Effect of Particle Size on the Optical Properties of Silicon-Vacancy Centers in Nanodiamonds Fabricated by a Detonation Process

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1. Introduction

Nanodiamonds (NDs) with color centers—namely, fluorescent nanodiamonds (F-NDs)—have attracted considerable attention as ideal fluorescent markers for biomedical applications such as bioimaging/sensing.[1–7] In comparison with quantum dots and organic dyes, F-NDs not only have the advantage of greater chemical stability and lower toxicity but also exhibit nonfading and nonblinking photoluminescence (PL) at room temperature.[8,9] In addition, in the quantum information field, F-NDs are considered promising single-photon sources that function at room temperature.[10,11] Among more than 500 types of diamond color centers discovered thus far,[12] nitrogen-vacancy (NV) centers are widely known to function as fluorescent markers and single-photon sources; both their applications and fundamental properties have been actively investigated.[13–17] As a result of numerous studies related to NV centers, despite advances in the photonics field,[17] NV centers have been found to not be ideal fluorescent markers. The two nonideal properties of an NV center are as follows. First, the zero-phonon lines (ZPLs) for NV0 and NV+ centers are located at 2.16 and 1.95 eV, respectively, and are outside the near-infrared biological window (1.31–1.77 eV).[17–19] Second, the luminescence is spread over a large phonon sideband accompanied by the ZPLs at room temperature.[20,21] Therefore, other color centers have been investigated and a silicon-vacancy (SiV) center has recently been proposed as a promising color center.[20] The SiV center has a split-vacancy structure in which a silicon atom is located between two carbon vacancies and exhibits two advantageous optical properties.[21,22] First, an SiV center exhibits a ZPL at 1.68 eV, which lies within the near-infrared region and exhibits a narrow spectral width of 5 nm at room temperature.[23,24] Second, emission from a SiV center has a large Debye–Waller factor (DWF), and ≈70% of its total optical emission is concentrated in the ZPL.[25] These optical properties make SiV centers a promising alternative to NV centers as fluorescent markers.

Given the aforementioned background, the synthesis of NDs containing SiV centers (SiV-NDs) has been actively studied. In 2011, SiV-NDs with a size of 70–80 nm were produced by crushing diamonds containing SiV centers synthesized by chemical vapor deposition (CVD).[26] In 2019, 10 nm SiV-NDs were synthesized by a high-pressure, high-temperature (HPHT) method.[24] However, the production volume was limited to the laboratory scale. The next challenge was to establish a practical-scale synthesis method that would accelerate the application research...
of SiV-NDs. To address this issue, our group focused on a detonation process that produces NDs with an average particle size of 4–5 nm through the detonation of explosives such as a mixture of 2,4,6-trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX). The simplicity of the process enables the production of detonation nanodiamonds (DNDs) in large quantities (tens or hundreds of tons per year) at low cost. We have recently succeeded in the straightforward synthesis of SiV-NDs via a detonation process using aromatic Si compounds as a Si source.

SiV-NDs fabricated by the detonation process (SiV-DNDs) with high production volume have the potential to greatly advance the biomedical field. For future applications, it is necessary to determine the optical properties of SiV centers in the extremely small DNDs, not those in bulk diamonds. Although the optical properties of SiV centers in few nanometer-sized NDs synthesized by CVD and HPHT or collected from meteorite fragments have already been reported, color centers in DNDs fabricated by the detonation process have not been studied in detail except in the case of NV centers. In the present article, we investigate SiV-DNDs spectroscopically, clarify the temperature and excitation-energy dependence of the luminescence intensity and linewidth of the ZPL as well as that of the luminescence lifetime, and compare them with typical SiC centers in bulk diamond. These unique optical properties of SiV centers in DNDs, as revealed by our spectroscopic measurements, show that the surface effect stemming from the extremely small particle size of DNDs enhances electron–phonon coupling and increases the nonradiative transition probability of SiV-DNDs. Moreover, because of the detonation process, the electronic states of the SiV centers inside the DNDs are not uniform. Aggregates of SiV-DNDs with slightly nonuniform electronic states exhibit the ZPL with inhomogeneous broadening. However, with regard to photostability, we find that the luminescence emitted by SiV centers in DNDs does not fade, like the luminescence emitted by well-known color centers such as the NV center. This understanding of the optical properties and the electronic states of SiV centers in DNDs, as gained from our systematic investigation, provides a foundation for the practical application research of SiV-DNDs as a biomarker and single-photon emitter.

