Recent Progress and Application of Synthesized Diamond
(Present Status and Future of Vapor Phase Deposition of Diamond)

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Diamond is known as the most difficult material to machine and a costly material. These have been limited the application of diamonds in a small area. The method to make diamonds from gas phase was reported by Setaka et al. in 1981 and many Japanese successfully developed various methods of diamond deposition. Diamond can essentially be deposited from the mixed gas consisting of hydrogen and methane and the diamonds made by this technique have the same characteristics as IIa diamonds which do not contain any impurity elements. The application of diamond films have already started. Tools, speaker diaphragms and X-ray windows are the products used presently. As diamond has many useful characteristics for electrical applications, expectations to use in electric parts and devises are quite common. The development of diamond devices using vacuum deposited diamond film has already begun. For the future application of this technology, improvement of this process for obtaining higher quality films and fabrication by lower cost is required.

Key-words: Diamond, Film, Chemical vapor deposition, Plasma, Optical property, Raman spectroscopy, Tool, Diamond semiconductor, Speaker diaphragm, Schottky contact, FET

1. Introduction

SYNTHESIS of diamond was first reported in 1955 by General Electric and has been progressed to make not only grit but also sintered diamond. Nowadays, more than 95% of diamond in use is artificial diamonds. However, practical applications of diamond has been limited in abrasives, cutting tools and wear-resistant parts. In 1984, Sumitomo Electric Industries commercialized diamond heat sinks made of high pressure synthesized single-crystal diamonds. They are used in electrical application such as laser diodes or microwave devices.

Significant progress can be seen in the development of gas phase deposition of diamonds. As the machining of diamonds is quite difficult and costly, a method to make diamond having near net shape is required. Moreover, the size of high pressure synthesized diamond is limited less than 10 mm and a larger diamond is also desired to utilize.

In this report, the author wishes to review the technologies of diamond synthesis from gas phase and to discuss the applications of diamond film.

2. Diamond synthesis from vapor phase

The major innovation of this technology was performed by Setaka et al. in 1981.1) Though many researchers tried to obtain diamond from gas phase, reproducible deposition and reasonable growth rate for application had not been reported before their publication. Spitsyn et al. first succeeded in depositing diamond on other substrate materials than diamonds in 1976.2) They used a chemical transport reaction using some activation means for the reaction. However, they did not show their apparatus and no one could reconfirm their results.

After Setaka’s report on the development of hot filament CVD, many Japanese researchers rushed into this technology, as with the fever of high temperature superconductivity, and succeeded in developing various methods. Thanks to the development of electronic industries, the background technology of thin film deposition helped to develop many technologies.

Basic technologies of making diamond from gas phase are categorized in the following four basic
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There are more than 30 modified methods but they are limited in CVD methods. Diamonds from gas phase are so called 'CVD Diamonds'.

Although there are many methods, the principle of diamond formation is summarized in the following conditions.

1. Hydrogen is needed in reactant gas,
2. One or more activation means are needed,
3. Substrate temperature is from 400°C to 1000°C.

Many kinds of gas, such as hydrocarbon, alcohol, ketone, carbon oxide, carbon halide etc., are found to be suitable source gases. In contrast, no one has succeeded in making diamond from a reactant gas which does not contain any hydrogen atoms. Recent reports indicated the possibility to make diamonds lower than 150°C.

Figures 1 and 2 show the schematic drawing of hot filament CVD and microwave plasma CVD. The typical deposition conditions using hot filament CVD are;

- Reactant gas: 1% CH₄ 99% H₂
- Pressure: 40 Torr
- Filament temperature: 2050°C
- Substrate temperature: 900°C
- Deposition rate: 1 μm/H

Setaka et al. suggested that, under these conditions, atomic hydrogens are made by the reaction of such high filament temperature and atomic hydrogens play as forming precursor of diamond deposition and etching graphite codeposited with diamonds. Using plasma assisted CVD, the electron temperature of hydrogen was found to be as high as 5000 K.

3. Characteristics of CVD diamond

Typical surface morphology of diamond film deposited on silicon is shown in Fig. 3. As the nucleation site of diamond deposition is quite low in density, rubbing the surface with diamond grit is needed to make film. Figure 4 shows cross section of 30 μm thick diamond film. The columnar structure is seen in this picture.

