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Chapter

Growth of Diamond Thin Film and Creation of NV Centers

Yaping Ma, Junbo Chen and Chenhui Wang

Abstract

Nitrogen-vacancy (NV) center is one type of special defects in diamonds. NV center not only can be used as sensors for temperature, stress detection, magnetic field, etc., but also has potential applications for quantum computing due to its unique physical properties. Therefore, the growth of diamond and creation of NV centers are significant for the future technologies. In this chapter, some methods for growing diamond thin film are introduced first, including traditional high-pressure-high-temperature (HPHT) and chemical vapor deposition (CVD) methods. The second part will focus on the current commonly used approaches to create NV centers. Inter-growth and post-growth processes are mainly utilized for the creation of NV centers during and after the growth of thin film, respectively.

Keywords: diamond growth, NV center, physical properties, high-pressure-high-temperature, chemical vapor deposition, growth mechanism, inter-growth, post-growth

1. Introduction

Diamond, composed of carbon elements, is an allotrope of graphene. Diamond, which is the hardest substance on earth, possesses high electron and hole mobility, the highest known thermal conductivity, extremely low thermal coefficient of thermal expansion, and a wide band gap and optical transparency window spanning from the near ultraviolet to the far infrared (IR), and chemical inertness, which make it a unique and desirable solid-state material for several forefront technological applications, especially in the quantum field [1, 2].

In 1963, it was discovered that diamond nanoparticles can be synthesized by the detonation of carbon-based explosives [2]. Since then, a new pathway has been opened to synthesize diamonds. High-temperature-high-pressure, chemical vapor deposition (CVD), and other methods for synthesizing diamond are being developed. It was not until 1965 that Dyer et al. discovered the nitrogen-vacancy center (NV center) with good optical properties and long coherence time of electron spin to rapidly push diamond to the research upsurge, including catalysis, biomedicine, quantum computing, etc [3]. The negatively charged NV centers in diamond have great potential applications in quantum sensing and quantum communication due to their unique long coherence time.

Nowadays, the method of synthesizing nitrogen-doped diamond has been developed rapidly. In the synthesis process of diamond, high-pressure-high-temperature (HPHT) and chemical vapor deposition methods will be introduced. After diamond synthesis, femtosecond laser, electron irradiation, and ion implantation methods can be used for nitrogen doping. However, the current approaches still cannot synthesize NV centers with high permutations. Not only that, the concentration of NV centers is not very high, and the coherence time is only on the order of milliseconds [4]. Therefore, we have to face a lot of challenges to overcome, and the NV centers still requires further studies.

2. Physical properties of NV center in diamond and their potential applications

The NV center is a unique defect in diamond, made up of a substitutional nitrogen atom (N) and a vacancy (V) at one of the closest neighboring sites of the diamond crystal lattice (**Figure 1a**) [6]. The neutral state NV0 and the negatively charged state NV⁻, which have extremely different optical and spin characteristics, are the two distinct varieties of this defect that have been discovered so far [7, 8]. Only the negatively charged state of the defect (NV⁻) is interesting for quantum computing and sensing, since it can provide a spin triplet ground level which can be initialized, coherently manipulated with long coherence time and readout by pure optical techniques. The followings will focus on the negative charge defect NV⁻ (denoted as NV center defect).

This C_{3v} symmetry defect behaves like an artificial atom nested in the diamond matrix and exhibits a broadband photoluminescence (PL) emission with a zero-phonon line at 1.945 eV ($\lambda_{ZPL} = 637$ nm), making it possible to detect individual NV center using optical confocal microscopy at room temperature [9, 10]. Furthermore, the NV centers exhibit perfect photostability without photobleaching or blinking, which can enable the construction of very reliable single-photon sources operating at room temperature and be applied in biology, where NV defects are used as fluorescent labels [11–13]. In addition, the ground level with a spin triplet state 3A_2 , whose sublevels are divided in energy by spin–spin interaction into a singlet state of spin projection $m_s = 0$ and a doublet $m_s = \pm 1$, separated by $D = 2.87$ GHz in the absence of a magnetic field, is a crucial characteristic of the NV center (**Figure 1b**). Here, m_s stands for the spin projection along the intrinsic quantization axis of the NV defect, which corresponds to the axis connecting the nitrogen and the vacancy ([111] crystal axis) [14]. The NV defect can be optically excited through spin-conserving transitions to a spin triplet 3E excited state, which is an orbital doublet with a zero-field splitting $D_{es} = 1.42$ GHz at room temperature, exhibiting the same quantization axis and gyromagnetic ratio as in the ground level [15]. After optically excited in the 3E level, the NV center can relax to ground level through two various transition routes, including the same radiative transition path producing a broadband red PL and another transition path involving non-radiative intersystem crossing (ISC) to singlet states (**Figure 1b**). Since non-radiative ISCs to the 1E singlet state are highly spin-selective, whereas optical transitions are mostly spin-conserving ($m_s = 0$), the shelving rate from the $m_s = 0$ sublevel is substantially less than those from $m_s = \pm 1$. Furthermore, the NV defect prefers to decay from the lowest 1A_1 singlet state toward the ground state $m_s = 0$ sublevel [16, 17]. Consequently, these spin-selective processes use optical pumping

