Characterization of Optical and Spin Properties of Single Tin-Vacancy Centers in Diamond Nanopillars

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Abstract

Color centers in diamond have attracted much interest as candidates for optically active, solid-state quantum bits. Of particular interest are inversion-symmetric color centers based on group-IV impurities in diamond because they emit strongly into their zero-phonon lines and are insensitive to electric field noise to first order. Early studies of the negatively-charged tin-vacancy (SnV\(^-\)) center in diamond have found the SnV\(^-\) to be a promising candidate: it has high quantum efficiency, emits strongly into its zero-phonon lines, and is expected to have a long \(T_2\) spin coherence time at 4 K. To develop the SnV\(^-\) into a spin qubit requires further characterization, especially of the spin and optical properties of individual SnV\(^-\) in nanofabricated structures. In this work we isolate single SnV\(^-\) centers in diamond nanopillars and characterize their emission properties and their spin response to a magnetic field. We observe narrow emission linewidths that are spectrometer-limited, as well as a strong polarization dependence of each transition. We also find the Zeeman splitting under a magnetic field to be in good agreement with theoretical prediction. Our results pave the way toward future employment of single SnV\(^-\)s for optically accessible quantum memories.
I. INTRODUCTION

Color centers in diamond have emerged in recent years as candidates for solid-state, optically active quantum bits (qubits)\textsuperscript{1-3}. A strong spin qubit candidate of this type should have strong emission into a narrow-linewidth transition, good immunity to environmental fluctuations, and long spin coherence time. The negatively charged silicon-vacancy (SiV\textsuperscript{−}) center, in particular, has garnered a lot of attention in recent years for fulfilling two of these three criteria: strong (\(\sim 70\%\)) emission into its four zero-phonon lines (ZPL) and immunity to electric field noise to first order\textsuperscript{4}. However, the SiV\textsuperscript{−} suffers from short coherence times at 4 K (\(\sim 100\ \text{ns}\))\textsuperscript{5} and low quantum efficiencies (\(\sim 10\%\))\textsuperscript{6,8}. Thus, other color centers with potentially better optical and spin properties must be explored.

The negatively charged tin-vacancy (SnV\textsuperscript{−}) center and SiV\textsuperscript{−} belong to the same class of inversion-symmetric color centers comprised of an interstitial group-IV impurity atom accompanied by a split vacancy in the diamond lattice, shown in Fig. 1(a). Thus, SnV\textsuperscript{−} has some of the favorable properties of the SiV\textsuperscript{−} along with some added benefits. Notably, preliminary measurements have estimated the quantum efficiency of SnV\textsuperscript{−} to be around 80\%\textsuperscript{7}, a significant improvement over that of SiV\textsuperscript{−} \(\sim 10\%\)\textsuperscript{6,8}. Considering that the SnV\textsuperscript{−} has a Debye-Waller factor of 40\%\textsuperscript{9}, the overall probability that an excited SnV\textsuperscript{−} will emit into one of its ZPL is approximately 30\%, compared to 7\% for SiV\textsuperscript{−}. Furthermore, the SnV\textsuperscript{−} is expected to have improved spin coherence times (\(T_2\)) over the SiV\textsuperscript{−}\textsuperscript{5} because of its 17-fold greater ground-state splitting of \(\sim 850\ \text{GHz}\) (Fig. 1(b)). This larger splitting reduces the probability of single-phonon-mediated transitions between ground states, the primary mechanism of spin decoherence in SiV\textsuperscript{−}\textsuperscript{5}. The SnV\textsuperscript{−} is thus expected to have long \(T_2\) at 4 K\textsuperscript{9}, making the operating conditions of SnV\textsuperscript{−} more feasible.

Central to exploring the SnV\textsuperscript{−} as a qubit candidate is the thorough study of the optical and spin properties of individual SnV\textsuperscript{−}s. In this work, we study single SnV\textsuperscript{−} centers in diamond nanopillars and characterize their optical and spin properties. In particular, we observe spectrometer-limited linewidths and a clear polarization dependence of the emission at 5.6 K. We also investigate the behavior of a single SnV\textsuperscript{−} in an external magnetic field at 1.7 K and compare our experimental results to theoretical predictions. Our findings enable further investigations into the spin properties of the SnV\textsuperscript{−} and incorporation of the SnV\textsuperscript{−} into more sophisticated nanophotonic structures, two crucial steps toward implementation
of SnV$^-$ as a spin qubit in a quantum network.