2. Experimental Section

2.1. Fabrication and Characterization of Undoped- and SiV-DNDs

To synthesize undoped-DNDs, a mixed explosive consisting of 60 wt% TNT and 40 wt% RDX was prepared by compression to form a cylindrical charge with a total mass of 1,000 g (hereinafter referred to as “TR-explosive”). For the synthesis of SiV-DNDs, 10 g of triphenylsilanol (TPS-OH) (Tokyo Chemical Industry) as a Si-dopant was added in the course of the aforementioned explosive preparation (hereinafter referred to as “Si-explosive”). Because the Si-dopant was a powdery solid at room temperature and pressure (the melting point of TPS-OH is 152–154 °C), it could be well mixed with TNT and RDX powders and the resultant mixtures could be molded by pressing into a cylindrical shape. The grain size of each powder was adjusted to be less than 1 mm.

Each of these two explosives was detonated under a CO₂ atmosphere. The detonation products were purified with an acid mixture (H₂SO₄ + HNO₃) at 150 °C for 5 h. After cooling to 70 °C, the reaction mixtures were added to deionized (DI) water and heated (150 °C) again for 5 h. The precipitates were then rinsed with DI water. After drying, the crude products were treated with aqueous 8 M NaOH at 70 °C for 8 h. Alkali-treated precipitates were added to DI water at room temperature, and the pH of the resultant mixtures was adjusted to 3–4 by addition of aqueous 1 M HCl. The crude suspension was centrifuged (CR22G, Hitachi Koki) at 8000 × g for 10 min, and the precipitates were separated and added to DI water. These procedures of adding aqueous HCl and centrifuging were repeated. The collected precipitates were then rinsed with DI water and dried. Finally, only the sample obtained from Si-explosive was air-oxidized in O₂/N₂ (4/96 vol %) at 470 or 570 °C for 2 h. The DNDs obtained from the TR- and Si-explosives were characterized by powder X-ray diffraction (XRD) (SmartLab, Rigaku) analysis using Cu-Kα radiation (λ = 1.54 Å). The average crystallite sizes, which were approximately the average particle sizes of the DNDs, were then calculated using Scherrer’s formula on the basis of the (111) diffraction peak, which was the most intense diffraction peak in the XRD patterns. The samples for optical measurements were prepared by dropping 100 μL of 10 wt% aqueous suspension of each DND onto a glass substrate and drying it (drop-cast sample). Unless otherwise noted, these drop-cast samples were used in subsequent optical measurements. To confirm the construction of SiV centers and evaluate the temperature conditions under air-oxidation, the DNDs produced from Si-explosive were characterized by PL spectroscopy using a Raman spectrometer (Lab RAM Evolution, HORIBA) equipped with a narrow-linewidth laser with an excitation energy of 2.33 eV.

2.2. Investigation of the Optical Properties

The PL measurements of undoped- and SiV-DNDs were performed using the handmade system schematically shown in Figure 1. A laser system (Pharos, Light Conversion) operating at 1 kHz with a 200 fs pulse width and 0.2 mJ pulse energy at

![Figure 1. Schematic of the optical system for photoluminescence (PL) experiments (OPA: optical parametric equalizer; CCD: charge-coupled device).](image-url)
an output energy of 1.20 eV was used to pump an optical parametric amplifier (Orpheus-HP, Light Conversion) and to generate excitation pulses with an energy in the range of 1.80–3.54 eV. The excitation laser beam was guided through a circular pinhole for all optical experiments. Luminescence was spectrally dispersed by a spectrometer (SpectraPro HRS-300, Acton Research) equipped with a 150 groove mm⁻¹ grating and was detected using an air-cooled charge-coupled device (PIXIS 256, Princeton Instruments). In the case of low-temperature measurements, the samples were cooled using a He cryostat.

For time-resolved PL measurements of SiV-DNDs, the same optical system shown in Figure 1 was employed. The samples were excited by an excitation laser with an energy of 2.34 eV. Luminescence was detected by a streak camera (C14831, Hamamatsu Photonics) interfaced to a spectrometer (SpectraPro 300i, Acton Research) equipped with a 50 groove mm⁻¹ grating. Using this optical system, we recorded the time-resolved spectra on a timescale of 100 and 20 ns with a time resolution of 0.14 and 0.027 ns, respectively.

The photostability of SiV centers in the DNDs was evaluated according to the method of Reineck et al. [37] as follows. A colloidal solution of SiV-DNDs was prepared by sonicating 750 mg of the SiV-DNDs in 15 mL of DI water using an ultrasonic horn (UP-400S, Hielscher Ultrasonics) at 180 W for 3 h to ensure proper dispersion. The dispersion was then centrifuged (CR22G, Hitachi Koki) at 13 200 × g for 1 h. The supernatant was separated, and DI water was added to the separated supernatant to prepare SiV-DNDs at a concentration of 1 wt%.