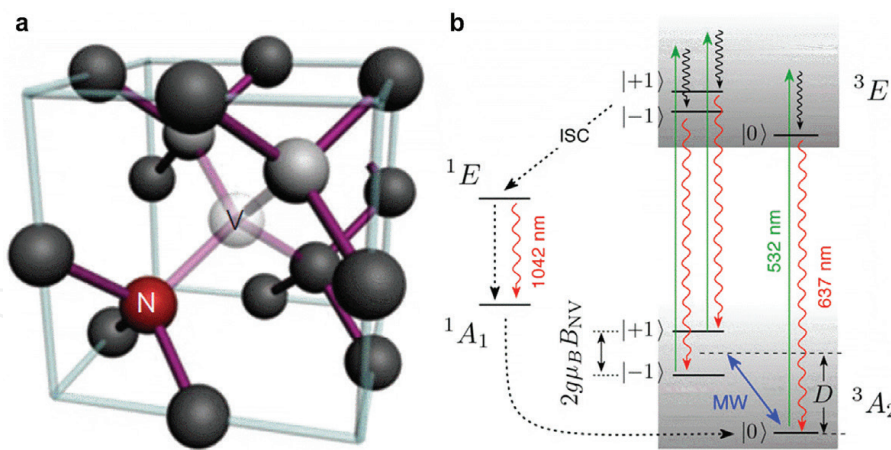


Figure 1. (a) Atomic structure of the NV defect in diamond. (b) Schematic diagram of energy levels in NV defect. Spin conserving optical transitions from the 3A_2 spin triplet ground state to the 3E excited state are shown with solid arrows. The dashed arrows indicate spin selective intersystem crossing (ISC) involving the singlet states 1E and 1A_1 . The infrared (IR) transition occurring at 1042 nm between the singlet states is also shown. Reproduced with permission from ref. [5]. Copyright 2014 IOP Publishing Ltd.

to achieve substantial electron spin polarization into $m_s = 0$. Moreover, due to the non-radiative ISCs, the PL intensity of the NV center will become higher when the state is $m_s = 0$ populated. Indeed, by providing a resonant microwave (MW) field, a single NV defect that was initially prepared in the $m_s = 0$ state by optical pumping can be driven to the $m_s = \pm 1$ spin state, leading to a decrease in the PL signal. This property has been widely applied recently in the context of diamond-based quantum information processing, where the NV defect is investigated as a solid-state spin qubit [18].

Neglecting the hyperfine interaction with nearby nuclear spins in the diamond lattice, the spin Hamiltonian of the level can be written as:

$$H = (hD + d^{\parallel} E_z) \left[S_z^2 - \frac{S(S+1)}{3} \right] + g\mu_B \mathbf{B} \cdot \mathbf{S} - d^{\perp} \left[E_x (S_x S_y + S_y S_x) + E_y (S_x^2 - S_y^2) \right] \quad (1)$$

where z is the NV defect quantization axis, h is the Planck constant, d is the ground triplet state permanent electric dipole moment, E is the electric field, μ_B is the Bohr magneton, $g \approx 2.0$ is the electron g-factor, B is the applied magnetic field, S is the electron spin operator, and S_x , S_y , and S_z are the Pauli matrices [20]. The axial zero-field splitting parameter D is ~ 2.87 GHz resulting from spin-spin interaction between the two unpaired electrons of NV defect [5]. The measured axial (d^{\parallel}/h) and non-axial (d^{\perp}/h) components of the ground triplet-state permanent electric dipole moment are $\sim 0.35 \pm 0.02$ and 17 ± 3 Hz cm V $^{-1}$, respectively [20]. In addition, the axial splitting parameter D is related to the temperature due to the combination effects of thermal expansion and electron-phonon interactions [19]. Therefore, the NV center in diamond offers unique possibilities to be employed as a nanoscale sensor for detection and imaging of magnetic fields, electric fields, and temperatures (**Figure 2**). For instance, the measurement principle for magnetometry applications of NV defect is comparable to that of optical magnetometers based on the precession of spin-polarized atomic gases [22]. The

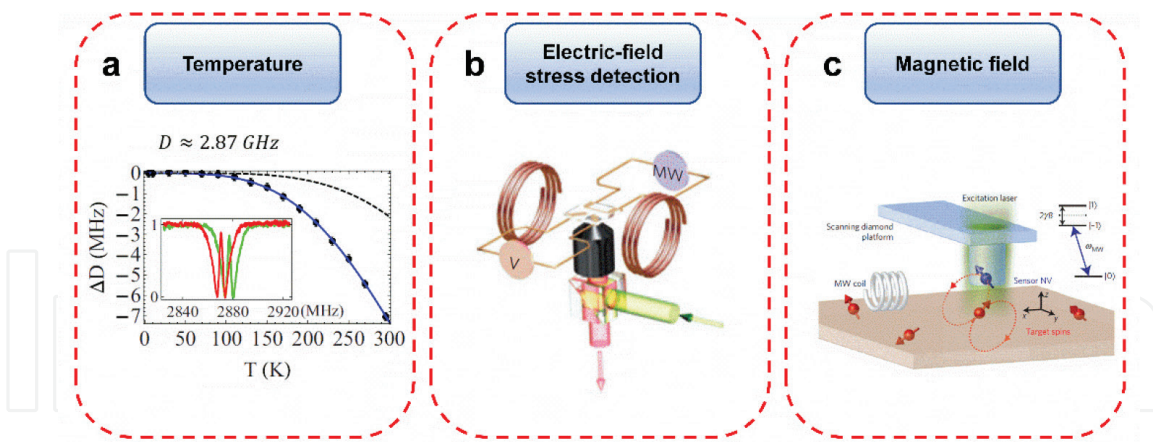


Figure 2.

