}$ fall in the $\approx 17 - 35$ meV region (yellow shaded area) region while those localized on the $3 \times C$ atoms around $V_{Si}$ are located in the $\approx 35 - 115$ meV region (blue shaded area).

B. Temperature dependent reionization spectra

We conclude that the HR theory $V_{C}V_{0}^{0}_{Si}$ reproduces well the experimental spectrum, therefore we can apply this theory in for understanding the temperature dependent reionization. Ionization energy of point defect can be approximated by the corresponding charge transition levels which are positions of the Fermi level in the band gap, where total energy of two charge states is equal. According to preliminary ab initio studies$^{27,44-46}$ three charge transition levels of $V_{C}V_{Si}$ fall into the band gap of SiC as $(+/0), (0/−)$ and $(−/2−)$ levels valid for all inequivalent $V_{C}V_{Si}$ configurations. We showed in a previous study$^{27}$ that the energy separation between the $(+/0)$ level and the VBM ($E_{VBM}^{+/0} \approx 1.1$ eV) is somewhat smaller than that between the $(0/−)$ level and the CBM ($E_{VBM}^{0/−} \approx 1.2 - 1.3$ eV) for all $V_{C}V_{Si}$ configurations. As a result we addressed the dark state of the divacancy as $V_{C}V_{−}$, i.e. the single negative charge state into which $V_{C}V_{0}^{0}_{Si}$ is converted upon photoexcitation below the reionization threshold energy. The corresponding experimental threshold energies and calculated charge transition levels are listed in Table III.

However, qubit state of the divacancy is the neutral charge state, i.e. $V_{C}V_{0}^{0}_{Si}$. Consequently, in order to manage optical manipulation of $V_{C}V_{0}^{0}_{Si}$ at the usual excitation energies of 1250-1320 meV (940-990 nm) the negative charge state should be optically converted to the neutral charge state, i.e. the optical reionization process of $V_{C}V_{−} \rightarrow V_{C}V_{0}^{0}_{Si}$ should
Figure 6. Calculated temperature dependent transition probability density functions for HR absorption spectra of the $V_C V_{Si} \rightarrow V_C V_{Si}^0$ transition for (a) $V_C V_{Si}(hh)$, (b) $V_C V_{Si}(hk)$, (c) $V_C V_{Si}(kk)$ and (d) $V_C V_{Si}(kh)$ at 0 K (black lines), 150 K (red lines), 300 K (blue lines), 450 K (green lines) and 600 K (magenta lines).

be carried out. To this end, a possible solution is to raise the temperature giving rise to phonon-assisted reionization of $V_C V_{Si}$. In order to investigate thoroughly the $V_C V_{Si} \rightarrow V_C V_{Si}^0$ reionization process we simulated the corresponding HR absorption spectra for all $V_C V_{Si}$ configurations as shown in Fig. 6. Here we note that, we only considered the electronic transition of $e \rightarrow CBM$ being the lowest energy electronic transition resulting in the neutral charge state. Furthermore, we assume that the electron promoted to the CBM dissipates and hence the process indeed results in $V_C V_{Si}^0$. By raising the temperature, PSB in the corresponding absorption spectra appears also at lower energies than that of the ZPL giving rise to probability of the afore mentioned electronic transition at lower-than-ZPL energies.

Table III. Experimental threshold energies of photoionization\textsuperscript{27} which is approximated by the (0/-) charge transition levels for all $V_C V_{Si}$ configurations referenced to the CBM. The corresponding HR ($S_i$) and DW ($w_i$) factors are also provided.

