Advances in Nitrogen-Vacancy color centers in diamond for magnetometry: Advantages and Challenges

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https://doi.org/10.5109/7158033

出版情報：Proceedings of International Exchange and Innovation Conference on Engineering & Sciences (IEICES). 9, pp.417-422, 2023-10-19. 九州大学大学院総合理工学府
バージョン：

Advances in Nitrogen-Vacancy color centers in diamond for magnetometry: Advantages and Challenges

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Abstract: *Color centers in diamonds have promising and unique properties that can be optimized and engineered for several quantum-sensing applications. The negatively charged Nitrogen-vacancy (NV) center is one of the outstanding candidates due to its stable luminescence and spin features. It has a long coherence time that can be initialized and manipulated with high accuracy at room temperature. Nonetheless, many parameters, namely; nonradiative centers, complex defects, and nitrogen-based defect centers can severely affect the desirable properties of these NV centers. In this review, we highlight the recent advances of color center fabrication, parameters optimization, and current challenges to enhance these properties, with main focus on magnetometry applications.*

Keywords: NV centers; quantum sensing; magnetometry

1. INTRODUCTION

Recently, Nitrogen-vacancy in diamonds has attracted much attention due to its unique stability, photoluminescence, and spin properties. These properties can be initialized and measured with high accuracy at ambient conditions [1-3]. On the other hand, diamond is super stable material, so it is considered as an optimum hosting material to these color centers. Moreover, diamond is chemically inert, so it can be used in biomedicine sensing applications [4,5].

Diamond in its natural form, can be classified into several types depending on the impurities within the crystal structure. One of the most common defects in diamond is the Nitrogen atom that has almost the same size of carbon [6]. Figure 1 demonstrates the several types of diamonds and their related defects [7]. Nitrogen-vacancy color centers consist of a substitutional Nitrogen atom (also called C-center or P1-center) [8] and adjacent vacancy [9], missing carbon atom (also called GR1 center) as shown in Figure 2.

Nitrogen-vacancy can be excited in three different states with respect to its charge; neutral (NV^0), positively (NV^+), and negatively charged (NV^-) [10]. The negatively charged Nitrogen-vacancy is a promising candidate for applications due to its perfect spin properties such as stable charge state and long coherence time. On the other hand, many applications require a specific configuration and distribution of NV^-, such as high concentration is required for biomedical imaging applications [11]. Additionally, these color centers should be near to the surface of hosting diamond to enhance the imaging process because deep centers may produce less photoluminescence (PL) signal. NV centers also have many applications in quantum bits as single photon emitters and quantum communications. NV^- has a significant potential in quantum sensing applications such as quantum thermometry, electric field, pressure, strain, and AC/DC magnetometry in both single and ensemble NV^- forms [12]. Single NV^- shows a large coherence time as long as 2μs ensuring the high sensitivity [13]. additionally, ensemble of NV^- with high concentration may show less coherence time, yet it introduces a higher concentration of color centers that can enhance the functionality of the sensing process as discussed in the article.

The rest of our article is organized as follows: in section 2 we demonstrate the fabrication mechanisms of NV centers in diamond starting from the native color centers formation during the deposition process to the implantation of nitrogen into pure diamond grains and introducing the vacancies to the nitrogen-rich diamond plates. In section 3 we discuss the applications of NV centers in AC and DC magnetometers and the parameters that control these applications. In section 4 we illustrate the limitations and challenges of the current techniques and protocols and provided some proposed solutions to enhance the sensing process. Finally, in the conclusion we summarized the major points that have been illustrated and highlighted in the focus of this review article.

2. Formation of NV centers in diamond

Formation of NV centers in diamond can be obtained through several mechanisms depending on the type of diamond plate in addition to desirable concentration and spin properties of NV centers [14]. For pure diamond, the concentration of nitrogen is relatively small. Nitrogen implantation can enhance this concentration and introduce the desired vacancies [15].