![SnV$^-$ center in diamond](image)

**FIG. 1.** SnV$^-$ center in diamond. (a) Schematic of the physical structure of the SnV$^-$ center in diamond. Gray spheres represent carbon atoms, the purple sphere represents a tin atom, and the dashed circles outline the vacant carbon lattice sites. The high-symmetry axis is along [111]. (b) Schematic energy level diagram. The excited- and ground-state manifolds are each split into two states by spin-orbit coupling. In an unstrained SnV$^-$, the ground-state splitting is $\sim 850$ GHz, and excited-state splitting is $\sim 3000$ GHz. Four optical transitions are allowed, represented by red arrows labeled A, B, C, D in order of decreasing energy.

**II. ISOLATION OF SINGLE TIN-VACANCY CENTERS**

Starting with electronic grade, single crystal diamond, we perform a boiling tri-acid (1:1:1 nitric:sulfuric:perchloric acids) clean. We then etch 300 nm with oxygen (O$_2$) plasma. This sample is sent to Cutting Edge Ions for $^{120}$Sn$^+$ ion implantation at 370 keV, with a dose of $2 \times 10^{11}$ cm$^{-2}$. Stopping and Range of Ions in Matter (SRIM) simulations predict a depth of $\sim 90$ nm. The implanted diamond is then annealed at 800$^\circ$C for 30 minutes and 1100$^\circ$C for 90 minutes. To make the pillars, we first grow 200 nm of silicon nitride (Si$_x$N$_y$) by low-pressure chemical vapor deposition. Nanopillars, ranging in diameter from 140 nm to 300 nm, are then defined by electron-beam lithography. Using Si$_x$N$_y$ as an etch mask, we etch 500 nm into the diamond with a directional O$_2$ plasma etch. A scanning electron microscope (SEM) image of a resulting nanopillar can be found in Fig. 2(a).

We verify that we have isolated single emitters in the diamond nanopillars by performing second-order autocorrelation ($g^{(2)}[\tau]$) measurements. A measurement of $g^{(2)}[\tau]$ for an emitter in a nanopillar under 1-mW, 532-nm excitation is presented in Fig. 2(b). The data are fit
FIG. 2. Single SnV$^-$ isolated in a nanopillar. (a) SEM image of a 500-nm tall nanopillar etched into implanted and annealed diamond. Neighboring bars are used to help locate pillars in 2D photoluminescence maps. (b) Second-order autocorrelation measurement for a single SnV$^-$ in a nanopillar. The data are represented in black dots. The solid red curve is a fit of Eq. 1 to the data. From the fit, we find $g^{(2)}[0] = 0.23 \pm 0.02$.

to the function

$$g^{(2)}[\tau] = 1 - c \left( (1 + b)e^{-|\tau|/\tau_1} - be^{-|\tau|/\tau_2} \right),$$

where $b$, $c$, $\tau_1$, and $\tau_2$ are fitting parameters$^{10}$. $\tau_1$ provides an estimate of the excited state lifetime of the emitter. $\tau_2$ is the decay time on the photon bunching and relates to a third shelving state in the system. For the emitter presented in Fig. 2(b), the $g^{(2)}[0] = 0.23\pm0.02$, indicating that this emitter is indeed a single emitter. $\tau_1$ and $\tau_2$ were found to be 4.8\pm0.1 ns and 103\pm10. ns, respectively. The estimated emitter lifetime $\tau_1$ of 4.8 ns is on par with previous measurements of $\sim 5$ ns$^7$.

