Influence of hydrogen implantation on emission from the silicon vacancy in 4H-SiC

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The silicon vacancy (V_{Si}) in 4H-SiC is a room temperature single-photon emitter with a controllable high-spin ground state, and is a promising candidate for future quantum technologies. However, controlled defect formation remains a challenge, and recently it was shown that common formation methods such as proton irradiation may in fact lower the intensity of photoluminescence (PL) emission from V_{Si} as compared to other ion species. Herein, we combine hybrid density functional calculations and PL studies of proton-irradiated n-type 4H-SiC material to explore the energetics and stability of hydrogen-related defects, situated both interstitially and in defect complexes with V_{Si}, and confirm the stability of hydrogen in different interstitial and substitutional configurations. Indeed, V_{Si}-H is energetically favorable if V_{Si} is already present in the material, e.g., following irradiation or ion implantation. We demonstrate that hydrogen has a significant impact on electrical and optical properties of V_{Si}, by altering the charge states suitable for quantum technology applications, and provide an estimate for the shift in thermodynamic transition levels. Furthermore, by correlating the theoretical predictions with PL measurements of 4H-SiC samples irradiated by protons at high (400 °C) and room temperatures, we associate the observed quenching of V_{Si} emission in the case of high-temperature and high-fluence proton irradiation with the increased mobility of H$_i$, which may initiate V_{Si}-H complex formation at temperatures above 400 °C. The important implication of hydrogen being present is that it obstructs formation of reliable and efficient single-photon emitters based on silicon vacancy defects in 4H-SiC.

I. INTRODUCTION

Solid-state single-photon emitters and controllable spin centers are currently in high demand for applications within quantum computing, communication, imaging and sensing. Silicon carbide, and the 4H polytype due to its mature material processing and fabrication in particular, is a promising host for qubit defects. 4H-SiC harbors several candidate defects exhibiting desirable properties such as single-photon emission in the near-infrared and stable and controllable spin states, even at room temperature [1,2]. However, although isolated point defects can be detected and identified in 4H-SiC, both controlled formation and fully reliable detection of the defects remain a challenge.

Promising qubit contenders in 4H-SiC include the silicon vacancy (V_{Si}) [3], the silicon-carbon divacancy ($V_{Si}V_C$) [4], the carbon antisite-vacancy pair ($C_{Si}V_C$) [5] and the nitrogen-vacancy center (N_CV_{Si}) [6]. The high fraction of V_{Si} emission directed into the zero-phonon line (ZPL) [7], along with the higher stability of V_{Si} emission energies towards stray electric fields [8–10] and device fabrication [11] as compared to the complexes, mark the silicon vacancy as a frontrunner for quantum technology applications.

V_{Si} can inhabit two different lattice sites in 4H-SiC, the hexagonal (h) and pseudo-cubic (k), and therefore exists in two configurations. Accordingly, photoluminescence (PL) spectra from n-type 4H-SiC typically showcase two ZPLs related to V_{Si}: V1 at 1.438 eV assigned to the negative V_{Si} at a

hexagonal lattice site, $V_{Si}^-(h)$, and V2 at 1.352 eV attributed to $V_{Si}^-(k)$ [8,12]. Despite the promising properties of V_{Si}, emission from V_{Si} remains low, and is commonly enhanced by nanostructuring of the 4H-SiC surface to form waveguides for single-defect spectroscopy [13,14]. Furthermore, only the negative charge state of V_{Si} manifests single-photon emission and millisecond spin coherence times [13]. Recently, the 2− and 3− charge states were shown to be more stable than V_{Si}^- in n-type material, by correlating density functional theory (DFT) calculations to deep level transient spectroscopy (DLTS) measurements [9]. Indeed, substantial enhancement of emission from V_{Si} ensembles [9] and control of the charge state of isolated V_{Si} defects [15] was recently demonstrated via application of electric fields, and attributed to selective population of the bright and dark charge states.

In contrast to the carbon vacancy, which is commonly present even in state-of-the-art epitaxial 4H-SiC material [16], the silicon vacancy is challenging to form thermally. With a formation energy of ~ 7.5 eV in the neutral charge state [1,9], which is predominant under the intrinsic conditions that manifest at high temperatures, only approximately 10^7 cm^{-3} of silicon vacancies can be formed by annealing 4H-SiC at 2000 °C. Accordingly, irradiation and ion implantation are the methods of choice for silicon vacancy formation. Unfortunately, the placement of isolated defects during an irradiation procedure is inherently randomized, but proton beam writing [17] or irradiation through nano-scale apertures [18] enhance the reproducibility when single defects are desired. To successfully employ silicon vacancies as efficient single-photon sources for quantum cryptography or reliable multi-level single spins for quantum computing, comprehensive investigations into the effects of processing conditions on V_{Si} formation

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and emission are needed.

Recently, it was shown that V_{Si}-related PL is substantially weaker when the silicon vacancies are formed by hydrogen implantation compared to that of, e.g., helium [18]. A possible explanation involves the implanted hydrogen atoms preferentially occupying V_{Si} sites, thereby altering the optoelectronic properties of the defect and effectively quenching the V1 and V2 emission lines. Helium, on the other hand, is inert, and may have a reduced impact on the V_{Si} emission. A theoretical study suggested that hydrogen is readily captured by silicon and carbon vacancies in 3C-SiC, while preferring the V_{Si} site over that of V_C [19]. However, vacancy-hydrogen complex formation is possible also in the 4H polytype, motivating for further investigation. Indeed, a deep-level defect at 0.73 eV below the conduction band edge, observed by DLTS, was tentatively attributed to the V_{Si}-H complex [20].

In the present work, we explore the impact of hydrogen on the formation and properties of V_{Si} in 4H-SiC theoretically, by employing density functional calculations, and interpret our findings in light of photoluminescence measurements. We propose that the interstitial H configuration is lowest in energy, and that formation of the V_{Si}-H complex is energetically favorable during, e.g., irradiation and subsequent heat treatments. Complex formation likely results in a quenching of V_{Si}-related emission, and we propose hydrogen as an obstacle for efficient creation of reliable single-photon emitters using silicon vacancies in 4H-SiC. Moreover, we reaffirm that H migrates substantially slower in n-type than p-type material, and find that 400-500 °C is likely sufficient for H to react with V_{Si} in n-type 4H-SiC. Finally, we study V_{Si}-related emission experimentally in n-type 4H-SiC samples, irradiated with protons to different fluences and at different temperatures, and attempt to explain our observations in light of the theoretical findings presented herein.

