

Monoisotopic Ensembles of Silicon-Vacancy Color Centers with Narrow-Line Luminescence in Homoepitaxial Diamond Layers Grown in $\text{H}_2\text{-CH}_4\text{-}^{[x]}\text{SiH}_4$ Gas Mixtures ($x = 28, 29, 30$)

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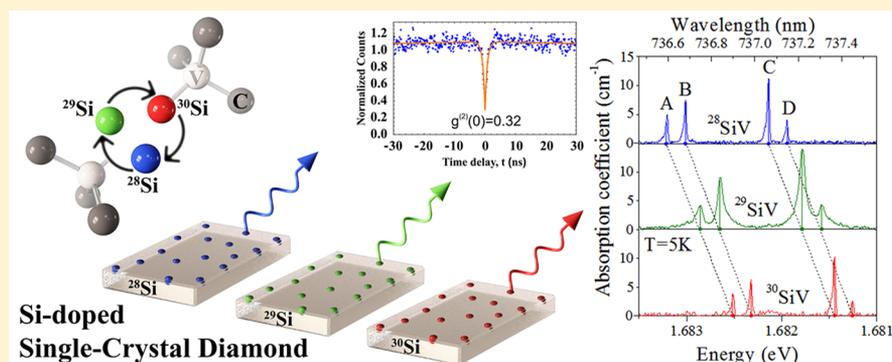
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Supporting Information



ABSTRACT: Silicon-vacancy (SiV^-) color center in diamond is of high interest for applications in nanophotonics and quantum information technologies, as a single photon emitter with excellent spectral properties. To obtain spectrally identical SiV^- emitters, we doped homoepitaxial diamond films *in situ* with ^{28}Si , ^{29}Si , and ^{30}Si isotopes using isotopically enriched (>99.9%) silane SiH_4 gas added in $\text{H}_2\text{-CH}_4$ mixtures in the course of the microwave plasma-assisted chemical vapor deposition process. Zero-phonon line components as narrow as ~ 4.8 GHz were measured in both absorption and luminescence spectra for the monoisotopic SiV^- ensembles with a concentration of a few parts per billion. We determined with high accuracy the Si isotopic energy shift of SiV^- zero-phonon line. The SiV^- emission intensity is shown to be easily controlled by the doped epilayer thickness. Also, we identified and characterized the localized single photon SiV^- sources. The developed doping process opens a way to produce the SiV^- emitter ensembles with energy confined in an extremely narrow range.

KEYWORDS: diamond, CVD synthesis, silicon-vacancy center, doping, silicon isotope, photoluminescence, optical absorption

Color centers in diamond, emitting across the visible and near-infrared spectrum, provide a material platform for quantum information science and applications in photonics and, more specifically, in quantum information technologies.^{1–4} The negatively charged silicon-vacancy (SiV^-) color center in diamond is of increasing interest for nanophotonics^{1–7} due to its excellent spectral properties, including

a strong zero-phonon line (ZPL) at 737 nm wavelength, which contains about 70% of the fluorescence from this color center, and the weak phonon sideband.^{7–9} This, being coupled to the absence of spectral diffusion effects in SiV^- , allows generation

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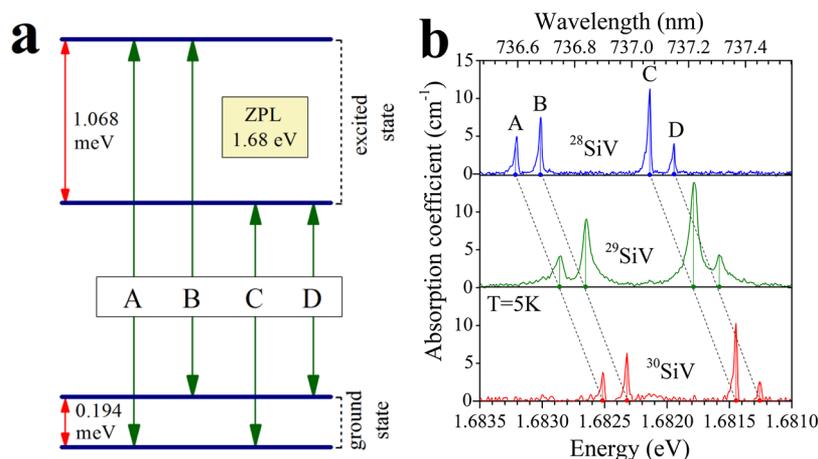