Additionally, vacancy creation can be performed by several mechanisms. Depending on the ion’s energy and fluence. When the ion with high energy collides with a carbon atom in the diamond lattice, the carbon is displaced and leaves a vacancy behind. Yet, if the energy

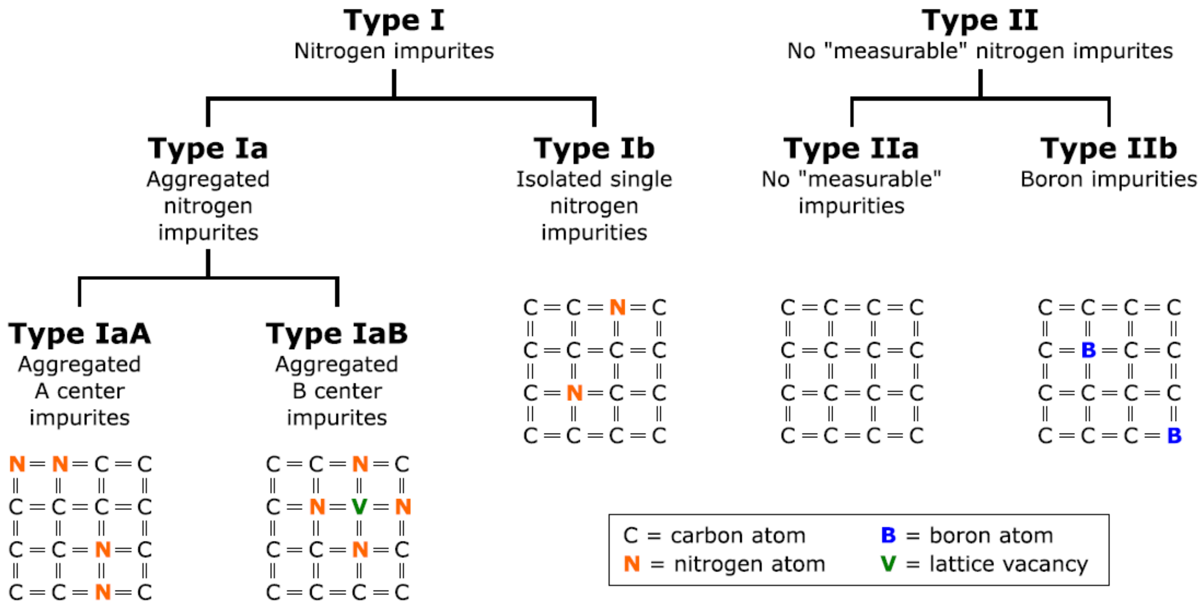

Figure 1. Represents the different classes of diamond depending on the type and concentration of impurities within the grains [copyrights permission from reference (7)].

of this ion was not high enough, the displaced carbon can move for a short distance away from its original position and recombine very fast [16].

Consequently, when the displaced carbon atom has enough energy, it can displace more atoms that make more vacancies. Indeed, there is a threshold damage cannot be excused because after this limit the diamond grains cannot be recovered or repaired during the post thermal annealing treatment. The depth profile and the vacancies concentration can be simulated for optimizing the irradiation does depending on the irradiating ion and energy. Figure 4 illustrates the number of vacancies created by electron irradiation with different energy. In addition, it also shows the maximum depth can be reached by the electron as a function of irradiation energy [17].

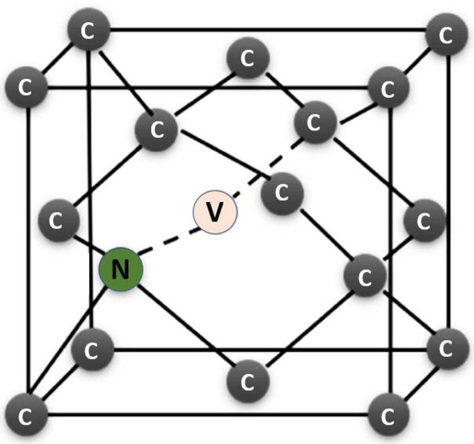

Figure 2. Illustrates the crystal structure of NV center consists of a displaced carbon atom (vacancy) adjacent to substitutional N atom (P1-center).

2.1 Native NV centers fabrication

The first technique is directly constructing the NV centers in diamond lattice structure during the deposition process [18]. This technique can be used mainly in chemical vapor deposition (CVD) [19]. Yet, the resultant NV concentration in this case is very small (a few parts per billion) and many applications require high concentration of the color centers.