II. METHODOLOGY

A. Theory

Hydrogen-related defects in 4H-SiC were studied using density functional theory as implemented in the *Vienna ab initio simulation package*, or VASP, code [21–24]. The electronic ground state was obtained within the Kohn-Sham formalism, using the projector augmented-wave (PAW) method [25] and plane-waves to describe core and valence electrons, respectively. 400-atom hexagonal supercells were constructed from $5 \times 5 \times 2$ primitive cells along the main axes. The lattice constants used for 4H-SiC were obtained using the Perdew-Burke-Ernzerhof functional (PBE [26]), and PBE-level lattice parameters were chosen because PBE was mainly used when studying H diffusion.

Defect formation was accomplished by adding one hydrogen (H) atom to form a hydrogen interstitial (H_i), and removing a Si atom to form a silicon vacancy (V_{Si}) or a V_{Si}-H complex. The defect geometries were first optimized at the PBE-level by employing $2 \times 2 \times 2$ Γ-centered Brillouin-zone (BZ) sampling and relaxing until the maximum force was below

0.01 eV/Å. Starting from the resulting defect configuration, a Γ-only relaxation succeeded within screened hybrid density functional theory (HSE06 [27,28]) until maximum forces were below 0.05 eV/Å. From these results, formation energy diagrams for all defects were constructed. The stopping criterion for the electronic self-consistent loop was set to 10^{-6} eV, and the plane-wave energy cut-off to 420 eV.

For the silicon monovacancy, the formation energies are based on calculations from Ref. [9], where we employed a 96-atom orthorombic supercell, the HSE06 functional and $2 \times 2 \times 2$ Monkhorst-Pack type BZ-sampling. Note that mirroring effects might influence the defect energetics for smaller supercells. However, the minimum distance between defects is 10 Å for V_{Si} in the 96-atom supercell, and the calculated thermodynamic charge-state transition levels agree with those obtained for V_{Si} in tests with 400-atom supercells, and when comparing to experiment [9], within $\sim$ 0.1 eV. During migration, the defect strain field extends over a larger volume and particularly when a complex is involved. A larger 400-atom supercell was therefore used to study migration of interstitial hydrogen and formation of hydrogen-vacancy complexes herein. This method was previously successfully employed to study migration of the carbon vacancy (V_C) in 3C- and 4H-SiC [29], and excellent overlap between theory and experiment was found.

Electronic structure calculations employing the HSE06 functional appear to adequately capture the energetics of defects within 4H-SiC, as demonstrated in Refs. [9,29] by combining DFT calculations with DLTS measurements for V_{Si} and V_C, respectively. The band gap of the orthorombic supercell becomes 3.17 eV when employing the $2 \times 2 \times 2$ MP **k**-mesh, which is close to the experimental value of 3.27 eV [30]. The Γ-only HSE06 calculations employing hexagonal supercells yield a band gap of 3.48 eV. When discussing charge state transition levels herein, the calculated figures will refer to the valence band edge.

The formation energy of a semiconductor point defect is given by [31,32]

$$E^f(q) = E^{total}_{defect}(q) - E^{total}_{bulk} - \sum_i \Delta n_i \mu_i \\ + q(\varepsilon_{VBM} + \varepsilon_F) + E^{FNV}. \quad (1)$$

Here, E^{total} refers to the total energies of the defective and pristine supercells, Δn_i is the number of atoms added (positive) or removed (negative), μ_i is the chemical potential for a particular species (Si, C or H), ε_{VBM} is the valence band maximum (VBM) and ε_F is the Fermi level position relative to VBM. Within this work, the chemical potentials were estimated by relaxations of bulk diamond, Si and hydrogen gas (H_2 in a periodic box) until all forces were below 0.005 eV/Å. E^{FNV} is a correction term to account for the use of charged and finite-sized supercells, and we have employed the extended Freysoldt, Neugebauer and Van de Walle (FNV) correction scheme [33–35] herein.

From the formation energy diagrams of the different defects, we can estimate the binding energy of a corresponding

complex, here exemplified by V_{Si}-H:

$$E^{b}[(V_{Si}\text{-H})^{3-}] = E^{f}(V_{Si}^{2-}) + E^{f}(H_{i}^{-}) - E^{f}[(V_{Si}\text{-H})^{3-}]. \quad (2)$$

The binding energy depends on the charge state of the final defect complex, and thereby the Fermi level, and must be positive to ensure the stability of the complex in question. To obtain the complete dissociation energy needed to break up the complex, the migration barrier of the most mobile constituent (here H_i) is added to E^b.

Minimum energy paths (MEP) for defect migration were studied at the PBE-level using the climbing image nudged elastic band (CI-NEB) method [36,37], Γ-only BZ sampling, 420 eV cut-off energy and between seven and eleven intermediate images. The forces were relaxed until the maximum force was below 0.01 eV/Å for all migration paths. NEB calculations require fixed initial and final geometries, and a chain of intermediate images are formed to provide an initial guess for the path of the migrating species. The images are connected via spring forces to keep them at a suitable distance, and are then collectively optimized, with the climbing image approach ensuring that the highest-energy image lands at the MEP maximum. Finally, the transition state electronic structure was refined by self-consistent field (SCF) calculations employing HSE06 for select migrational pathways.

Within the present work, we study seven different configurations of H_i, and eight different migration paths involving axial and basal migration for two charge states (+ and −). This is not exhaustive, as a fully comprehensive investigation into the nature of H_i in 4H-SiC is outside the scope of this work. We leave a full qualitative summary of H_i to other works [19,38,39], although one should note that semi-local functionals are employed and Ref. [19] concerns the 3C polytype. Instead, our aim is to determine if hydrogen is likely to alter the electronic structure and optical transitions of V_{Si} when both defects are present in 4H-SiC material, and explore the likelihood of V_{Si}-H complex formation. Therefore, to understand recent experimental findings, we focus on illuminating a representative behavior for H in 4H-SiC and consider closely how hydrogen interacts with silicon vacancies. Higher-order complexes between V_{Si} and more than one H atom were not considered herein, but could contribute to the overall picture.