Table 1. Yield and primary particle size of SiV-DNDs after the air-oxidation.

| Air-oxidation conditions | Yield [wt%] | Average particle size [nm] |
|------------------------|------------|--------------------------|
| Temperature [°C]       | Time [h]   |                          |
| 470                    | 2          | 86.3                     |
| 570                    | 2          | 4.6                      |

The particle sizes of the DNDs prepared from the Si-explosive differ depending on the air-oxidation temperature. The temperature conditions and yields of the air-oxidation product of the DNDs obtained from Si-explosives are shown in Table 1. The DNDs oxidized at 470 °C hardly lost weight, whereas those oxidized at 570 °C lost 95.4 wt%. The high-temperature condition caused an increase in particle size and a decrease in yield. Osswald et al. reported similar results in 2008 [39]. They presumed that larger particles observed after the oxidation treatment were present in the sample before the treatment. In fact, Stehlik et al. examined the size distribution of DNDs in detail and showed that

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3. Results and Discussion

3.1. Characterization of Fabricated DND Samples

The XRD patterns of the purified detonation products obtained from the TR- and Si-explosives are shown in Figure 2a–c. Because all the patterns show three major diffraction peaks that originate from the (111), (220), and (311) planes of diamond, all the products are confirmed to have a diamond crystal structure. The average particle sizes of the DNDs were calculated on the basis of the (111) diffraction peak in each pattern using Scherrer’s formula. For the undoped-DNDs produced from TR-explosives, the average particle size was 6.3 nm. For the DNDs prepared from Si-explosive under air-oxidation temperatures of 470 and 570 °C, the sizes were 8.1 and 10.8 nm, respectively. These values are larger than those of undoped-DNDs. The particle size distribution of these air-oxidized DNDs is discussed in Section S1, Supporting Information. These results indicate that DNDs can be obtained from TR- and Si-explosives. Note that
the distribution increased from a few nanometers to tens of nanometers.\textsuperscript{[40]} Given the values in Table 1 and those reported previously, our experiments suggest that especially small DNDs, such as those with a single-digit-nanometer diameter, were decomposed/combusted and that only the relatively large particles survived the air-oxidation process at 570 °C.

The PL spectra of the air-oxidized DNDs prepared from the Si-explosive were recorded at room temperature. Figure 3a,b shows PL intensity maps at 1.68 eV, which is a ZPL of SiV centers, for the air-oxidized DNDs treated at 470 and 570 °C, respectively. The maps comprise 10,201 data points, each of which corresponds to a 1 μm × 1 μm region. In Figure 3c,d, the representative PL spectra for the DNDs prepared under different air-oxidation conditions are shown. These measurement points correspond to points 1–6 and i–vi indicated in Figure 3a,b, respectively. These measurement points are located not only in bright points (1–3 and i–iii) but also in dark points (4–6 and iv–vi). Those baselines were subtracted in the method discussed in detail in Section 3.2.1. The spectra represented by data points 1 and i have a distinct peak centered at 1.68 eV. This peak position is in agreement with the well-known energy of the ZPL of SiV centers.\textsuperscript{[41]} In addition, the X-Ray fluorescence (XRF) elemental analysis of the SiV-DNDs before air-oxidation (immediately after alkaline treatment) reveals that Si atoms were definitely introduced into the DNDs (details are provided in Section S2, Supporting Information). These results mean that the DNDs generated from the Si-explosive contain SiV centers (SiV-DNDs) irrespective of the air-oxidation temperature. However, as shown in Figure 3c, little or no luminescence from SiV centers was observed from the dark points in Figure 3a. In contrast, all the data points in Figure 3b show the ZPL of the SiV centers (Figure 3d). The number of data points in the maps in Figure 3a,b where the ZPL of SiV centers are observed, such as spots 1 and i, were counted. For SiV-DNDs obtained in 86.3 wt% yield after oxidation at 470 °C (Figure 3a), only 1349 points were observed. However, for the SiV-DNDs obtained in 4.6 wt% yield after oxidation 570 °C (Figure 3b), 10,139 points were observed and the SiV centers were dispersed over the entire measurement.