2.2 N ions implantation

For diamond plates with low nitrogen concentration [N] introducing the N atoms and vacancies required to create the NV centers can be performed by N implantation. Typical energy of implantation is a tens KeV is used to implement the N and create vacancies [15]. The depth profile of this process shows that N can go deep hundred nanometers down the surface. This limited depth helps to create the color centers near surface which is preferable for many applications. However, the damage occurred by the nitrogen ions is huge and negatively affects the crystal structure. On the other hand, the concentration of created color centers is limited and to enhance the concentration, the implantation energy or fluence should increase. This increase severely affects the hosting diamond and reduces the sensitivity [20].

2.3 Ion irradiation

For the Nitrogen-rich diamond, vacancies can be introduced through the irradiation of electrons, protons or even gamma-rays [11]. The concentration and depth profile of the created vacancies can be optimized by adjusting the irradiation energy and dose fluence. The most common irradiation process is electron irradiation which provides a homogeneous vacancy distribution that is suitable for many applications. Furthermore, subsequent thermal annealing is a keyword for NV^- formations [21]. Thermal energy makes the vacancies mobile and can be trapped by the existing P1-centers to form NV centers in the neutral charge state as shown in equation [1]. The temperature should be higher than 800 ºC to activate the NV center's formation.

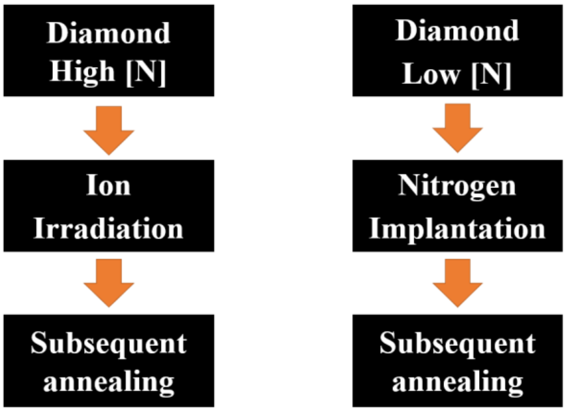

Figure 3. Schematic chart represents the most common techniques for NV centers formation in diamond. For the diamond plates with high [N] L.H.S, vacancies can be introduced by the ion irradiation followed by sufficient annealing recipe. For low [N], R.H.S, both nitrogen and vacancies can by introduced by N impanation that should also be followed by sufficient annealing as described inside the text.

Higher temperature can help the diamond lattice to recover from the damage caused during the irradiation process [22]. On the other hand, sufficient annealing can lead to removal the other undesirable defects that could be formed during the treatment that negatively affect the properties of NV^- centers such as N-based defects and vacancies clusters.

$$P1 + V^0 \rightarrow NV^0 \qquad \text{(i)}$$

The neutral NV center gets the negative charge from other near color center according to equation [2].

$$P1 + NV^0 \rightarrow NV^- + N^+ \qquad \text{(ii)}$$

Nevertheless, the conversion efficiency from P1 centers to NV centers is still limited compared to the desirable ratio [23]. Table 1 demonstrates an example of electron irradiation with energy of 3 MeV and different initial p1-centers concentration. The maximum reached conversion efficiency in this case is 16% which is considered a relatively high ratio compared to the recent results. Yet, this result shows that further investigations should be done in order to enhance the conversion rate [24].

On the other hand, the residual P1 centers have a negative effect on the spin properties of the NV. P1 centers severely affect the coherence time and dephasing time of the NV centers. Therefore, many applications require a high concentration of NV centers, and to increase the concentration of the NV centers, within the limit ratio of conversion, the initial P1 centers must be high. This P1 concentration. From this point of view, fine tuning the whole parameters such as P1 concentration, vacancies fluence and annealing recipe may lead to optimizing the concentration of NV centers along with their spin properties.

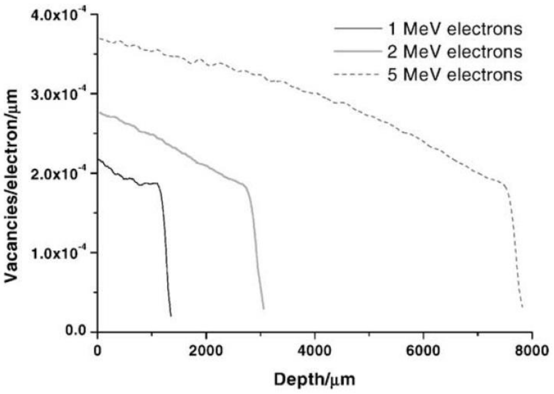

Figure 4. The number of created vacancies due to electron irradiation with 1, 2, and 5 MeV [copyrights permission from reference (17)].

