Doubly-charged silicon vacancy center, Si-N complexes, and photochromism in N and Si co-doped diamond

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Diamond samples containing silicon and nitrogen are shown to be heavily photochromic, with the dominant visible changes due to simultaneous change in total SiV0/− concentration. The photochromism treatment is not capable of creating or destroying SiV defects, and thus we infer the presence of the optically-inactive SiV2−. We measure spectroscopic signatures we attribute to substitutional silicon in diamond, and identify a silicon-vacancy complex decorated with a nearest-neighbor nitrogen, SiVN, supported by theoretical calculations.

I. INTRODUCTION

Diamond, as with other wide-band-gap semiconductors, has recently attracted attention as a host for optically-active point defects with potential applications in quantum communication [1], nanophotonics [2, 3], and quantum information processing (QIP) [4]. In addition to in quantum communication [1], nanophotonics [2, 3], and QIP applications, we have studied silicon and nitrogen co-doped diamond from as-grown to a treatment temperature of 2400 °C using a combination of optical absorption spectroscopies and EPR. We identify the neutrally-charged silicon-vacancy-nitrogen complex SiVN0 through combined experimental measurements and theoretical modeling, and tentatively assign an infrared absorption mode at 1338 cm−1 to substitutional silicon.

A. Charge transfer

It is well established that as an insulator, defects in diamond may exist in more than one charge state in the same crystal simultaneously. For charge states which are dominated by the charge dynamics of nitrogen donors (the dominant impurity in the majority of synthetic diamond), a “charge transfer” protocol has been established to drive between the two extremal states [16, 24, 25]. Above-band-gap UV excitation (λ<225 nm) of a sample typically maximizes the concentration of nitrogen donors, N0, which in turn tends to favor the neutral charge state of other defects. Heating the sample at 550°C in the absence of light enables thermal excitation of electrons/holes, reversing the process and yielding N+ while typically maximizing the concentrations of negatively-charged versions of defects present. This has been previously demonstrated in several defects including SiV [16], NV [20], NVH [24], N3V [27], and N5V [28].

This charge instability can be a great advantage when studying fundamental defect properties as it enables multiple charge states of the same defect to be studied in the same crystal. In a single-electron charge transfer process (e.g. X0 to X− rather than X+ to X− for a given defect X), we expect at least one of the charge states to be EPR-active. EPR is capable of absolutely quantifying the concentration of a defect and is therefore fundamentally the source of the optical absorption cross-section values for most defects in diamond [29]. Where charge transfer is present, the loss (gain) of the EPR-active charge state can be equated to the gain (loss) in the other, allowing an optical absorption cross-section to be extracted for the non-EPR-active state. The major assumption made in the above procedure is that there are only two charge states of the defect accessible through the charge transfer protocol, and therefore the loss of one must equal the gain in the other. If this is not the case, and some charge population is lost to a third charge state, then an incorrect optical absorption cross-section for the non-
EPR-accessible charge state will be extracted.

II. EXPERIMENTAL DETAIL

A. Method and samples

Seven samples were grown in a microwave-plasma chemical vapor deposition (CVD) reactor: Samples A–F were grown simultaneously and doped with natural abundance silicon (via the addition of silane to the growth gases) and 100% $^{15}$N-enriched nitrogen; Sample G was doped with natural abundance silicon and nitrogen (Table I). Secondary ion mass spectrometry measurements on samples grown in the same conditions indicated $[N_d] = 9(2)$ ppm through the bulk, and a silicon incorporation uniformity to ±10%: we were unable to quantify the silicon due to the lack of a suitable reference sample. Growth substrates (all {001}-oriented) and non-diamond material were removed from all samples post-growth to leave free-standing plates. Samples B–F were each subsequently annealed under stabilizing pressure (6–8 GPa) for 1 h at 1600, 1800, ..., 2400 °C, respectively: each sample was annealed only once (i.e. Sample D was annealed at 2000 °C only). Sample G was annealed at 1800 °C for 100 h under stabilizing pressure. All samples were polished post-anneal to remove any etched or graphitic material and provide parallel, low-roughness faces for optical measurements. Each sample was approximately $3 \times 3 \times 1.6$ mm.

