Quantitative Analysis of Spectral Characteristics and Concentration of Ensembles of NV⁻ Centers in Diamond

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Abstract: On account of their outstanding photo-luminescence properties, NV⁻ (Nitrogen-vacancy) centers in diamond make possible the high-sensitivity detection of physical quantities. The concentration of NV⁻ centers is one of the main factors that affect the sensitivity in detecting macroscopic physical quantities. This paper studied and analyzed the relationship between the dose of electron irradiation and the concentration of NV⁻ centers. We found that after electron irradiation into diamond, luminescence centers of 524.7 nm, 541.1 nm, 578 nm and 648.1 nm were formed, which is necessary for producing NV⁻ centers. After annealing at high temperature ($\geq 800\text{ }^{\circ}\text{C}$) and in vacuum ($\geq 10^{-7}\text{ Pa}$) on diamond, NV⁻ centers were formed when vacancies were bound by nitrogen atoms. We also obtained the rules of NV⁻ concentration as a function of electron irradiation, which followed Boltzmann distribution. In addition, the number of NV⁻ produced by electron injection was limited by 16 ppm for diamond with a nitrogen content of 100 ppm regardless of the increment of vacancies concentration. This study is the basis of quantitative preparation of NV⁻ centers, and further lays a foundation for the application of NV⁻ centers to the precise measurement of macroscopic physical qualities.

Key words: NV⁻ centers, Fluorescence spectra, Electron irradiation, Concentration

1 Introduction

A variety of lattice defects are commonly found in diamond crystals [1-3]. Nitrogen vacancy (NV) defects in diamond which are caused by nitrogen impurities

exist in two forms: neutrally charged centers (NV^0 centers) and negatively charged centers (NV^- centers)^[4]. NV^- centers have attracted much attention in recent years due to their good stability, long coherence time of electron spin, and capability of being controlled by laser and microwave pulses^[5,6]. The utilization of single NV^- centers can realize high sensitivity nanoscale and macroscopic detection of physical quantities. Notably, high-density ensembles of NV^- centers are the prerequisite of improving the sensitivity^[7]. Take magnetic detection as an example, magnetic detection with ensembles of NV^- centers under ambient condition can theoretically achieve sensitivity as high as that of a superconducting quantum interference device^[8]. The solid-state nuclear magnetic resonance (NMR) gyroscope^[9] based on Berry phase shifts in NV^- centers in diamond, which was introduced by M. P. Ledbetter et al., can realize angular rate measurement with an ideal sensitivity of $10^{-5} \text{ rad s}^{-1} \text{ Hz}^{-1/2}$ when the concentration of NV^- centers is $10^{18} / \text{cm}^3$ ^[10].

Vacancies in diamond with high nitrogen content can be obtained by the irradiation of high-energy particles (such as electrons and neutrons)^[11], and accordingly NV^- centers in diamond can be produced by subsequent annealing in vacuum at a temperature of above **700 °C**^[12]. Particle irradiation is an appropriate means of introducing defects in a predetermined manner^[13,14]. In early irradiation experiments, heavy particles like neutrons are adopted^[15], but defects introduced by the irradiation of heavy particles are relatively complex, which may produce mono-vacancy, bi-vacancy and even larger vacancy clusters, thus bringing great difficulty in control. In contrast, defects introduced by electron irradiation are relatively simple^[15]. High-energy electron irradiation can produce a great many vacancy defects, and the vacancies are more uniformly distributed. With different doses of electron injection, NV^- centers with different concentrations can be produced^[16]. T. Nobauer et al.^[17] created dense ensembles of NV^- centers in diamond by neutron and electron irradiation. They concluded that highest densities of NV^- at neutron fluences on the order of 10^{17} cm^{-2} and electron doses of 10^{18} cm^{-2} , with spin resonance linewidths of 6 MHz. They also obtained that lower electron energies increase the ratio of centers in the desired negative charge state to those in the neutral one. Annealing at **900 °C** during the irradiation reduces the spin resonance linewidth, which is very useful for in hybrid quantum systems and magnetometry. However, few research was focused on the concentration estimation of NV^- centres which is critical on sensitivities for quantum sensors.

This paper mainly studied the preparation and the concentration measurement of NV^- centers in type Ib diamond. Through injection of different doses of electrons into diamond and subsequent annealing, NV^- centers with different concentrations were obtained^[18]. Meanwhile, the spectra characteristics of NV^- centers with different concentrations were represented through Raman spectrometer, and the relationship

between the concentration of NV⁻ centers and the dose of electron injection was further explored, which was of significance to controllable preparation of NV⁻ centers with different concentrations. Finally, the rule of NV⁻ concentration as a function of vacancy contents was quantitatively described in the letter. The study lays a foundation for the application of NV⁻ centers in the field of macroscopic detection.