B. Experiment

Experimentally, we study PL emission from 4H-SiC samples that are proton-irradiated to different fluences and at different temperatures, to better understand the optimal formation conditions for V_{Si}. 4H-SiC samples holding 10 μm epitaxial layers purchased from Cree, Inc were employed. The epi-layers were n-doped (nitrogen) with net carrier concentrations in the epi-layer of 1×10^{15} cm^{-3}, as determined by capacitance-voltage measurements. We study n-type 4H-SiC samples implanted with 1.5 MeV protons having a projected range of $\sim 20\,\mu$m, according to collision Monte Carlo calculations as manifested in the SRIM (Stopping and Range for Ions in Matter) code [40]. The samples were irradiated to fluences
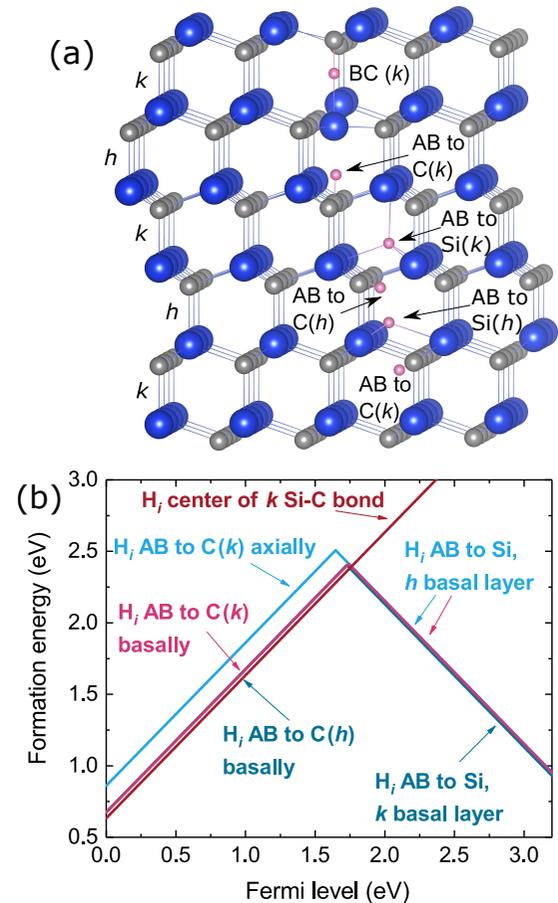
FIG. 1. (a) Favorable positions for H_i in the 4H-SiC lattice, with the different lattice site configurations (h and k) highlighted to the left. Si atoms are shown in blue, C in gray and H in pink. The anti-bonding (AB) to C and bond-centered (BC) configurations reflect the positive charge state, while negative H is AB to Si. (b) Formation energy diagrams for various configurations of H_i. The energy of VBM is offset to zero.

of 1×10^{13} cm^{-2}, 5×10^{13} cm^{-2} and 1×10^{14} cm^{-2}, dubbed low, medium and high fluence, respectively. All implantations were performed with the samples tilted $\sim 8°$ off with respect to the surface normal to reduce channeling, and at either room temperature (RT) or 400 °C (so-called hot implantation). Note that hot implantation is common in silicon carbide device processing, and is used to alleviate damage during implantation of dopants. Employing the dynamic annealing figure of 3 % for V_{Si} estimated in Ref. [9], we arrive at V_{Si} concentrations in the 10^{16}-10^{17} range at the Bragg peak maximum.

Photoluminescence measurements were carried out at 10 K using a closed-cycle He refrigerator system (Janis, CCS450) and 675 nm wavelength cw-laser of 1 mW power as an excitation source. The focused laser beam, impinging on the sample surface at ~ 27 degree angle, yielded an excitation intensity of < 100 Wcm^{-2} and polarization perpendicular to the optical c-axis of 4H-SiC. PL signal was collected in a back-scattering geometry by a microscope objective (Mitutoya, LWD 10X), spectrally filtered (long-pass LP 750 filter) and analyzed by

imaging spectrometer (Horiba, iHR320) coupled to EMCCD camera (Andor, LM658M) with a spectral resolution below 2 nm.

As 4H-SiC is virtually transparent to below-band gap illumination, the luminescence can be collected from the whole sample depth [9]. Consequently, in the experiments described herein we are probing both the proton irradiation tail and the Bragg peak of implanted hydrogen ions, and can collect luminescence deriving from defects located in either region. The V1 and V2 ZPLs are associated with the negative charge state of h and k V_{Si}, respectively [3,7], but no PL signal has (to the best of our knowledge) been attributed to complexes between V_{Si} and H. V_{Si} requires high energies, and therefore irradiation, to form [1,29], and post-irradiation annealing is commonly performed to alleviate implantation damage and remove non-radiative channels. As this effect was something we wanted to probe herein, no post-irradiation annealing was performed.

III. RESULTS

A. Theory

1. The hydrogen interstitial

A selection of H_i configurations is presented in Figure 1, where 1(a) displays the preferred lattice sites with hexagonal and pseudo-cubic sites labeled as h and k, respectively, and 1(b) contains formation energy diagrams for H_i. We find that interstitial hydrogen is amphoteric in 4H-SiC, with a negative-U character for the $(+/-)$ transition near mid-gap. Upon altering the charge state, the H_i configuration also changes. The most stable configuration for H_i^+ is at (approximately) the center of a Si-C bond (bond-centered or BC), in contrast to the finding of Ref. [38]. However, the antibonding (AB) state (to C) which is most stable in Ref. [38] lies less than 0.05 eV higher in energy, and should be attainable at room
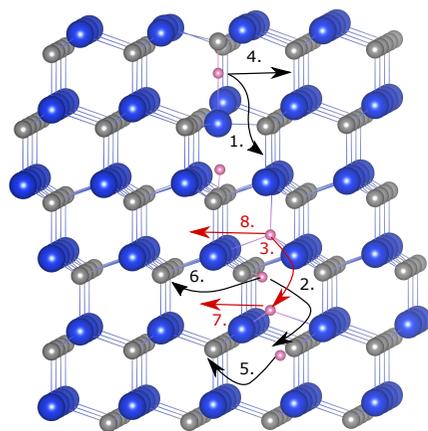
temperature. Generally, H_i^+ attaches to a location with high electron density, i.e., either at the bond-centered site, or at the AB site to the C atom which is the anion species in SiC. In n-type material, on the other hand, H_i^- will dominate, preferring the AB to Si configuration. For both V_C [41] and V_{Si} [9], the k site is more stable than the h one in n-type material, by ~ 0.1 eV. However, regarding sub-lattice site preference, no unified trend has been identified for H_i herein.