The possible applications of NV defect in the detection or imaging of temperature, electric fields, and magnetic fields. (a) Reproduced with permission from ref. [19]. Copyright 2014 American Physical Society. (b) Reproduce with permission from ref. [20]. Copyright 2011 Nature Publishing Group. (c) Reproduced with permission from ref. [21]. Copyright 2013 Nature Publishing Group.

applied magnetic field is evaluated through the observation of Zeeman shifts of the NV defect electron spin sublevels. In fact, the Zeeman effect occurs when a magnetic field is applied near the NV defect, lifting the degeneracy of $m_s = \pm 1$ spin sublevels and causing the emergence of two resonance lines in the ESR spectrum. Therefore, a single NV defect can act as a magnetic field sensor with an atomic-sized detecting volume [23, 24].

Additionally, the NV defect in diamond holds great promise for quantum communication applications, and its special structure enables spin states to be measured at room temperature [25]. Weakness of spin-orbit coupling and high Debye temperature of diamond ensure long spin-lattice relaxation time for NV-electron spins, [26, 27] making NV defect in diamond a promising candidate for quantum computing and quantum communication. After a single NV center in diamond absorbs a photon (532 nm), NV center will relax to emit a photon (637 nm). Subsequently, the emitted photon can be captured to optically readout the spin state. After a certain period of time, the NV center is reset, allowing the aforementioned processes to be repeated. Therefore, the controlled generation of single photons based on NV defect in diamond is significant for applications in quantum communication [28, 29]. Moreover, room-temperature quantum entanglement with the lifetime of milliseconds between two single NV defect spins in diamond can be realized for the future room-temperature quantum device [30].

3. Growth methods of diamond

There are two commonly used methods to grow diamond crystals, including high-pressure-high-temperature (HPHT) and chemical vapor deposition (CVD) methods. The phase diagram of carbon in **Figure 3** demonstrates that diamond is stable in the HPHT region. The HPHT methods are carried out under conditions that are in the diamond region of the phase diagram, while the CVD methods are conducted under circumstances corresponding to the graphite phase.

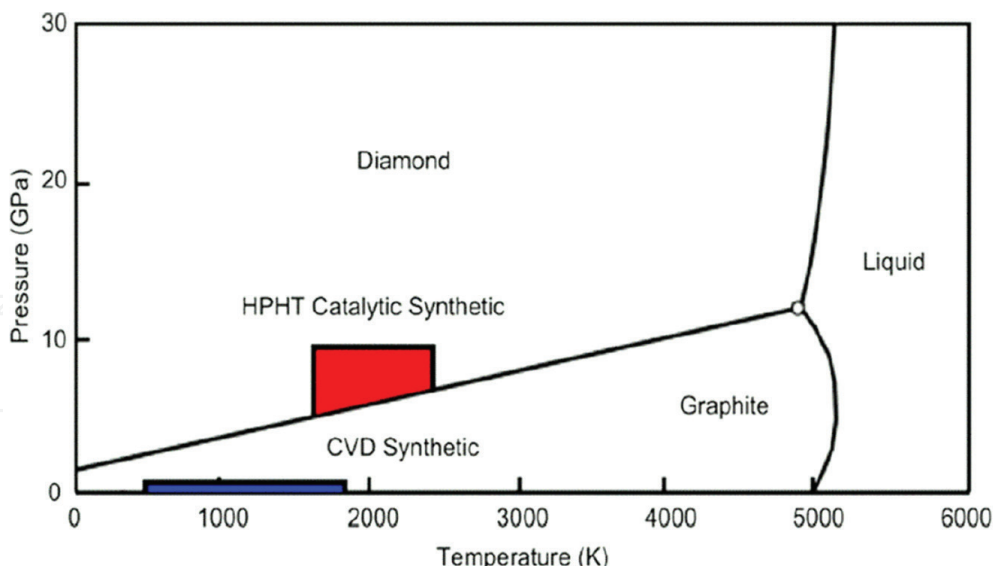


Figure 3. Phase diagram for carbon revealing the pressure and temperature regions with HPHT and CVD synthesis can occur. It is notable that CVD is a nonequilibrium process. Reproduced with permission from ref. [31]. Copyright 2020 American Chemical Society.

3.1 HPHT

Nature is the source of theoretical reference for cultivating diamonds under high-temperature and high-pressure environments. In fact, by placing diamond seed crystals in a high-temperature and high-pressure environment that simulates the formation of natural diamonds, the carbon atoms are adsorbed from the carbon source onto the seed crystals to grow diamond single crystals [32, 33].