CVD diamond is essentially a diamond which contains no impurity atoms. Collins et al. reported on the optical absorption of diamond film. The absorp-
tion edge was found to be 225 nm which is the same as $\mu m$. Recently, Imai et al. reported that the absorption edge of CVD diamond film with a thickness of 100 $\mu m$ was also 225 nm.\(^9\)

Small amounts of impurity phases can be measured by Raman spectroscopy.\(^10\) Figure 5 shows a typical spectrum of Raman shift obtained from CVD diamond film deposited by microwave plasma CVD whose reactant gas consisted of 1% CH$_4$. The Raman shift of diamond is observed at 1332 cm$^{-1}$ and graphite and amorphous phase can be easily identified because the Raman shift of such phases are observed at 1360 and 1580 cm$^{-1}$ (graphite) and 1500 cm$^{-1}$ (amorphous).

4. Realized and anticipated applications of CVD diamond

CVD technology of diamonds is considered for application in the following manner.

1. Fabricating diamond coated composite material,
2. Fabricating three dimensional shaped and large diamonds,
3. Making high purity diamonds.

4.1 Tools

Diamond is not a suitable material to cut steel or iron. The major uses of diamond cutting tool are for cutting aluminum alloy and plastics. Recent requirements to make automobiles light has made aluminum alloy common in automobiles. As a strong aluminum alloy is required, the content of silicon has been increased. For example, A 390, which contains 17% silicon, is believed to be useful for the engine block but a sufficient tool has not yet been developed.

In order to apply diamond films in this field, ‘Diamond Coated Tools’ is the common expectation. Many have tried to develop diamond coated inserts and found that the adhesion strength between diamond and cemented carbide is not sufficient for practical application. The reason is believed to be that diamond consists of covalent bonds and does not have any compound phase.

However, in tool application other than cutting, strong adhesion is not required. Figure 6 shows a Tape Automated Bonding (TAB) tool made of CVD diamond film.\(^11\) The life time of this tool was found to be about 10 times longer than made of sintered diamond.

The second way to apply CVD diamonds in tools is to use thick diamond film like sintered diamond. In 1989, we started to sell small diameter endmills made of CVD diamonds.\(^12\) Diamond films having a thickness of 100 $\mu m$ are made by hot filament CVD. They are cut by laser and the substrates are dissolved by acid. These blanks are brazed on a submount made of cemented carbide. Characteristics of this endmill are shown in Fig. 7. The tool life was found to be several or 10 times longer than that of cemented carbide.

4.2 Electric parts

Diamond is well known as the most suitable material for acoustic parts because of its large sound velocity (18,200 m/s). The authors developed a diamond coated speaker diaphragm as the first product of CVD diamond.\(^13\) Diamond coating improved the highest sound of an alumina diaphragm from 35,000 Hz to 50,000 Hz.

A diamond diaphragm is considered to be an ideal one. The poor machinability makes it impossible to make a diaphragm of natural diamond. A free standing diamond diaphragm fabricated by the CVD method was developed in 1990. Diamond deposition was carried out by hot filament CVD on silicon substrate. After the deposition, silicon substrates were dissolved by a mixed acid of HF and HNO$_3$. Figure 8 is a photograph of this diaphragm. The thickness is
30 μm and the distribution of thickness is controlled to be within 10%. The sound velocity was measured by the vibration method and the result was 16,500 m/s which is a little less than the value of single crystal diamond. The properties of the speaker which this diaphragm was used are shown in Fig. 9. The highest frequency of this speaker was 80,000 Hz which is the highest sound that a dynamic speaker can generate.

Heat sinks are the most expected application of CVD diamonds. The heat conductivity of CVD diamond is quite dependent on conditions of deposition. The author measured the heat conductivity of 300 μm thick CVD diamond film obtained by hot filament CVD and the result was 16 W/cm · K. This value is considered to be sufficient for application in the same manner as single-crystal diamonds.

### 4.3 Active and passive devices

Diamond is one of the wide band gap semiconductors and has relatively high mobility, low dielectric constant and high break-down voltage. Anticipated applications of semiconducting diamond are as refractory integrated circuits, blue emitting diodes, antiradiation devices etc.