Interstitial hydrogen migration in 4H-SiC was studied for eight different atomic hops (both axial and basal) using the CI-NEB method, the PBE functional and Γ-only $\mathbf{k}$-point sampling. The migration pathways for various jumps of H_i are illustrated in Figure 2, with black arrows symbolizing H_i^+ and red arrows H_i^-. Activation energies for the corresponding pathways of H_i in the $+$ and $-$ charge states, and explanations for the numbering in Figure 2, are summarized in Table I. The table contains migration barriers for H_i deduced from PBE-NEB, and select activation energies are refined by hybrid-SCF calculations. The charge state of H_i is found to significantly impact the migration barrier, with $E_A \geq 0.5$ eV for both axial and basal migration of H_i^+ (at PBE-level), and $E_A \geq 2.2$ eV for basal and ≥ 2.4 eV for axial H_i^- migration. This agrees with experiments, which have demonstrated that hydrogen migrates much faster in p-type than n-type material [42]. Moreover, the migration barriers found herein for H_i^+ are very similar to those of Refs. [38,43], while the ones for H_i^- are lower than the ~ 3 eV found in Ref. [38]. It is also interesting to note that like V_C [29], we find that the migration of interstitial H in 4H-SiC is anisotropic, with H traveling faster along the basal directions than along the main crystalline axis. Assuming a jump frequency in the 10^{13} s^{-1} range, a migration barrier of 0.5 eV translates into room temperature hydrogen motion, while a ≥ 2.2 eV barrier prevents H diffusion (beyond ~ 1 μm) below 500 °C.

The charge state of H_i impacts not only the activation energy for diffusion, but also the form and nature of the pathway of motion. The minimum energy paths (MEPs) for H_i migration in 4H-SiC are illustrated in Figure 3, with 3(a) and

FIG. 2. Migration pathways for H_i in 4H-SiC. The jumps correspond to those of Table I. Black arrows designate migration of H_i^+, and red arrows that of H_i^-.

TABLE I. Activation energies (E_A) for different axial and basal jumps of H_i^+ and H_i^- in 4H-SiC (see Figure 1 for the notation, and Figure 2 for illustrations of the migration paths). The PBE and HSE data columns refer to the two steps of the calculation, namely (1) the climbing image NEB run and (2) the SCF calculation to refine the transition state within HSE06. All activation energies for individual jumps are calculated with respect to the energy of the initial state.

Jump	Activation energy, E_A (eV)			
Charge state	$q = +1$		$q = -1$	
Functional	PBE	HSE	PBE	HSE
1. Axial BC(k) $\rightarrow$ BC(h)	0.49	0.61		
2. Axial AB C(h) $\rightarrow$ C(k)	0.65			
3. Axial AB Si(k) $\rightarrow$ Si(h)			2.36	2.67
4. Basal BC(k)	0.51			
5. Basal AB to C(k)	0.51			
6. Basal AB to C(h)	0.50	0.45		
7. Basal AB to Si(h)			2.19	2.28
8. Basal AB to Si(k)			2.62	
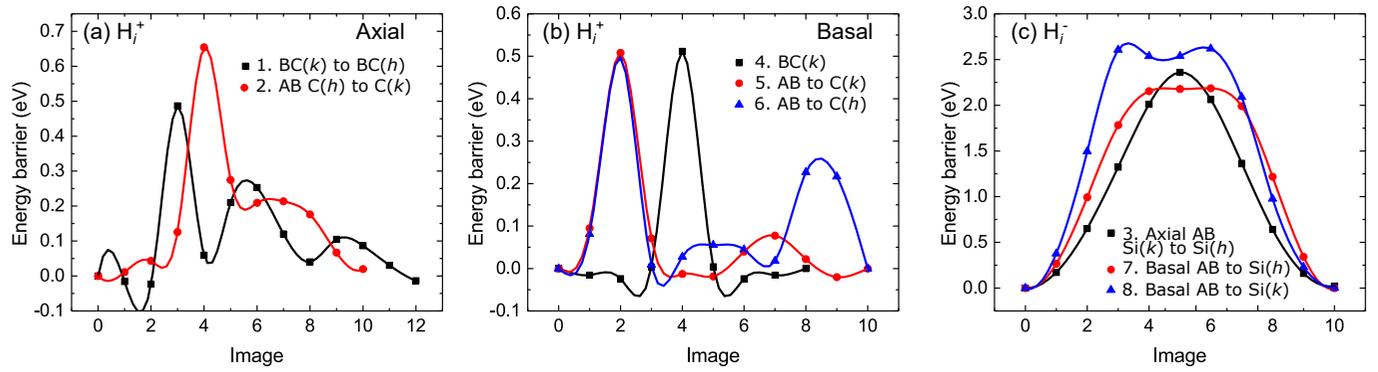
FIG. 3. Potential energy surfaces for migration of H_i in 4H-SiC. The migration paths are as outlined in Figure 2, and are calculated using the CI-NEB method at the PBE-level. Panel (a) shows the minimum energy path (MEP) for H_i^+ migrating axially and (b) for H_i^+ moving basally, while (c) depicts basal and axial migration of H_i^-. The solid lines are cubic-spline interpolations of the data obtained from CI-NEB calculations, and are intended as eye-guides.

3(b) showcasing the potential energy surfaces for H_i^+ migrating axially and basally, respectively, while 3(c) contains the MEPs for axial and basal H_i^- jumps. The pathways are identified with numbers in the legends, corresponding to those in Table I. H_i^+ prefers to reside either at a bond center or in an antibonding configuration to a C atom, which is accompanied by MEPs with several intermediate transition states and local minima (Figs. 3a and 3b). The oscillations largely correspond to rotations of the C-H bonds, while the highest-lying transition state structures are often similar to the ground-state configurations of H_i^-, and involve AB to a Si site. Note that the differences in x-coordinates between the different atomic hops in Figure 3 only correspond to the number of intermediate images employed in the CI-NEB calculations, and do not reflect absolute distances in the supercell.