2 Experimental Details

Type Ib diamond samples used in the experiments are high-pressure high-temperature (HPHT) synthetic diamond purchased from Sumitomo Electric, with a nitrogen content of approximately 100 ppm. The dimension of each diamond is 1.4 mm×1.4 mm×1 mm, and the polished surface is <100>. The lattice constant of the diamond is 0.357 nm^[19]. Each unit cell contains 8 carbon atoms, whose content is $8/a^3 = 1.76 \times 10^{23} \text{ cm}^{-3}$. As a result, the atom content in diamond with a nitrogen content of 1ppm is correspondingly $1.76 \times 10^{17} \text{ cm}^{-3}$.

Electron irradiation was performed using high energy electron accelerator on 4 diamonds with the number of S₁, S₂, S₃ and S₄, respectively, and the irradiation dose and energy is shown in Table 1. During irradiation, the diamonds were placed in a home-made water-cooled copper cup, which could ensure that the temperature of the diamond samples was less than 100 ppm, so as to reduce carbon-vacancy recombination^[20]. The duration of irradiation was 2s, 1 h, 2 h, and 3 h, respectively. After the irradiation, the samples were sealed in homemade vacuum quartz tubes (see Fig.1) to be subjected to thermal annealing at 850 °C in vacuum ($1 \times 10^{-7} \text{ Pa}$) for 2 hours in annealing furnace.

Table 1. Parameters for Electron Injection on Diamonds.

Sample	Irradiation dose (e ⁻ /cm ²)	Irradiation energy (MeV)
S ₁	2×10^{14}	7 MeV
S ₂	1.58×10^{17}	10 MeV
S ₃	3.15×10^{17}	10 MeV
S ₄	4.74×10^{17}	10 MeV

The fluorescence and Raman spectroscopy of the diamond samples were

measured utilizing Renishaw's inVia Raman spectrometer. The laser wavelength of the spectrometer was 514.5 nm, and the power was 5 mW. The exposure time was as long as 10 s. For this spectrometer, the fluorescence spectra as a function of the Raman spectra in diamond is given by^[21]

$$\lambda_{PL} = \frac{1}{\frac{1}{\lambda_{laser}} - \nu_{Raman}} \quad (1)$$

In this equation, ν_{Raman} is the position of the Raman scattering peak, λ_{laser} is the wavelength of laser, and λ_{PL} is the fluorescence wavelength corresponding to the position of the Raman scattering peak.

3 Results and Discussion

(1) Homogeneity of Diamonds

Type Ib diamonds are yellow due to their high nitrogen content. During injection of high-energy electron beams into diamonds, electrons could thoroughly penetrate through the diamonds and inelastically collide with carbon atoms in diamond lattices because the irradiation energy (7 MeV) of the electron beams was much higher than the that of C-C bonds (approximately 97 keV)^[22] in diamonds. Consequently, atoms in the diamond lattices run away from the original positions, and defects like self-interstitials and vacancies were formed in the diamond crystals^[23]. As a result, the diamond became darker in color after being subjected to electron irradiation, as shown in Fig. 1(a). Since the penetration depth of electrons in diamond (10 mm@7 MeV, 15 mm@10 MeV)^[24] was much larger than the sample thickness (1 mm), energy was assumed to be uniformly deposited in diamond, and produced vacancies were relatively uniform.

A Thorlab Optical Coherence Tomography (OCT) imaging system was adopted to detect the homogeneity of the diamond before and after irradiation. The scales as both diamond are 3000 times. During the measurements, the diamonds was placed at an inclination of 10 degrees when scanning, so as to reduce the specular reflection caused by the roughness of the diamond surfaces. Fig. 1(b) shows the homogeneity of the side view of S₄ marked in dotted black lines before (left) and after (right) irritation of electron beam. From this image, it can be seen that the side surfaces of the diamond were comparatively rough, and the lateral boundaries of the diamond is visible clearly. Besides, there is no obvious changes occurred before and after electron irradiation, which reflects that the internal structures of S₄ were stable and uniform. Diamonds of S₁, S₂ and S₃ shows the similar homogeneity properties to S₄ after electron irradiation.

Fig.1. Photography (a) and homogeneity (b) of Diamond S₄ Before and After Electron Irradiation.

