

# Research and Application Progress of Boron-doped Diamond Films

Guangqiang Hou, Jingyan Ye, Jiaxing Han, Zhenghang Han, Xiang Yu \*

School of Materials Science and Engineering, China University of Geosciences (Beijing), Beijing, China

\* Corresponding author: yuxiang@cugb.edu.cn

**Abstract.** Thanks to its unique structure, diamond has many excellent properties, such as high hardness, low birefringence, high thermal conductivity, good chemical stability, etc., but pure diamond has extremely high resistivity (up to  $10^{12} \Omega \cdot m$ ), which is an insulator, so it is usually doped to expand the application of diamond in the electrochemical field. B atoms have a very small radius, which is an ideal material for doping diamond, and B-doped diamond has good electrical conductivity. In this paper, on the basis of introducing the phase composition and structure of boron-doped diamond (BDD) film, the common methods for preparing BDD film are analyzed, and the application status and prospect of its application in electrochemistry and other fields are summarized.

**Keywords:** Boron-doped diamond film, Chemical vapor deposition, Electrochemical field.

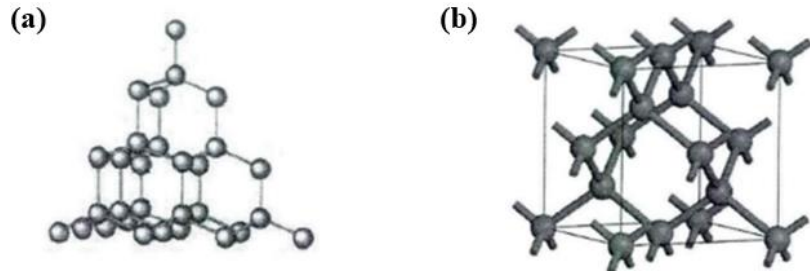
## 1. Introduction

Diamond has high electron and hole mobility, high breakdown voltage, and high bandgap width, which can be five times that of silicon, and its electron affinity is small, which can be obtained under lower electric field large emission current, so it has great application potential in the semiconductor field, but pure diamond has extremely high resistivity (up to  $10^{12} \Omega \cdot m$ ), and is an insulator, so diamond is usually doped to improve its conductivity. At present, diamond doping is mainly divided into P-type and N-type, among which P-type doping is relatively mature, usually doped with boron (B) element; B atoms have a small radius, which is an ideal material for doping diamond. B-doped diamond has good electrical conductivity and can become a conductor, semiconductor or superconductor, which greatly broadens its application fields in physics, chemistry, biology and so on. In this paper, on the basis of introducing the phase composition and structure of the BDD film, the chemical vapor deposition and ion implantation methods for preparing the BDD film are analyzed, as well as the correlation between their physical properties and material composition, structure, and preparation process conditions. Application status and prospects in the field of chemistry.

## 2. Structure and performance of BDD

### 2.1. Structure of Diamond

The elemental composition of diamond is C. C atoms are connected by covalent bonds to form atomic crystals, and the ortho-tetrahedral structure of diamond is given in Figure 1 (a). From the hybrid orbital theory, it can be concluded that the four orbitals of carbon atoms,  $2s$ ,  $2P_x$ ,  $2P_y$ ,  $2P_z$ , will form four  $sp^3$  hybrid atomic orbitals, and the four  $sp^3$  electrons and the surrounding carbon atoms generate four  $\sigma$  bonds respectively, forming a tetrahedral structure with bond length  $0.154 \text{ nm}$ , bond angle  $109^\circ 28'$ , and bond energy  $347 \text{ kJ/mol}$ . From the cellular point of view, the usual sense of Diamond belongs to the face-centered cubic structure, belongs to the equiaxed crystal system, has strong covalent bonds and high atomic density, as shown in Figure 1. (b), the primary cell contains two unequal carbon atoms, the number of atoms per unit cell  $Z=8$ , and the lattice constant at  $298 \text{ K}$  is  $0.356683 \text{ nm}$ .



**Figure 1.** Schematic diagram of the ortho-tetrahedral structure and crystal structure of diamond:(a) Schematic diagram of the ortho-tetrahedral structure of diamond (b) Schematic diagram of the crystal structure of diamond [1]

## 2.2. Properties and applications of diamond

The unique structure of diamond gives it many excellent properties, such as high hardness, low bi-folding rate, high thermal conductivity, good chemical stability, etc. Therefore, diamond has excellent performance in mechanical, optical, thermal, acoustic, chemical, and electrical fields [2].