As a consequence of the charge transfer effect (IA), the annealing behavior of a given defect can be confused with its charge transfer properties if care is not taken to initialize the crystal to a known state before each measurement. We therefore perform all measurements immediately following either UV exposure (the ‘UV state’) or heating in the dark at 550 °C for 20 min (the ‘heated state’): the sample is kept in the dark between treatment and measurement. For the UV state, samples were exposed using the xenon arc lamp of a DiamondView instrument for 6 min per face; heating was performed under a dry nitrogen atmosphere in a tube furnace (Elite Thermal Systems Ltd.) for 20 min at 550 °C. EPR measurements were performed at X-band using a Bruker EMX-E spectrometer with 90 dB attenuator to avoid microwave power saturation, and ER4122SHQ resonator. EPR measurements were quantified by comparison to a standard reference sample containing 270 ppm N$_0^0$ and were performed below microwave power saturation. Ultraviolet-visible (UV-vis) and IR absorption measurements were performed in PerkinElmer Lambda 1050 and Spectrum GX spectrometers, respectively.

B. Computational method

Density functional theory within the supercell approach was employed using the AIMPRO software pack-

之初我考虑的annealing study performed on the samples which were grown simultaneously (samples
TABLE II. Details and references for techniques and absorption cross-section coefficients employed in the quantification of defects at each annealing stage.

<table>
<thead>
<tr>
<th>Defect</th>
<th>Technique</th>
<th>Note</th>
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<td>10</td>
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<tr>
<td>N\textsuperscript{+}</td>
<td>IR</td>
<td>1332 cm\textsuperscript{-1}</td>
<td>11</td>
</tr>
<tr>
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<td>IR</td>
<td>3123 cm\textsuperscript{-1}</td>
<td>12</td>
</tr>
<tr>
<td>NVH\textsuperscript{-}</td>
<td>EPR</td>
<td></td>
<td>13</td>
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<td></td>
<td>14</td>
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<tr>
<td>N\textsubscript{2}VH\textsuperscript{0}</td>
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<td></td>
<td>14</td>
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<tr>
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<td>3107 cm\textsuperscript{-1}</td>
<td>14</td>
</tr>
<tr>
<td>SiV\textsuperscript{0}</td>
<td>EPR</td>
<td></td>
<td>15</td>
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<tr>
<td>SiV\textsuperscript{-}</td>
<td>UV-vis</td>
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<td>16</td>
</tr>
<tr>
<td>SiVN\textsuperscript{0}</td>
<td>EPR</td>
<td></td>
<td>this work</td>
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</table>

A–F). Each sample was initialized into the UV state and measured by IR and EPR to quantify the defects present — see Table II for details on quantification method for each defect.

Sample A is dominated by nitrogen-related complexes, with the most abundant identified defects being N\textsuperscript{0}/+ and NVH\textsuperscript{0/−} [Fig. 1]. The only identified silicon-related centres are SiV\textsuperscript{0/−} which are present at approximately 100 ppb combined. Any concentrations of SiVH\textsuperscript{0} [15] and SiV\textsubscript{2}H\textsuperscript{0} [20] are below EPR detection limits (≈1 ppb). Sample A is visually brown but heavily photo/thermochromic, varying from deep brown to brown-pink in the UV and heated states, respectively.

Between samples A and F, approximately 4.5 ppm of substitutional nitrogen has been lost in addition to 1 ppm of NVH\textsuperscript{0/−}, and is accompanied by the production of approximately 0.3 and 1.0 ppm of N\textsubscript{2}VH\textsuperscript{0} and N\textsubscript{3}VH\textsuperscript{0}, respectively. Together with SiVN\textsuperscript{0} this corresponds to a total of 4.0 ppm nitrogen, accounting for the majority of the lost N\textsuperscript{0}/+ and NVH\textsuperscript{0/−}. However, a significant concentration of nitrogen-related defects remain unidentified. As N\textsubscript{3}VH contains three nitrogen atoms, a small error in its oscillator strength would have a dramatic effect on our ability to quantify total nitrogen in the high-temperature annealed samples.
FIG. 2. a) IR absorption spectra of Sample A (top) and Sample F (bottom) in the two extremal charge states. The two regions give the defect-induced one-phonon absorption (left) and C-H stretch region (right): the intrinsic multiphonon absorption has been subtracted. b) The one-phonon of two as-grown samples grown under similar CVD conditions: both are nitrogen-doped but silicon was added to the growth gases of one. The primary difference is the feature at approx. 1340 cm$^{-1}$ in the silicon-containing sample, which is tentatively assigned to substitutional silicon [22]. The remaining peaks are reported in studies of solely nitrogen-doped CVD material [24]. c) Difference spectra between Sample A (as-grown) and samples treated at the given temperatures. The change in the 1338 cm$^{-1}$ mode is highlighted.

