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Study on Preparation Process and Electrical Properties of Diamond PN Junction

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Abstract. Diamond PN junctions exhibit exceptional properties such as high electric breakdown field, the largest bandgap and the highest thermal conductivity compared to any known materials. These unique attributes make diamond highly suitable for high-power, high-frequency and harsh-environment applications. Currently, chemical vapor deposition (CVD) and high-pressure high-temperature (HPHT) methods can be used to synthesize diamond substrates. Among these, synthetic diamond produced by CVD has garnered significant interest due to its distinctive combination of exceptional electrical and thermal properties. However, its extremely high mechanical hardness and smaller substrate size pose substantial challenges for the implementation of device technology. This paper aims to explore the distinguished properties of diamond in electronics and the preparation process of diamond PN junctions, focusing on synthesis technologies, doping issues and terminal technologies. All of these are critical for maximizing the dependability and performance of electronic devices based on diamonds. By addressing these challenges, the research seeks to forward the application of diamond in various high-performance electronic devices, highlighting its capacity to improve device durability and effieciency in harsh operating conditions. The insights provided will contribute to a deeper understanding of the material's capabilities and the technological advancements necessary to harness its full potential in electronic applications.

Keywords: Diamond; PN junction; Synthesis techniques.

1. Introduction

Diamond, known for its unparalleled hardness and thermal conductivity, has emerged as a promising material for electronic applications due to its exceptional electrical properties. As a semiconductor, diamond boasts a wide bandgap of 5.47 eV, significantly surpassing that of conventional semiconductors like silicon (1.12 eV) and gallium arsenide (1.42 eV). This wide bandgap endows diamond with superior thermal stability and the ability to operate at higher voltages and temperatures. Additionally, diamond exhibits an extraordinary thermal conductivity of over 2000 W/mK, which is crucial for dissipating heat in high-power devices, thereby enhancing their performance and reliability.

The high carrier mobility of diamond allows for faster electronic switching speeds, while its strong dielectric breakdown field, exceeding 10 MV/cm, makes it capable of withstanding high electric fields without breaking down. These properties are complemented by diamond's high saturation velocity, which enables rapid carrier transport, and its low carrier concentration, which minimizes leakage currents, thus enhancing the efficiency of electronic devices. Moreover, diamond's exceptional chemical stability ensures it remains inert in harsh environments, making it suitable for extreme conditions applications.

In the context of diamond PN junctions, these properties translate into significant advantages for various electronic applications. The performance of diamond PN junctions, which consists of P-type and N-type diamond layers is critically dependent on their composition and structure. These junctions find applications in high-frequency field-effect transistors (FETs), high-power switches, and Schottky diodes, where their unique properties can be fully leveraged.

The production of diamond PN junctions involves sophisticated synthesis techniques, including the high-pressure high-temperature (HPHT) method, chemical vapor deposition (CVD), and microwave plasma chemical vapor deposition (MPCVD). Single-crystal and polycrystalline diamonds are

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typically produced among the prepared diamonds. The preparation methods of single crystal diamond mainly include HPHT method and MPCVD method. The CVD method and HPTH method are used to prepare polycrystalline diamond, which are relatively more mature and enable large-scale production.

Each of these methods offers distinct advantages and challenges, particularly in terms of achieving uniform and effective doping. P-type doping in diamond is relatively well-understood, typically achieved using boron, while N-type doping remains challenging due to the difficulty in incorporating donors such as phosphorus or nitrogen into the diamond lattice.

The paper further investigates diamond terminal technology, which is essential for optimizing the performance of diamond-based devices. Diamond terminals are designed to handle high current densities and voltages, ensuring efficient and reliable operation in demanding applications.

To conclude, this paper provides a comprehensive overview of the preparation processes and electrical properties of diamond PN junctions. By examining their unique characteristics, practical applications, and production challenges, the study aims to underscore the potential of diamond as a transformative material in the field of electronics, paving the way for next-generation high-performance devices.

2. Excellent Electrical Properties of Diamond as PN Junction

2.1. Wide Bandgap

Diamond has the largest bandgap among all known materials. Its bandgap energy is approximately 5.47 eV, which endows diamond with unique applications in the field of optoelectronics, electronics, and optics.