The potential energy surfaces for H_i^- migration (Fig. 3c) are strikingly different from those of H_i^+, having either a single transition state near mid-way along the path (axial jump), or two transition states similar in energy with a small local minimum in between (both basal jumps). In the former case, the transition state occurs as H_i^- passes through a square constructed of two C and two Si atoms. For basal(k) migration (blue curve), the first transition state of H_i^- is anti-bonded to C(h), while the subsequent local minimum and second barrier involve a rotation of the bond, and passing between two Si atoms on the way to the final configuration (AB to Si(k)). The transition state for H_i that is AB to Si(h) (red curve in Fig. 3c) is, in fact, similar to the AB to Si(k) configuration, with the difference being that the former is stable when the three basal atoms are Si(h), while the latter is stable when they are Si(k). Therefore, for the negative charge state in particular, we find a pronounced effect of the crystal field (depending on whether the H atom resides in a h or k lattice plane) on the preferred configuration of interstitial hydrogen.

2. The V_{Si}-H complex

If a silicon vacancy is present in the material, H may prefer the substitutional over the interstitial configuration. The formation energy diagrams of V_{Si}-H (calculated as described in Section II) and V_{Si} (calculated as in Ref. [9]) are presented in Figure 4. We observe that while the formation energy of H_i is significantly lower than that of the V_{Si}-H complex for all Fermi levels, the V_{Si}-H complex will be energetically favorable if V_{Si} is present in the material. Indeed, after proton implantation both V_{Si} and H are present, and the formation of V_{Si}-H is likely.

For the V_{Si}-H complex, we find that the H atom prefers to sit closer to the axial or one of the three basal C atoms (termed the axial and basal configurations, respectively). The four configurations differ in energy by less than 0.1 eV for $V_{Si}(h)$-H, and all configurations are expected to be available to both com-
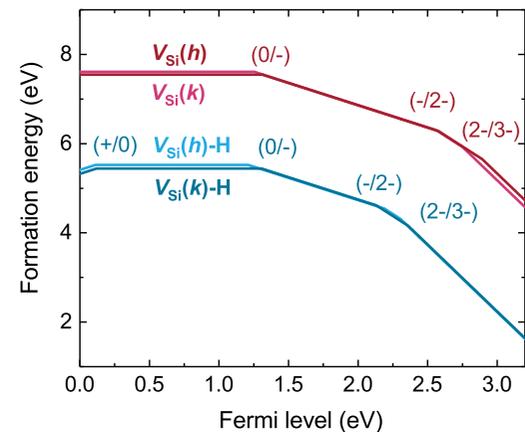
FIG. 4. Formation energy diagram for the silicon vacancy and the V_{Si}-H complex, in both the h and k configurations. The total energies of V_{Si} are from Ref. [9], and the VBM energy is offset to zero.
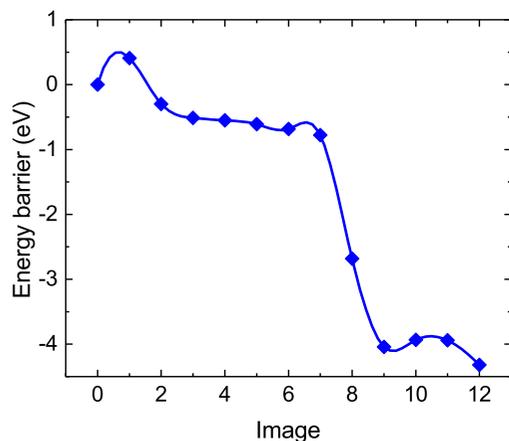
FIG. 5. Minimum energy path for dissociation of $(V_{Si}(k)\text{-}H)^{3-}$, as calculated using the CI-NEB method, the PBE functional and Γ-only BZ sampling. The starting image was $V_{Si}(k)$ with a H atom two lattice vectors away. The solid lines are cubic-spline interpolations of the data obtained from CI-NEB calculations, and are intended as eye-guides.

plexes (h and k) at room temperature. The C-H bond length is between 1.10-1.11 Å for all charge states and both h and k V_{Si}, in close agreement with the 1.12 Å found for C-H bonds in 3C-SiC [19]. Similarly to that for V_{Si}, the C atoms surrounding the V_{Si}-H complex experience a slight breathing relaxation, which is more prominent for the positive and neutral charge states than for the three acceptor states. Contrary to what is found for V_{Si}, the V_{Si}-H complex is more stable in the k than h configuration in p-type and slightly n-type material, and vice versa in highly n-type material, although the difference in stability is minor (see Fig. 4). Interestingly, the shape of the formation energy diagram is strikingly similar for V_{Si} and V_{Si}-H, with only minor differences apart from the predicted stability of $(V_{Si}\text{-}H)^+$ in highly p-type 4H-SiC.

Next, we consider the binding energy of V_{Si}-H. Importantly, to ensure that silicon vacancies do not inadvertently disappear, processing steps intended for quantum applications utilizing V_{Si} should not involve heat treatments exceeding 400-600 °C [5,9,44,45]. In this temperature range, the Fermi level resides around 0.5 eV below the conduction band edge in n-type material, and the V_{Si}-H complex will likely inhabit the 3− charge

TABLE II. Spin state of V_{Si} and the V_{Si}-H complexes, as calculated using hybrid DFT for different charge states. The results for $V_{Si}(h)$ and $V_{Si}(k)$ are from Ref. [9].

Charge state	$V_{Si}(k)$	$V_{Si}(h)$	$V_{Si}(k)$-H	$V_{Si}(h)$-H
$q = +$	N/A	N/A	0	1
$q = 0$	1	1	3/2	3/2
$q = -$	3/2	3/2	1	1
$q = 2-$	1	1	1/2	1/2
$q = 3-$	1/2	1/2	0	0

state (see Fig. 4). If the defect dissociates into $(V_{Si}\text{-}H)^{2-}+H_i^-$, the energy raises by 4.35 eV (binding energy). Of course, the dissociation kinetics are limited by a dissociation barrier, which must be at least as high as the binding energy plus the migration barrier of the faster-diffusing product. These figures ensure that V_{Si}-H will remain stable in n-type 4H-SiC at most operating conditions. Interestingly, Refs. [46,47] predicted that dissociation of complexes between V_{Si} and H is the rate limiting step for H diffusion in irradiated n-type 4H and 6H SiC, with dissociation energies being in the 3.5-4.9 eV range. The relevant experimental conditions involve temperatures above 1300 °C [48], resulting in Fermi levels around midgap and leaving H_i in the positive charge state. The binding energy of V_{Si}-H will then likely differ from the n-type case.