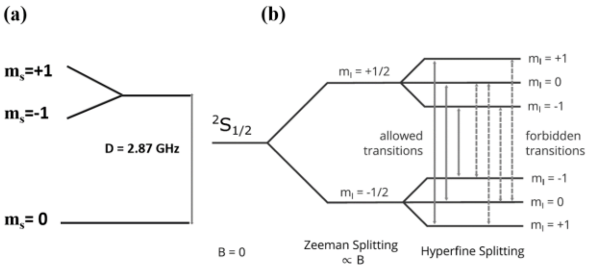

Figure 5. (a) represents the energy levels diagram for NV centers with zero filed splitting (D=2.87 GHz between m_s= 0 and $m_s = \pm1$. The $m_s = \pm1$ levels experience Zeeman shift in the existence of magnetic field B. (b) represents the p1-centers spin states with allowed transitions (solid lines) and forbidden transitions (dashed lines) [12].

Table 1. The first column represents the electron irradiation energy in (MeV), second column represents the final concentration of negatively charged NV centers, and the third column illustrates the conversion efficiency from the initial P1-centers to NV [24].

E (MeV)	NV (ppm)	Conversion efficiency (%)
3	0.06	2
3	0.16	1.6
3	0.24	2.5
3	0.54	5.4
3	0.75	7.5
3	11.6	14.5
3	14.6	16

3. Magnetometry

Magnetometry is measuring the magnitude and direction or a projection of a magnetic field. Therefore, negatively charged NV centers have spin-1 triplet spin states in the ground state electronic structure. These ground states can be split into singlet spin state projection m_s = 0 and doublet $m_s = \pm1$ separated by D = 2.87 GHz with zero bias magnetic field [25, 26]. Magnetic field sensing by NV centers depends on the Zeeman splitting of the spin states. Figure 5 illustrates the Zeeman splitting for NV^- and P1-ceters that proportional to the magnetic field B [12].

Equation 3 [27] shows the sensitivity of dc magnetometry as a function of NV^- concentration (N) and dephasing time T_2^* , and the sensitivity of ac magnetometry as a function on N and the coherence time T_2.

$$\eta_{DC} \propto \frac{1}{\sqrt{N\,T_2^*}} \quad , \quad \eta_{AC} \propto \frac{1}{\sqrt{N\,T_2}} \qquad \text{(iii)}$$

Consequently, enhancing the concentration of color centers in addition to dephasing/coherence time will lead to better sensitivity. However, as discussed before, increasing the concentration of NV centers requires increasing the P1-centers in diamond that affect the dephasing time and coherence time for dc and ac magnetometry respectively.

Thus, to emphasize the impact of these parameters (as indicated in Table 2) on the sensitivity we will discuss the dephasing time in deep detail [7]. We can roughly express the dephasing time as follows.

$$\frac{1}{T_2^*} \sim \frac{1}{T_2^*(e)} + \frac{1}{T_2^*(n)} + \frac{1}{T_2^*(S)} + \frac{1}{T_2^*(E)} + \frac{1}{T_2^*(T)} + \frac{1}{T_2^*(other)} \qquad \text{(iv)}$$

Table 2. Parameters' indication of Dephasing time equation.

$\frac{1}{T_2^*(e)}$	Represents the dephasing from the electronic spin bath including the NV^- centers and P1-centers.
$\frac{1}{T_2^*(n)}$	The dephasing due to nuclear spin path and mainly occurred due to ^{13}C isotope.
$\frac{1}{T_2^*(S)}$	The dephasing due to internal strain and strain degradation within the diamond lattice
$\frac{1}{T_2^*(E)}$	Electric field variation dephasing
$\frac{1}{T_2^*(T)}$	Dephasing caused by the temperature degradation.
$\frac{1}{T_2^*(other)}$	The dephasing of other related factors can contribute in case of absence of the first mentioned parameters