B. Photochromism and evidence for SiV$^{2-}$

In previous studies of nitrogen-doped brown CVD diamond, samples which were annealed above 1600 °C became less brown, with higher temperatures corresponding to a greater reduction of brown color [24, 25, 50]. The present samples display the same behavior, with samples E and F (2200 and 2400 °C, respectively) appearing near-colorless by eye in the heated state. Contrary to previous studies, the present samples treated at >2000 °C remain heavily photochromic, varying from a deep grey-blue to near-colorless in the UV and heated states, respectively.

UV-Vis measurements of Sample D in the UV state show strong absorption from both SiV$^-$(737 nm) and SiV$^0$(946 nm) [Fig. 3]. The spectrum of the former reveals the optical structure associated with the second excited state of SiV$^-$ [14, 51] which has been reported previously in photoluminescence excitation [22, 53]. Comparison of the absorption spectra in the UV and heated states confirms that the photo/thermochromism is dominated by dramatic changes in the concentration of SiV$^-$ and SiV$^0$ [Fig. 3]; this is the case for samples A–F. The visible photochromic color change in the present samples is much more extreme than the color change reported in nitrogen-doped CVD samples [24] due to the incredibly broad absorption band of SiV$^0$ compared to the relatively broad and weak absorption bands associated with NVH in purely nitrogen-doped material [Fig 3].

The processes employed during the charge transfer procedure are not capable of destroying or creating SiV and we conclude that we are efficiently driving to a third charge state of SiV. The photochromic behavior of the samples is consistent with driving to a negatively- (rather than positively-) charged state. DFT studies of SiV predict that SiV$^{2-}$ is a stable and electronically saturated system with no internal optical transitions or accessible spin levels and is thus difficult to spectroscopically observe [24]. We therefore infer the presence of SiV$^{2-}$ by the absence of SiV$^-$ and SiV$^0$ in the heated charge state.
C. Discussion

Doubly-charged defects are well-characterized in other group-IV semiconductors (e.g. Si \([53,56]\) and Ge \([57,58]\)) but have not been previously reported in diamond despite several theoretical predictions \([23,59,60]\). Generally, this is a result of the paucity of very shallow donors and acceptor states in diamond, which are required to stabilize the chemical potential suitable for these doubly-charged states (in the absence of negative-U effects \([61]\)). However, in SiV the \((2−/−)\) transition is relatively deep (approximately mid-gap \([54]\)), yielding a stable charge state even for deep nitrogen donors (at approximately \(E_{\text{CC}} \approx 1.7\) eV \([62]\)).

Despite its lack of internal transitions, we still expect transitions from the SiV\(^{2−}\) ground state to the conduction band, which are theoretically predicted at \(\approx 4\) eV \([54]\). As a defect-to-band transition, this will manifest as spectrally broad rather than a sharp transition. There is a small change in the absorption gradient \(< 250 \text{ nm}\) (\(< 5\) eV) between the UV and heated states, but any absorption in this region is dominated by NV\(^0\) absorption \([\text{Fig. 3}]\) \([63]\) and hence difficult to isolate.

In Sample D we measure the UV state concentrations of SiV\(^{−}\) and SiV\(^0\) as 110 ppb and 380 ppb, respectively \([\text{Fig 2}]\), using the conversion factors given in \([16]\): in the heated state the concentration of both charge states is below 1 ppb and therefore all SiV defects are in the 2− charge state, requiring 870 ppb of donor charges between the two states. The corresponding loss in NV\(^0\) from UV to heated states is 2.3 ppm, more than accounting for the SiV-related charge effects. This relationship is true at all annealing temperatures. As a result, the changes in donor concentrations cannot be attributed solely to SiV and it is therefore difficult to quantify the latent SiV\(^{2−}\) concentration in the UV state. Upper limits can be estimated based on the assumption that the only donor is NV\(^0\); however, this is known not to be the case in these samples (e.g. NVH\(^−\)), other photochromic peaks in \([\text{Fig 2}]\).