Dissociation of $(V_{Si}\text{-}H)^{3-}$ into the relevant constituents was studied using CI-NEB and a starting configuration with the H atom situated approximately two lattice vectors away from the vacancy (to enable relaxation). The resulting MEP is shown in Figure 5, and we find that the dissociation barrier is indeed the binding energy plus the migration barrier of H_i, with no large capture barriers being present. In n-type 4H-SiC, where migration of H_i was found to have E_A above 2.2 eV (at the PBE-level), we anticipate that migration of interstitial hydrogen is the limiting reaction for V_{Si}-H complex formation.

The silicon vacancy is a promising candidate for quantum technology applications, having millisecond spin coherence times and single-photon emission associated with the negative charge state. It is thus relevant to consider the effect of hydrogen on the electro-optical properties of V_{Si} when an isolated vacancy is transformed into the V_{Si}-H defect complex. As only the negative charge state (V_{Si}^-) has well-known opto-spin signals, it is particularly interesting to scrutinize the energetics of V_{Si}-H as compared to that of V_{Si}^-.

Table II summarizes the ground state total spin of both V_{Si} configurations and the V_{Si}-H complexes for all relevant charge states. Interestingly, $(V_{Si}\text{-}H)^+$ appears to change spin states between the h and k V_{Si} configurations. This happens because the electronic structure of $(V_{Si}(k)\text{-}H)^+$ organizes as $a_1^2 e^0$, while in $(V_{Si}(h)\text{-}H)^+$ the a_1 and e levels become very close, resulting in a parallel spin configuration.

In the negative charge state, the ground state spin of V_{Si} (h and k) is $S = 3/2$. We observe that a corresponding high-spin configuration does exist for the V_{Si}-H complex, but now in the neutral charge state. This is so because the reaction of V_{Si}^- with H^+ displaces one of the singlet gap states of V_{Si}^- into the valence band (due to C-H bond formation), along with two electrons. However, magnetic and optical manipulation of the V_{Si} spin state, as needed for quantum applications, relies on optical detection of the V1 and V2 ZPLs. Accordingly, a crucial question is whether photoluminescence from V_{Si}-H follows that of V_{Si}. Although they do not provide the full picture, the Kohn-Sham single-particle states that result from DFT calculations may illuminate how the electronic structure of V_{Si} changes upon addition of H to form the V_{Si}-H complex.

The five upper electrons inhabiting the V_{Si}^- defect states are expected to distribute in an $a_1^2 a_1^1 e^2$ configuration in the ground state, with the first excited state (V1 and V2) being $a_1^1 a_1^2 e^2$ [49]. Accordingly, the optical transitions are minority spin-
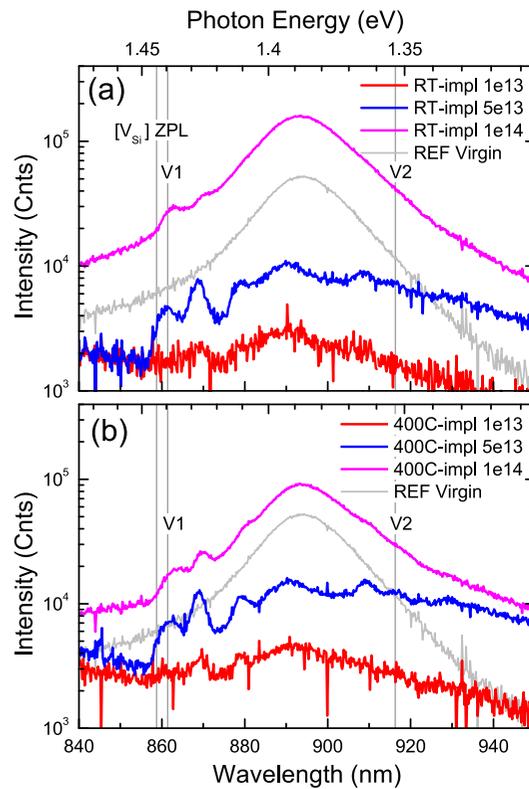
FIG. 6. Emission from n-type 4H-SiC (proton implanted to different fluences) collected at 10 K, for implantation at (a) RT and (b) 400 °C, with the V_{Si}-related emission lines V1 and V2 highlighted.

channel transitions. The relevant charge states of V_{Si}-H are $q = -$, $2-$ and $3-$, as these are most likely present in n-type material. V_{Si} is metastable in p-type 4H-SiC, and rapidly transforms into $C_{Si}V_C$ for Fermi levels below mid-gap. The electronic structures of V_{Si}-H are $a_1^2 e^2$, $a_1^2 e^3$ and $a_1^2 e^4$ for the charge states $-$, $2-$ and $3-$, respectively. Indeed, the $-$ and $2-$ states could have excited states similar to V1', where an electron from the singlet is promoted to the doublet. However, upon comparing, e.g., $V_{Si}(k)^-$ to $(V_{Si}(k)$-H$)^0$, we observe that there are no longer any occupied spin-down energy levels within the band gap for the complex. All spin-down electrons are confined to the valence band. Moreover, there are only two unoccupied levels within the gap, as compared to four for V_{Si}. Upon complex formation the energy difference between the highest occupied and lowest unoccupied Kohn-Sham energy levels is lowered by ~ 0.6 eV, indicating a drastic change in emission when V_{Si} transforms into V_{Si}-H. Moreover, the $3-$ state does not have excited states because the levels are fully occupied, and thus formation of $(V_{Si}$-H$)^q$ complexes may explain the PL quenching.

To summarize, we find from theoretical considerations that the V_{Si}-H complex is stable in n-type 4H-SiC, with thermal formation (given the presence of V_{Si}) restricted by the migration barrier of interstitial hydrogen. Even though high-spin configurations likely exist for the V_{Si}-H complex, capturing an H atom is found to significantly impact the electronic configuration of V_{Si}, resulting in an alteration of the optical transition

and quenching of V_{Si}-related photoluminescence.

B. Experiment

In Ref. [18], the effect of H implantation on V_{Si}-related PL was compared to that of He implantation. Considering the reported results, the assumption that formation of the V_{Si}-H complex quenches luminescence from V_{Si} in turn necessitates that He does not complex with V_{Si}, or that V_{Si}-He complexes retain the luminescence properties of isolated V_{Si}. Herein, we investigate the effect of fluence and temperature during hydrogen implantation on the V_{Si} luminescence intensity, to corroborate the theoretical predictions above.