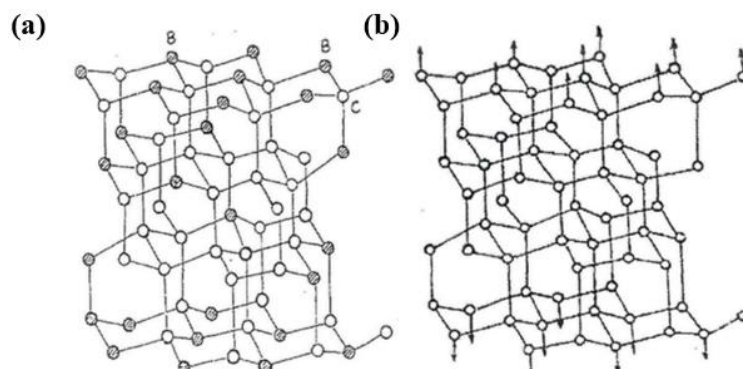
CVD diamond films basically retain the good mechanical properties of natural diamond with high hardness, high modulus of elasticity, good compressive and tensile properties, and low coefficient of friction, so diamond films have been widely used in tools and drills, pressure sensors, and bearing materials.

Diamond has a wide range of high transmittance from the vacuum UV band (0.22 $\mu$ m) to the far infrared millimeter band without any absorption peaks except for a weak absorption peak near 5 $\mu$ m due to two-phonon absorption, and behaves transparently, so it is often used as a window material or coating for lasers and detectors [3-4]. In addition, diamond also has visible fluorescence, a luminescent property, which mainly originates from electromagnetic radiation generated by electronic state jumps in the band gap due to its impurities and lattice defects, and can be applied in the field of imaging [5].

Diamond has a high elastic modulus and Young's modulus, and the propagation speed of sound waves in diamond crystals is extremely fast, up to 18.2 km/s, and is commonly used as the diaphragm of high-fidelity loudspeaker tweeters [6]. Diamond has good chemical stability and high corrosion resistance, and is often used as a corrosion-resistant protective layer; in addition, diamond is one of the isomers of carbon, so it has good biocompatibility and has a wide range of applications in biology and medical fields.

## 2.3. Structure of BDD

The atomic radius of B is very small and can be easily incorporated into the diamond crystal. As shown in Figure 2, B atoms will replace some of the C atoms on the surface and inside, and its main structure is not changed. It has been found that the electrical conductivity, oxidation resistance, heat and corrosion resistance of diamond can be substantially improved by doping with B atoms.



**Figure 2.** Schematic diagram of the structure of boron-containing and ordinary diamond: (a) Boron-containing diamond structure (b) Ordinary diamond structure [7]

## 2.4. Electrochemical properties of BDD membranes

The electrochemical properties of diamond films were also greatly enhanced by doping with B atoms. Qi [8] prepared BDD films on P-type (100) silicon substrates using a DC hot-cathode CVD method with liquid trimethyl borate as the boron source, and found that BDD films have a wide potential window, very high oxygen precipitation potential, low background current, good stability and maintain good catalytic activity for most organics.

Li et al [9] prepared BDD electrodes with different boron doping concentrations by solid boron doping using boron trioxide as the boron source and found that the appropriate boron doping concentration helps to improve the electrochemical performance of BDD electrodes, and in their samples, the quality of boron doping is optimal and the potential window is maximum at a mass concentration of 2 g/L. More or less than this concentration will reduce its potential window.

## 3. Preparation method of BDD membrane

The main doping methods for BDD are chemical vapor deposition (CVD), ion implantation and high temperature and high pressure (HTHP), among which HTHP is mainly used for the growth of single crystal diamond substrates and less for doping.

### 3.1. CVD doping

The common CVD methods are hot filament chemical vapor deposition (HFVCD), and microwave plasma chemical vapor deposition (MW-PCVD). Table 1. compares the advantages and disadvantages of the two common CVD methods. MW-PCVD method is the most widely used method for high quality diamond film deposition, but it is commonly used for laboratory diamond film preparation because of its expensive equipment.