![Intensity mapping of PL at 1.68 eV for air-oxidized silicon-vacancy (SiV)-NDs fabricated by the detonation process (SiV-DNDs) treated at: a) 470 and b) 570 °C. The PL spectra corresponding to points: c) 1–6 and d) i–vi indicated in (a) and (b), respectively.](image-url)
region. The increased number of points indicating SiV centers in the high-temperature-treated samples might be attributable to the increased average particle size and yield after the treatment (Table 1). According to Shershulin et al., the smallest oxygen-terminated diamond particle that can hold a stable SiV color center is 8 nm. After the air-oxidation at 570 °C, such especially small DNDs, which represent 95.4 wt% of the total mass, are decomposed/combusted and only the originally large particles (4.6 wt% of the total mass) capable of emitting SiV luminescence survive. As a result, the concentration of SiV-DNDs is increased. In addition, defects quenching the PL from color centers might have been eliminated by air-oxidation at the higher temperature. On the basis of these results, we used the SiV-DNDs oxidized at 570 °C (4.6 wt% yield) for subsequent optical measurements.

### 3.2. Investigation of the Optical Properties

#### 3.2.1. PL Spectra

The PL spectra of SiV- and undoped-DNDs excited at room temperature by the laser with an excitation energy of 2.34 eV are shown in Figure 4a (black and red dots, respectively). The PL intensity of the undoped-DNDs is normalized by the PL intensity of the SiV-DNDs at 1.80 eV. The PL spectra of the SiV-DNDs are composed not only by the ZPL at 1.68 eV with a phonon sideband originating from SiV centers but also by a broadband originating band without peaks as a baseline. A similar broad background has been observed in the spectra of SiV-center-containing diamonds fabricated by other methods. The shapes of the PL spectrum of our undoped-DNDs and those of other undoped-NDs are similar. In the case of NDs with a size of 5–50 nm, this broadband luminescence presumably originates from surface defects. Therefore, the broad background observed from SiV-DNDs originates in the diamond structure irrespective of the SiV centers. In fact, the subtracted spectrum between SiV- and undoped-DNDs, indicated as blue dots in Figure 4a, shows a typical shape of the SiV luminescence spectrum. As shown in Figure 4b, the ZPL of SiV centers in the subtracted spectra can be well-fit with a Gaussian curve. The linewidth of the ZPL and DWF are 0.0318 eV (14.4 nm) and 0.47, respectively. The DWF is calculated as the area ratio of the subtracted spectrum to the Gaussian curve. Here, in the case of typical SiV centers in bulk-sized diamonds, the linewidth and DWF are ≈5 nm and 0.7, respectively. Although the DWF of SiV centers in DNDs can be underestimated because the luminescence originating from other defects might not be completely subtracted as the baseline, the DWF of the SiV centers in DNDs is seemingly small compared with that of typical SiV centers. Therefore, the SiV centers in DNDs exhibit a ZPL with wider homogeneous and/or inhomogeneous broadening and have stronger electron–phonon coupling. Note that the PL spectrum in Figure 4b is the average of those for different SiV centers in DNDs, as obtained by recording the spectrum for a range of ≈30 μm (the size of the excitation laser beam) in the drop-cast sample. However, for multiple spots observed with a scanning increment of 1 μm × 1 μm using a system with a higher spatial resolution of ≈1 μm (Figure 3), the obtained PL spectra show various shapes depending on the measurement spot. Therefore, the linewidth and DWF calculated from Figure 4 are the mean values for various SiV-DNDs.

#### 3.2.2. Temperature Dependence of the PL Spectra

We measured the temperature dependence of the luminescence intensity of the SiV-DNDs. Figure 5a shows the PL spectra of SiV- and undoped-DNDs at 4–300 K, normalized by the excitation power. As evident in Figure 5c, for the normalized spectra in Figure 5b, the spectral shape for the undoped-DNDs is almost independent of temperature. Therefore, the PL spectrum of the undoped-DNDs at 4 K, which exhibits the highest signal-to-noise (S/N) ratio among the spectra of undoped-DNDs, was used as a baseline for the SiV luminescence. The subtracted spectra in Figure 5d were obtained via the method described in Section 3.2.1. The luminescence intensity of the ZPL in the subtracted spectra, in which only the luminescence from SiV centers is included, was estimated by fitting the shape of the ZPL with a Gaussian function. As shown in Figure 5e, the PL intensity of the ZPL of SiV centers shows a temperature dependence expressed by the Arrhenius equation.