Figure 1. (a) Electronic level scheme of the SiV^- center with split ground and excited states. The four ZPL transitions in PL or absorption are denoted as A–D. (b) Absorption spectra of SiV^- centers with isotopes ^{28}Si , ^{29}Si , and ^{30}Si . ZPL peaks shift to lower energies with Si mass increase. Dashed lines show the trends for lines A–D positions.

and detection of indistinguishable, single photon emitters (SPEs).^{10–12}

To produce an ensemble of such identical SiV^- sources (with exactly the same narrow ZPL positions), local variations to the emitter environment, such as a stress, should be minimized.¹⁰ Other factors shifting the SiV^- emission line are the presence of carbon ^{13}C isotope in diamond lattice¹³ or Si isotope atoms.^{14,15} Silicon has three stable isotopes, ^{28}Si with an abundance of 92.22%, ^{29}Si (4.89%), and ^{30}Si (3.09%), and the separation between SiV^- ZPL for the isotopes differing by a mass $\Delta m = 1$ is about 80 GHz.¹⁵ The selected Si isotopes can be incorporated in diamond by ion implantation.¹² An annealing is required in order to reduce residual defects and stress caused by the implantation-induced damage and thus to narrow the ZPL position distribution; however, it is not clear if perfect restoration of the diamond lattice by the thermal treatment can be attained.

Another method to form SiV^- centers is *in situ* doping with Si atoms in the course of the diamond chemical vapor deposition (CVD) process. The CVD technique with a gaseous impurity precursor allows controlled and uniform doping both depthwise and laterally. Several groups reported on the photoluminescence (PL) spectra of SiV^- centers in CVD diamond doped from silicon-containing gases like silane SiH_4 ,^{13,16–21} tetraethoxysilane,²² or tetramethylsilane.²³ In all cases, the formed SiV^- centers contained all three Si isotopes with natural abundance. Here we realized *in situ* doping of single crystal diamond with silicon using silane isotopically enriched with respect of each of the three isotopes, ^{28}Si , ^{29}Si , and ^{30}Si , and studied optical spectroscopic properties of the produced SiV^- centers at room and low temperatures. We obtained very narrow ZPLs in optical absorption and PL for each isotope and found a distinct shift of the SiV^- ZPL and Si-related local vibration mode with the change in Si isotope mass.

The epitaxial Si-doped diamond films have been grown by microwave plasma chemical vapor deposition (MPCVD) at pressures of 130 Torr in 6% CH_4/H_2 mixtures with a small addition of silane SiH_4 similar to the procedure described elsewhere.^{13,19} Polished (100) oriented type IIa high pressure, high temperature (HPHT) diamond plates (nitrogen content ~ 600 ppb) were used as the substrates in the experiments with ^{28}Si and ^{30}Si doping, while the ^{29}Si doped epilayer was

deposited on a single crystal CVD diamond (<40 ppb nitrogen) substrate. The dimensions of the substrates were $2.5 \times 2.5 \times 0.5$ mm³.

A constant ratio of silicon to carbon contents in the gas mixture $[\text{Si}]/[\text{C}] = 0.5\%$, which was close to the optimum value for enhancing SiV^- PL intensity found in previous studies, was maintained.^{19,21} The Si isotope purity of silane was 99.997% for ^{28}Si , 99.909% for ^{29}Si , and 99.944% for ^{30}Si according to the producer (Devyatykh Institute of Chemistry of High-Purity Substances, RAS). The substrate temperature during growth was measured with a two-color pyrometer, Williamson 81-35-C, and was kept at 1100 ± 20 °C. The deposited diamond films doped with ^{28}Si , ^{29}Si or ^{30}Si isotopes had an identical thickness of 5.0 ± 0.1 μm , which was *in situ* controlled with low-coherence interferometry^{24,25} (see Supporting Information for more details on the sample preparation).

We measured the optical absorption (ABS) and photoluminescence (PL) spectra at low temperatures (5 K) using a high-resolution FTIR spectrometer, Bruker IFS 125 HR, equipped with a Si-detector and a closed-cycle He cryostat, Cryomech PT403. The spectral resolution in these measurements was 0.1 cm⁻¹ or better (see more details on spectroscopic instrumentation in Supporting Information). For the PL spectra, the excitation of an orange diode laser beam (wavelength 635 nm, power 50 mW) was focused on the sample in a spot of about 0.5 mm in diameter.