| Signal | Config. | $E_{\text{rel}}$ [eV] | $E_{0/\text{CBM}}$ [eV] | $S$ | $w$ |
|--------|---------|----------------|----------------|----|----|
| PL1    | $hh$    | 1.310          | 1.245           | 2.691 | 0.068 |
| PL2    | $kk$    | 1.310          | 1.209           | 3.038 | 0.048 |
| PL3    | $hk$    | 1.321          | 1.307           | 2.490 | 0.083 |
| PL4    | $kh$    | 1.281          | 1.174           | 3.267 | 0.038 |
In this case the position of the no-phonon absorption line is approximated by the corresponding charge transition levels and thus ZPLs of the reionization spectra are shifted to the experimentally determined reionization threshold energies ($E_{rei}$) listed in Table III. Regarding the PSB, sharp features appearing within the $\approx 100$ meV phonon energy range at beyond the ZPLs are present at even 600 K for $hh$ and $hk$ configurations, while those of $kk$ and $kh$ configurations almost completely disappear. This implies that contribution of the $3 \times Si$ atom around $VC(h)$ to these features is more significant than that of the $3 \times Si$ atom around $VC(k)$. Furthermore, features are more dominant for $VCV_{Si}(hh)$ than for $VCV_{Si}(hk)$ implying the same trend for the $3 \times C$ atoms around $V_{Si}$. In summary, based on the absorption spectra, the hexagonal environment of $VC/Si$ allows the presence of more localized phonons and hence a stronger electron-phonon coupling.

One basic assumption of the HR theory is that normal modes and vibrational frequencies are identical in the initial and final states (see Sec. II A). Consequently, we use the $VCV_{Si}^{0}$-related ground state modes and frequencies for calculating the reionization spectra as we did for the PL spectra (see Subsec. III A). Thus, the same IPR analysis is valid here as for the $VCV_{Si}^{0}$-related PL spectra, i.e. in the phonon energy region of $\approx 17 – 35$ meV the phonon modes are mostly localized in the $3 \times Si$ atom neighboring the $VC$ while those falling in the $\approx 35 – 115$ meV region are mostly localized on the $3 \times C$ atoms around the $V_{Si}$ with the IPR of $\approx 1 – 5$.

The corresponding HR and DW factors are listed in Table III. Similarly to the reionization spectra the same correspondence was found in the HR and DW factors between the $hh-hk$ and $kh-kk$ $VCV_{Si}$ configurations. In particular, the $hh-hk$ pair exhibits the higher HR factors and thus the lower DW factors. The lowest HR factor (highest DW factor) corresponds to $VCV_{Si}(kh)$ while the highest HR factors (lowest DW) factors belongs to $VCV_{Si}(hk)$.

C. Charge state control of divacancy defects in 4H SiC

Energy balance of phonon-assisted reionization can be expressed as $E_{rei} = E_{ex} \pm E_{ph}$, where $E_{ex}$ represents the photoexcitation energy and $E_{ph}$ stands for the energy of the absorbed (+) or emitted (−) phonon. Accordingly, employing excitation energies lower than $E_{rei}$ requires presence of phonons in the system in addition to the zero-point motion. The required photoexcitation energy at 0 K is $E^{\text{min}}_{ex} = E_{rei}$ as listed in Table III.
Figure 7. (a) Numerical temperature dependent transition probability density functions of the HR absorption spectra for the $V_{C_{V_S}}(hh) \rightarrow V_{C_{V_S}}^0(hh)$ transition. PSB below the ZPLs given rise at elevated temperatures are enlarged and the corresponding reionization threshold energies ($E_{\text{min}}^\text{ex}$) are indicated by vertical dashed lines, whereas the CTP of $w/2$ are represented by shaded under-curve areas. (b) CTP for the $V_{C_{V_S}}(hh) \rightarrow V_{C_{V_S}}^0(hh)$ transition. Half of DW factor, i.e. $w/2$ is indicated in the expanded part of the CTP.

Since the calculated reionization spectra are normalized (they are PDFs), exciting with the energy of $E_{\text{ex}}$ results in the total transition probability, i.e. cumulative transition probability (CTP) of

$$\text{CTP}(E_{\text{ex}}) = \int_0^{E_{\text{ex}}} \text{PDF}(\varepsilon) d\varepsilon,$$

where $\varepsilon$ is the variable for the energy in the reionization spectra.