Equation 4 shows the basic parameters that affect the dephasing process. First, the electronic spin path dephasing is controlled by the paramagnetic defects within the diamond lattice. The magnetic dipole interaction between NV^- and other defect centers in addition to special inhomogeneity and random orientation leads to dephasing of NV^- centers. The effect of electronic spin path is a combination of mainly three parameters P1-centers, NV^0, and NV^-. The P1-centers are fundamental component to fabricate NV^- defects and as discussed before the conversion efficiency from P1 to NV can reach up to 25%. The residual P1 (has a spin state of S = ½) contribute to the dephasing mechanism. Moreover, the existence of NV^- cannot be occurred in absence of NV^0 defects (also has a spin state of S = ½). Finally, when the concentration of the NV^- increases, the NV^-_ NV^- mutual interaction also contribute to the dephasing process [28].

On the other hand, the effect of nuclear spin path is due to the interaction between the ^{13}C isotope which has a nuclear spin (S = ½) and the NV^-. ^{13}C isotope natural concentration represents about 1.1% equivalent to 10700 ± (800) ppm. Being a natural abundance, reducing the concentration of ^{13}C isotope is not practically convenient. Yet, the effect of ^{13}C isotope dominates in case of pure diamond / low nitrogen concentration, typically [p1] < 0.4 ppm. When the nitrogen concentration increases, the effect of nuclear spin path can be ignored due to the dominantly of P1-centers [13].

The other effects, strain, and electric field degradation may have occurred during the posttreatment process such as ion irradiation / implantation. These parameters can be minimized by enhancing the diamond plate quality or sufficient thermal annealing at T=1800 °C [29].

4. Limitations and challenges

The sensing process depend on several parameters starting with the quality of the diamond plate and the initial defects that exist within the grains. The initial concentration of P1-centers which is the basic ingredient in fabricating the NV centers also has a significant impact especially due to the limited conversion efficiency. The irradiation or implantation can enhance the degradation of internal strain and affect the quality of a diamond. The basic limitations can be summarized as follows.

1- NV centers have a high sensitivity to magnetic field variation and this sensitivity depends on the distance between the magnetic field and the NV centers. For that reason, fabrication of NV centers on / near the diamond surface can help in optimizing this term [30].

2- NV^0 are contributing to the background noise since there is an intersection between the phono side band of the two defects, this limitation requires high NV^- / NV^0 ratio to enable efficient functionality [31].

3- Formation of nonradiative defects besides other complex defect centers affects the sensitivity of NV centers [32].

4- NV centers are limited to four different orientations, and all are equally probable to enhance the resolution and prevent the dead points. However, the spatial resolution of sensing using NV centers is limited to the nanoscale, and covering large is a complicated process [33].

5- The initialization and readout mechanisms by laser beam affect thermally the local positions of the diamond plate enhance the temperature degradation within the diamond and this degradation reduces the efficiency of magnetometry [34].

6- In biomedical imaging, diamond is chemically inert and typically biocompatible, however, the size of the diamond host should be within the nanoscale. So, NV centers in nanocrystalline diamonds are more applicable [5].

5. Conclusion

Nitrogen-vacancy color centers in diamond have a wide range of applications especially in nanoscale sensing. The formation of these color centers can be optimized based on the application objectives using N implantation into pure diamond or electron irradiation to the nitrogen-rich diamond plates. The fundamental input in this process is the nitrogen, nevertheless the conversion of P1-centers to NV is much limited. Consequently, the residual P1 reduces the sensitivity of sensing based on the NV centers. Moreover, nonradiative defects and other complex centers and the local strain occurred during the posttreatment also reduce the sensitivity. Higher sensitivity can be approached by using high quality diamond plates in addition to sufficient subsequent annealing that helps in repairing the damage within the diamond crystal structure. For the magnetometry, we discussed the parameters that control the efficiency and sensitivity of sensing including the dephasing time and the color centers concentration. We illustrated that enhancing the concentration of negatively charged NV along with optimizing the concentration of P1 can help in enhancing the sensitivity. For future work, there is a significant potential in using the color centers in diamond in a wide spectrum of applications. Yet, the approached sensitivity is much less than the theoretical limit which means that a deep understanding of the effect of controlling parameters and carefully engineering them will lead to enhancing the efficiency. On the other hand, optimizing the readout protocols can severely enhance functionality and reduce the setup-based scenarios that limit applications of these color centers.

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