The negatively charged SiV^- center is formed by an interstitial silicon atom in between two neighbor vacancies (split-vacancy structure) along the $\langle 111 \rangle$ axis of the diamond lattice.²⁶ The energy levels of the SiV^- center display spin-orbit split of 0.19 and 1.07 meV (47 and 259 GHz) of ground and excited electronic states, respectively,²⁷ thus resulting in a four-line fine structure of the ZPL at ~ 737 nm (Figure 1a). The corresponding transitions, observed at low enough temperatures,^{10,14,27} are denoted in Figure 1a as A, B, C, and D in the order of decreasing of the transition energy. The presence of minor Si isotopes ^{29}Si and ^{30}Si in addition to the main isotope ^{28}Si is known to result in 12-line ZPL structure for ensembles of SiV^- centers with natural isotope compositions^{14,15,27} since each isotope produces own, shifted four-peak system in spectra.

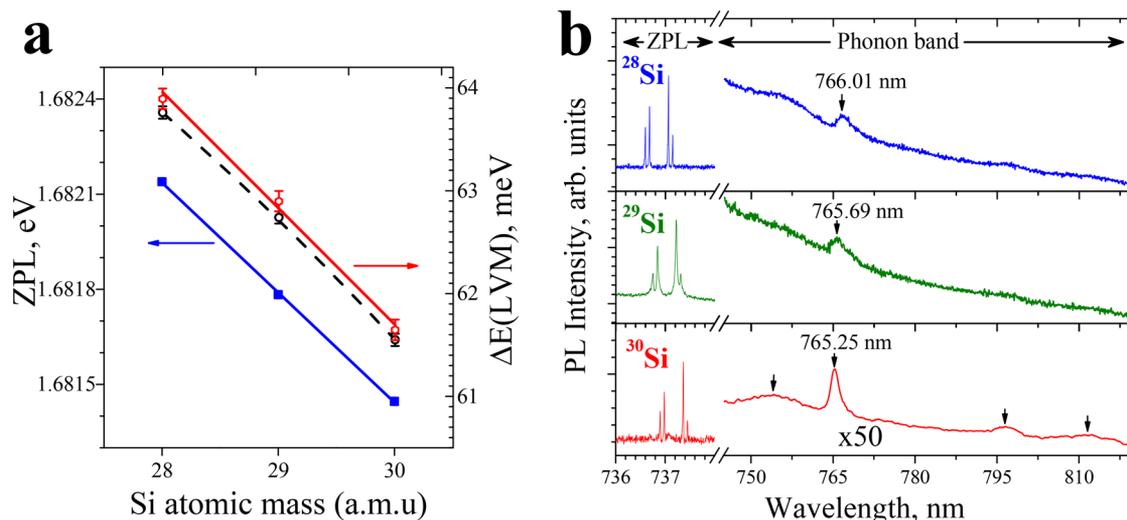


Figure 2. (a) Energies for transition C in ZPL (squares) and local vibration mode (circles) versus Si isotope mass as determined from the absorption and PL spectra, respectively. The bars show the measurement errors. Red and black circles are experimental data in the present work and from Dietrich et al.,¹⁵ respectively. The lines are guides for the eye. (b) SiV⁻ PL spectra for three Si isotopes excited at 473 nm wavelength. Zoomed ($\times 50$) phonon bands are shown on the right side. The components of the phonon band are marked by arrows. The LVM band at ~ 766 nm shows a blue shift with the increase of Si atom mass. All the spectra are taken at 5 K.

In preliminary experiments, after annealing of the samples in vacuum at 1400 °C for 1 h, we observed a significant narrowing of ZPL components due to stress relaxation in diamond; moreover additional new SiV⁻ centers were formed, increasing the PL intensity by a factor of 2 (see Figure S1 in Supporting Information). Particularly, for a film with isotope ²⁸Si, the strongest line C revealed the full width at half-maximum (fwhm) of 0.28 cm⁻¹ (0.035 meV, 8.4 GHz) and 0.22 cm⁻¹ (0.027 meV, 6.6 GHz) before and after the annealing, respectively. Further, all the spectroscopic measurements at low temperatures were performed for the annealed samples.