The ionization threshold at cryogenic temperature is the ZPL energy of reionization, i.e. the adiabatic reionization energy. This corresponds to $\text{CTP}(E_{\text{rel}} = E_{\text{ZPL}}) = w/2$ with assuming symmetrical broadening of the ZPL peak of the photoionization spectrum. By increasing the temperature the phonon excited states of the negative divacancy are occupied according to the Bose-Einstein function thus the effective gap between the defect ionization energy and the conduction band minimum decreases which results in a lower threshold energy of photoionization. In other words, the phonon-assisted photoionization results in
PDF(ε) > 0 for ε < E_{ZPL} energy. One can find the threshold reionization energy at a given temperature for each configuration for which the ionization probability is equal to that of at T = 0 K i.e., PDF(ε) = w/2 is fulfilled.

We show the corresponding CTP(ε) at temperatures of T = 0 K, 150 K, 300 K, 450 K, 600 K function for the hh configuration in Fig. 7. In Fig. 7 (a) CTP(ε) is shown as area under the curve of the corresponding PDF(ε) while CTP(ε) as line plot is shown in Fig. 7 (b). CTP(ε) at all investigated temperatures is similar to the lineshape of the cumulative distribution function of the Boltzmann distribution, however at low temperatures (at 0 K and 150 K, black and red lines in Figs. 7) the lineshapes become wavy at around the ZPL energy for V_CV_{Si}(hh). We note that the temperature broadening of the ZPL emission is not considered in our study that may affect the results that is particularly manifested at low temperatures.

We also indicated $E_{ex}^{min}$ at the afore-mentioned temperatures in Fig. 7 (a) and depicted for all V_CV_{Si} configurations at temperatures of 0...600 K in 50 K steps in Fig. 8. Accordingly, $E_{ex}^{min}(T)$ exhibits a plateau up to $\approx 150-200$ K and at higher temperatures it decreases for all V_CV_{Si} configurations. Or, in other words, value of $E_{ph}^{min}(T)$=0 in our approximation for $T < \approx 150 – 200$ K and increases for $T > \approx 150 – 200$ K. In order to gain further insight to the temperature dependence of the phonon threshold energy, $E_{ph}^{min}(T)$, we employed the Boltzmann distribution [$f(\epsilon,T)$] as the low concentration limit of the Bose-Einstein distribution for the phonon bath appearing in the region of $[0, E_{rei}]$ as

$$f(\epsilon,T) = \frac{1}{kT} \cdot \exp\left(\frac{\epsilon - E_{rei}}{kT}\right),$$

where $k = 8.617 \cdot 10^{-5}$ eV/K is the Boltzmann constant. Calculation of the area under the curve (that is now required to be $w/2$) in the region of $[0,E_{rei}]$ can be performed by direct integration of the Boltzmann distribution as

$$\int_0^{E_{ex}^{min}} \frac{1}{kT} \cdot \exp\left(\frac{\epsilon - E_{rei}}{kT}\right) d\epsilon = \frac{w}{2}$$

By evaluating the integral of Eq. 14 and rearranging the equation we arrive at

$$E_{ph}^{min}(T) = -\ln\left[\frac{w}{2} + \exp\left(\frac{E_{rei}}{kT}\right)\right] \cdot kT$$