Since Strong and Wentorf from G.E. company successfully grew large diamond crystals by temperature-gradient approach in 1971, [34] the growth technology of gem-quality diamond has gradually become mature and commercialized. HPHT methods can be categorized into the solubility-gradient, temperature-gradient, no-catalyst conversion, and shock compression approaches. In fact, HPHT methods are widely used to grow diamond in industry. In the solubility-gradient approach, diamond powders can be prepared by solving graphite in a molten metal (Fe, Ni, or Co, etc.) under HPHT conditions [35]. However, it is difficult to prepare high-quality single-diamond crystals with dimensions greater than 1 mm by the solubility-gradient approach. The temperature-gradient approach to grow large diamond crystals is illustrated in **Figure 4**. First, the carbon source is usually placed at high temperature, and the crystal seed is placed at low temperature. The growth process of diamond single crystals is the dissolution and recrystallization of diamond. As the carbon concentration in the solvent metal catalyst depends on the temperature, there is a temperature difference (20–50°C) between the high-temperature and the low-temperature ends, which causes the carbon to diffuse from the high-temperature end to the low-temperature end and precipitate on the crystal seed, leading to the epitaxial growth of the diamond crystals [34, 36]. However, in the production process at high temperature and high pressure, a very critical step is to stimulate the carbon source such as graphite and other materials required for diamond growth to release free carbon atoms. Under normal conditions, this can only be achieved at a temperature of 2000°C and the pressure of several MPa, which is much more stringent than the natural diamond formation conditions in nature.

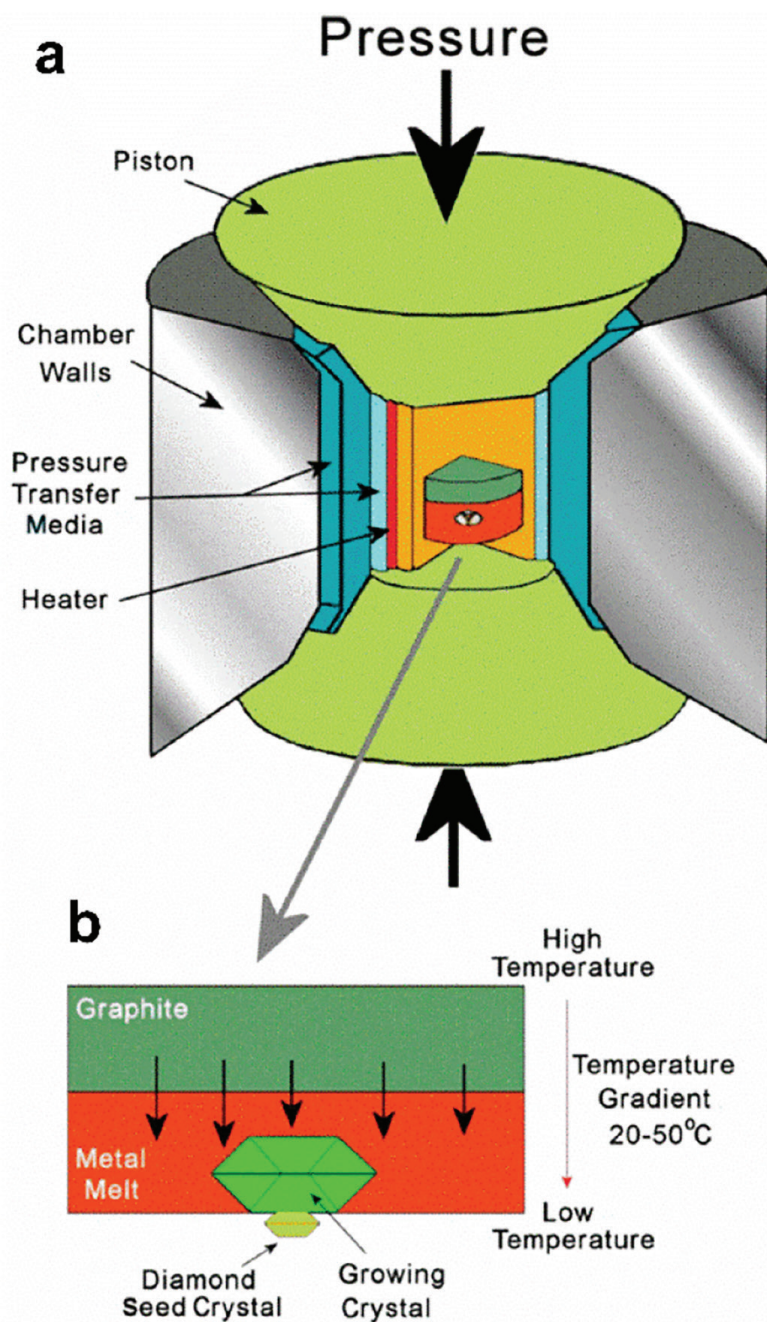


Figure 4. Schematic diagram of (a) an HPHT press that applies high pressures and temperatures to a cell holding graphite, a metal melt, and a diamond seed crystal. These circumstances cause (b) the graphite to dissolve in the metal and precipitate on the seed crystal, therefore spreading the diamond lattice. Reproduced with permission from ref. [31]. Copyright 2020 American Chemical Society.

Therefore, to avoid the stringent conditions in HPHT method, metal catalysts are utilized in the synthesis of diamond, because the adding catalysts can efficiently reduce the phase transition activation energy of diamond, resulting in the decrease of the temperature from more than 2000°C to the actual 1200–1500°C. However, due to the utilization of metal catalysts in HPHT method, there will be a small amount of nearly undetectable metal impurities in the diamond, which make the diamond possess some unique physical properties, such as a certain weak magnetism.