2.2. High Thermal Conductivity

Diamond also has the highest thermal conductivity (T_C) of any material known. The T_C of a high-purity, single-crystal CVD diamond is greater than 2200 $\mathrm{W} \cdot m^{-1} \cdot K^{-1}$ at room temperature of 25℃ (298K), and it even reaches 4500 $\mathrm{W} \cdot m^{-1} \cdot K^{-1}$ when it is -100℃ (173K). The extremely high thermal conductivity enables diamond to dissipate heat more easily during the initial stage of thermal management in diamond-based high power devices [1].

2.3. High Carrier Mobility

Single-crystal CVD diamond exhibits both the highest electron and hole mobilities at room temperature of any wide-bandgap semiconductor materials, which leads to very fast carrier transport in the diamond PN junction. Electron and hole mobilities of about 4500 $cm^2V^{-1}s^{-1}$ and 3800 $cm^2V^{-1}s^{-1}$, respectively, have been measured in intrinsic, single-crystal CVD diamond at room temperature [1].

2.4. Strong Dielectric Breakdown Field

A semiconductor material with a high electric breakdown field is preferred for many applications. This holds true for high-frequency FETs as well as power components like switches and diodes meant to block many kilovolts. For this reason, devices with smaller dimensions can be engineered to turn on faster, provided that larger electric fields can be tolerated [1]. The dielectric breakdown strength of diamond is more than thirty times greater than that of silicon (Si) and three times greater than that of silicon carbide (SiC) [2].

2.5. High Saturation Velocity

The conductivity is determined by the saturation velocity in high electric fields. Regarding saturation velocity, diamond has a real advantage in that its high saturation velocity is reached in fields of ~10 kV/cm, which is relatively easy to approach compared to SiC, the saturation velocity of which is close to its practical electrical breakdown strength [1].

2.6. Low Carrier Concentration

The low quiescent current in the PN junction is crucial for energy-saving electronic devices, which can greatly reduce power consumption. In addition, the low quiescent current also greatly reduces the leakage current when the PN junction is reverse biased, improving the device stability. In this regard, diamond typically has a very low carrier concentration, indicating there are fewer free carriers in the PN junction and therefore a low quiescent current.

2.7. Chemical Stability

The highly symmetrical crystal structure and strong covalent bonds in diamond make it extremely stable for working as PN junctions in some challenging environment.

3. Diamond PN Junction

3.1. Composition and Structure of Diamond PN Junction

Diamond PN junctions, characterized by their unique electrical properties and exceptional performance, are generally composed of a p-type and a n-type region within a diamond crystal. The p-type region of the diamond PN junction is commonly created by dopant boron (B), which introduces acceptor levels in the diamond lattice, resulting in the creation of holes as the majority carriers. Similarly, the n-type region is formed by doping the diamond with phosphorous (P) or nitrogen (N). These atoms introduce donor levels, leading to the presence of electrons as the majority carriers. The junction is eventually formed where the p-type and n-type regions meet within the diamond crystal [2].

3.2. Applications of Diamond PN Junction

The wide bandgap and high thermal conductivity make diamond PN junction an appropriate material for high-power switching devices and for semiconductor lasers. For high-power switching devices, low on-resistance, fast switching property and high blocking voltage are required simultaneously in order to minimize the energy loss [3]. The wide bandgap of diamond makes it highly sensitive to ultraviolet (UV) light while being insensitive to visible and infrared light. This characteristic renders diamond PN junctions particularly suitable for UV photodetectors, which can be utilized in applications such as environmental monitoring, flame detection and biomedical imaging. Diamond PN junction has also become a competitive candidate material for radio frequency power amplifiers, which are suitable for equipment requiring high frequency performance such as wireless communication and radar systems [4]. A comparison of the characteristics of diamond and other typical semiconductor materials is shown in Figure 1.

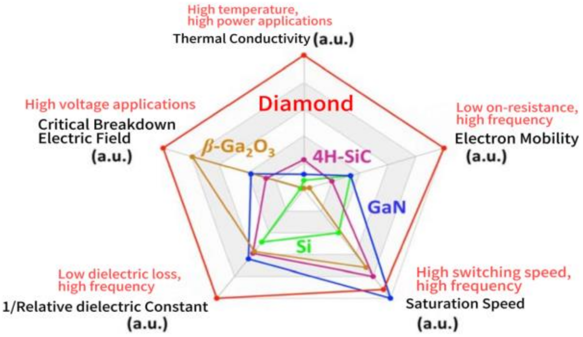

Figure 1. Characteristics advantages of diamond compared to other common semiconductor materials [5].

