Synthetic Diamond for Nitrogen Vacancy Sensor and Its Applicability

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Synthetic diamonds have been widely used in industrial applications due to their high purity and low crystal defects compared to natural diamonds. It is also possible to endow specific electrical and magnetic properties by doping with different types of elements, and is expected to be applied in various fields such as sensing and measurement. We have succeeded in producing a diamond with the world's highest level of purity and lowest level of defects by using our unique high-pressure and high-temperature method. Furthermore, we have created a highly sensitive sensor with the nitrogen vacancy (NV^-) center by electron beam processing and ion implantation in cooperation with Nissin Electric Co., Ltd. This paper introduces the high quality diamond synthesized for the NV sensor and its applicability.

Keywords: diamond, electron-beam processing, ion implantation, nitrogen vacancy (NV^-) center, sensing

1. Introduction

Uses of diamond are not limited to jewelry. It is known as a fundamental material for various technologies ranging from heavy industries to semiconductors and other leading-edge industries. Sumitomo Electric Industries, Ltd. began research of synthetic single-crystal diamond (Sumicrystal) in the 1970s and succeeded in the world's first mass production of diamond (Photo 1). Sumicrystal has high hardness and high thermal conductivity. Moreover, our technology can decrease crystal defects and dislocations to extremely low level compared to natural diamonds. Due to these excellent properties, Sumicrystal has been used in a wide range of applications, such as grinding wheels, dressers, drawing dies, cutting tools(1), drills, end mills, throwaway inserts, and heat spreaders. Furthermore, Sumitomo Electric succeeded in developing colorless high-purity diamond called Sumicrystal Type II in 1995. It has been used as a material for various optical components and pressure-resistant windows.

In recent years, the NV^- center in diamond has been the focus of attention in the ultra-high-sensitivity sensor and quantum information device fields. Since diamond-based NV sensors are highly sensitive even at room temperature, diamond becomes a promising material for biosensors such as cytosensors, magnetoencephalography and magnetocardiography. Automobile sensors, and atomic-level fine magnetic field sensors have also been proposed. Moreover, diamond offers superb quantum controllability, which can be exploited to apply it to quantum computers*1 and quantum repeaters*2 in the near future. This paper reports on a diamond NV sensor currently in joint development with Nissin Electric Co., Ltd.

2. The NV Sensor and Its Required Properties

Ultra-high-sensitivity sensors, also known as NV sensors, can operate even at room temperature because of their unique NV^- center pair in diamond, as shown in Fig. 1. In order to introduce the NV^- center into diamond lattice, a trace amount of nitrogen (N) is added firstly during synthesis. Then the vacancy (V) is introduced by using electron-beam processing*3 or ion implantation*4.

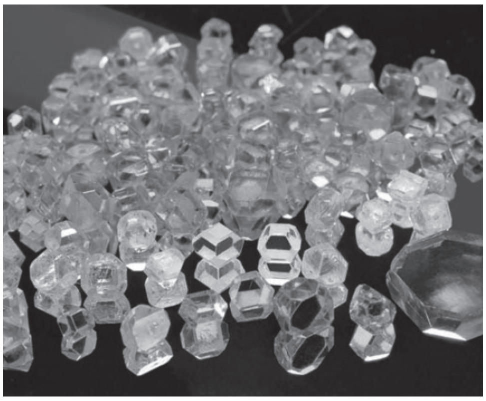

Photo 1. Synthetic single-crystal diamond

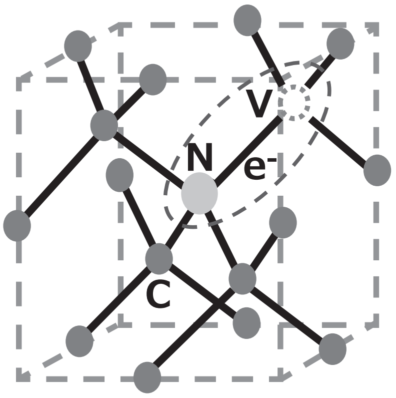

Fig. 1. NV^- center in diamond lattice

Eventually, the NV$^-$ center can be formed by annealing the diamond.