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Here we note that $E_{rei}$ approximated by $E_{(0/-)}^{CBM}$ (see Sec. IIIB) does not depend on temperature in our derivation. Since values of $E_{rei}$ are around 1300 meV (see Table III) and temperature does not exceed 600 K in our calculations, $\exp\left(\frac{E_{rei}}{kT}\right) \sim 10^{-12}$ (and became notable at only around $10^4$ K) and hence negligible with respect to the calculated DW values of $w/2 \approx 0.03 - 0.09$ (see Table III). In this way $E_{ph}^{\text{min}}(T)$ can be approximated as

$$E_{ph}^{\text{min}}(T) \approx -\ln\left(\frac{w}{2}\right) \cdot kT$$

yielding linear characteristics for $E_{ph}^{\text{min}}(T)$ with the slope of $m = -\ln(w/2) \cdot k$. Furthermore, since $w/2 < 1$, $E_{ph}^{\text{min}}(T)$ increases with $T$ within this approximation. As a result, reionization threshold energy can be expressed as

$$E_{ex}^{\text{min}}(T) = E_{rei} - E_{ph}^{\text{min}}(T) \approx E_{rei} + \ln\left(\frac{w}{2}\right) \cdot kT.$$  

Linear behavior of $E_{ex}^{\text{min}}(T)$ is manifested also in the numerical values plotted in Fig. 8. However, as we have already noted, $E_{ex}^{\text{min}}(T)$ is constant for $T \approx 150 - 200$ K, particularly, it takes the value of $E_{rei}$. The reason behind is that below 150-200 K the PSB is so weak that CTP of $w/2$ can only be reached by completing the PSB with a fraction from the ZPL contribution. Since treatment of the ZPL is beyond the scope of the Boltzmann-distribution, linearity of $E_{ex}^{\text{min}}(T)$ is violated by the ZPL contribution at low temperatures. Nevertheless, properties of $E_{ex}^{\text{min}}(T)$ at $T \approx 150 - 200$ K might be elucidated by a finer division of the temperature range and by applying finer resolution of the calculated reionization spectra that is now 0.5 meV. However, in this study reionization probability around room temperature ($\approx 300$ K) is in focus and hence low temperature characterization of $E_{ex}^{\text{min}}(T)$ is beyond our recent scope. Nevertheless, for $T \approx 150 - 200$ K $E_{rei}(T)$ decreases and at room temperature (300 K) it reaches 1250-1320 meV (940-990 nm) which is around the usually applied excitation wavelength for exciting $V_C^0V_{Si}^0$.

This procedure is demonstrated for $hh$ configuration in Fig. 7. We reiterated this procedure for the other configurations and the results are summarized in Fig. 9. Since the CTP of the electronic transition is proportional to the emission rate, Eq. 17 provides a prediction for excitation laser detuning upon temperature fluctuations in order to maintain a constant emission intensity. We also note that Eq. 17 is valid for any kind of point defect and PL spec-
trum within the employed approximations by substituting $E_{\text{rei}}$ with the corresponding ZPL energy. We emphasize that the actual phonon-assisted reionization may be observed for ε with PDF(ε) < w/2 depending on the integration time and other factors in the experiments that are discussed in Sec. III D.

D. Experimental aspects

The above consideration shows that the quenching behavior of the divacancy in all configurations is distinctly different at low temperature (say, < 2 K) and at elevated temperatures. While at low temperature there is a distinct threshold for the excitation energy for each divacancy configuration, below which quenching of the corresponding PL is observed but can be recovered using higher-energy repump illumination. Above the threshold the PL of the corresponding divacancy configuration does not quench even if no repump is applied. At higher temperatures, however, there are no distinct thresholds because phonon-assisted photoionization of the VV$^-$ charge state becomes possible, whereas no phonons are available at low temperature for this process. Given a fixed excitation energy $E_{\text{ex}}$, the minimum energy of a phonon $E_{\text{ph}}^{\text{min}}$ that can combine with the incident photon to produce phonon-assisted photoionization of VV$^-$ is given by the energy balance quoted in the beginning of Sec. III C,