![Figure 4](https://www.advancedsciencenews.com/2200342/5.png)

**Figure 4.** a) PL spectra of SiV- and undoped-DNDs, plotted as black and red dots, respectively. The PL intensity of undoped-DNDs is normalized by the PL intensity of the SiV-DNDs at 1.80 eV. The subtracted spectrum of SiV- and undoped-DNDs is plotted as blue dots. b) A Gaussian fitting curve for the subtracted spectrum in (a). The black dots and red line indicate the original data and the fitted curve, respectively.
$I_{\text{SiV}} = \frac{I_0}{1 + A \exp\left(\frac{E_a}{k_B T}\right)}$  

(1)

where $I_0$, $A$, and $k_B$ are the PL intensity at low temperature, a pre-exponential factor, and the Boltzmann constant, respectively. The activation energy ($E_a$) obtained by the fitting is 21.2 meV. All the fitted values are reported in Table 2.

**Table 2.** Fitting parameters of Equation (1) by Arrhenius plot.

| Parameter | Value   |
|-----------|---------|
| $I_0$ [arb. units] | $(4.4 \pm 0.2) \times 10^5$ |
| $A$ [arb. units] | $8.8 \pm 3.9$ |
| $E_a$ [meV] | $21.2 \pm 0.5$ |

**Figure 5.** PL spectra of: a) SiV- and b) undoped-DNDs at each investigated temperature. c) Normalized PL spectra of undoped-DNDs calculated from (b). d) Subtracted spectra between the PL spectra of SiV-DNDs at each temperature and undoped-DNDs at 4 K. e) Temperature independence of the PL intensity of the SiV centers in DNDs (black dots). The red line is the curve fitted using the Arrhenius equation.

**Figure 6.** a) PL spectra of the SiV- and undoped-DNDs at 4 K plotted as black and red dots, respectively. The PL intensity of the undoped-DNDs is normalized by the PL intensity of the SiV-DNDs at 1.71 eV. The subtracted spectrum between the SiV- and undoped-DNDs is shown as blue dots. b) Gaussian fitting curve for the subtracted spectrum in (a). The black dots and red line indicate the original data and the fitted curve, respectively.
dependence of the luminescence linewidth for SiV centers only, we prepared the subtracted spectrum shown in Figure 6a (blue dots) using the aforementioned method. The linewidth of the ZPL of SiV centers in the subtracted spectrum is 0.014 eV (6.5 nm), as calculated by fitting a Gaussian function (Figure 6b). The linewidth of the ZPL at 4 K is narrower than that at room temperature (Figure 4b), indicating that the homogeneous linewidth decreases to a limit that depends on the measurement temperature. However, the linewidth of the ZPL of SiV centers in DNDs is sufficiently wider than that of the ZPL for a typical SiV center in bulk-sized diamond (according to Bolshakov et al., 4.5 nm at 298 K and 0.3 nm at 5 K [49]). Thus, the ZPL of SiV centers in DNDs has a broad inhomogeneous linewidth. The dependence of the peak position of the ZPL on the stress in the diamond lattice has been reported in detail [41,50]. The location of each SiV center in the DNDs varies from the center to the surface. According to the distance from the surface, the lattice distortion is inhomogeneously distributed around the SiV structure. Because the SiV-DND sample used in the present study is an aggregate of particles, the PL spectra are observed as an ensemble of individually peak-shifted ZPLs.

3.2.4. Time-Resolved PL Measurements

Time-resolved spectroscopy was performed using a streak camera to measure the luminescence lifetime of the SiV centers excited at 2.34 eV. Figure 8a shows a time-resolved PL spectrum around the ZPL of SiV centers during approximately 100 ns. The luminescence peak of the SiV centers is clearly observed in the time-integrated spectrum in Figure 8b. Figure 8c,d show the decay curves for the luminescence from SiV-DNDs; these curves were extracted by integrating over the spectral ranges of 1.65–1.72 eV and 1.76–1.84 eV, respectively. Notably, luminescence from SiV centers is observed only in the range of 1.65–1.72 eV. Both decay curves reach baselines after ~90 ns. This timescale appears to be too long because the well-known luminescence lifetime of SiV centers in bulk diamond is 1.0–2.4 ns [20]. To determine the time constant of this longer component, we fit both decay curves in the time domain after 25 ns using

\[ F(t) = F_0 + F_{\text{Long}} \exp(-t/\tau_{\text{Long}}) \]  

where \( F(t) \) is the luminescence intensity at time \( t \), \( F_0 \) is the baseline, and \( F_{\text{Long}} \) and \( \tau_{\text{Long}} \) denote the pre-exponential factor and lifetime of the long-lived component, respectively. As shown by a red line in the inset of Figure 8c,d, both decay curves were successfully fitted with a common \( \tau_{\text{Long}} \) in Equation (2) (the value of \( \tau_{\text{Long}} \) is reported in Table 3). In fact, Figure 8a indicates that the ZPL of SiV centers is observed only in the time region earlier than 25 ns. Therefore, the longer component has no relation to SiV centers in the DNDs, likely because of the presence of the other defect centers in the DNDs, such as NV centers. Actually, NV centers are known to normally be present in DNDs [51], and their luminescence lifetime is \( \approx 10 \) ns [52,53].