The NV$^-$ center is negatively (−) charged when one electron is captured. It creates a state sensitive to magnetism, electric field, and temperature, which is known as the triplet spin state. The state of the NV$^-$ center can be detected sensitively by light even with a single spin, while other methods such as electron spin resonance (ESR) require many spins. Moreover, each carbon atom is joined to other four carbon atoms with strong covalent bonds in diamond lattice, which makes the disturbances in diamond lattice extremely low. As a result, the NV$^-$ center can be measured with high-sensitivity even at room temperature. These facts make diamond promising for very convenient use in high-sensitivity sensors and quantum computers.

The sensitivity of the NV sensor can be expressed by the following equation.

$$\eta \propto \frac{1}{C\sqrt{\mathrm{n}_{NV}\cdot T_2}} \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \quad (1)$$

where C is the contrast, η is the sensor sensitivity, n_{NV} is the number of NV$^-$ centers, and T_2 is the electron spin coherence time.(2)

The sensor sensitivity increases with decreasing η. Therefore, in order to develop a high-sensitivity sensor, it is necessary to either make n_{NV} larger or T_2 longer. However, a larger n_{NV} usually results in a shorter T_2, which can be caused by the nuclear spin attributable to the nitrogen in the NV$^-$ center, the inclusion of foreign elements, and crystal defects. In order to optimize this trade-off, several different kinds of methods that make T_2 longer are currently being explored from material and process points of view.(3) Since the length of T_2 is closely related to the properties of diamond, we consider that it is effective to have a longer T_2 by reducing impurities and crystal defects in diamond lattice, thereby reducing noise from their spins.

3. Diamond Synthesis Process for NV Sensors

Diamond synthesis processes are roughly divided into high-pressure high-temperature (HPHT) process*5 and chemical vapor deposition (CVD) process*6.

Development of a high-sensitivity NV sensor requires a high-quality diamond of high purity and few defects, which is close to a perfect crystal. To synthesize diamond through a CVD process, it is common to adopt homoepitaxial growth using single-crystal diamond as a seed substrate. A drawback involved in this process is that lattice defects such as dislocations are likely to occur during the growth from the substrate interface, resulting in a short T_2. It has been difficult to synthesize high-quality diamond since only small substrates are currently available and it is extremely difficult to obtain a seed substrate with few dislocations and few crystal defects, as described later. In comparison, the HPHT process synthesizes diamond in an ultra-high-pressure and ultra-high-temperature region in which diamond is stable. Therefore, it is easier to yield high-purity and low-defect diamond. Consequently, we used the HPHT process to synthesize diamond for NV sensors.

3-1 High purification technology

To improve the sensitivity of NV sensors, it is necessary to achieve a high level of purification by controlling the amount of nitrogen and eliminating foreign elements. Diamond synthesized through the HPHT process commonly contains 10 to 200 ppm nitrogen in a single-substitutional form, which is known as the Ib type (Photo 2). Since NV$^-$ centers are susceptible to faint magnetic fields, controlling nitrogen impurities with spin is a challenge. We developed a technology to use titanium as a nitrogen getter during synthesis and control nitrogen to a level of a few ppm.(4) Moreover, in addition to nitrogen, foreign elements such as boron (B) and nickel (Ni) are also readily contained in the crystal. To avoid these inclusions, raw materials must be highly purified. High-purity diamond thus produced is raising huge expectations about its use in NV sensors.

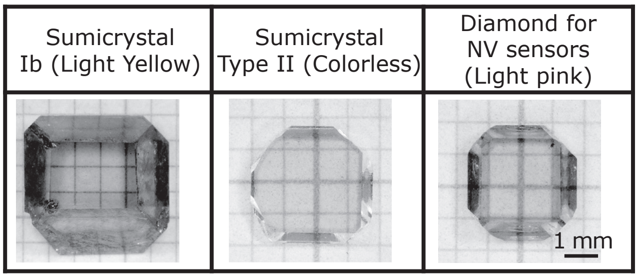

Photo 2. Different types of synthetic single-crystal diamond

3-2 Defect reduction technology

Diamond synthesized through the HPHT process offers superb crystallinity and a very low level of variation between crystals. However, close observations of crystal defects by means of X-ray topography reveals radially extending needle-like dislocation defects, as shown in Photo 3.(4)

These types of defects are presented in most diamonds synthesized through the HPHT process and affect the sensitivity of NV sensors (due to a short T_2). To counter this problem, Sumitomo Electric's proprietary crystal growth