(2) Fluorescence Spectroscopy of NV⁻ Centers in Diamond

The fluorescence spectrum of diamond of S₀ without irritation and annealing is shown in Fig. 2(a). Fig. 2(b) shows the spectrums of S₁, S₂, S₃ and S₄ after electron Irradiation but without annealing which is marked in pink, blue, red and black lines, respectively. The irradiation duration for S₁, S₂, S₃ and S₄ is 10 s, 1 h, 2 h and 3 h, respectively. Fig. 2(c) is the spectrums of all the diamond after annealing which is marked in lines of S₁, S₂, S₃ and S₄, respectively. The annealing duration is 2h for all the samples. The infrared spectrum of diamond S₄ is measured and given in Fig. 2(d).

In Fig. 2(a), an intrinsic Raman peak in 552 nm wavelength, which accounts for the diamond carbon content, occurred only in diamond without any treatment.

In Fig. 2(b), the peaks of 552 nm are still obviously visible for S₁, S₂, S₃ and S₄, which is the intrinsic peaks of the diamonds. Further, there exist strong and wide phonon sidebands (PSBs) at a position around from 560 nm to 630 nm after electron injection for samples S₂, S₃ and S₄. In contrast, this band cannot be visible in the spectrum of S₁. In addition, intensity of PSBs dramatically increased with the irradiation extend. These PSBs were generated by various nitrogen-vacancies^[25], which has features of high vibrational coupling capacity, and generally induces strong and wide PSBs. Interestingly, the similar phenomena happened for the spectrum peaks at 524.7 nm and 541.4 nm of diamond samples S₂, S₃ and S₄; while, these peaks cannot be visible in the spectrum of S₁. Incidentally, the energy band between 541.4 nm and 524.7 nm is corresponding to 72.9 meV.

Origin of the peak at 523.7 nm has been explained by some researchers but

cannot reach the final conclusion. K. Y. Wang et al found that this peak was commonly existed in HTHP synthetic diamond after electron irradiation^[26]. Zhang et al maintained that the generation of the peak was due to defects formed by nitrogen-centric impurity interstitial atoms^[27]. In our experiment, due to the instrument calibration and temperature, peak at 523.7 nm shifts to 524.7 nm. This peak increases with the increment of electron injection doses and disappeared after annealing at temperature of 850 °C (Fig. 2(c)).

A peak at 648.1nm occurred only in sample S₄ after irradiation, of which the electron injection dose was the greatest. This peak will disappear after annealing, and was caused by interstitial atoms. The inset shows the fluorescence spectrum as a function of the wavelength from 630 nm to 670 nm. Interestingly, two accompanying peaks existed at 637.7 nm and 658.8 nm, both of which wavelength differences between 637.7 nm are 31 meV, respectively. Besides, the energy values corresponding to the peaks at 637.7 nm, 648.1 nm and 658.8 nm are 1.9457 eV, 1.9145 eV and 1.8834 eV, respectively. The source of the two peaks was due to the Stokes/anti-Stokes vibration of the lattices between 637.7 nm/658.8 nm and 648.1 nm, respectively.

The peak at 681.1 nm of S₄ in Fig. 2(b) was aroused, while for S₁, S₂ and S₃, this peak at 681.1 nm cannot be observed. In consideration of the energy band for defect lattice between 681.1 nm and 648.1 nm of 92.7 meV, which is smaller than that of the maximum displacement energy (165 meV)^[28] of diamond phonons, this peak is the the phonon replica of the defect at 648.1 nm. Similarly, the peak at 723 nm existed in S₄ but disappeared in S₁, S₂ and S₃ due to the local vibration mode of the center at 648.1 nm, what is because the energy band of the peak away from the 648.1 nm center was 198 meV, was greater than that of the maximum displacement energy (165 meV) of diamond phonons.

In Fig. 2(c), the spectrum of S₁ is amplified by 1000 times marked in pink line in Fig. 2(c). Compared S₁ to the other samples, it shows that the intrinsic peak of diamond became relatively weaker in the fluorescence spectrum after electron irradiation and annealing because of the scale. Notably, a sharp emission peak become obviously increased at 637.3 nm after annealing for S₂, S₃ and S₄, where the zero-phonon line (ZPL) of NV⁻ centers was located. Further, the wide PSBs of NV⁻ centers ranging from 650nm to 850 nm were visible in the spectra in blue, red and black lines. Besides, intensity of PSBs dramatically increased with increasing of the irradiation powers for S₂, S₃ and S₄, respectively. And the intensity for S₂, S₃ and S₄ reached maximum at approximately 700 nm. All the results show that assemble NV⁻

centers was successfully fabricated after electron irradiation and annealing process. Notably, PSBs of NV^- centers were quite wide, and their fluorescence intensity was larger than that of the NV^- ZPL as shown in Fig. 2(c)^[29]. In addition, origin of the peak at 662.1 nm is still not clear and needed to be further understood.