The Si ion implantation followed by high-temperature annealing in vacuum is often used to produce SiV⁻ centers in diamond.^{12,28,29} The heating to 800 °C is required to make vacancies moveable, while the temperatures 1000–1100 °C are preferable to anneal other defects and reduce the stress. As an example, Evans et al.¹² found that increase of the annealing temperature from 800 to 1100 °C results in about 100 times narrowing of transition C width distribution (for ensemble), from 3–4 nm (800 °C anneal) to 0.03 nm (15 GHz, 1100 °C anneal). As the CVD growth in the present work was performed at already high $T = 1100$ °C, it was reasonable for us to go to even stronger annealing at temperature as high as 1400 °C to achieve further ZPL narrowing.

Figure 1b displays the fine structure of split SiV⁻ ZPL for each Si isotope, with extremely narrow components, as measured in absorption spectra at temperature $T = 5$ K. The width (fwhm) of line C in ZPL is 0.020 meV (4.8 ± 0.5 GHz) and 0.027 meV (6.5 ± 0.6 GHz) for ³⁰Si and ²⁸Si isotopes, respectively (see also Figure S3 for more details), which, to our knowledge, are the smallest values ever reported for SiV⁻ ensembles. For *single* SiV⁻ centers, ZPL components as narrow as 136 MHz for epitaxial films doped from gas phase¹⁰ and 270 MHz²⁸ and 320 ± 180 MHz¹² for ²⁸Si ion-implanted diamond, only several times larger than the lifetime-limited line width of 94 MHz,¹⁰ were observed by other authors. For SiV⁻ ensembles much wider ZPLs (component C) have been reported so far, from 8 GHz (fwhm)¹⁵ to 15 GHz³⁰ in low

strain homoepitaxial CVD diamonds and up to ~ 580 GHz for HPHT nanodiamonds.³¹ The observed broadening of C line for the ²⁹Si isotope to 0.065 meV (15 GHz) (Figure S3b) we associate with enhanced stress in epilayer grown on CVD diamond substrate, the latter being more defective compared to the HPHT substrates used for epitaxy with ²⁸Si and ³⁰Si doping.

We note that the presence of carbon isotope ¹³C in the amount of 1.07% in diamond with natural isotope composition cannot result in ZPL broadening but the relatively large ZPL shift only. The replacement of all ¹²C atoms by ¹³C ones causes SiV⁻ ZPL blue shift $\Delta E_{12/13}$ of 1.78 meV (14.36 cm⁻¹).¹³ Then, we assume that the energy levels of SiV⁻ center are sensitive to six nearest C atoms only. If there are one ¹³C atom and five ¹²C atoms in the surrounding, the probability of this configuration is $p = 6 \times 0.0107 \approx 0.06$ (the probability to meet two ¹³C atoms is negligible). Then, the ZPL shift for this configuration is $(1/6)\Delta E_{12/13} \approx 0.3$ meV (2.4 cm⁻¹), much larger than the width of ZPL components measured here. Therefore, monoisotopic diamond^{10,42} should be preferably used for Si doping to produce multiple identical single photon emitters.

Figure 2a summarizes all three ZPL absorption spectra at 5 K for SiV⁻ centers with isotopes ²⁸Si, ²⁹Si, and ³⁰Si. The positions of ZPL components demonstrate a systematic shift, $\Delta\nu$, to longer wavelengths with Si atom mass increase from $m = 28$ to $m = 30$ (Figure 1b). Particularly, the component C for ²⁸Si moves by 0.35 meV (84.6 ± 0.5 GHz) for ²⁹Si and further to 0.69 meV (167 ± 0.5 GHz) for ³⁰Si isotopes, in excellent agreement with the average value $\Delta\nu = 166 \pm 2$ GHz reported by Dietrich et al.¹⁵ for a collection of PL spectra taken from individual SiV⁻ emission sites with natural isotopic composition of silicon. Note, however, the four-time better accuracy for peak position in the present work. Our data on the absorption/PL isotopic shift for SiV⁻ with ²⁸Si and ³⁰Si are close also to the value of 0.70 ± 0.01 meV previously reported for SiV⁻ ensembles in HPHT crystals with natural isotopic composition of silicon,¹⁴ with ZPL peak width of a few tens of gigahertz. The isotope induced shift in the peak C position shows an

almost linear dependence on the Si atom mass, as displayed graphically in Figure 2a. Other ZPL components, lines A, B, and D, reveal the identical shift.