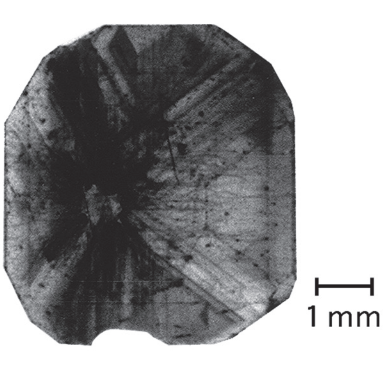

Photo 3. X-ray transmission topograph of diamond

technology was deployed, which resulted in success in synthesizing diamond with virtually no dislocation defect, as shown in Photo 4.(5)

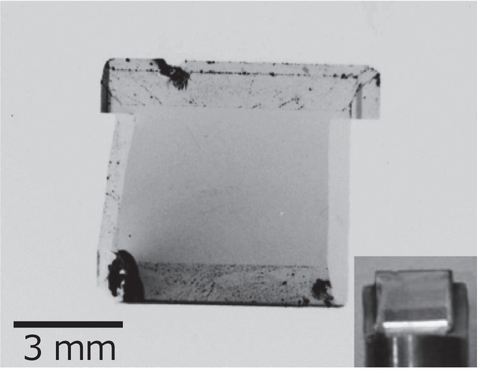

Photo 4. X-ray transmission topograph of low-defect diamond

A large defect-free region of 5 mm in diameter is presented at the center of this diamond. The diamond thus synthesized is the closest to a perfect crystal among currently obtainable diamonds and has already been provided as a sample to research institutes in Japan and abroad. Moreover, using the CVD process described at the beginning of this chapter and this diamond as a seed substrate, large low-defect diamond can be synthesized.

4. NV Sensor Fabrication Technology

The development of a defect reduction technology approaching perfect crystals and high-purification and nitrogen concentration control technologies for controlling nitrogen concentration to a level of a few ppm has enabled us to provide diamond for NV sensors. Following this, Sumitomo Electric explored NV sensor fabrication and application technologies with Nissin Electric and its group companies.

NV sensor fabrication methods include the following: 1) Implantation of nitrogen ions into high-purity diamond, 2) Electron-beam processing of diamond with pre-implanted nitrogen, and 3) Doping nitrogen during diamond synthesis through a CVD process. Vacancies formed during ion implantation or electron-beam processing move in the diamond crystal at a high temperature of 600°C or above and bond with nitrogen, forming the NV^- centers.

Ion implantation enables controlling nitrogen concentration in the direction of depth through the control of acceleration energy and designing a two-dimensional NV^- center arrangement through the use of a mask. Thus, further advanced utilization of diamond is being explored.

Regarding the CVD process, it has been reported that N-V axes were aligned on a (111) diamond substrate in a direction perpendicular to the surface with a probability close to 100%.(6)

4-1 Ion implantation

Nissin Ion Equipment Co., Ltd. has a medium-current ion implanter compatible with 300 mm wafers in a cleanroom (Class 1). This implanter can implant various ion species and even cluster or molecular ion species. It also implants ion species while heating the substrate. The company is also engaged in subcontract implantation (Table 1). Ion implantation requires expertise to set conditions because the method also produces other forms of nitrogen than the substitutional form. Nonetheless, using the EXCEED system in the current development, NV^- centers were produced.

Table 1. Summary of Ion Implanters

Model	Ion species	Dose	Energy	Other
EXCEED 3000AH	N^+, N_2^+, B^+, BF_2^+, P^+, As^+, In^+, Sb^+, etc.	5E10~1E17	5~750 keV	
CLARIS	N_2^+, $B_{18}H_x^+$, $C_{16}H_x^+$, $C_7H_x^+$, P_4^+, etc.	5E10~1E17	4~80 keV	Cluster
IMPHEAT	N^+, N_2^+, Al^+, P^+, B^+, etc.	5E10~1E17	5~960 keV	Substrate temperature: up to 500°C

4-2 Electron-beam processing

NHV Corporation provides various irradiation services (Table 2). The company uses several transfer methods suitably according to irradiation materials and conditions. The company can also handle indefinitely shaped small substrates such as diamond. Using the EPS-3000 system in the current development, irradiation parameters for diamond a few mm in thickness were ascertained to achieve vacancy introduction into the diamond and NV^- centers were formed.