In principle, the NV^0 ZPL peak should be aroused at 575 nm; whereas it cannot be detected in our measurement in Fig. 2(c). Possibly, NV^- centers take a large concentration, and contents of NV^0 centers was too small to be detected in the fluorescence spectrum. Considering the different conditions compared to that in Ref. [20], another possibility of invisible of the NV^0 ZPL peaks in diamond from Sumitomo is due to the short time and high energy during irradiation in our experiment.

In order to verify whether the crystalline form of the diamond after electron irradiation and annealing was modified into amorphous carbon, the infrared spectrum of diamond S4 was tested using Fourier Transform Infrared Spectroscopy (FT-IR) Microscope (Nicolet iN10) with the wavelength sweep from 500 nm to 3000 nm, as shown in Fig. 2(d). Peaks of 2030 cm^{-1} , 2160 cm^{-1} and 2350 cm^{-1} were available which suggests that the diamond wasn't modified into amorphous carbon after electron irradiation and subsequent annealing, because Eigen frequencies of diamond in infrared spectra lied between 1500-2680 cm^{-1} . Besides, the spectral peaks at 1130 cm^{-1} and 1344 cm^{-1} present in Fig. 2(d) was associated with the localized vibrational modes of C-N bonds^[30]. In addition, the fluorescence generated by NV^- centers in diamond after electron irradiation and subsequent annealing was increasing, and the intrinsic peak of diamond became weaker.

Fig.2. Fluorescence Spectrogram of NV centres in Diamond. (a) Pure Diamond. (b) After Electron Irradiation and before Annealing. (c) After Annealing for S_2 , S_3 and S_4 . (d) The infrared spectrum of diamond S_4 .

3.3 Concentration of NV⁻ Centers

Quantitative analysis of a substance can be realized by Raman spectroscopy. If the detection direction is perpendicular to that of the laser incident, the Raman scattering peak intensity I_R collected is given by^[31]

$$I_R = (I_L \sigma k) P c, \quad (2)$$

wherein, I_L , σ , k represent the laser intensity, the absolute Raman scattering cross section, and measurement constant (such as the optical collection efficiency, the optical transmission of the Raman spectrometer, and the field effect of the sample), respectively. P and c represents the optical path length, and the concentration of the samples, respectively. Under the same experimental conditions, if substances with different concentrations have the same values of I_L , σ , P and k , the Raman scattering peak intensity I_R is proportional to c . Namely, substance concentration c can be obtained from I_R .

Multi-point measurements were performed on the diamond samples S_2 , S_3 and S_4 , and the obtained intensities of NV⁻ Raman scattering peak (3755 cm^{-1}) were 2625.77, 5991.28 and 10837.8, respectively. Consequently, intensities of NV- Raman scattering peak as a function of Raman shift were shown in Fig. 3 for S_2 , S_3 and S_4 .

Fig. 3 Raman Spectra of Diamond (after calibration).

We estimated that the production rate of vacancies was approximately 2.9 vacancies/e⁻/cm at **7 MeV** and 3.4 vacancies/e⁻/cm at **10 MeV** according to Ref. 23. And the concentration of vacancies V (ppm) produced by electron injection can be calculated as $V = (\mu * e) / (1.76 \times 10^{17})$. Where, μ represents the yield of vacancies after electron injection, e represents the electron injection dose.

Therefore, the variation of Raman scattering peak intensity of NV⁻ centers as a function of vacancies concentration of V is calculated and shown in Fig. 4 by the curve (1), which reflects that the concentration of NV⁻ centers grows exponentially as V increases. Accordingly, the concentration variation of NV⁻ centers as a function of V was also obtained, as shown in Fig. 4 by the curve (2) and summarized in Table 2. From Fig. 4, vacancies with the concentrations of 5ppm diamond with a nitrogen content of 100 ppm could produce NV⁻ centers of **0.3 ppm**^[20], and the corresponding intensity was 4790.34 in Fig. 4.

Fig. 4 Concentration of NV Centers Estimated for S₁, S₂, S₃ and S₄.

Table 2 Concentration of NV Centers.