4. The Production Process of Diamond PN junction

As mentioned before, diamond gains outstanding electrical properties and a stable crystal structure. But these excellent properties of diamond rarely present in the same stone, so that's why diamond synthesis by the high-pressure, high-temperature (HPHT) processes and chemical vapor deposition (CVD) has been responsible for its commercial use in engineering applications [1]. The potential of diamond could be seen by contrasting its properties with other wide-bandgap materials, which are also rival materials for high-frequency and high-power electronic device application. It is noticeable that the qualities of carrier mobility and thermal conductivity in a CVD diamond even receive higher values than in a natural diamond as a positive consequence of the CVD method (The electron mobility, hole mobility and thermal conductivity of natural diamond are $200{\sim}2800\ cm^2V^{-1}s^{-1}$, $1800{\sim}2100\ cm^2V^{-1}s^{-1}$ and $22\ Wcm^{-1}K^{-1}$ respectively, and these corresponding qualities in a CVD diamond are respectively $4500\ cm^2V^{-1}s^{-1}$, $3800\ cm^2V^{-1}s^{-1}$ and $24\ Wcm^{-1}K^{-1}$) [1].

4.1. High Pressure High Temperature (HPHT) Method for Diamond Synthesis

In 1955, Bundy and others from General Electric Company in the United States synthesized diamond by simulating the formation process of natural diamond, which is called the high-pressure high-temperature (HPHT) method. The HPHT method is now mainly used to prepare high-quality single crystal diamond as a base material for PN junctions.

Diamonds produced using the High Pressure High Temperature (HPHT) method possess the same hardness and crystal structure as natural diamonds. Given the cost-effectiveness of this method, HPHT diamonds are widely utilized in industrial applications, primarily for cutting and grinding tools.

The synthesis of HPHT diamonds occurs in an atmospheric environment where nitrogen (N2) is predominant in the air. This results in a significant incorporation of nitrogen impurities within the HPHT diamonds, which often manifest as a yellow coloration. Due to limitations in crystal quality, HPHT diamonds are generally not suitable for direct use in device fabrication. However, HPHT diamonds are frequently employed as substrate materials. A high-quality diamond thin film can be epitaxially grown on these substrates, which can then be utilized for the manufacturing of diamond devices. Therefore, by leveraging the HPHT method for substrate production, it becomes feasible to combine cost efficiency with the superior properties of high-quality epitaxial diamond films for advanced applications [5].

4.2. Chemical Vapor Deposition (CVD) Method

Currently, most laboratory-grown diamonds are produced using a method known as Chemical Vapor Deposition (CVD), which is also mainly used to grow diamond films and achieve uniform doping to form p-type and n-type regions. Like the 'electronic grade' single-crystal CVD diamond plates shown in Figure 2, these plates are presently offered for commerce and can serve as the foundation for electronic components like FETs and Schottky diodes [1]. CVD is a technique that decomposes a hydrocarbon gas mixture into active radicals and deposits diamond onto a substrate under specific conditions. Compared to the High-Pressure High-Temperature (HPHT) method, the advantages of CVD include the ability to synthesize large, high-quality diamonds on various substrates, and the precise control over the impurities and properties of the synthesized diamonds. Additionally, CVD can be conducted at lower pressures and temperatures, significantly reducing the cost of the diamond synthesis process.

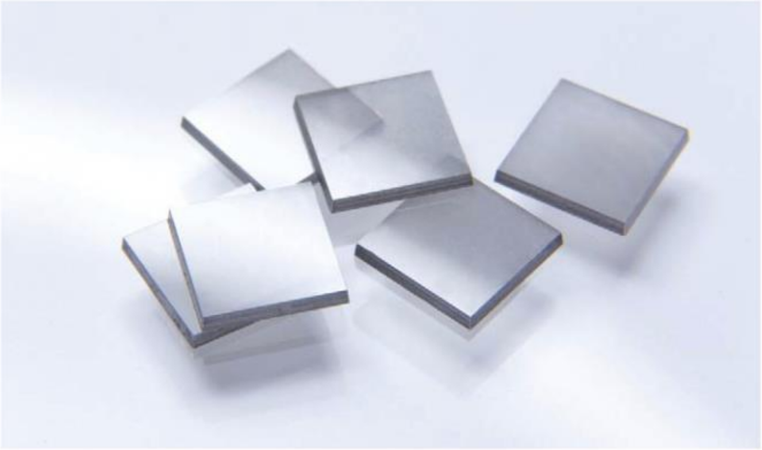

Figure 2. Commercially synthesized electronic-grade single-crystal CVD diamond plates [1].