Table 2. Summary of Electron-Beam Processing Systems

Model	Acceleration voltage (kV)	Max. irradiation width (cm)	Max. sheeting Dimensions (cm)	Carrier
EBC-200	150~200	100	–	Film・Sheet (Φ40 cm, 200 kg/m)
EBC-300	150~300	60	60×60×3	Wafer, etc. (External Carrier Unit equipped)
EPS-750	300~750	120	120×80×7	Wafer, Film, Sheet
EPS-800	400~800	60	60×100×7	Wafer, Sheet, Wire, etc.
		180	180×130×8	Wafer
EPS-3000	1000~3000	180	180×90×15	Wafer, Film・Sheet

4-3 Basic characteristics of NV sensors

We fabricated NV sensors by performing electron-beam processing and annealing on various synthesized diamond substrates. Figure 2 presents changes in the full-width at half-maximum (FWHM) of an optically detected magnetic resonance*7 spectrum against the nitrogen concentration of diamond.

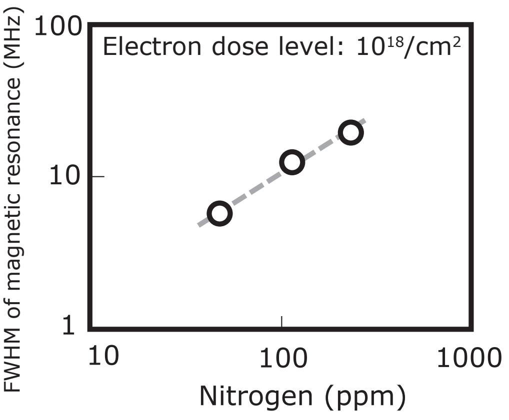

Fig. 2. Nitrogen concentration dependence of FWHM of optically detected magnetic resonance

The graph reveals that the FWHM increases with increasing nitrogen concentration. It is likely that, at a high nitrogen concentration: distances between an NV^- center and its adjacent nitrogen atom or NV^- center that has spin become small; disturbances increase; and the spin coherence time becomes short.

According to Equation (1), and depending on applications, the sensitivity of an NV sensor can be enhanced either by raising fluorescence intensity (the number of NV^- centers: n_{NV}) or by making the spin coherence time (T_2) longer. The optimal solutions vary with specific needs. Even so, as described above, NV sensor prototypes have made exploration of the optimal solution possible.

5. NV Application Technology

Sumitomo Electric and Nissin Electric are commonly operating in the electricity sector. Taking this business sector as an example, Chapter 5 describes forms of NV sensor usage. Common magnetic sensors convert magnetic signals to electrical signals and transmit them via conductors. Accordingly, they capture noise other than magnetic signals. In contrast, NV sensors only detect the magnetic field around them and transmit signals optically, contributing to reduced electrical noise from electric wires; in other words, their measurements are electrically isolated. This enables the sensor to be installed in proximity to a high-voltage power line, providing strong signals and achieving high-performance measurements. Moreover, diamond offers superb environmental resistance and is therefore expected to function as a sensor stably for a long period even in a harsh environment. To adapt to these various applications, we constructed prototype modules with an embedded NV sensor block.

5-1 Pen-shaped module

First, using Sumitomo Electric's optical technology, we constructed a prototype module of a pen-shaped NV sensor (Photo 5). The pen-shaped casing of this model contains diamond with NV^- centers in it, as well as a laser diode (LD), a multiplexing/demultiplexing module, a microwave coil, and a photodetector. To transmit and receive LD control signals, photodetector signals, and microwave signals, electric cables are drawn in or out. This small sensor head with only thin cables attached enables measurements conveniently in proximity to the magnetic field to be measured.