Figure 6 shows the effect of different proton fluences on V_{Si}-related emission for (a) RT and (b) 400 °C hydrogen implantation. One can observe dramatic developments in the PL spectra of 4H-SiC upon irradiation, with the broad background emission (gray band) representing the virgin material being quenched after the lowest fluence irradiation and then gradually recovering at higher fluences. The intensity of the silicon vacancy-related signal is increasing with the proton fluence, and such a dependency remains linear within the 10^{11}-10^{14} cm^{-2} fluence range, as shown earlier in Ref. [9]. Upon comparing Figures 6(a) and 6(b), we notice that the signal intensity overall increases for the 400 °C implant, while V_{Si}-related features seem to sharpen. This effect can be attributed to the reduction in non-radiative channels at elevated temperatures.

Figure 7 displays a baseline-subtracted and zoomed-in version of Figure 6, and compares RT and 400 °C irradiation for the three different proton fluences (a-c). In Figure 7(a), for the lowest proton fluence, the V1 and V2 ZPLs are barely visible as the V_{Si} concentration is below the detection level, but the elevated temperature seems to enhance the overall signal. Both V1 and V2 are clearly visible in Figures 7(b) and 7(c), with V1 being much more prominent than V2. The total luminescence and amount of features appear greater for the 400 °C implant in all three cases. For the intermediate case, illustrated in Figure 7(b), irradiating at 400 °C clearly impacts the V_{Si} content in the sample compared to that of the RT sample. The V1 peak is almost twice as strong for the high temperature irradiation. The moderate proton fluence of 5×10^{13} cm^{-2} falls within the scope studied in Ref. [9], where we correlate the proton fluence dependence of the V1 emission intensity to the same dependence of the S center observed in DLTS spectra of n-type 4H-SiC. Therefore, we can conclude that an increase in V1 intensity is accompanied by a similar increase in the V_{Si} concentration. Consequently, for the medium fluence (5×10^{13} cm^{-2}), we can anticipate more silicon vacancies and fewer non-radiative channels for the sample irradiated at 400 °C than the one irradiated at RT.

Interestingly, Figure 7(c) demonstrates the opposite behavior for V1 when comparing to Figure 7(b). In fact, the V1 peak is found to be stronger after implanting at RT than at 400 °C for the highest proton fluence. The discrepancy in temperature dependence between Figures 7(b) and 7(c) is intriguing, and challenging to explain from standard considerations con-
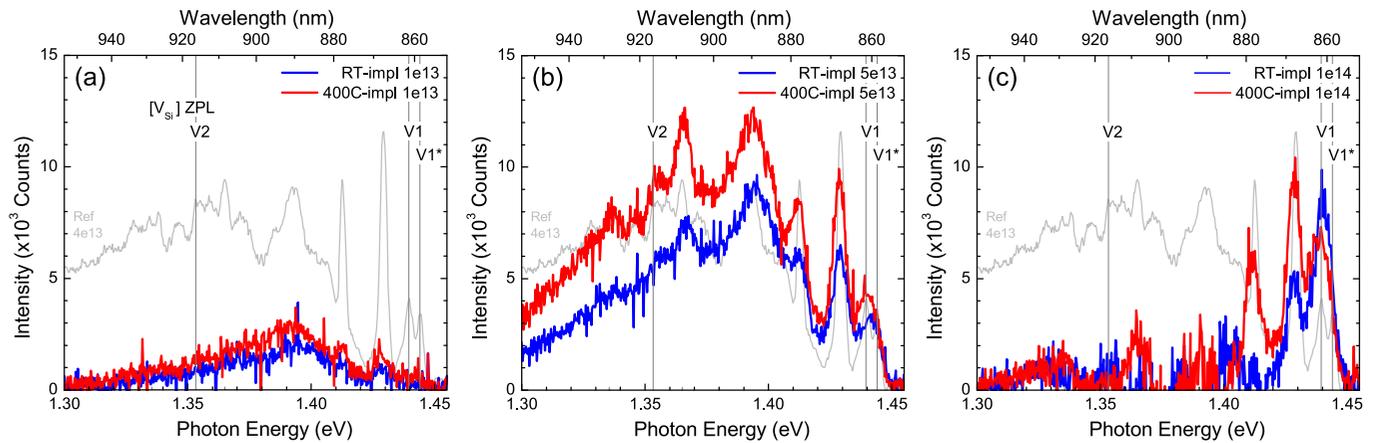
FIG. 7. Emission from n-type 4H-SiC, proton implanted at RT (blue lines) and 400 °C (red lines), collected at 10 K, for proton fluences of (a) 1×10^{13} cm^{-2}, (b) 5×10^{13} cm^{-2} and (c) 1×10^{14} cm^{-2}, with the V_{Si}-related V1 and V2 emission lines highlighted. The gray PL spectra in the background are for reference, and derive from a V_{Si}-rich sample from Ref. [9].

cerning irradiation and temperature alone.

IV. DISCUSSION

The DFT calculations corroborate that hydrogen migrates faster in p-type material than in n-type, as previously established experimentally [42]. However, raising the temperature above 400 °C during implantation could render the H atoms mobile, even in n-type material. Accordingly, during hot implantation H is likely to migrate, and potentially encounter an implantation-induced and nearby V_{Si} and form V_{Si}-H complexes, resulting in reduced emission from V_{Si} centers. Indeed, H migration in irradiated material is expected to be limited by dissociation of H-related complexes [46,47], with outdiffusion of H not commencing until above 1300 °C [48].

Post-implantation annealing should result in a similar effect on V_{Si} as that of hot implantation. Indeed, Wang et al. [18] demonstrated that the V_{Si}-related PL increased in intensity after post H-implantation anneals up to 300 °C, while He-implantation resulted in increasing PL intensities up to 500 °C. Importantly, silicon vacancies are metastable in n-type 4H-SiC, and anneal out between 400-600 °C [5]. Hence, one may speculate that the lower stability of V_{Si} after H implantation as compared to that of He may be related to formation of V_{Si}-H, and larger complexes thereof, assuming that H becomes mobile at or above 400 °C.