The extremal charge states are unstable at room temperature in all of the present samples. Time-lapse absorption measurements of SiV\(^{−}\), performed in the absence of ambient light, show that after UV treatment of Sample F the concentration of SiV\(^{−}\) increases by approximately 70% over 9 h. Ambient light increases the rate of this change, and significant color changes are visible after 2 h in ambient. The changes cannot be described by a simple coupled model with constant leakage rates from SiV\(^0\) → SiV\(^{−}\) and SiV\(^−\) → SiV\(^{2−}\). Instead, the increase is well-described by a hyperbolic function, as expected by multiple overlapping thermal processes. This is consistent with the present material containing multiple thermally-activated donors/acceptors at room temperature.

The existence of SiV\(^{2−}\) casts doubt on the optical absorption cross-section for SiV\(^{−}\) given in \([16]\). The cross-section for SiV\(^0\) was calibrated by directly measuring its concentration by EPR and equating it to the absorption strength measured by UV-Vis. However, the cross-section for SiV\(^−\) was calibrated via charge transfer between SiV\(^0\) and SiV\(^−\) using the protocol given in \([1A]\) the loss of the former was equated to the gain in the latter. The assumption was that only two charge states were involved in the process: any loss or gain of population to or from SiV\(^{2−}\) was unaccounted for, and would result in a modified absorption cross-section than the one given in \([16]\). The concentrations of SiV\(^−\) given by the cross-section are within approximately a factor of two of the expected concentration based on charge balance arguments. However, the potentially high concentration of SiV\(^{2−}\) in these samples makes a more precise statement impossible at this time. A future study based on intrinsic or even p-type material should bias between SiV\(^−\) and SiV\(^0\), allowing both present charge states to be quantified simultaneously and reliably. We note that even with the present uncertainty, our results remain incompatible with the \(1 \times 10^{−13}\) meV cm\(^−2\) value derived from first-principles calculations \([63]\).

IV. THE SILICON-VACANCY-NITROGEN DEFECT

A. Defect identification

The spin Hamiltonian for a single electron, multiple nucleus system is given by

\[
H = \mu_B \mathbf{B} \cdot \mathbf{S} + \sum_i^N S_i^\text{T} \cdot \mathbf{A}_i \cdot \mathbf{I}_i + I_i^\text{N} \cdot \mathbf{Q}_i \cdot \mathbf{I}_i,
\]

with \(i\) summed over the nuclei. These terms represent the electronic Zeeman, electron-nuclear hyperfine, and nuclear quadrupole interactions, respectively. Application of magnetic field lifts the degeneracy of the electronic states \(m_S\) via the Zeeman interaction, with transitions between the states driven by high frequency (typically microwave) magnetic fields — the electron paramagnetic resonance phenomenon. Each nucleus splits the electron resonance line into \(2I + 1\) lines, where \(I\) is the nuclear spin of the isotope in question (1 (0) for \(^{14}\)N (\(^{15}\)N) and 0 (1/2) for \(^{28}\)Si (\(^{29}\)Si) respectively). The quadrupole interaction (characterized by the tensor \(\mathbf{Q}\)) is nonzero only for nuclei with \(I \geq 1\).

EPR measurements of samples D-F reveal a previously-unidentified multi-line \(S = 1/2\) spectrum at approximately \(g = 2.004\) \([\text{Fig 4}]\). Initial investigations indicated that spectrum can be accurately simulated using a spin Hamiltonian of a monoclinic C\(_{1h}\) defect which possesses a 100% \(I = 1/2\) nucleus with a small hyperfine interaction. With the external magnetic field \(B||(1\ 1\ 1)\), a C\(_{1h}\) defect (principal axis \((1\ 1\ 0)\) ) possesses three inequivalent orientation sets with relative populations 1:1:2. Each population further has its electronic resonance split by interaction with the \(I = 1/2\) nucleus, yielding the three orientation classes highlighted in \([\text{Fig 4}]\).
As Samples A–F are $^{15}$N-enriched, the nucleus involved could either be $^{15}$N or $^1$H. An additional sample, Sample G, was grown under similar conditions to Samples A–F but with natural abundance nitrogen rather than $^{15}$N-enriched gasses and subsequently annealed at 1800 °C for 100 h. EPR measurements of Sample G again exhibit a previously-unidentified multi-line $S = 1/2$ spectrum at approximately $g = 2.004$ but the spectrum is significantly more complex than in the $^{15}$N-doped samples [Fig 3]. This spectral change under nitrogen isotope change confirms the presence of nitrogen at the defect. Due to the isotopic abundances we identify this nucleus as a single nitrogen atom, eliminating hydrogen as a possibility.