$$E_{\text{rei}} = E_{\text{ex}} + E_{\text{ph}}^{\text{min}} \quad (18)$$

Here we assume that $E_{\text{ex}} < E_{\text{rei}}$, hence $E_{\text{ph}}^{\text{min}} > 0$. All phonons with energies $E_{\text{ph}} > E_{\text{ph}}^{\text{min}}$ also contribute to phonon-assisted photoionization, hence the cumulative transition probability CTP($E_{\text{ex}}$) is given by Eq. 12. From practical point of view, it may be desirable to have
Figure 9. Theoretical dependencies of the cumulative transition probability on the temperature for the four divacancy configurations as denoted for each curve, and for the two excitation wavelengths used in the experiment. The inset displays an energy diagram of the phonon-assisted photoionization illustrated on the hk divacancy configuration. The charge transition levels (0/−) are labelled with the corresponding configuration and the experimentally determined energy separation from the conduction band. The two bold vertical arrows represent the two experimental laser energies whereas the wavy arrows represent the phonons with minimum energies needed for reionization of the divacancy from negative to neutral charge state.

the possibility for optical charge state control also at elevated temperatures. This can be achieved by using lower excitation energies $E_{\text{ex}}$, because these provide lower $\text{CTP}(E_{\text{ex}})$, hence the quenching behaviour can be preserved also at elevated temperatures. It is clear that if $E_{\text{ph}}^\text{min} \gg k_B T$ for given temperature $T$ (the case of lower-energy $E_{\text{ex}}$) the amount of phonons available for phonon-assisted reionization is negligible and $\text{CTP}(E_{\text{ex}}) \approx 0$. Note that $E_{\text{ex}}$ is bound from below by the condition $E_{\text{ex}} > E_{\text{ex}}^{\text{ZPL}}$, where $E_{\text{ex}}^{\text{ZPL}}$ refers to the corresponding divacancy configuration. Our goal here is to examine the concept of phonon-assisted reionization by comparing the quenching properties at higher temperatures for two excitation energies, both below the thresholds, but one of which is close to the threshold while the other is far enough so that $E_{\text{ph}}^\text{min} = E_{\text{rei}} - E_{\text{ex}} \gg k_B T$.

The energy diagram (inset in Fig. 9) depicts the two excitation cases for $E_{\text{ex}} = 1.270 \text{ eV}$ (976 nm), and $E_{\text{ex}} = 1.177 \text{ eV}$ (1053 nm) which have been used in the experiments presented below. Both excitations are below the thresholds for all divacancy configurations, but the former is close to the thresholds (only $\approx 11 \text{ meV}$ lower than the threshold for PL4, cf.
Table II), whereas the 1.177 eV excitation is about 100 meV (up to 140 meV for the different configurations) below all thresholds. As a consequence, the condition $E_{\text{min}}^{\text{ph}} \gg k_B T$ is fulfilled only for the second excitation at 1.177 eV, as long as the temperature does not exceed room temperature. The CTPs as a function of temperature for the two used excitations and for the four divacancy configurations are calculated using Eq. 12 and displayed in Fig. 9 in the temperature range 0 – 350 K. Using these dependencies we can make qualitative comparison with the experimental data presented in Fig. 10 and obtained using these two fixed laser excitations, 976 and 1053 nm. The repump laser beam used in these experiments is at 532 nm directed unfocused on the sample with power density of the order of 1 mW/cm$^{-2}$. On the other hand, the excitation beam (976 or 1053 nm) is moderately focused on the sample to a spot of $\sim$1 mm diameter, with estimated power density at the sample of the order of several watts per cm$^{-2}$. The experimental conditions are detailed in Ref. 27.