The experiments demonstrate different effects of temperature on V_{Si}-related emission, depending on the proton fluence used for hydrogen implantation (Fig. 7). Firstly, C and Si interstitials are expected to migrate rapidly at 400 °C, but not at RT, due to migration barriers of ~ 1 eV [50] resulting in fewer non-radiative channels in the samples irradiated at 400 °C as compared to the RT ones. Secondly, V_{Si} defects may start to anneal out in this temperature range, due to migration of H$_i$, recapturing of self-interstitials or transformation into C$_{Si}V_C$ [5]. The migration of H$_i$ and subsequent complex formation would be dependent on the average distance between V_{Si}'s,

and hence fluence dependent.

The diffusivity D of hydrogen is expected to follow an Arrhenius behavior in 4H-SiC, according to

$$D = D_0 e^{-E_A/kT}, \quad (3)$$

where D_0 is the exponential prefactor, E_A the activation energy for migration, k the Boltzmann constant and T the temperature [29]. If we assume that $D_0 = 4 \times 10^{-3}$ cm^2/s for H [51] and $L = \sqrt{Dt}$, and estimate that the samples are at 400 °C for $t = 1$ hour, the diffusion length of H$_i$ becomes $L = 22$ nm for a migration barrier of $E_A = 2.2$ eV (see Table I). Using SRIM, we estimate that the V_{Si} concentration at the top of the implantation Bragg peak is 1.3×10^{16} cm^{-3} for the low fluence (10^{13} cm^{-2}), 7×10^{16} cm^{-3} for the medium fluence (5×10^{13} cm^{-2}) and 1.3×10^{17} cm^{-3} for the high fluence (10^{14} cm^{-2}), assuming a dynamic annealing factor of 3 % for V_{Si} [9]. These concentrations translate into mean distances between silicon vacancies (in all directions) of approximately 45 nm, 25 nm and 20 nm, respectively. As the peak concentration of H is 3-4 times larger than that of Si vacancies, we assume that formation of V_{Si}-H is limited by the V_{Si} distribution. Hence, for the low fluence (10^{13} cm^{-2}) and medium fluence (5×10^{13} cm^{-2}) the diffusion length of H$_i$ is not sufficient to efficiently form V_{Si}-H, while for the high fluence (10^{14} cm^{-2}) complex formation is viable, and is one potential explanation for the fluence dependence observed in Figure 7, and the temperature dependence observed in Ref. [18].

In conclusion, we find that the likelihood of a hydrogen atom diffusing far enough to encounter, and potentially form a complex with, a silicon vacancy increases with the proton irradiation fluence. Hence, hot hydrogen implantation might render H mobile and increase the amount of V_{Si}-H complexes as compared to the corresponding RT process. If maximum yield of isolated V_{Si} defects is desired and a sample volume containing the Bragg peak of H is to be probed, hydrogen should be avoided as the implantation species, with He being a more promising candidate. Alternatively, the issue can be circumvented by laser creation of point defects, as recently

demonstrated for V_{Si} in silicon carbide [52,53].

So far, no optical signal has been unambiguously assigned to complexes of V_{Si} and H, as the H-lines, which are located around 3.15 eV in hydrogen-rich 4H-SiC and were originally assigned to V_{Si}-H [54], were later attributed to a hydrogen dimer bound to a carbon antisite ($C_{Si}H_2$) [55]. Hence, we remain unable to directly probe V_{Si}-H formation. Electrical characterization may offer a viable alternative, as deep level transient spectroscopy (DLTS) measurements of n-type 4H-SiC have shown that hydrogen-related and irradiation-induced defects introduce deep levels within the 4H-SiC band gap [20]. Recently, we demonstrated that the silicon vacancy is electrically active in n-type 4H-SiC, by assigning the $(-/2-)$ and $(2-/3-)$ charge state transitions of h and k V_{Si} to the S-center, a deep-level defect consisting of two different transition levels that are sporadically observed in DLTS spectra of n-type 4H-SiC [9]. Interestingly, the predicted transition levels of V_{Si}-H are ~ 0.1 eV, 1.2-1.3 eV, 2.2 eV and 2.3-2.4 eV above the valence band maximum (Fig. 4), which is within the range found for hydrogen-related deep levels using DLTS [20]. However, complexes between hydrogen and carbon vacancies (V_C-H) may also be electrically active [56], and are thus potential candidates for the measured defect levels.

The contribution of the zero-point (vibrational) energy has not been considered herein. Indeed, H is very light, and the energy of each configuration should have the contribution of approximately $\hbar\omega/2$, where ω is the vibrational frequency of the stretch mode for the Si-H or C-H bond. Although it should have a limited impact on the calculated location of electronic levels, zero-point motion affects formation and migration energies (see for instance Ref. [57]). For migration, the contribution of vibration to the energy barrier is expected to be found mainly in the ground state, as the transition state bonds are weaker than the ground state ones. Thus, we expect the absolute error bar of our calculations, arising from vibrations of light H atoms, to be in the 0.1-0.2 eV range (see Ref. [19]).

V. CONCLUDING REMARKS

In summary, we study hydrogen-related defects in 4H-SiC, and find that H_i may exist both interstitially and embedded in defect complexes. As previously found, H_i is expected to migrate much faster in p-type than n-type 4H-SiC material, and migration of H may be limited by formation of complexes such as V_{Si}-H in n-4H-SiC. In fact, the V_{Si}-H complex is more stable than the isolated V_{Si} defect, and we find it likely that hydrogen may alter the spin and luminescence properties of V_{Si} in n-type 4H-SiC. Upon comparing to PL emission from n-type 4H-SiC samples that are proton irradiated to different fluences and at different temperatures, we find that elevated temperature implantations may induce H_i motion, causing formation of V_{Si}-H complexes and a reduction in the V_{Si}-related emission intensity. In conclusion, we predict that hydrogen could present an important obstacle towards reliable formation of, and optimal luminescence yield from, V_{Si} defects highly suitable for quantum technology applications.

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(a)

k

BC (*k*)

h

AB to C(*k*)

AB to Si(*k*)

AB to C(*h*)

AB to Si(*h*)

k

h

AB to C(*k*)

k

(b)

H_i center of *k* Si-C bond

H_i AB to C(*k*) axially

H_i AB to Si,
h basal layer

H_i AB to C(*k*)
basally

H_i AB to C(*h*)
basally

H_i AB to Si,
k basal layer

Formation energy (eV)

Fermi level (eV)