The angular variation of the spectrum [Fig 4] confirms that it belongs to a defect possessing monoclinic C$_{1h}$ symmetry and a small hyperfine interaction with the nitrogen [Table III], indicating essentially zero unpaired electron spin density on the nitrogen nucleus [65]. The similar magnitude of the quadrupole and hyperfine interactions allows “forbidden” transitions ($\Delta m_S = \pm 1; \Delta m_I \neq 0$) to acquire appreciable intensity, yielding more than three transitions per orientation and significantly increasing the complexity of the spectrum [Fig 4c]. This effect is observed in other nitrogen-related defects in diamond [28, 65].

A large number of purely nitrogen-related defects have been identified by EPR in diamond, including N$^0$, NV$^-$ [67, 65], interstitial nitrogen [69], and even substitutional nitrogen pairs [70]. It is thus unlikely that a new defect which involves only nitrogen would be identified in material which is novel due to its simultaneously high concentration of nitrogen and silicon. Therefore, we hypothesise that this defect must also contain silicon, whose 95% natural abundance of $^{28}$Si ($I = 0$) makes it difficult to identify without a high defect concentration.

A previous DFT study into silicon-containing defects in diamond identified SiVN as a simple and stable defect candidate in high-nitrogen high-silicon diamond [22]. DFT calculations of the hyperfine parameters of the silicon and nitrogen in SiVN$^0$ (improving on previously-reported values [22]) were used as a guide for experimental parameters [Table III]. To confirm the presence of silicon in the defect, long-term scans designed to increase the signal-to-noise enough to easily identify any $^{28}$Si-related spectrum (approximately 5% of the natural abundance of $^{28}$Si) were performed. These scans measured approximate replicas of the primary spectrum split by a nucleus of $I = 1/2$, approximately 5% abundant, which we identify as $^{28}$Si [Fig 5]. The hyperfine interaction strengths $A_{1,2,3}$ = 98.24, 98.13, 94.47 MHz are remarkably similar to the DFT-calculated values (87, 89, 92 MHz, respectively) and directions. A similar case is found for the nitrogen hyperfine, where the experimentally-measured values are within 0.3° of the DFT-calculated values. When taken in conjunction with the dopant and treatment history of Sample G, these data are enough to conclusively assign the observed spectrum to the defect SiVN [Fig 6].

Comparison of the spin Hamiltonian tensors shows that the hyperfine and $g$-tensors retain the monoclinic symmetry of the defect geometry [Table III]. Using the standard approach to hyperfine analysis [72], we may make estimates of the unpaired electron spin density probability. Approximating the $^{28}$Si interaction as
FIG. 5. EPR spectrum of Sample G with $B\parallel\{111\}$. Experimental data in black; simulation in red. Additional panels show the $^{29}\text{Si}$ hyperfines on each side of the primary spectrum. As expected, their intensity is 5% of the primary spectrum. Simulation generated by EasySpin [24] using the spin Hamiltonian parameters given in Table III.

an axial, dipolar interaction, we obtain isotropic and anisotropic components of 96.9 and $-1.24\text{MHz}$, respectively. By comparison with tabulated values for 100% localization [73], this corresponds to an approximate unpaired electron spin density probability of 3% on the silicon. In conjunction with a negligible localization on the nitrogen, we conclude the majority of the localization is on the nearest-neighbor carbons, as expected from the DFT-computed wavefunction [22]. Unfortunately, signal-to-noise limitations mean we have not been able to identify the 1.1% $^{13}\text{C}$ signal associated with these neighbors.