Figure 10. Experimental spectra of the divacancy emission obtained at different temperatures with the simultaneous application of the IR laser and the 532 nm repump laser (denoted NQ, or non-quenched) and with the IR laser alone after a long term quenching ($Q$, or quenched). The panels to the left (right) refer to the 976 nm (1053 nm) IR laser, respectively. The two bottom panels show also the anti-Stokes part of the spectra and illustrate the upconversion in the emission of the silicon vacancy.
We compare now the quenching behaviour of the divacancy emission at different temperatures when the two different excitations are used. The experimental spectra obtained at different temperatures are presented in Fig. 10. The spectra with the infrared laser excitation alone (976 or 1053 nm) are obtained after switching off the repump laser and quenching the divacancy PL for about 1/2 hour, and are referred to further as the “quenched” spectra (denoted by $Q$ in Fig. 10). The rest of the spectra are with the repump laser applied in addition to the infrared excitation; under these conditions the divacancy PL is stable and the spectra are denoted by NQ for “non-quenched” in Fig. 10. One can see from the spectra that at liquid He temperature (3.5 K) the divacancy PL quenches about 10 – 30 times for each of the two excitations, as expected because both excitation energies are below the thresholds for all divacancy configurations. Also, at this temperature essentially no phonons are available for phonon-assisted reionization, hence the accumulation of the divacancy in the negative charge state is irreversible for both IR excitations used. We notice also that in the particular sample used in these experiments the quenched PL never reaches zero intensity, similar to sample 1 of Ref. 27.

At 80 K, however, we notice differences in the quenching behavior of one of the divacancy configurations ($kh$). Namely, with the 976-nm excitation the PL4 line corresponding to the $kh$ configuration shows nearly the same intensity in the “quenched” spectrum as in the “non-quenched”, i.e., it does not quench. We notice here that the relative contribution of the PL4 line in the spectra at 80 K is strongly reduced compared to the spectra at 3.5 K, but this behavior is not understood at present. The rest of the lines (PL1 – PL3) do quench exhibiting large intensity contrast (similar to that at 3.5 K) between the “quenched” and “non-quenched” spectra for both excitations. We notice further that the PL4 also quenches in a way similar to that at 3.5 K if the 1053-nm excitation is used. Referring to the CTP plots in Fig. 9 we notice that at temperature $T = 80$ K only the $kh$ configuration (corresponding to the PL4 line) exhibits $\text{CTP} \approx 0.003$ for 976-nm excitation, while for the rest of the divacancy configurations at 976 nm and all configurations at 1053 nm the CTP is essentially negligible (< $10^{-4}$) for both excitation wavelengths. Thus, the experimental data for the PL4 line implies that for CTP of only 0.003 (0.3% probability of phonon-assisted ionization of $VV^-$) the reionization process outcompetes the accumulation of the divacancy in the negative charge state. Consequently, for CTPs in the $10^{-4}$ or low $10^{-3}$ range one may expect to notice impact of the phonon-assisted reionization on the quenching process. This
provides a means to define semi-quantitatively the experimental conditions when the rate of the phonon assisted reionization is comparable with the rate of capture of electrons to neutral divacancies, thus creating negatively-charged ones. We can define that this condition (similar rates of ionization an reionization) is true if the quenched spectra exhibit roughly 50% (say, between 30% and 70%) of the intensity of the non-quenched ones.

At temperatures higher than 80 K the contribution of the $kh$ configuration (PL4 line and phonon sideband) in the spectrum can be neglected owing to the abovementioned rapid decrease of the PL4 intensity with increasing temperature. Thus, we investigate the behavior of the PL1-PL3 lines, the phonon sidebands of which coalesce into a broad band extending between 1100 and 1320 nm. Note that also the threshold energies of these three configurations ($hk, hh$ and $kk$) are rather close according to the energy diagram inset in Fig. 9. At 150 K the contributions from the these three divacancy configurations are still discernible via their zero-phonon lines, although the latter are much broader and weaker than at helium temperature. However, the dominant contribution to the spectrum at this and higher temperatures comes from the PSBs of each configuration, which overlap to form a single band concealing the individual contribution from the different configurations. Therefore, in the following we shall compare the intensities of the broad bands in the “quenched” and “non-quenched” spectra, looking for each IR excitation for the temperature when the intensity in the quenched spectrum is roughly half of the intensity in the non-quenched one.