3.2 CVD

Chemical vapor deposition (CVD) for diamond growth generally needs the use of plasma, which can be generated by various plasma sources, including microwave, DC, or RF plasma. The gas source containing methane (CH_4) gas diluted with H_2 gas can be transformed to CH_3 and H radicals for the diamond growth.

Figure 5a shows the principle of CVD diamond growth method [31]. The microwave or DC heating can lead to the generation of H and CH_3 radicals. H radicals play an important role in the CVD process. The roles of H radicals are as follows: (1) the H radicals can etch the graphite phase on the diamond surface to let diamond continuously grow; (2) the H radicals can terminate with dangling bonds on the diamond surface to maintain the sp^3 hybridization of the surface carbon atoms; (3) the H radicals can react with CH_4 molecules to produce CH_3 radicals; and (4) the H radicals can react with diamond surface H to activate the surface bond. The current realization of the reaction mechanism for CVD diamond growth [38] shown in **Figure 5b** illustrates that two carbon atoms for a dimer structure with H-terminated bonds on the diamond surface first. After one of surface H atoms reacts with an H radical to desorb to produce the surface dangling bond, a CH_3 radical from the vapor phase will adsorb on the reactive dangling bond to form a bond with the surface C atom. Then the H radical of CH_3 radical desorbs and breaks the dimer bond. Finally, the CH_2 radical forms the bond with the other surface C atom.

The preparation of diamond by hot filament (DC-plasma) CVD is one of the most widely used methods at present (**Figure 6**). It has the characteristics of simple preparation process, cheap equipment, and mature technology. In the production process of diamond, there are many parameters that affect the quality of diamond film, including filament type, methane concentration (CH_4/H_2 ratio), substrate temperature, distance between substrate and filament, nitrogen pollution, carbon source selection, etc. One of the important influencing factors is the C:H ratio, which can influence the concentration of activated CH_3 and H radicals. As shown in the scanning electron microscopy (SEM) images as shown in **Figure 7**, with the increase of methane concentration in a certain range, the grain size and surface roughness of diamond decreased, and cauliflower-like particles appeared on the surface.

The microwave plasma CVD (MPCVD) method is similar to the hot filament CVD (HFCVD) method, in which the gas molecules are transformed into active

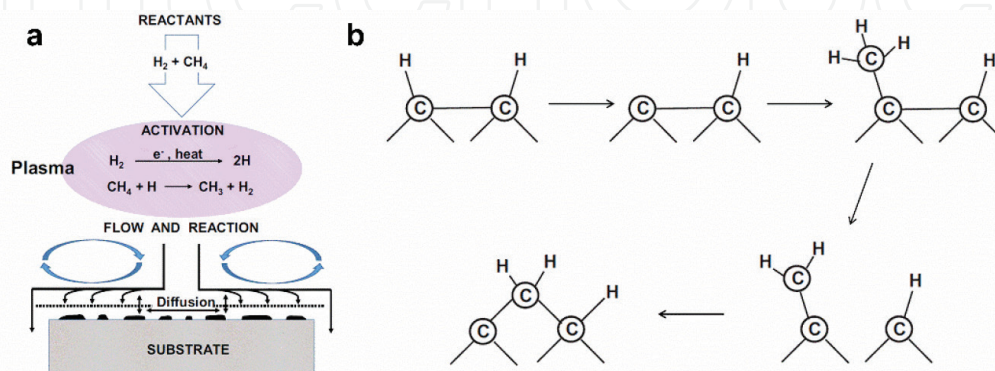


Figure 5. (a) Principle of plasma CVD diamond growth, and (b) the mechanism of surface chemical reaction of CVD diamond growth. Reproduced with permission from ref. [37]. Copyright 2016 Elsevier Ltd.

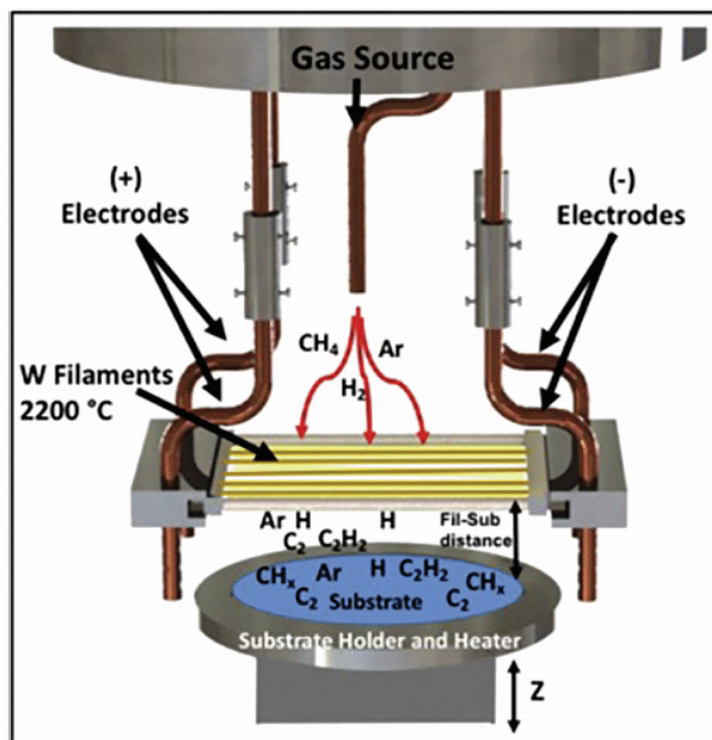


Figure 6. Setup of polycrystalline diamond growth by hot filament CVD (HFCVD). Reproduced with permission from ref. [39]. Copyright 2017 Microscopy Society of America.