III. OPTICAL PROPERTIES

The photoluminescence spectrum of a single SnV$^-$ in a nanopillar is presented in Fig. 3(a). The C and D transitions of the emitter are found to be 842 GHz apart, close to the $\sim 850$ GHz expected, indicating that this emitter is under minimal strain. The photoluminescence data in Fig. 3(a) is spectrometer-limited, so we report upper limits on the linewidths of transitions C and D: 13.2 GHz and 17.4 GHz. These linewidths are an improvement over previously reported values in bulk$^{7,11}$. This improvement in linewidth may be attributed to the lower implantation dose compared to Refs. 7 and 11 or the longer anneal time than Ref. 7 used in our work.
The average linewidths for 38 pillars are $24 \pm 11$ GHz and $36 \pm 20$ GHz for C and D, respectively. The combined data for transitions C and D of 38 pillars are presented in Fig. 3(b). Because the narrowest lines are spectrometer-limited, the averages are likely skewed higher. Also, the distribution in Fig. 3(b) appears bimodal for both transitions, indicating that two different types of pillars were surveyed: those with single emitters and those with multiple closely overlapping emitters. The latter generally results in linewidths broader than those expected from a single emitter.

Furthermore, we estimate the inhomogeneous broadening present in the emitters by plotting the average photoluminescence spectra of 44 pillars, as shown in Fig. 3(c). The C and D transitions appear in the plot as two distinct peaks and have been fit to Gaussian distributions. From the fits, we find the full widths at half-maxima of the C and D transitions to be $271 \pm 8$ GHz and $583 \pm 27$ GHz, respectively. Raman tuning has been used to tune the ZPL of a SiV$^-$ up to $100$ GHz\textsuperscript{12,13}. Thus, it may be possible in future works to overcome a significant portion of the inhomogeneous broadening found here.

We also study the polarization of the emission into the C and D transitions for a single SnV$^-$. The emission intensity of the C and D transitions are plotted as a function of the polarization in Fig. 3(d). The SnV$^-$ studied displays a clear polarization dependence in its emission. The strong polarization dependence is, as expected, similar to that of SiV$^-$ in diamond\textsuperscript{14} and is consistent with previously reported room-temperature absorption data for SnV$^-$\textsuperscript{15}. From Fig. 3(d) we observe that the dipole moments associated with the C and D transitions projected onto the [001] diamond surface are roughly perpendicular to one another.

IV. ZEEMAN SPLITTING

We explore the spin properties of a single SnV$^-$ and compare our experimental results to theoretical predictions. When a magnetic field is applied to a SnV$^-$ center, the two-fold spin degeneracy is lifted and the two branches of the excited- and ground-state manifolds each split into two more states. Consequently, each of the original optical transitions splits into four: two spin-conserving transitions that are strongly allowed and two spin non-conserving transitions that are only weakly allowed by magnetic field components orthogonal to the symmetry axis of the emitter. A schematic diagram of the energy levels and optical transi-
FIG. 3. PL spectrum and polarization dependence. (a) Photoluminescence spectrum of a single emitter in a pillar taken at 5.6 K. Data are presented as black points joined by black lines. (b) Histogram of linewidths for the C and D transitions of 38 pillars. Bars corresponding to D transition data are stacked on top of the C transition bars. Spectrometer-limited (cutoff $\sim 15$ GHz) is marked with diagonal lines. (c) Average photoluminescence spectrum of 44 pillars. C and D peaks are two distinct, broad peaks on either side of 2.00 eV. The red line is a double Gaussian fit to the two peaks. (d) Polarization dependence of the emission. Intensity of the C (blue dots) and D (green triangles) transitions as a function of angle, normalized to the maximum value of transition C.

For our theoretical model, we solve for the eigenstates of the Hamiltonian derived in Ref. 9:

$$\hat{H}_{\text{eff}}^{g,u} = -\hbar \lambda^{g,u} \hat{L}_z \hat{S}_z + \mu_B f^{g,u} \hat{L}_z B_z + \mu_B g_S \hat{S} \cdot \mathbf{B} + 2\mu_B \delta^{g,u} f S_z B_z + \hat{\Upsilon}_{\text{strain}},$$

where the $z$-direction is along the symmetry axis of the emitter. The superscripts $g$ and $u$ respectively denote the parity of the states: even (gerade) and odd (ungerade). For SnV$^-$ and similar negatively charged group-IV-based color centers, the ground state corresponds to $g$ and excited to $u$. The sign on the effective spin-orbit coupling (first) term opposes that of Hamiltonians previously used to model other negatively charged group-IV-based
color centers. In the form $x = \{x^g, x^u\}$, where $x$ is a parameter, the values given in Ref. 9 for the parameters in Eq. 2 are $\lambda = \{850, 3000\}$ GHz, $f = \{0.154, 0.098\}$, and $\delta_f = \{0.014, 0.238\}$. We study an emitter under minimal strain, so we neglect the $\hat{\Upsilon}_{\text{strain}}$ term.