We observe from Fig. 10 that our criterion is fulfilled for the 976-nm excitation at $T = 150$ K, when the intensity of the phonon sideband is about 1/2 of the intensity in the non-quenched one. The corresponding CPTs for the 976 nm excitation are $1.5 \times 10^{-3}$, $3 \times 10^{-3}$ and $3 \times 10^{-3}$ for the $hk, hh$, and $kk$ configurations, respectively. These values are in good agreement with our anticipation that the phonon-assisted reionization rate is comparable with that of the divacancy ionization to $VV^-$. Further temperature increase to 200 K completely inhibits the quenching as seen from the corresponding spectrum for 976 nm excitation in Fig. 10. On the other hand, the quenching is well pronounced for the 1053 nm excitation at both temperatures, 150 K and 200 K. For this excitation (1053 nm), one notices significant change in the quenching contrast only at 250 K, when the intensity of the “quenched” spectrum is about 30% of that of the “non-quenched” one, thus satisfying our criterion. The corresponding theoretical CPTs are $2.5 \times 10^{-4}$, $4.4 \times 10^{-4}$ and $4.6 \times 10^{-4}$ for the $hk, hh$, and $kk$ configurations, respectively. These values are 6 – 7 times smaller than the
corresponding CPTs at 150 K for the 976 nm excitation, but we still expect impact on the quenching properties for such values of the CPT. Thus, the experimental data is in reasonable agreement with the theory and we may conclude that the dominant reason for the loss of the quenching properties above 150 K quoted in Ref. 27 where 976-nm excitation has been used is the phonon-assisted reionization activated at this and higher temperatures. In contrast, the quenching property disappears completely only at room temperature when the 1053 nm excitation is used.

We notice the appearance of the luminescence of the silicon vacancy ($V_{\text{Si}}^-$) at elevated temperatures when the 976-nm excitation is used, via the upconversion mechanism discussed in Ref. 27. Indeed, at 250 K the spectrum obtained with 976-nm excitation is dominated by the contribution of $V_{\text{Si}}^-$, as shown in the bottom left panel of Fig. 10. However, the $V_{\text{Si}}^-$ spectrum can be discerned even below 200 K when 976-nm excitation is used. For instance, the Stokes part of the $V_{\text{Si}}^-$ luminescence is clearly visible in the spectrum at 200 K (left panels). In contrast, weak contribution from the upconverted $V_{\text{Si}}^-$ luminescence can be observed with 1053-nm excitation only at room temperature (293 K, bottom right panel); at 250 K or lower temperatures its contribution to the spectrum is negligible and the dominant luminescence is that of the divacancy. Since the upconverted $V_{\text{Si}}^-$ luminescence is associated with increased generation of free electrons, its appearance serves as an indicator of the rapid increase of the free-electron population with temperature when 976-nm is used, owing to the rapid increase of the CTP with increasing temperature for this excitation. On the contrary, the increase in the CTP (and the electron population) is much smaller with the 1053-nm excitation, so that the contrast between quenched and non-quenched spectra disappears only at 293 K and is associated with the weak appearance of upconverted luminescence from $V_{\text{Si}}^-$, as expected.

Thus, the experimental data suggests that the phonon-assisted divacancy reionization apparently influences the quenching behavior at temperatures and excitations for which the CTP is of the order of mid $10^{-4}$ – low $10^{-3}$, that is, well below 1%. We notice that this value is much smaller than the half of the Debye-Waller factor ($w/2$) used as a reference during the discussion of the probabilities in the previous section. We can understand the fact that low reionization probability (of the order of 0.1%) is sufficient to counteract the process of accumulation of the divacancy in the negative charge state, if we consider the model describing the quenching dynamics presented in Ref. 27. In this simplest model two
types of centrums are considered: traps capable to emit electrons to the conduction band as a result of photoionization (via the IR excitation) and divacancies capable of capturing electrons. Consequently, the traps can be in two states: with captured electron (capable to emitted an electron to the CB via photoionization), and with a missing electron (capable to recapture of free electron). The divacancies in this model are also assumed to have two charge states: neutral (capable of capturing electron) and negatively-charged (with captured electron). The latter state cannot be photoionized using IR excitation below the threshold, hence the accumulation of divacancies in the negative charge state leads to quenching of the luminescence from the neutral charge state.