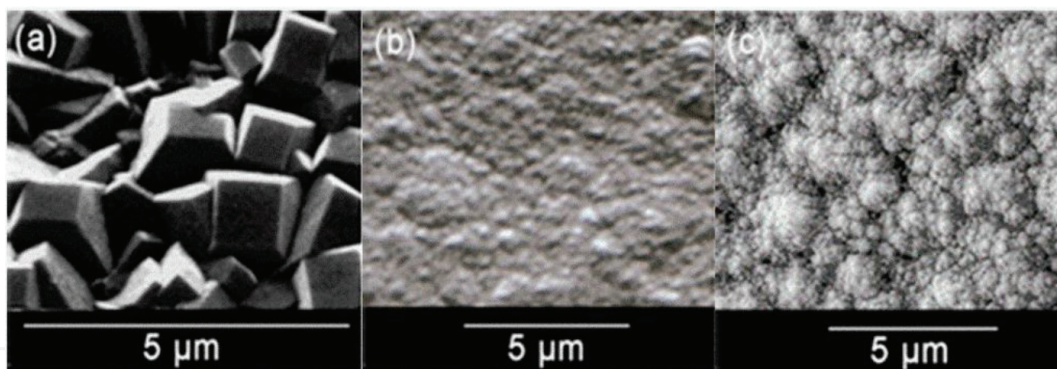


Figure 7. (a–c) Examples of different morphologies of undoped polycrystalline CVD diamond films grown using different C:H ratios in the source gas: (a) faceted microcrystalline diamond typically grown under standard deposition conditions, with <2% CH₄ in H₂, (b) smoother nanocrystalline diamond grown as before, but with >4% CH₄ in H₂, and (c) “cauliflower” nanocrystalline diamond grown with >4% CH₄ in H₂. Reproduced with permission from ref. [31]. Copyright 2020 American Chemical Society.

carbon-containing groups and H atoms by injecting energy. The plasma density of MPCVD is higher than that of HFCVD so that high-purity diamond can be prepared. Due to the limitation of microwave wavelength and microwave resonator, a large-area uniform film cannot be obtained. Therefore, MPCVD is not suitable for industrial production. In order to further improve the quality and growth rate of diamond, the improvement and innovation of microwave cavity have become the focus of research. The stability of microwave frequency and the singleness of microwave energy will still be the direction that needs to be overcome in the future. With the development of GaN devices, the third-generation semiconductor solid-state microwave source

will possibly replace the magnetron and become an inevitable choice for the modularization and miniaturization of high-power and high-stability microwave sources. In addition, the addition of multi-beam energy coupling excitation plasma such as radio frequency, laser, and other energy will also open a new platform for MPCVD equipment.

Despite the polycrystalline diamond grown by CVD techniques, the growth of ultrathin diamond film has also attracted extensive attention. In the past years, theoretical calculations based on density functional studies have predicted the chemically induced transformation of multilayer graphene into a diamond-like film [40, 41]. Recently, in experiment, the fluorination of graphene sheets in Bernal-stacked bilayer graphene generated by CVD over a single-crystal CuNi(111) surface can cause the creation of interlayer carbon-carbon bonds, resulting in a fluorinated diamond monolayer [42].

4. Creation methods of NV defect in diamond

The development of diamond NV centers has been relatively mature so far. Not only can NV centers be formed during diamond growth (inter-growth methods), but also ions, electrons, and laser beams can be used to obtain holes after diamond growth and then combine with nitrogen atoms to form NV centers (post-growth methods).

4.1 Inter-growth methods

The formation of NV centers in diamond can be realized during the growth of diamond by CVD (inter-growth). By adding a nitrogen gas source in the mixed gas source, the NV centers can possibly be created during the diamond growth. There are several advantages to grow NV defect by inter-growth method: (1) by adjusting the gas-phase environment and growth conditions, the NV defect concentration of the diamond film can be controlled within 200 ppb, ideally suitable for optical and electronic applications; [43] (2) The NV centers by this method can not only achieve a high concentration, but also the lifetime of electron spin coherence in ground state can reach the order of milliseconds. However, the inter-growth method by CVD to create NV defect has obvious drawbacks, like the uncontrollable formation site of NV defect, which needs further investigations. By optimizing the nitrogen concentration in the range of 0.2–20 ppm and E-beam irradiation conditions to study the formation of NV defect in CVD-grown diamond, the spin-spin coherence times of 45.5–549 μs for CVD diamond containing 168–1 ppb NV centers can be achieved [44]. In addition, with low growth temperature to enhance the nitrogen incorporation and with N_2O as a dopant gas for diamond growth by CVD on [113]-oriented substrate, the obtained nitrogen-doped diamond combines a high NV defect creation yield and long coherence time of several tens of μs together with a partial preferential orientation, which are desirable requirements for diamond-based sensors (**Figure 8**) [45].