To investigate the short luminescence components, we recorded time-resolved spectra over a time range of \( \approx 20 \) ns. Figure 9a shows the PL decay around the ZPL of SiV centers. Figure 9b,c shows the decay curves of the luminescence from SiV-DNDs, which were extracted by integration over the ranges of 1.65–1.72 and 1.76–1.84 eV, respectively. These luminescence decay curves can be represented by setting \( \tau_{\text{Long}} = 10 \) ns, as follows

![Figure 7](image-url)

Figure 7. a) PL spectra as a function of excitation energy for SiV centers in DNDs produced by subtracting PL spectra of SiV- and undoped-DNDs. These PL intensities are normalized by the peak intensity of the PL spectrum excited by a 1.80 eV laser (red line). b) PLE spectrum produced by plotting the PL intensity at 1.68 eV against the excitation energy in (a). The PLE spectrum of typical SiV centers is based on Häußler et al. [25]. The PL intensity of the SiV centers in DNDs and a typical SiV center is normalized by the PL intensity excited at 2.3 eV.


\[ F(\tau) = F_0 + \sum_{i=1}^{N} F_i \exp(-\tau/\tau_i) + F_{\text{Long}} \exp(-\tau/\tau_{\text{Long}}) \]

where \( F(\tau) \) is the luminescence intensity at time \( \tau \), \( F_0 \) is the baseline, \( F_i \) and \( F_{\text{Long}} \) are pre-exponential factors, and \( \tau_i \) denotes lifetimes. As shown in Figure 9b, the decay curve of the luminescence from SiV-DNDs in the range of 1.65–1.72 eV is well-fitted with the tetra-exponential model (\( N = 3 \) in Equation (3)). However, the decay curve of SiV-DNDs’ luminescence in the range of 1.76–1.84 eV is successfully fitted with tri-exponential components (\( N = 2 \) in Equation (3)). These fitting parameters are shown in Table 4. Because \( \tau_1 \), \( \tau_2 \), and \( \tau_{\text{Long}} \) are commonly observed in both decay curves, they are presumed to be the same components originating from the ND structure. The time constant of \( \tau_3 = 0.56 \pm 0.04 \) ns observed only from the decay curve in the range of 1.65–1.72 eV is attributed to the luminescence lifetime of the SiV centers. The contribution of the luminescence from the SiV centers was evaluated by the two different sets of experimental data shown in Table 5: the decay curve and the PL spectrum in the range of 1.65–1.72 eV. Note that the calculation of the contribution based on the time-integrated PL spectrum is performed using the PL spectra shown in Figure 4a, which were recorded under the same conditions as the time-resolved spectroscopy measurements. \( A_{\text{Subt}} \) and \( A_{\text{SiV-DNDs}} \) are the areas of the subtracted and PL spectra of SiV-DNDs (blue and black dots in Figure 4a) in the energy range of 1.65–1.72 eV, respectively. The two calculated values in Table 5 are 0.43 and 0.50, which are consistent. Here, the decay curve in the range of 1.76–1.84 eV without SiV centers was well fitted by a tri-exponential component. Although we attempted to fit this decay curve using a tetra-exponential model having an additional component with a time constant of 0.56 ns, the component did not substantially contribute to the fitting results (details are provided in Section S4, Supporting Information). These results suggest that the third term in Equation (3) in the range of 1.65–1.72 eV is attributable to luminescence from SiV centers. Decay curves in the range of 1.65–1.72 eV obtained from other spots in the sample were also fitted by a tetra-exponential model with the same fitting parameters as in Table 5, including \( \tau_1 \) in the range of 0.56 ± 0.04 ns (details are provided in Section S5, Supporting Information). Although the luminescence lifetime of 0.56 ± 0.04 ns obtained in the present study for SiV-DNDs is shorter than the well-known

Table 3. Parameters for decay curves represented in Figure 8c,d and fitted by Equation (2).

| Energy range [eV] | \( F_0 \) [arb. units] | \( F_{\text{Long}} \) [arb. units] | \( \tau_{\text{Long}} \) [ns] |
|------------------|----------------|----------------|----------------|
| 1.65–1.72        | \( 2.5 \times 10^{-4} \) | \( 0.04 \pm 0.03 \) | \( 10.1 \pm 0.3 \) |
| 1.76–1.84        | \( 6.7 \times 10^{-4} \) | \( 0.12 \pm 0.01 \) | \( 10.5 \pm 0.2 \) |