The PL ZPL spectra at low temperatures exactly replicated the well-resolved fine structure seen in absorption spectra (Figure S2, Supporting Information). To monitor the isotope-induced changes in phonon band a series of PL measurements were performed at $T = 5$ K under excitation at $\lambda = 473$ nm wavelength at the power density of ~ 0.2 W/cm². The spectra were taken from an area of 20×100 μm^2 and recorded with CCD matrix Spec-10 (Princeton Instruments) with spectral resolution of 0.07 nm. The phonon band in SiV⁻ PL exhibits systematic variation with Si isotope mass (Figure 2b). The strongest peak at ~ 766 nm (~ 64 meV), known as the local vibration mode (LVM) related to a single Si atom,^{13,15,33} shifts to shorter wavelengths from 766.01 nm for ²⁸Si to 765.25 nm ³⁰Si with the band position for ²⁹Si between them, while the PL ZPL position experiences an opposite red shift. The other three features in the phonon band (they are shown by small arrows in Figure 2b) do not experience the isotopic shift, so they are not local vibration modes as discussed in refs 15, 33, and 41. Particularly, the peaks at 127 meV (797 nm) and 152 meV (811 nm) belong to LA-phonon mode^{32,43} and LO-phonon mode^{32,43} of diamond lattice, respectively.

Eventually, the LVM energy determined as its distance from line C in ZPL reduces linearly with Si atomic mass from $E_{28} = 63.9 \pm 0.1$ meV for ²⁸Si to $E_{29} = 62.9 \pm 0.1$ meV for ²⁹Si, and to $E_{30} = 61.6 \pm 0.1$ meV for ³⁰Si as plotted in Figure 2a. The obtained LVM values for SiV⁻ ensembles are very close, within 0.1–0.7 meV, to the LVM data reported by Dietrich et al.¹⁵ for single SiV⁻ centers (shown by dashed in Figure 2a).

The following ratios of energies of the phonon peak $E(\text{LVM})$ are obtained: $E_{28}/E_{29} = 1.016 \pm 0.002 \approx 1.0177 = (m_{29}/m_{28})^{1/2}$, $E_{28}/E_{30} = 1.036 \pm 0.002 \approx 1.0357 = (m_{30}/m_{28})^{1/2}$, and $E_{29}/E_{30} = 1.020 \pm 0.002 \approx 1.0171 = (m_{30}/m_{29})^{1/2}$, where m_i is the Si atomic mass. These ratios are in agreement with those calculated from a simple harmonic oscillator model with the phonon frequency $\omega = (k/m)^{1/2}$, where k is spring constant and m is oscillating mass corresponding to the silicon atom. Thus, the local vibration mode at ~ 64 meV includes one silicon atom, not bonded to a carbon atom, in accord with arguments by Dietrich et al.¹⁵ based on spectral analysis of single SiV⁻ centers. On the small interval of the masses, the ZPL and LVM energies linearly decrease with the Si atomic mass (Figure 2a).

The absolute content of the centers, [SiV⁻], in the three samples was found from integrated absorption of the ZPL peak $A_{1.68}$ (the total area under the ZPL in $\text{meV}\cdot\text{cm}^{-1}$) measured at 77 K using calibration constants for 77 K reported in ref 17:

$$A_{1.68} = [(3.4 \pm 0.6) \times 10^{-15} \text{ meV}\cdot\text{cm}^2] \times [\text{SiV}^-] \quad (1)$$

The SiV⁻ abundance was 1.2 ± 0.3 , 4.8 ± 0.6 , and 1.4 ± 0.3 ppb for the samples doped with ²⁸Si, ²⁹Si, and ³⁰Si, respectively (see Table S1 in Supporting Information), that gives the area density of the PL sources of $(1\text{--}4) \times 10^2$ μm^{-2} for film thickness of 5 μm . Taking into account the size of the probed area, the ABS spectra in Figure 1b summarize the signals from about 10^7 individual SiV⁻ centers.

The Si incorporation efficiency, f , in the (100) diamond growth face upon doping from silane in the plasma, defined as the ratio of Si concentration in diamond to that in gas, $f = [\text{Si}/\text{C}]_{\text{dia}}/[\text{Si}/\text{C}]_{\text{gas}}$, was found in our previous work²¹ to be $(1.1 \pm$

$0.5) \times 10^{-3}$. Then, with $[\text{Si}]/[\text{C}]_{\text{gas}}$ of 5×10^{-3} in the present experiment, the concentration of the main isotope $[\text{SiV}^-/\text{C}]_{\text{dia}} \approx 5.5$ ppm could be expected; thus, only a small fraction of 0.02% of all incorporated silicon was converted to SiV⁻ centers according to this consideration.