The CVD synthesis of diamonds was first reported by scientists from the former Soviet Union, Derjaguin et al. in 1968. They used a chemical transport reaction method to deposit diamond films on non-diamond substrates, though the deposition rate was very slow. In 1981, Spitsyn and colleagues from the Institute of Physical Chemistry in the former Soviet Union initially demonstrated the principles of CVD diamond synthesis. They utilized atomic hydrogen in a reducing atmosphere to inhibit graphite crystallization, thereby successfully ensuring the selective growth of diamond. In 1983, Japanese scientist M. Kamo and his team successfully achieved the epitaxial growth of diamond films using the Microwave Plasma CVD (MPCVD) method. Since then, this method has been widely used to grow high-quality diamond films and has sparked a global surge of research interest in diamonds [5].

In a typical CVD process, hydrocarbons, commonly methane (CH4), provide the carbon source for diamond growth, while hydrogen (H2) plays a crucial role in initiating reactions between gas-phase radicals and surface species. Currently, there are various methods to excite the reactant gases into active radicals, including thermal methods, discharge methods (such as DC, RF, microwave, or laser), and combustion flame methods. Compared to other methods, the MPCVD technique offers advantages such as the absence of electrode contamination, high plasma density, and easy control over the size, making it the internationally recognized best method for growing high-quality single-crystal diamonds [5].

Since there are multiple obstacles in impurity control of synthesizing high-purity silicon wafers in the laboratory, it is worth mentioning that the MPCVD method is a simple and efficient way to synthesize high-purity diamond substrates suitable for electronic device applications in the laboratory. This represents a unique advantage of diamond semiconductors [5].

4.3. Doping Challenges in Diamond PN Junctions

Doping in diamond, which involves introducing impurity atoms into the diamond crystal lattice to create either p-type or n-type semiconductor regions, presents unique challenges compared to other semiconductor materials. The wide bandgap of diamond necessitates the use of specific dopants that can effectively donate or accept electrons. Boron is commonly used for p-type doping, while phosphorus, sulfur, and nitrogen are potential candidates for n-type doping.

4.3.1. P-type Doping

At present, the p-type doping technology of diamond is relatively mature. For the main dopant of p-type doping, boron impurities can be easily integrated into natural diamond and microwave plasma chemical vapor deposition (MPCVD) diamond, with no crystal orientation problem. Diamond can be transformed from an insulator to a p-type semiconductor or even a superconductor by boron doping, where boron atoms exist as the main impurity in diamond.

However, while the implementation of boron (B) doping is relatively straightforward, its high activation energy presents a significant challenge for the application of B-doped diamond in electronic devices. The relationship between B concentration and activation energy in room-temperature B-doped diamond has been shown in Figure 3, It indicates that at low B doping concentrations($\sim 10^{16} cm^{-3}$), the activation energy is approximately 0.36 to 0.37 eV. This high activation energy results in an activation rate of B less than 0.1% at room temperature, leading to relatively high resistivity in B-doped diamond. As the B concentration and temperature increase, the activation energy gradually decreases, which also highlights the poor thermal stability of B-doped diamond [5].

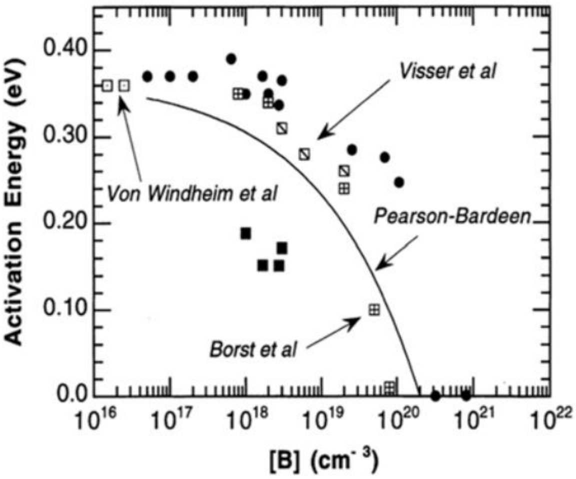

Figure 3. Relationship between B concentration and activation energy in B-doped diamond [5].