**U b** diamond is a p-type semiconductor, which was reported in 1952. The first report of a diamond transistor was carried out by Geis et al. in 1987 using synthesized single-crystal diamond and point contacts. They reported that the transistor was operated even at 500°C.

Epitaxial growth of diamond is considered to be a key technology to fabricate diamond devices. The authors endeavored to obtain high quality epitaxial films and found that using (100) substrate and 6% CH₄ in the reactant gas of microwave plasma CVD
makes good epitaxial films.\textsuperscript{16)\textsuperscript{17}) Boron-doped epitaxial films were obtained which characteristics was found to be quite similar to natural IIb diamonds.\textsuperscript{17)}

As an n-type semiconductor is hard to obtain, Schottky junctions have been studied by many researchers. Rectifying behavior using poly-crystal line and epitaxial film have been reported. However, the surface roughness of epitaxial films affects the rectifying behavior.\textsuperscript{16)\textsuperscript{17}) Typical surfacemorphologies of epitaxial film grown from a reactant gas consisting 0.5\% and 6\% CH\textsubscript{4} are shown in Fig. 10. Figure 11 shows the Schottky behavior of aluminum electrode on these films. The difference of forward and reverse current was found to be affected by surface morphology.

A FET and a light emitting diode are successfully fabricated using boron-doped epitaxial films and Schottky contacts.\textsuperscript{19)\textsuperscript{21)} Figure 12 shows the characteristics of diamond MESFET reported by Shiomi et al. Electro-luminescent devices have also been reported using Schottky junctions. The report of blue emission by point contact suggest the possibility of ultra-violet emission. The photo-conductivity of CVD diamond has been reported and light sensors are the expected application using this characteristic. The fabrication of a thermistor using boron-doped film was reported by Nakahata et al.\textsuperscript{22)} The superiority of this device is its operation at elevated temperatures as high as 600°C.

4.4 Others

X-ray window used in EPMA was commercialized in 1988. As the transmission of soft X-rays is strongly affected by the atomic number and thickness of the window, diamond film as thin as 4000Å or less is needed.

The demands of fine lithography technology require X-ray lithography and a mask blank made of diamond is expected. Windischmann reported on a diamond X-ray mask having dimension of 50 mm.\textsuperscript{23)\textsuperscript{24)} A large and thin free standing film (2 µm) are required for this application.

The optical transparency of diamond is essentially quite flat in wavelength larger than 225 nm. The quality of diamond for this application is considered to be quite high and the improvement of the quality of film is required.

5. Future development and problems to be solved

Several commercial products of CVD diamonds have been developed and significant progress in new applications of diamonds has been made. As mentioned previously, CVD diamond resolved the limitation of diamond application. However, several targets are being considered for study to make use of CVD diamonds practically in various fields.

(1) Distinguish phases other than diamond,
(2) Low temperature deposition,
(3) Low cost process.

CVD diamond film is confirmed to be type II a diamond by measurement of optical transmission. However, uncertain absorption from 500 nm to the absorption edge was observed. Of course, contamination by nitrogen can be controlled using CVD methods. However, contamination by hydrogen is confirmed by Imai et al.\textsuperscript{11)}

The reported lowest temperature of diamond formation is 400°C. Almost all common metals can be coated at this temperature. The adhesion strength of diamond films is lower than that of ceramic films. One of the reasons is that a compound with diamond has not been found.

The cost of diamond is essentially determined by the deposition rate and size of equipment. However, the quality of CVD diamond obtained at high growth rates is not sufficient for application and the improvement of film quality is desired. The study of mechanisms of diamond formation is promising in solving this problem. The role of atomic hydrogen is progressively understood in recent studies. The author considers these studies to be helpful for the better understanding of film formation other than diamond from gas phase.

References


Naoji FUJIMORI was born in 1949. He received Master Degree in Metallurgy from Tokyo University in 1975. He has engaged in Sumitomo Electric Ind. Ltd. since 1975. He is the Chief Research Associate of Itami Research Laboratories. His research is focused on thin film processing and application, especially diamond film.