For the measurements in a magnetic field, our sample is cooled to 1.7 K in an attoDRY2100 with a superconducting magnet. The magnetic field is applied out of the plane of the chip, along the [001] direction, which shall be denoted as $z'$. We apply magnetic fields $B_{z'}$ from 0 T to 9 T, inclusive, in 1 T increments. We perform photoluminescence spectroscopy with 532-nm excitation. To collect spectra of the inner transitions with finer resolution, we use a double monochromator. The resulting double monochromator data as a function of field is presented in Figs. 4(b) and (d). A detailed explanation of how the data in Figs. 4(c) and (e) were extracted from the raw spectra can be found in the Supplemental Materials.

We plot the experimental and theoretical frequencies of the four peaks comprising C and D in Figs. 4(c) and (e). To correct for a slow spectral drift, we center the inner and outer frequencies pairwise about their average frequency. We apply the same correction to the theoretical plots. As can be seen in Fig. 4(c) and (e), the experimental data are in good agreement with the predicted behavior based on Eq. 2. We also note that the $f$ and $\delta_f$ values used in Eq. 2 provided by Ref. 9 are based on values for SiV$^-$. The good agreement between our data and the theoretical predictions indicates that the difference between $f$ and $\delta_f$ values for SiV$^-$ and SnV$^-$ are quite small and within the error of our measurements.

V. SUMMARY AND OUTLOOK

We have studied the optical properties of single SnV$^-$ centers that have been isolated in diamond nanopillars. We were able to generate emitters with spectrometer-limited linewidths of $< 20$ GHz. These linewidths are an improvement over previously measured linewidths in bulk diamond and demonstrate that emitters can be incorporated into nanostructures without degrading the optical properties. SnV$^-$ linewidths may be further improved by lower implantation dose and a longer high-temperature anneal. We also observe a strong polarization dependence of the emission. Lastly, we observed the behavior of a single SnV$^-$ as a function of magnetic field and find it to be in good agreement with theoretical predictions.
FIG. 4. Behavior of SnV\(^-\) in an external magnetic field \(B_z'\). (a) Schematic energy level diagram of SnV\(^-\) when a magnetic field is applied. Each of the original optical transitions splits into four transitions. Two of each set of four transitions are spin-conserving and thus strongly allowed (bold arrows), and the other two are weakly allowed (thin arrows). Transitions C (red) and D (dark red) are represented by arrows, numbered 0 to 3 in order of decreasing energy. (b) Stacked spectra of inner transitions C1 and C2 as a function of \(B_z'\) collected with a double monochromator. Transition frequency is with respect to the central transition frequency at 0 T. Solid red lines are double or single Lorentzian fits to the data (black points). (c) Location of central frequencies of all four C0, C1, C2, and C3 transitions. Error bars on the filled data points are the error on the central frequency fit parameter. The unfilled shapes are points approximated by eye. Points that could not be fit nor approximated by eye were omitted. Solid lines are functions derived theoretically from Eq. 2 and correspond to data of the same color. (d) Same as (b) for transition D. (e) Same as (c) for D transitions.

Presented by Thiering and Gali\(^9\). Our findings indicate that the SnV\(^-\) is a promising candidate for a spin qubit and warrants further investigation. Future works include characterizing the spin coherence time \(T_2\) of the isolated emitters and fabricating more sophisticated nanostructures such as photonic cavities resonant with SnV\(^-\) ZPLs, two necessary steps in order to implement the SnV\(^-\) as an optically interfaced spin qubit.
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At the time of submission of this manuscript, we became aware of a very recent, similar work.17

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