**Table 1.** Advantages and disadvantages of two types of CVD methods

Name	Advantages	Disadvantages
HFVCD	The name is easy to operate and simple equipment. Suitable for the preparation of large size BDD membrane electrodes.	Poor stability and easy contamination. Cannot be used to deposit high quality diamond films.
MW-PCVD	No electrode discharge contamination and electrode corrosion. Wide operating pressure range. High plasma density. Large volume of uniform plasma can be generated. Can be deposited on complex surfaces.	High equipment price. Difficult to deposit large area films. Low deposition rate.

### 3.2. Ion injection method

The ion injection method is to inject boron ions directly into the diamond matrix by using electric field acceleration, etc. on the already prepared diamond film. The efficiency of ion injection is high, but because of the tight carbon-carbon bond, it is difficult to diffuse boron ions over long distances and high-energy ion injection can lead to severe damage to the surface structure, which requires annealing to remove the surface damage layer and avoid graphitization. preparation is very complicated, so although high-energy ion injection can damage the diamond surface structure, it is still a promising alternative method to produce such microstructures. And to reduce the degree of surface damage, multiple ion implantation one-annealing cycle processes are usually used for the preparation of diamond P-type semiconductors [11-12].

## 4. Current Status of BDD Membrane Applications in Electrochemistry

BDD membrane has good electrochemical properties, and has a broad development prospect in the fields of electrode materials, treatment of electrochemical wastewater, detection of trace organic compounds, etc.

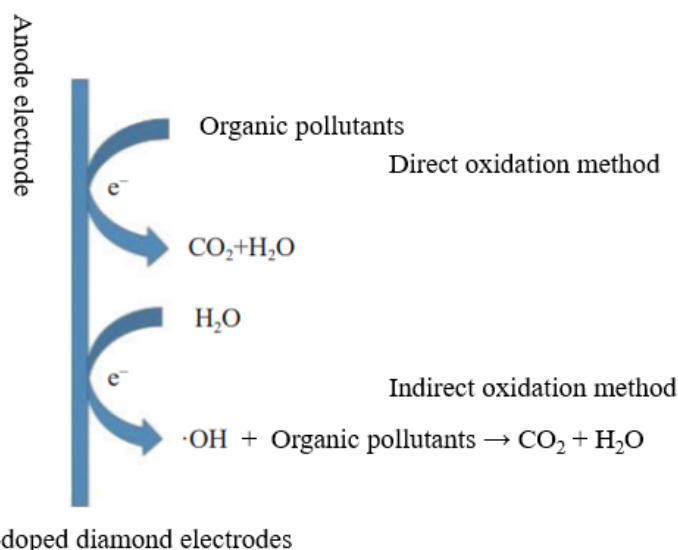
### 4.1. Electrode material

BDD films have good electrical conductivity and can be used as electrode materials, while BDD electrode materials have more advantages over common metal electrodes due to their high forbidden band width, low background currents, and excellent mechanical properties and chemical stability. For example, Tully Joshua J et al [13] made BDD rotating ring-disk electrodes, and the experimental surface, BDD electrodes have low background currents, a wide solvent potential window in aqueous solutions, and good chemical and electrochemical stability in acid-base solutions, which are ideal electrocatalyst carriers.

And Qinghai Yang et al [14], by modulating the boron doping concentration and fluorination modification of BDD film, comprehensively optimized the electrode's resistance to erosion and abrasion, electrochemical corrosion resistance and oil sparing performance, which can realize the long-term stable operation of the electroconductive water content sensor under harsh downhole conditions.

### 4.2. Wastewater Treatment

The application of BDD membrane in the field of wastewater is mainly to use it as an anode material, using its oxidation to generate free radicals to decompose toxic and harmful substances in water, making them harmless CO<sub>2</sub> and H<sub>2</sub>O, Figure 3 shows the schematic diagram of BDD wastewater treatment, BDD membrane electrode in wastewater treatment has many specific advantages, such as high ozone generation rate, not easy to produce secondary pollution, high chemical and electrochemical stability, etc. The BDD membrane electrodes developed by ICRI have been commercially applied.



**Figure 3.** Schematic diagram of boron-doped diamond wastewater treatment [15]

Thanks to the excellent electrochemical properties of BDD membrane electrodes, there are numerous studies on the application of BDD membrane electrodes in wastewater treatment, involving various types of organic wastewater treatment and many fields such as printing and dyeing, pulp and tanning, pharmaceuticals, pesticides, and petrochemicals. For example, Bany Abdelnabi Ahmad A et al [16] investigated the optimal setup of BDD membrane electrodes to produce strong active oxidizing substances from tap water, and the results showed the best performance of the electrolysis process using two long rolls of BDD/Nb mesh as the anode electrode and one long roll of BDD/Nb mesh as the cathode electrode.