4.2 Post-growth methods

4.2.1 Ion implantation method

The NV centers can be generated by nitrogen ion implantation after the formation of diamond film. Nitrogen ion implantation provides an NV positioning accuracy that

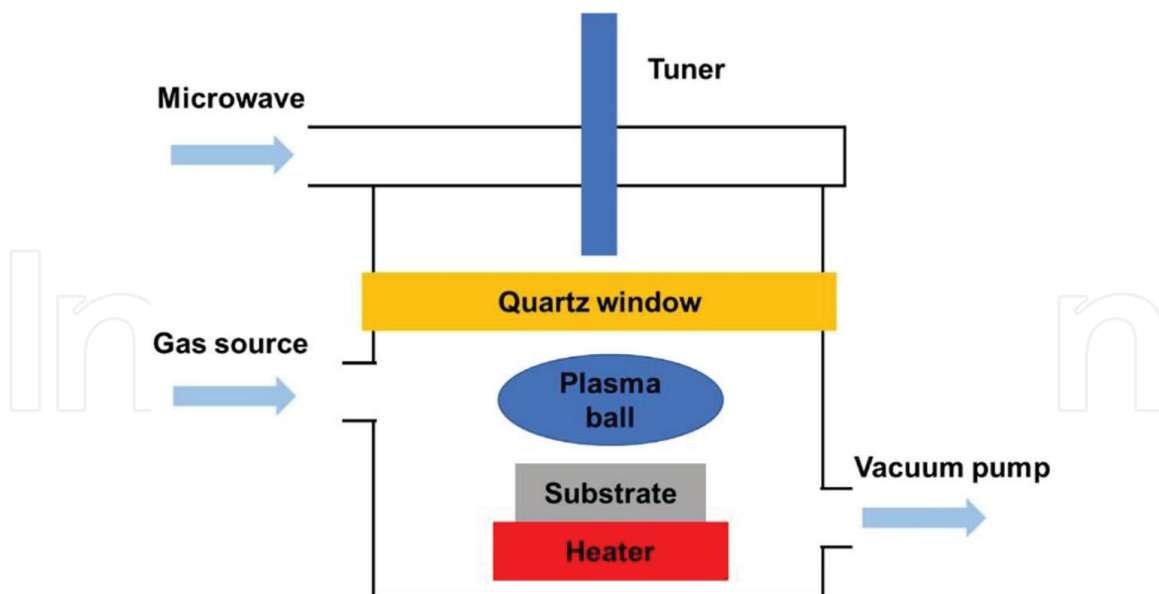


Figure 8. Schematic illustration for the creation of NV defect in diamond by CVD.

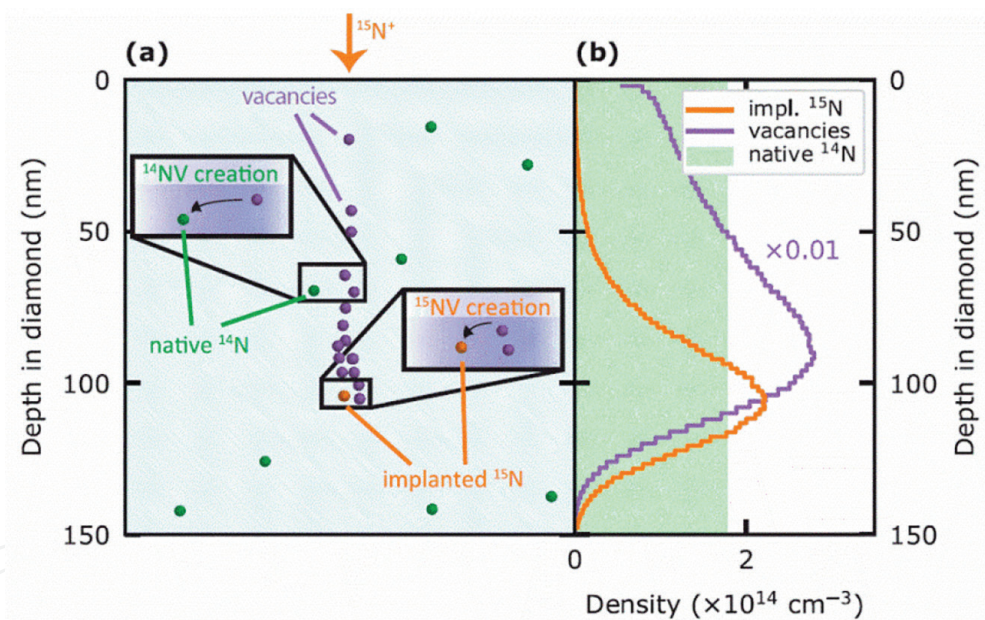


Figure 9. The creation of NV defect via nitrogen ion implantation. (a) Schematic illustration of implanted $^{15}\text{N}^+$ leaving a trail of vacancies until settling into a final position. Vacancies mobilized by annealing can bind a nitrogen atom (implanted or native) to form an NV defect, and (b) a SRIM simulation using the parameters in sample shows the distribution of implanted nitrogen and created vacancies. Reproduced with permission from ref. [47]. Copyright 2019 American Physical Society.