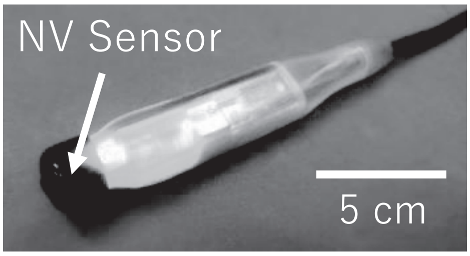

Photo 5. Exterior of pen-shaped module

5-2 Antenna-type module

To install a sensor in proximity to high-voltage power equipment, bringing the sensor thoughtlessly close to the equipment can result in a ground fault because coaxial cables used to transmit microwaves are made of metal. To address this challenge, a prototype NV sensor module transmitting and receiving microwaves was constructed to achieve electrically isolated measurement. The configuration illustrated in Fig. 3 was used to confirm for the first time that magnetic field signals of a simulated power line (50 Hz alternating current of 30 A) could be measured at a maximum distance between antennas of 10 m.

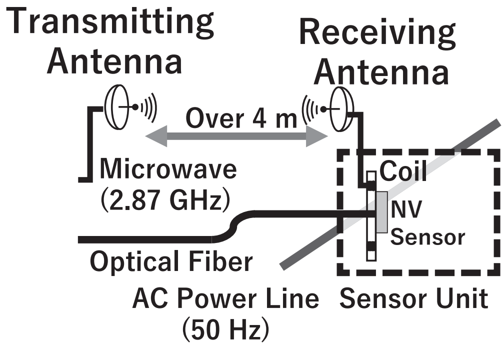

Fig. 3. Experimental system for alternating magnetic field (electric current) measurement

Figure 4 shows the experimental results for a distance between antennas of 4 m. Changes over time in signal intensity were observed to correspond to changes in the alternating magnetic field. The experiment proved that NV sensors can be installed for measurement in high-voltage areas without the use of a metal cable.

Diamond NV sensors, as described above, are expected to come into increasing use as convenient high-

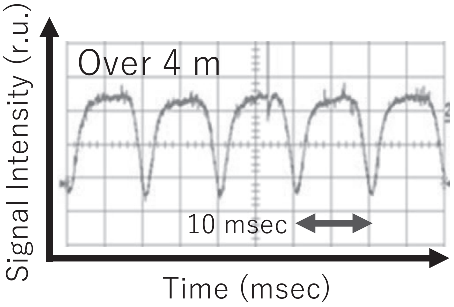

Fig. 4. Alternating magnetic field (electric current) measurement results

sensitivity sensors in various applications and environments.

6. Conclusion

This article described high-sensitivity NV sensors incorporating high-pressure synthesized single-crystal diamond and their applicability. Expectations are high for its use in various areas, including magnetoencephalography, magnetocardiography, automobile sensors, and remote measurement in harsh environments. This paper reported on procedures used to synthesize raw material diamond, NV$^-$ center formation, and application technologies. Going forward, for the commercialization of the NV sensor, we intend to develop high-quality diamond products and sensor module products and explore their applications.

- Sumicrystal is a trademark or registered trademark of Sumitomo Electric Industries, Ltd.
- EXCEED, CLARIS, and IMPHEAT are trademarks or registered trademarks of Nissin Electric Co., Ltd.

Technical Terms

*1 Quantum computer: The next-generation computer based on quantum effect, which has overwhelming processing power in comparison with nowadays computers in specific calculation field. On the other hand, the current quantum computer made with superconducting devices can only be operated at an extremely low temperature close to absolute zero.

*2 Quantum repeater: A repeater means for enabling long-distance quantum information communications based on quantum entanglement. Since the information sent and received is nearly impossible to be duplicated, it is possible to extend the distance of quantum cryptography by using multiple quantum repeater systems.

*3 Electron-beam processing: A technology of irradiating a sample with high-energy electron beams. It can be used for cross-linking treatment to polymer products or controlling the behavior of semiconductor carriers.

*4 Ion implantation: A technology of irradiating a sample with high-energy ions. It can be used for creating doped layers on semiconductors.

*5 High-pressure high-temperature (HPHT) process: A technology used to produce synthetic diamond from graphite as the start material under the conditions of 1350°C and 5 GPa, by using an ultra-high pressure generator,.

*6 Chemical vapor deposition (CVD) process: A technology used to produce synthetic diamond below atmospheric pressure by decomposing source gases (hydrogen and methane) by plasma to react chemically on a substrate.

*7 Optically detected magnetic resonance: A phenomenon in which fluorescence intensity reflects the resonance state of electron or nuclear spin under the effect of a magnetic field, with the resonance state caused by a specific microwave frequency and magnetism.

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