To demonstrate that the SiV⁻ PL intensity, I_{SiV^-} , and the area density of SiV⁻ centers can be tuned simply by the film thickness (deposition time), we produced a series of epitaxial films with thickness varied from 1.5 to 5.0 μm on HPHT (111) diamond substrates using the silane gas with isotope ³⁰Si at deposition parameters identical to those described above for (100) epilayers. The (111) oriented substrates were chosen since, structurally, SiV⁻ center lies along the $\langle 111 \rangle$ axis of the diamond lattice,^{26,35} so the emission of the SiV⁻ dipole exhibits a strong directionality, which is maximized along the normal to (111) plane; therefore the PL collection efficiency should be higher for Si-doped (111) face. We measured the PL spectra for the doped (111) epilayers at room temperature (RT) with a LabRam HR840 spectrometer in a confocal configuration (see details in Supporting Information) and observed a strong SiV⁻ ZPL at 738 nm with intensities exceeding the Raman peak (Figure 3). The SiV⁻ intensity increases proportionally to

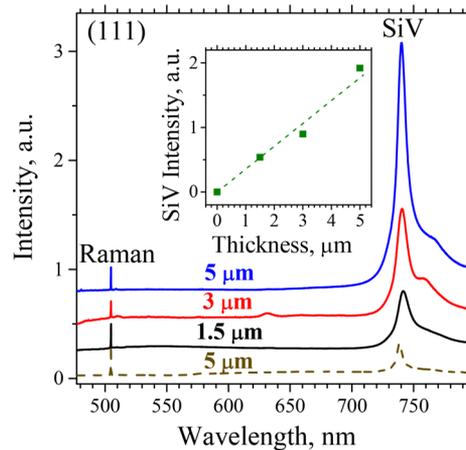


Figure 3. PL spectra at room temperature for diamond films of different thicknesses, grown on and doped from silane with ³⁰Si isotope, on (111) oriented substrates (solid lines) and on (100) oriented substrate (dashed line). The excitation wavelength is 473 nm. Inset: the plot of the integral intensity of SiV⁻ ZPL versus the film thickness on (111) plane, demonstrating a linear dependence.

the film thickness, suggesting that Si doping occurs almost uniformly across the film thickness (see inset in Figure 3). The PL SiV⁻ intensity for the 5 μm thick film on the (111) plane is about 8 times stronger than that for the film with the same thickness grown on the (100) plane (see the spectrum shown by dashed line in Figure 3), indicating a similar enhancement factor in the PL emission collection. The SiV⁻ ZPL width (fwhm) for the epilayers on the (111) surface strongly increased ($\Delta\lambda = 11.2$ nm for 1.5 μm thick film, 10.5 nm for 3 μm film, and 8.5 nm for 5 μm film) compared to $\Delta\lambda \approx 4.8$ nm for a 5 μm thick epilayer on the (100) face. This indicates high stress of the diamond films on the (111) oriented substrates, which, however, progressively relaxes with the film thickness. Because of the ZPL broadening, the isotope-induced line shift (0.15 or 0.30 nm), which is 15–35 times smaller than the ZPL width at RT, cannot be detected at room temperature.

Since stress may be generated at the film/substrate interface, there is a concern about possible enhanced stress and ZPL broadening in very thin (sub-micrometer) epi-films, based on the data for (111) diamond samples. To check if such high stress does appear in the films with (100) orientation, we prepared a sample with the ^{28}Si doped films of $0.9 \pm 0.1 \mu\text{m}$ thickness on (100) HPHT diamond substrate at similar growth parameters. In contrast to the epilayers on the (111) substrates, we still observed narrow ZPL peaks at 5 K (with C line width as small as $0.025 \pm 0.003 \text{ meV}$) as confirmed by the absorption spectrum in Figure S5 (Supporting Information). This indicates the validity of the approach to form single monoisotopic SiV^- spectra with narrow inhomogeneous distribution based on the use of ultrathin films, preferably on (100) substrates.