enables the integration with on-chip photonic devices [46]. Furthermore, this method can create a single NV center or a new NV defect coupling with the nearby NV defect. However, in the process of bombarding diamond with nitrogen ions, severe lattice damage in diamond is inevitable, resulting in damaging the ground state of NV defect and weakening the spin coherence time. Fortunately, it has been found that high-temperature annealing can recover part of the damaged lattice. In order to distinguish NV defects formed by implanted nitrogen atoms from the NV defects formed by

native ^{14}N atoms, ^{15}N isotope atoms were used to create NV defect by ion implantation and annealing procedure (**Figure 9**) [47, 48]. It is observed that NV centers formed by implanted ^{15}N atoms exhibit broadened optical linewidth (>1 GHz) and higher strain than that formed by native ^{14}N atoms (<500 MHz). The poor optical coherence of NV centers formed from implanted nitrogen is not resulted from an intrinsic effect related to the diamond or isotope, but the influence of lattice damage by ion bombardment [47]. Meanwhile, a mass-produced NV color center array with positioning accuracy of tens of nanometers can be achieved by using nitrogen ion implantation [49].

4.2.2 Femtosecond laser irradiation method

The femtosecond laser irradiation used to generate NV defects can cause strong damage to diamond, even more leading to graphitization. In 2017, Chen et al. used a single-pulse laser writing to controllably generate NV centers on the diamond surface without the occurrence of macroscopic crystal graphitization, which promoted the development of femtosecond laser irradiation for NV defect generation [50].

The principle of the femtosecond laser method shown in **Figure 10a** is that electron beam, generated by ionizing the air due to the strong electric field formed by the propagation of the femtosecond laser, can lead to the generation of vacancies in diamond. After annealing process, the produced vacancies can combine with nitrogen atoms to form NV defects [53]. Compared with ion implantation, the NV defect generated by femtosecond laser irradiation method possesses a narrower optical linewidth and a longer decoherence time. The NV color centers in diamond exhibit a narrow optical linewidth of 13.05 ± 0.2 MHz and a long decoherence time of 445 ± 27.6 μs [51].

4.2.3 Electron beam irradiation method

The principle of electron beam irradiation technique is to use electron beam to irradiate diamond to generate vacancies, which can bind with nitrogen atoms to form NV defects after high-temperature annealing, as shown in **Figure 10b**. The concentration and depth of the generated NV defects can be controlled by adjusting the energy

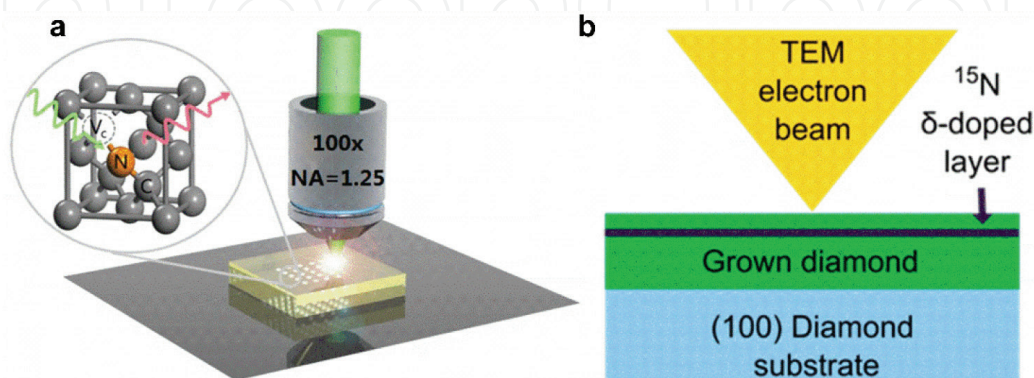


Figure 10.
(a) Schematic of the preparation of NV defect in diamond using femtosecond laser irradiation. Reproduced with permission from ref. [51]. Copyright 2022 AIP Publishing, and (b) Schematic of the generation of NV defect in diamond by electron beam irradiation in a transmission electron microscope (TEM). Reproduced with permission from ref. [52]. Copyright 2016 American Chemical Society.

of electron beam, the irradiation time, and the distance between the diamond and the electron beam gun. In 2017, a TEM-based method was used to create localized NV defect with coherence time exceeding 1 ms [52].

Due to the high sensitivity and high spatial resolution of TEM-based technique, it is well suited for the creation of NV defects. By using electron beam irradiation with the energy of 200 keV followed by high-temperature annealing at 1200°C, a surface density of $\sim 2500 \mu\text{m}^{-2}$ of NV defects in diamond can be achieved. This technique can enable the given arbitrary in-depth control of NV centers.

5. Conclusions

In this chapter, we have summarized the potential applications of NV defect in diamond, including sensors for the detection of temperature, electric and magnetic fields as well as quantum communication and computing. Furthermore, the growth methods of diamond are introduced, such as HPHT and CVD methods. For the creation of NV defects in diamond, NV centers can be generated during the grow of diamond by adding nitrogen gas source in the mixed gas source. Additionally, NV defects can also be obtained after diamond growth, notably ion implantation, femto-second laser irradiation, and electron beam irradiation methods.

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Conflict of interest

The authors declare no conflict of interest.

Appendices and nomenclature

NV	nitrogen vacancy
HPHT	high-pressure high temperature
CVD	chemical vapor deposition
ISC	intersystem crossing
PL	photoluminescence
MPCVD	microwave plasma CVD
HFCVD	hot filament CVD

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