While Sedlazeck Klaus P et al [17] found that BDD membrane electrodes have high decomposition rates in degrading organic pollutants such as tetrachloroethylene, MTBE and clopidogrel, but this degradation is accompanied by the production of metabolites, which can be further improved by any combination of two degradation methods, zero-valent iron and UV radiation in a fluidized bed reactor and the addition of hydrogen peroxide. Removal rates.

Clematis Davide et al [18] summarized the effectiveness of BDD membrane electrodes in degrading toxic or biodegradable organic compounds in real wastewater, such as municipal wastewater, hospital wastewater, groundwater, petrochemical wastewater, and wastewater from agri-food activities, and showed that BDD can effectively treat such real wastewater and can remove pollutants in different environments. Nevertheless, further efforts are needed to develop a broader market, and the next phase of research should be directed towards cell design and optimization of electrochemical systems and integration with other water treatment and renewable energy sources.

With the increasing pressure and demand for disinfection, traditional disinfection methods such as disinfectants, alcohol, and UV light have gradually failed to meet the public demand due to their inherent defects, and there is an urgent need for a new type of disinfection that is safe, environmentally friendly, and highly efficient. The BDD electrode system used for ozone disinfection has the characteristics of high disinfection efficiency, environmental protection and no pollution, high chemical and electrochemical stability. It can make up for the shortcomings of traditional methods and has high economic and social benefits.

### 4.3. Detection of trace organic compound components

Conventional electrodes usually have high background currents when detecting trace organic compound components, which leads to inaccurate detectors. The surface of BDD membrane electrode has good inertness, which can make up for the shortcomings of conventional electrodes, and because of its wide potential window and good biocompatibility, BDD membrane electrode has gradually become an ideal electrode material for determining the composition of trace organic compounds by simple amperometric method. Currently, BDD membrane electrodes have been investigated for the detection of amino acids, peptides and proteins, nucleobases, nucleases, nucleotides, and DNA/RNA [19].

For example, Henderson Skye et al [20] investigated the preparation of nanoparticles and Nafion-modified boron-doped gold BDD microelectrodes and their application in the *in vitro* detection of nitric oxide (NO) in mouse colon; Boonkaew Suchanat et al [21] proposed boron/nitrogen co-doped diamond-graphene nanowall-structured (DGNW) integrated with screen-printed graphene electrode (SPGE) for the detection of serotonin (5-HT) as a model system and applied the method to synthetic urine samples, the results showed that the DGNW modified electrode has good anti-pollution properties and biocompatibility; while Dushna Olha et al [22] firstly combined a working boron-doped diamond electrode (BDDE) with a novel screen-printed sensor to form a planar electrochemical cell consisting of a working boron-doped diamond electrode (BDDE) and a novel screen-printed sensor was first used for voltammetric determination of the alkaloid atropine (ATR).

Although BDD membrane electrodes still have some drawbacks in detecting trace organic compound components, such as poor surface fabricability and processability, they still have great potential in this field because of their excellent electrochemical properties and biocompatibility.

## 5. Conclusion

BDD membranes are superior to ordinary diamond membranes in terms of heat resistance, wear resistance, chemical inertness, oxidation resistance and compressive strength, especially in the field of electrochemistry, BDD membranes have tremendous performance advantages. Therefore, with the rapid development of modern industry in recent years, BDD membranes gradually show great application prospects in the fields of electrode materials, treatment of electrochemical wastewater, detection of trace organic compounds, making capacitors and optoelectronics, etc. High concentration

BDD membrane electrode is becoming an alternative material to traditional electrode with its excellent electrochemical and physical properties.

With further research on the microscopic mechanism of BDD membrane and continuous improvement of its preparation process, the comprehensive performance of BDD membrane will be further improved, and the application of BDD membrane will be further expanded with a very broad prospect.