The linearity of PL intensity, I_{SiV} , versus the film thickness, h , should be valid until the latter becomes less than the information depth, H , at which the signal contribution of deeper layers with $h > H$ becomes less than 50%. In our confocal optical scheme, we had $H \approx 6 \mu\text{m}$ as was estimated from the geometry of collection of backscattered light and from Raman spectra measurements of CVD diamond films enriched with isotope ^{13}C of different thicknesses.³⁶ Therefore, the doped films with thickness up to $5 \mu\text{m}$ satisfied this criterion. To operate with SiV^- single photon emitters, their area density in the doped layer preferably should be on the order of $0.2\text{--}0.4 \text{ SiV}^-$ per μm^2 to be able to spatially separate the emitters (with interdistance of $\sim 1.5\text{--}2 \mu\text{m}$) using a confocal optical scheme for PL photon collection.^{10,28} Of course, the area density of SiV^- centers, up to $4 \times 10^2 \mu\text{m}^{-2}$ in the films studied here, is far beyond this requirement; however, the linear plot in Figure 3 (inset) indicates a possibility to tune the total PL intensity through growth of very small thickness to form a two-dimensional ensemble of the sufficiently spaced emitters. For SiV^- emitter concentration of 1.2 ppb upon our doping parameters, the film thickness adequate for SiV^- density of $0.4 \mu\text{m}^{-2}$ should be as small as 2 nm, the value that could be achieved, in principle, using a delta-doping technique³⁷ or by tuning the growth parameters (CH_4 content and substrate temperature) in a microwave plasma to almost balance the growth and hydrogen-induced etching rates, and obtain very low growth rates.^{2,4,27} A more rational way would be, however, to reduce the Si doping level by 1 or 2 orders of magnitude by the use of highly diluted SiH_4 in the process gas mixture²¹ to make the Si-doped layers of thickness 10–100 nm acceptable.

The PL from SiV^- centers in the diamond film with ^{28}Si isotope for a sample with the reduced concentration of SiV^- sites was performed at room temperature using a home-built confocal setup combined with a Hunbury Brown-Twiss interferometer³⁸ (for details see Supporting Information). A typical distribution of the PL emission under continuous wave laser excitation (532 nm wavelength) on the area of $6.2 \times 6.2 \mu\text{m}^2$ is shown in Figure 4a. The brightest emission spots are clusters of the SiV^- centers, while some of less intensive sites correspond to single emitters. The autocorrelation function, $g^{(2)}(\tau)$, taken for one such site (it is marked by the red circle in Figure 4a) displays a dip to 0.32, confirming its single photon emitter signal (Figure 4b).

PL emission kinetics for a single SiV^- center in this film was investigated using a picosecond diode laser (532 nm wavelength). An example of the PL intensity decay kinetics, $I(t)$, is displayed in Figure 4c. Since the lifetime of the SiV^-

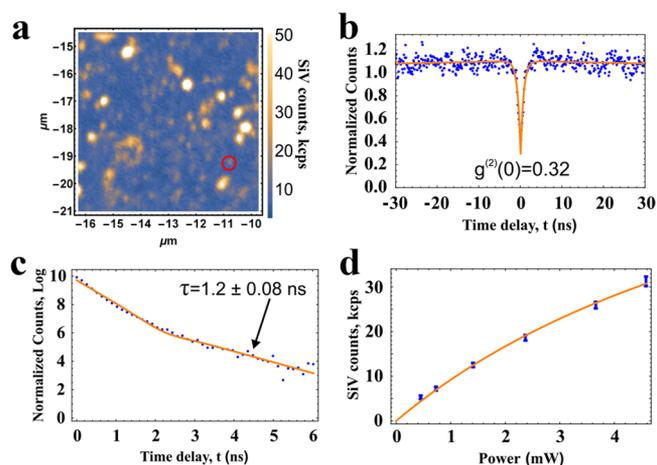


Figure 4. (a) Distribution of PL emission at room temperature of SiV^- centers with ^{28}Si isotope (integrated signal within the spectral band of $740 \pm 13 \text{ nm}$) on $6.2 \times 6.2 \mu\text{m}^2$ area. (b) Autocorrelation function $g^{(2)}(\tau)$ measured for a single SiV^- center from the site shown by red circle on PL map at the laser pump power of 4.5 mW. (c) PL emission kinetics: dots with error bars are the measured data; the solid line is fitting with a single exponent function $I(t) = I_0 \exp(-t/\tau)$ for times $t > 2 \text{ ns}$, with decay time $\tau = 1.2 \pm 0.08 \text{ ns}$. (d) Dependence of the photoluminescence signal of a single SiV^- on excitation power at 532 nm wavelength. The line is the fit $I = I_s P / (P + P_s)$.