The expected charge state of SiVN can be calculated from the group theoretical descriptions of the SiV defects. Here, the neutral and negatively charged SiV defects possess two and one hole, respectively [54]. In replacing one of the neighboring carbon atoms with nitrogen the number of holes present in the defect must decrease by one: we thus expect the positive, neutral and negative charge states to possess 2 ($S = 0$ or 1), 1 ($S = 1/2$), and zero ($S = 0$) holes respectively, and we identify the new spectrum with SiVN$^0$. Charge transfer measurements on all samples are consistent with this description. The EPR spectrum is photochromic, with the concentration changing from approximately 400 to $<5\text{ppb}$ between the UV and heat-treated charge states in Sample F; the behavior of the defect is therefore qualitatively similar to the behavior of SiV$^0$. In the heated sample state, we observe no additional EPR spectra and deduce the dominant charge state is SiVN$^-$, which is $S = 0$ in its ground state and therefore EPR-inactive.

DFT calculations of the stability of different charge states of SiV and SiVN are consistent with the observed charge state behavior: the neutral charge states of both defects are stable at approximately the same chemical potential, while SiVN$^-$ is the stable charge state over almost all other chemical potentials [Fig 7]. These calculations also predict that a double negatively charged SiVN state can exist for high chemical potentials: this charge state would have one hole ($S = 1/2$) and is able to form due to a disruption to the atomic configuration. Structurally, SiVN can be compared to a SiV system with a nitrogen donor and therefore SiVN$^-$ presents an electronically saturated system, as discussed above. DFT calculations indicate that the addition of an extra electron to SiVN$^-$, producing SiVN$^{2-}$, breaks a C–N bond with the nitrogen effectively forming a $N_\text{r}$ structure bonded to the Si and two nearest-neighbor carbons. This geometric distortion to SiVN results in the lowering of a band gap state which is now accessible for excitation. Examining the orbital characteristics depicted by spin density isosurfaces from DFT, we observe the $N_\text{r}$-like [Fig 7c] configuration adopted by SiVN$^{2-}$ [Fig 7f], rather than retaining the configuration of the same band gap state in SiVN$^0$ [Fig 7h]. Calculations of the SiVN charge stabilities [Table IV] indicate that all three charge states are stable configurations, and of these SiVN$^-$ is least likely to dissociate.

We expect all charge states of the SiVN to be difficult to identify in IR absorption measurements. The mass of the elements involved, combined with the vacancy, suggests that defect vibrations will be below the 1332 cm$^{-1}$ lattice cutoff and therefore will contribute to the one-phonon absorption, rather than exhibiting sharp local vibrational modes. Unfortunately, the one-phonon IR absorption of samples D–G contain other unidentified contributions thus no spectrum can be associated with any charge state of SiVN at the present time.

B. Defect production

The addition of silicon (typically via silane) during CVD growth of diamond yields a grown-in (native) population of SiV centers [24, 75]. In an analogous situation to nitrogen, where substitutional nitrogen concentrations are typically orders of magnitude higher than the grown-in NV concentrations [24], we presume the majority of the silicon is incorporated as substitutional silicon [10], as discussed in II.A. Therefore, there is a substantial source of silicon available within the sample itself from
TABLE III. Spin Hamiltonian parameters measured for SiVN$^0$. The three principal values ($p_1$–3) and directions are given for each parameter. A positive tilt is given to mean away from [001] toward [110]; no tilt is required for the final principal value of each parameter, retaining the [1{T{0} mirror plane and reflecting the defect’s C$_{3v}$ symmetry.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
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<th>Dir.</th>
<th>Tilt (°)</th>
<th>$p_2$</th>
<th>Dir.</th>
<th>Tilt (°)</th>
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<td>+4.3</td>
<td>2.00549(5)</td>
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<td>+2.7</td>
<td>–3.59(1)</td>
<td>[1 1 2]</td>
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<td>–3.28(1)</td>
<td>[1 {T{0}</td>
</tr>
<tr>
<td>$Q^{(14)N}$ MHz</td>
<td>Exp.</td>
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<td>[1 1 1]</td>
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<td>+1.04(1)</td>
<td>[1 1 2]</td>
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<tr>
<td>$A^{(29)Si}$ MHz</td>
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<td>[2 2 1]</td>
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<td>±0.82(50)</td>
<td>[1 1 4]</td>
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FIG. 7. a) Schematic of the SiVN$^{0/-}$ defect, highlighting the defect’s (1 1 0) mirror plane. b) Calculated formation energies at varying chemical potentials, $\mu_e$, for SiV and SiVN with reference to the intrinsic diamond valence band maximum. Transition levels include charge density offset and Madelung corrections. The calculated conduction band minimum was at 4.27 eV. c–e) Electron density on bandgap states for c) the donor state in N$_2$; d) the state with an unpaired electron for SiVN$^{2-}$; e) the same state for SiVN$^0$. Comparison of d) and e) highlights the additional electron in an N-C antibonding orbital in SiVN$^{2-}$. Isosurfaces depict a surface of constant spin density: a common spin density threshold was chosen for d) and e) to allow comparison in the same structure; a higher threshold was chosen for c) due to the highly localized nature of the N$_2^0$ donor state.

growth.