Figure 8. a) Time-resolved PL spectrum around the ZPL of SiV centers in DNDs excited at 2.34 eV. b) Time-integrated spectrum at all measurement times in (a). Decay curves of the luminescence in the ranges of: c) 1.65–1.72 and d) 1.76–1.84 eV. The insets in (c,d) are magnified views of the decay curves in the time region from 25 to 104 ns. The black dots and red line indicate the experimental data and fitted curve based on Equation (2), respectively.
The luminescence lifetime of SiV-DNDs (1.0–2.4 ns),[20] the luminescence lifetime of SiV centers in nanosized diamond has been reported to be shorter than that of SiV centers in bulk diamond. For example, SiV centers constructed with 5 nm DNDs using a high-temperature annealing technique have been reported to exhibit a luminescence lifetime of 0.4 ns.[54] According to another report, the shortest luminescence lifetime is 0.2 ns.[55] The luminescence lifetime of SiV centers in DNDs in the present study is within the range of values reported previously. Note that the determined luminescence lifetime of SiV centers in DNDs (0.56 ± 0.04 ns) is estimated as an average value for a large number of SiV-DNDs present in the excitation spot of the samples. As shown in a previous investigation of NV centers, the luminescence lifetime of the color centers in NDs is known to slightly differ among individual particles and exhibits a certain distribution.[56,57]

### 3.2.5. Effect of Particle Size on the Optical Properties of SiV Centers in DNDs

Table 6 shows the key optical properties of SiV centers in DNDs measured in a series of spectroscopic experiments in the present study, along with those of the well-known SiV centers in bulk diamonds. According to the linewidths evaluated from the PL spectra at room and cryogenic temperatures, the ZPL of SiV centers in DNDs exhibit greater homogeneous and inhomogeneous broadening compared with the ZPL for typical SiV centers.

**Table 4.** Fitting parameters of Equation (3) for decay curves of luminescence from SiV-DNDs.

| Energy range [eV] | F_{0} [arb. units] | F_{1} [arb. units] | t_{1} [ns] | F_{2} [arb. units] | t_{2} [ns] | F_{3} [arb. units] | t_{3} [ns] | F_{Long} [arb. units] |
|------------------|-------------------|-------------------|-----------|-------------------|-----------|------------------|-----------|---------------------|
| 1.65–1.72        | 3.5 × 10^{-4}     | 0.56 ± 0.02       | 0.16 ± 0.01| 0.06 ± 0.02       | 1.6 ± 0.2 | 0.31 ± 0.01      | 0.56 ± 0.04| (4.4 ± 0.5) × 10^{-3}|
| 1.76–1.84        | 4.4 × 10^{-4}     | 0.74 ± 0.01       | 0.20 ± 0.01| 0.14 ± 0.01       | 1.5 ± 0.1 | –                | –         | (1.7 ± 0.1) × 10^{-2}|

**Table 5.** Contribution of luminescence from SiV centers.

| Calculation method of contribution | Decay curve | Spectrum |
|------------------------------------|-------------|----------|
| \( F_{1} t_{1} / \sum F_{i} t_{i} + F_{Long} t_{long} \) | A_{Sub}/A_{SiV-DND} |
| Calculated value                   | 0.43        | 0.50     |

Figure 9. a) PL decay around the zero-phonon line (ZPL) of SiV centers in SiV-DNDs excited by a 2.34 eV laser. b,c) Decay curves of the luminescence in the ranges of: b) 1.65–1.72 and c) 1.76–1.84 eV. The black dots and red line indicate the experimental data and the fitted curve based on Equation (3), respectively.
Table 6. The optical properties of SiV centers in DNDs and typical SiV centers.

| Spectroscopic method | Optical properties | SiV centers in DNDs | Typical SiV centers in bulk-sized diamond |
|----------------------|--------------------|--------------------|------------------------------------------|
| PL Linewidth (FWHM)  | 14.4 nm at rt[^1]  | ≈5 nm at rt[^2][39] |
|                      | 6.5 nm at 4 K      | 0.3 nm at 5 K[^4]  |
| PL DWF at rt[^5]     | 0.47               | 0.67[^6]           |
| Time-resolved PL Luminescence lifetime | 0.56 ± 0.04 ns | 1.2 ns[^7] |

[^1] Full-width at half-maximum;[^2] room temperature.