center excited state, on the order of 1 ns, is much longer than the length of the laser pulse, the PL signal recorded after the end of the laser pulse exhibits exponential decay; the actual signal observed consist of two exponents, a fast and a slow one. The fast exponential component corresponds to the background fluorescence signatures that do not have a slowly decaying exponential component. This was verified by focusing the microscope on a region containing no optically active color centers in the diamond film (dark areas in Figure 4a) and measuring the background fluorescence decay time collected from that region. The decay curve for times $t > 2 \text{ ns}$ is well fitted with an exponential function, $I(t) = I_0 \exp(-t/\tau)$. We, therefore, associate the long-lived exponential tail decay time $\tau = 1.2 \pm 0.08 \text{ ns}$ in Figure 4c with PL of the SiV^- center. This value is in agreement with literature data on SiV^- PL kinetics for different diamond materials and Si-doping methods, including CVD diamond nanopillars doping from silane ($\tau = 1.0 \text{ ns}$),³⁹ ion implantation (1.2 ns) in type IIa natural diamond films,⁴⁰ doping of isolated diamond nanoparticles (1.1 ns)⁹ and homoepitaxial diamond films (1.3 ns)⁴¹ with silicon in course of CVD process.

To assess the maximum possible count rate, we measured the power dependence of the count rate for the selected single SiV^- center (Figure 4d). As the absorption maximum of the SiV^- center is in the near IR (738 nm), it is relatively difficult to reach experimentally complete saturation with green excitation.⁴² We fitted the obtained dependence using the standard saturation model,⁹ $I_s \frac{P}{P + P_s}$, where I is the measured count rate, P is excitation power, and fitting parameters are the saturation power, P_s , and the extrapolated maximum number of counts, I_s . The background fluorescence has been subtracted. Following this procedure, it was found, that the SiV^- center in the diamond film has the fluorescence count rate $I_s = 89 \pm 11$ kilocounts/s and saturation power $P_s = 8.6 \text{ mW}$. This is quite comparable with single SiV^- obtained by ion implantation followed by annealing under green excitation at room

temperature.⁴⁴ Nevertheless, the difference in count rates significantly depends on collection efficiency in the confocal setup. We estimated the collection efficiency of 0.2% for our experiment (see Supporting Information for details).

In summary, we demonstrated the controllable *in situ* doping of epitaxial diamond layers with isotopically enriched silicon (²⁸Si, ²⁹Si, and ³⁰Si) by adding silane SiH₄ gas in H₂–CH₄ mixture in the course of the microwave plasma-assisted CVD process to form ensembles of monoisotopic SiV[−] color centers with very narrow (~4.8 GHz) ZPL components. The presence of the SiV[−] centers at 737 nm wavelength was revealed both in photoluminescence and in optical absorption spectra for each of the Si isotopes. The zero-phonon line in SiV[−] absorption at low temperature (5 K) exhibits a spectral shift to lower energies with Si mass increase, namely, by 0.69 ± 0.01 meV when the ²⁸Si isotope is replaced by the ³⁰Si, with a similar trend for ZPL in PL spectra. Based on the spectral shift of the peak around 64 meV in the phonon band, we confirmed it to be a local vibration mode related to a single Si atom, in agreement with the previously reported finding by Dietrich et al.¹⁵ for measurements of individual SPE within SiV[−] ensemble with natural Si isotope composition. The SiV[−] PL intensity is shown to linearly depend on the doped film thickness making it possible to control the area density of the color centers, in particular, by depositing ultrathin epitaxial films with rarely arranged centers. The developed doping method can be a viable alternative to Si ion implantation in diamond^{12,45,46} to form isotopically pure SiV[−] centers as identical single photon emitters. Our results have an impact on the application of single-photon sources for quantum optical information technologies. The doping with Si using CVD method potentially promises to form SiV[−] centers in very shallow layers using a special design of CVD system with a rapid change of gas flow, as was demonstrated recently for doping with boron and nitrogen.^{34,37} With such strong depth localization, the CVD doping could compete with ion implantation techniques.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsp Photonics.8b01464.

Details of diamond growth and doping procedures; annealing effect; spectroscopic setup, measuring the absolute concentration and mapping of SiV[−] centers (PDF)

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Notes

The authors declare no competing financial interest.

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