Sample	V(ppm)	NV ⁻ (ppm)
S ₁	3×10 ⁻³	≈ 10 ⁻⁴
S ₂	3	≈ 0.16
S ₃	6	≈ 0.38
S ₄	9	≈ 0.68

The concentration of NV⁻ centers as a function of vacancies as high as 100 ppm was estimated in points in Fig. 5, which was fitted by exponential function in dotted line, and Boltzmann distribution in blue line. The equation, obtained by Boltzmann distribution fitting, is given by

$$N_{NV^-} = 16.04193 - \frac{16.67504}{1 + e^{(V-38.29)/11.846}} \quad (3)$$

Where, N_{NV^-} indicates the concentration of NV⁻ centers, and V is the yield of vacancies generated by electron injection.

From these curves and Eq. (3), the concentration firstly tended to grow exponentially with increase of vacancies, which is consistent with the dotted line of exponential growth, only when the vacancy contents was less than 40 ppm. When the vacancy content was half (about 50 ppm) of the nitrogen content in diamond, it tended to negative exponential grow slowly. And it became almost stable when the vacancy concentration was greater than 100 ppm.

From Eq.(3), we can get the minimum detectable NVs concentration is given by

$$\frac{d(N_{NV^-})}{dx} = \frac{b \cdot e^x}{(1 + e^x)^2}, \quad (4)$$

here, $a = 16.04193$, $b = 16.67504$, and $x = (V - 38.29) / 11.846$,

$$\delta(N_{NV^-}) = \frac{d(N_{NV^-})}{dx} \cdot \delta x = \frac{b \cdot e^x}{(1 + e^x)^2} \delta x, \quad (5)$$

When $V = 0$, $x_{\min} = -38.29 / 11.846 = -3.23$. $\delta x = \delta V \approx 10^{-4} \text{ ppm}$ from Tab. 2.

Take the parameters into Eq. (5), we get

$$\begin{aligned} \delta(N_{NV^-}) &= \frac{b \cdot e^x}{(1 + e^x)^2} \delta x = \frac{16.67504 \times e^{-3.23}}{(1 + e^{-3.23})^2} \cdot 10^{-4} \\ &= 0.61 \times 10^{-4} \text{ ppm}. \end{aligned}$$

Therefore, it can be seen that the minimum detectable NVs concentration is $0.61 \times 10^{-4} \text{ ppm}$ using fluorescence method.

This Equation can give a predicts of NV^- centers concentration in diamond with a nitrogen content of 100 ppm generated by high-temperature annealing in vacuum under different electron injection doses. From this equation, it can be concluded that the maximum yield of NV^- centers generated in diamond with a nitrogen content of 100 ppm is about 16ppm when the yield of vacancies is smaller than 120 ppm.

This finding is supported by Ref. 9, in which type Ib diamond with a nitrogen content of about 100 ppm was adopted. In their research, the contents of NV^- centers of approximately at 10 ppm and 16 ppm were obtained by yields of vacancies were 45 ppm and 110 ppm, which is consistent well with that of Eq. (3).

Diamond with different nitrogen contents may finally produce NV^- centers with different concentrations^[20] even when the electron injection doses and the experimental conditions are the same. Therefore, the concentration estimation of NV^- centers using this method is only applicable to the situation of the diamond with high density nitrogen under high temperature and high pressure (HTHP) process.

Fig.5 Variation of Concentration of NV^- Centers along with Vacancies Generated by Electron Irradiation.

4 Conclusion

In conclusion, we have explored the effect of electron injection doses on the concentration of NV^- centers and introduced a concentration definition method for determining NVs. ~~In conclusion, a concentration definition method of NV^- centers in diamond was investigated in this research. And influence of electron injection doses on the concentrations of the NV^- centers was also explored.~~ Firstly, we found that the concentrations of NV^- centers and the dose of electron injection followed Boltzmann distribution, and the number of vacancies produced by electron injection was limited by 120 ppm ($2.1 \times 10^{19} \text{ cm}^{-3}$) for diamond with a nitrogen content of less than 100 ppm. Therefore, when diamond with a nitrogen content of 100 ppm was subjected to irradiation of 10 MeV high-energy electron beams and the injection dose was $10^{18} \text{ e}^-/\text{cm}^2$, the concentration of the finally produced NV^- centers was about 16 ppm.

Further, the changes in the fluorescence spectra of diamond before and after annealing showed that some unstable defect centers disappeared after annealing at 800°C in vacuum which was due to the movement of interstitial atoms. This study provides a rule for the accurately quantitative preparation of NV⁻ centers by utilizing diamond, and further lays a foundation for the application of NV⁻ centers to the precisely measurement of macroscopic physical qualities measurement.

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Graphical abstract

Variation of Concentration of NV –Centers along with Vacancies
Generated by Electron Irradiation.