Focusing on the time-resolved PL, we find that the luminescence lifetime of the SiV centers in DNDs at room temperature is shorter than that of typical SiV centers by approximately one-half. Therefore, the homogeneous broadening of the ZPL of SiV centers in DNDs can be estimated to be ≈10 nm if we assume the time–energy uncertainty relation. Because the linewidth is determined by the sum of homogeneous and inhomogeneous broadening, inhomogeneous broadening of SiV centers in DNDs is estimated to be 4–5 nm at room temperature. Here, the short lifetime of SiV centers in DNDs indicates that the non-radiative transition probability is higher than that of typical SiV centers. Moreover, the decrease of the DWF is caused by the stronger electron–phonon coupling of SiV centers in DNDs compared with that of typical SiV centers. The possible causes of the change in the electronic state of these SiV centers are the distortion of their split-vacancy structure and the influence of the surface potential due to the specific small particle size of SiV centers in the DNDs. The smaller the particle sizes of the SiV centers in DNDs, the more sensitive the internal SiV centers are to such surface effects compared with typical SiV centers in bulk diamonds. In addition, the distance of each SiV center from the surface in DNDs is not completely controlled by the detonation process. Therefore, the electronic states of the SiV centers vary, which results in inhomogeneous broadening in the PL spectrum obtained as an aggregate of SiV centers in DNDs.

The literature contains some reports on the optical properties of SiV centers in NDs, based on characterization using other methods.[24,31–34] Recently, Shimazaki et al. used a post-treatment method (high-temperature annealing at 1100 °C) to obtain DNDs with SiV centers.[34] Here, we compare the optical properties of two types of SiV centers in DNDs, where the SiV centers were formed using different fabrication methods. DNDs with SiV centers formed by a post-treatment exhibited a ZPL with a minimum linewidth of 7.7 nm and a luminescence lifetime of 0.4 ns. Because a post-treatment such as high-temperature annealing is known to dramatically decrease the inhomogeneous linewidth of SiV centers,[58] its linewidth might correspond to the homogeneous linewidth. The estimated values of the linewidth and luminescence lifetime are consistent with those of our SiV centers synthesized directly via the detonation process. Therefore, the two types of SiV centers in DNDs are affected by surface effects because of their very small particle size, and they exhibit similar optical properties except for inhomogeneous broadening, irrespective of the fabrication process. Although SiV centers synthesized directly inside DNDs are highly productive, they exhibit a relatively broad inhomogeneous linewidth.

3.2.6. Photostability of SiV Centers in DNDs

Finally, the photostability of SiV-DNDs is investigated. Photostability is an important optical property for materials used as fluorescent markers for bioimaging and sensing. In 2016, Reineck et al.[37] characterized the photostability of various fluorescent markers in detail by measuring their luminescence intensity over time. In their experiments, the fluorescent dye Alexa Fluor 647, Au nanoclusters, and carbon dots exhibited a decrease in luminescence intensity within a few minutes, whereas carbon nanotubes (CNTs) and NDs containing NV centers (NV-NDs) exhibited perfect photostability without fading. Figure 10 shows the normalized intensity of the ZPL of SiV centers, where the baseline has been removed. The intensity was normalized by the initial intensity (at 0 min). The SiV-DNDs exhibit stable luminescence with no decrease in intensity, similar to NV-NDs and CNTs.

4. Conclusion

SiV-DNDs with an average particle size of ≈10 nm were synthesized by a detonation process and investigated spectroscopically. The optical properties related to their electronic states were compared with those of typical SiV centers in bulk diamond. In the case of SiV centers in DNDs, the homogeneous and inhomogeneous broadening of the ZPL is greater than that for typical SiV centers. Broadening of the ZPL absorption band is also observed in the PLE spectrum. Moreover, the DWF and luminescence lifetimes of the SiV centers in the DNDs are smaller than those of typical SiV centers by ≈70% and 50%, respectively. These optical properties originate from the inherently small particle size of DNDs fabricated by the detonation process. The extremely small size of ≈10 nm causes an increase in the nonradiative transition probability and enhancement of electron–phonon coupling because of the significant surface effect of the SiV centers. Moreover, under the influence of the surface effect, the energy...
levels of each SiV center fluctuate. The variation of the SiV centers gives rise to inhomogeneous broadening of their ZPL. However, the photostability of the SiV centers does not change even when the particle size is extremely small. These fundamental optical properties and understanding of their origin are expected to accelerate the application of SiV-DNDs.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Data Availability Statement**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Keywords**

detonation nanodiamonds (DNDs), detonation process, photoluminescence, silicon-vacancy center (SiV center), time-resolved spectroscopy

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