4.3.2. N-type Doping

Currently, achieving n-type doping in diamond is significantly more challenging than p-type doping. In traditional semiconductor materials like silicon, n-type doping can typically be accomplished through thermal diffusion, ion implantation, or chemical vapor deposition. However, for diamond, the high bond energy between carbon atoms makes thermal diffusion impractical. Additionally, due to the relatively small lattice constant and atomic spacing, defects created during ion implantation are difficult to anneal, and it is challenging to substitute carbon atoms with dopant atoms.

At present, n-type doping in diamond is primarily achieved by introducing dopant gases during the chemical vapor deposition process, and it has been realized on diamond substrates with (001) and (111) orientations. Phosphorus (P) and nitrogen (N) impurities have very deep donor levels in diamond, with P having a donor level of 0.6 eV and N having a donor level of 1.7 eV. As a result of its lower donor level, P is considered a more promising candidate for n-type doping. However, due to its larger atomic radius compared to carbon and nitrogen atoms, phosphorus causes significant lattice damage that is difficult to repair. Consequently, the lack of effective n-type doping techniques for diamond remains a critical bottleneck in the development of diamond-based devices [5].

4.4. Diamond Terminal Technology

Diamond terminal technology is critical to the performance and reliability of diamond PN junctions. This structure is used to control the edge effect and electric field distribution around the PN junction, thereby improving the performance and stability of the device.

The commonly used diamond terminations include hydrogen, silicon, oxygen, hydroxide, fluorine, and nitrogen. Hydrogen, fluorine, and nitrogen terminations are generally achieved through plasma treatments with gases containing these elements. Silicon termination can be realized either by reacting SiO2 with diamond in a high-temperature reducing atmosphere or by annealing elemental silicon with diamond under vacuum conditions. Oxygen termination is mainly accomplished through strong acid cleaning, ozone treatment, or oxygen plasma treatment [5].

Advanced terminal technology ensures efficient injection of charge carriers at the PN junction interface, minimizing contact resistance and enhancing current density and overall device efficiency. Additionally, the electrical performance of diamond PN junctions could be improved by optimized terminal designs, which reduce parasitic resistance and capacitances. Incorporating surface passivation techniques within terminal technology protects the PN junction from environmental factors such as moisture and contaminants, preserving the device's performance and longevity.

5. Conclusion

In this paper, these remarkable properties position diamond as a superior material for high frequencies, high power, high temperatures or high voltages devices, making it highly desirable for the next generation of electronic devices. The intrinsic properties of diamond PN junctions allow for the development of robust and efficient devices like high-power switches, FETs and Schottky diodes. By enabling these devices to function in harsh conditions where traditional materials would fail, these innovations will broaden the scope of semiconductor and electronic technology.

The production processes for diamond PN junctions, generally including the High Pressure High Temperature (HPHT) method, Chemical Vapor Deposition (CVD), and Microwave Plasma Chemical Vapor Deposition (MPCVD), are crucial in realizing their practical applications. Each method offers distinct advantages and challenges. HPHT is beneficial for its cost-effectiveness and ability to produce synthetic diamonds similar to natural ones. In contrast, CVD and MPCVD offer greater control over the purity and quality of diamond films, which is essential for electronic applications.

One major obstacle in the fabrication of diamond PN junction is doping, specifically attaining efficient N-type doping. While P-type doping has seen more progress, N-type doping remains a hurdle due to the difficulty in incorporating donor atoms into the diamond lattice without compromising its properties. Advances in doping techniques and terminal technologies are essential to fully harness the potential of diamond-based electronic devices.

Diamond PN junctions are a promising candidate for next-generation electronic applications due to their outstanding characteristics. The entire potential of diamond in the semiconductor industry could only be exploited via persistent research and development in synthesis techniques, doping schemes and device fabrication. Diamonds hold unique features that have the capacity to completely change electronics by providing unparalleled power, speed and durability.

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