## References

- [1] Li Z X. Preparation, Electrochemical Properties and Surface Modification of Boron-doped diamond films [D]. Nanjing University of Science and Technology, 2012.
- [2] Liu W P. Research and Application of P-doped Diamond [D]. University of Science and Technology of China, 2006.
- [3] Zhang Q, Dong G X, Li Y Y, et al. Research Progress of High-Power Microwave window Materials [J]. China Ceramic Industry, 2014, 21 (05): 16 - 20.
- [4] Shen C, Cai X, Su X, et al. Wavelength-tunable narrow-linewidth gaseous Raman laser[J]. Applied Optics, 2021, 60 (18): 5465 - 5470.
- [5] Neu E, Arend C, Gross E, et al. Narrowband fluorescent nanodiamonds produced from chemical vapor deposition films [J]. Applied Physics Letters, 2011, 98 (24): 243107.
- [6] Yuan Z H, Lin S S, Hou H J, et al. Application of diamond-like film deposited by cathode Arc in Electroacoustics -- Development and Production of High fidelity DLC/Ti Treble speaker Diaphragm [J]. Guangdong Journal of Nonferrous Metals, 2005, 15 (1): 26 - 29.
- [7] Gou Q Q. The structure and synthesis mechanism of boron black diamond and its special performance discussion [J]. Journal of Jilin University (Natural Science Edition), 1978 (02): 35 - 42.
- [8] Qi W T. Preparation and Electrochemical Properties of Boron-doped diamond Film [D]. Mudanjiang Normal University, 2010.
- [9] Li H Q, Gao B H, Tan B M. Effect of boron doped mass concentration on electrochemical characteristics of BDD electrode [J]. Micro-nano Electronics Technology, 2016, 53 (12): 838 - 841.
- [10] Ynsa M D, Agulló-Rueda F, Gordillo N, et al. Study of the effects of focused high-energy boron ion implantation in diamond [J]. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, 2017, 404: 207 - 210.
- [11] Hu X J, Li R B, Shen H S, et al. Electrical and structural properties of boron and phosphorus co-doped diamond films [J]. Carbon, 2004, 42 (8-9): 1501 - 1506.
- [12] Zang J B, Huang H, Zhao Y C. Doped diamond [J]. Diamond and Abrasive Tools Engineering, 2002 (01): 16 - 18.
- [13] Tully J J, Zhang Z, Terrero Rodríguez I M, et al. Versatile DIY Route for Incorporation of a Wide Range of Electrode Materials into Rotating Ring Disk Electrodes [J]. Analytical Chemistry, 2022, 94 (27): 9856 - 9862.
- [14] Yang Q H, Gao W, Wei S B, et al. Surface treatment technology of downhole water content sensor [J]. Petroleum Exploration and Development, 202: 1242 - 1251.
- [15] Li L L, Chen G Q. Research progress of high-performance boron-doped diamond electrodes [J]. Diamond and Abrasive Tools Engineering, 2022, 42 (05): 543 - 551.
- [16] Öztürk G, Kul D. Comparison of carbon paste and boron-doped diamond electrodes for determination of cefepime in pharmaceutical dosage forms and biological samples [J]. Diamond and Related Materials, 2023, 131: 109532.
- [17] Sedlazeck K P, Vollprecht D, Müller P, et al. Decomposition of dissolved organic contaminants by combining a boron-doped diamond electrode, zero-valent iron and ultraviolet radiation [J]. Chemosphere, 2019, 217: 897 - 904.
- [18] Clematis D, Panizza M. Application of boron-doped diamond electrodes for electrochemical oxidation of real wastewaters [J]. Current Opinion in Electrochemistry, 2021, 30: 100844.

- [19] Baluchová S, Daňhel A, Dejmková H, et al. Recent progress in the applications of boron doped diamond electrodes in electroanalysis of organic compounds and biomolecules–A review [J]. *Analytica chimica acta*, 2019, 1077: 30 - 66.
- [20] Henderson S, Bhardwaj K, Perugachi V, et al. In Vitro Monitoring of Nitric Oxide Release in the Mouse Colon Using a Boron-Doped Diamond Microelectrode Modified with Platinum Nanoparticles and Nafion [J]. *Analytical Chemistry*, 2022, 95 (2): 1027 - 1037.
- [21] Boonkaew S, Dettlaff A, Sobaszek M, et al. Electrochemical determination of neurotransmitter serotonin using boron/nitrogen co-doped diamond-graphene nanowall-structured particles [J]. *Journal of Electroanalytical Chemistry*, 2022, 926: 116938.
- [22] Dushna O, Dubenska L, Vojs M, et al. Highly Sensitive Determination of Atropine in Pharmaceuticals, Biological Fluids and Beverage on Planar Electrochemical Cell with Working Boron-Doped Diamond Electrode [J]. *Electrochemical Acta*, 2022, 432: 141182.