We have not identified SiVN$^0$ in any as-grown samples (putting an upper limit on the as-grown concentration of approximately 0.5 ppb). We first observe SiVN$^0$ upon HPHT annealing at 2000°C (for one hour, or 100 h at 1800°C), and its concentration increases up to the maximum 2400°C temperature [Fig 1]. As is typical for vacancy-containing defects in diamond, we assume SiVN production must occur via vacancy-assisted migration of impurities, as the energy required for direct diffusion of substitutional nitrogen (8 eV [77]) and silicon is significantly higher than the vacancy-assisted mechanisms [78]. Furthermore, the diffusion barrier for NV$^-$ ($\approx 5$ eV [79]) is significantly lower than for SiV$^0$ ($\approx 6.5$ eV [22, 54]). At high temperatures where NV$^-$ is unstable, nitrogen may diffuse through the lattice by concerted exchange with a vacancy before the NV pair breaks up [79]. We therefore understand SiVN production to occur via the diffusion of vacancies and subsequent capture by Si$_x$, producing SiV; and the vacancy-assisted diffusion of nitrogen to SiV centers producing SiVN.

Recent reports of delayed luminescence at 499 nm from synthetic, silicon-containing samples suggested that the emission originates at Si$_x$N$_y$ or Si$_x$N$_y$V complexes [80]. The 499 nm luminescence is maximized on annealing at 1700°C and destroyed above 2000°C [80]. We do not observe this luminescence from any of the present samples at any annealing temperature. Additionally, the annealing behavior of SiVN is incompatible with the reported annealing behavior of the 499 nm defect and therefore we conclude that the luminescence does not originate at SiVN. Furthermore, as SiVN is the simplest variant of the Si$_x$N$_y$V defects, and defect aggregation in diamond typically develops from simple to more complex under higher annealing temperatures, it seems unlikely that the emission originates with any defect in this group.

TABLE IV. Binding energies ($E_{bind}$, see [13]) for each modeled defect through charge-conserving reactions. Displayed errors result from comparing values calculated using LDA and GGA functional.

<table>
<thead>
<tr>
<th>Defect</th>
<th>Components</th>
<th>$E_{bind}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiVN$^0$</td>
<td>SiV$^+$ + N$_2^+$</td>
<td>2.80(1)</td>
</tr>
<tr>
<td>SiVN$^-$</td>
<td>SiV$^+$ + N$_2^0$</td>
<td>4.4(1)</td>
</tr>
<tr>
<td>SiVN$^{2-}$</td>
<td>SiV$^2-$ + N$_2^0$</td>
<td>1.80(3)</td>
</tr>
</tbody>
</table>
V. CONCLUSION

The present samples, while dominated in total concentration by nitrogen-related defects, enable additional insight into silicon-related defects and processes which must occur even in lower-concentration samples. The first observation of a doubly-charged defect in diamond leads the way for future studies of other doubly-charged donors or acceptors, provided the (+/2+) or (−/2−) levels are sufficiently deep.

The existence of SiV\(^{2+}\) puts limits on the production efficiency of SiV\(^−\) qubits in nitrogen-doped material. Previous reports which interpreted the absence of SiV\(^−\) in n-type material as the presence of SiV\(^0\) should now be re-interpreted in terms of charge transfer between SiV\(^{2+}\) and SiV\(^−\), rather than SiV\(^0\) and SiV\(^−\) [81]. As UV light is expected to be required to directly ionize SiV\(^{2+}\) it is not clear that it will be possible to design a simple optical ionization protocol to drive SiV\(^2+\) → SiV\(^−\) — any pulse which ionizes SiV\(^{2+}\) is likely also to drive charge in other proximal defects, reducing overall charge stability of the ensemble. Devices which require SiV\(^−\) as the dominant charge state should therefore be intrinsic or only moderately n-type to avoid interference from SiV\(^{2−}\).

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