Naturally, there exist various traps capable of emitting electrons via photoionization, for instance, the nitrogen donors, the carbon vacancy, the silicon vacancy in double ($2^-$) and triple ($3^-$) negative charge states, etc. The model in Ref. 27 assumes only one kind of traps which may be thought as having the dominant capture cross section for electrons and the dominant concentration. If these were the nitrogen donors, for instance, then the capture cross section of ionized donors for electrons is “giant” owing to the possibility for capture via the excited donor states. On the other hand capturing of electrons occurs to the neutral divacancy which, therefore, is assumed to have much smaller capture cross section for electrons. Indeed, in order to reproduce correctly the shape of the time decay of the divacancy PL the model in Ref. 27 admits that the ratio of capture cross sections for electrons of the divacancy and the trap is $2 \cdot 10^{-3}$. In other words, an electron is emitted from traps and recaptured from traps many times before it eventually can be captured by the divacancy. On the other hand, one can assume that the probability for absorption of a photon which is stipulated by the optical-absorption cross section is similar for the traps and the divacancies. Recapturing of electrons is fast to the traps, but only about 0.1 % of the total free-electron population are captured to divacancies. Thus, the divacancy population in the negative charge state grows slowly, and this slow process can be counteracted by phonon-assisted reionization with a CTP of about 0.1 %.

To conclude this section, we can state that excitations with longer wavelength (lower energy) widen the temperature range in which the quenching phenomenon can be observed. However, in many cases when the silicon vacancy $V_{\text{Si}}^-$ is also present, excitation with too high photon energies (e.g., close to or even above the threshold of all divacancy configurations) leads at elevated temperatures to upconverted PL of $V_{\text{Si}}^-$ instead of excitation of the
divacancy PL, as illustrated in the low left panel of Fig. 10. Thus, if the PL of the divacancy is to be measured at higher temperatures or at room temperature, lower excitation energies are also preferable. It should be noted, however, that it might be possible to stabilize the divacancy PL by Fermi-level tuning even when excitations above the thresholds is applied, but this is a subject of a different study and will not be discussed here.

IV. CONCLUSIONS

In this paper, we have investigated the photoluminescence lineshape of neutral $V_CV_{Si}^0$(hh) qubits in 4H SiC at $T = 0$ K by DFT calculations. We obtained the corresponding PL spectra by using the HR theory and found that the corresponding PSB exhibits rich set of sharp features for all configurations. The sharp features originate from localized phonon modes and via IPR analysis we showed that in the phonon energy region of $\approx 17-35$ meV phonons are localized on the $3 \times Si$ atoms around the $V_C$ while those falling in the $\approx 35-115$ meV are localized on the $3 \times C$ atoms around the $V_{Si}$. We also calculated the corresponding HR and DW factors yielding the lowest HR factor (and thus the highest DW factor) for $V_CV_{Si}^0$(hh) implying $V_CV_{Si}^0$(hh) to be the most attractive $V_CV_{Si}^0$ qubit candidate.

We also calculated the temperature dependent $V_CV_{Si}^- \rightarrow V_CV_{Si}^0$ reionization spectra. We showed that for a constant cumulative transition probability — that is fixed to $w/2$ in our calculations — that the function of $E_{ex}^{\text{min}}(T)$ shows linear behavior in the temperature range of $\approx 200-600$ K providing a prediction for excitation laser detuning upon temperature fluctuations in order to maintain constant emission intensity. This result can be applied for general PL spectrum for any kind of point defect within the applied approximations.

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