SYNTHESIS OF DIAMOND FROM GAS PHASE AND ITS PROPERTIES

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1. Introduction

Since the results of diamond synthesis from gas phase by the chemical transport reaction were reported in 1981 [1], many efforts have been made for the studies on diamond obtained by chemical vapor deposition method (CVD diamond). The first report of diamond deposition on a heterogeneous substrate from gas phase in Japan was in 1982 [2]. Since then, a lot of deposition methods have been reported. Hot-filament method, microwave plasma method [3] and radio frequency method [4] are able to be mentioned as the processes developed at the early stage. The deposition of diamond was confirmed by these methods, and gained general acceptance.

The growth features of diamond obtained by this method appear to have much in common. One of the most interesting features is that the crystals have well-defined habits and often appear as octahedral, cubo-octahedral or multiply-twinned particles truncated by the substrate.

Efforts for development of diamond synthesis have been made to get high-speed growth rate and large deposition area. So far the growth rate of about 1 mm/hr [5] is the highest, and a relatively homogeneous diamond film has been obtained on a 4 inches silicon wafer in diameter by microwave plasma method [6].

CVD diamond has been also studied to reveal the properties and the texture. Single crystalline particles, polycrystalline films and epitaxially grown films are able to be synthesized by CVD method. Single crystalline particles are useful to reveal intrinsic properties of CVD diamond, because polycrystalline films seem to be stressed by the aggregation of particles. The film is useful for practical applications, for example, optical window, heat sink, diaphragm for speaker, cutting tool and etc. Application of the film for X-ray optical window has been studied because of the high X-ray transmission and exceptional mechanical properties of the film.

In this paper, synthetic methods and conditions for CVD diamond, and some optical properties of CVD diamond are reported.

2. Methods for Diamond Synthesis from Gas Phase

Methods developed for diamond synthesis from gas phase are classified into three categories as given below.

1) Chemical transport reaction method (CTR) [1]
2) Hot filament assisted chemical vapor deposition (HFCVD) [2]
3) Plasma enhanced chemical vapor deposition (PECVD)

CTR is the deposition method from gas phase reported at first. The feature is to be deposited in a closed tube. However, the synthetic procedure has not been reported in detail enough to be traced.

The deposits similar to that obtained by CTR have been obtained on non-diamond substrates such as silicon under activated hydrogen by HFCYD. Schematic drawing of the apparatus is shown in Fig. 1 [2]). The tungsten filament heated above 2000°C was placed above the substrate heated at 600-1000°C, on which diamond was deposited. This method is economical but may have the problems in the reproducibility and the operation for a long period considering the short life of the filament. The deposition system using plasma seems to be effective for the improvement of these points.

Fig. 1 Schematic drawing of the apparatus of hot filament chemical vapor deposition [2].
Plasma enhanced chemical vapor deposition (PECVD) can be divided into four groups, that is, microwave [3,7], rf [4,8], dc [9,10] and combustion [11], according to the activation techniques of gas. Moreover, each technique may be also grouped into cold (glow discharge) and thermal plasma methods. As a typical plasma method, the apparatus of microwave plasma is shown in Fig. 2, in which substrate is heated by the absorption of microwave and the heat transfer from plasma. Although the experimental conditions for diamond deposition are different in each method, features of deposits such as shape and growth rate among each method have indicated similar tendencies for methane concentrations and substrate temperatures.

3. Influence of deposition conditions

Diamond particles tend to turn from polyhedron to hemispherical shapes with increasing methane concentrations. Particles with crystallographic planes such as (111) and (100) are obtained at the lower methane concentrations. The Raman spectrum of hemispherical crystals showed the existence of graphitic carbon having the peaks at 1360 cm\(^{-1}\) and 1600 cm\(^{-1}\) in addition to diamond. As the methane concentrations decrease, the intensities of Raman line due to graphitic carbon in the deposits decrease.

Deposits grow larger with the rise of the substrate temperature. At temperatures higher than 950°C, apparent growth rate decrease, because the graphitization of the deposited diamond and the gasification reaction of diamond with hydrogen are not negligible. Twinned crystals appear and the ratio of the area of (100) plane to that of (111) plane increase with the rise of substrate temperatures.

<table>
<thead>
<tr>
<th>Substrate temperature (°C)</th>
<th>800</th>
<th>820</th>
<th>900</th>
<th>950</th>
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<tbody>
<tr>
<td>(111) poly</td>
<td>single</td>
<td>single</td>
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<td>single</td>
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<tr>
<td>(110) poly</td>
<td>single</td>
<td>single</td>
<td>single</td>
<td>single</td>
</tr>
<tr>
<td>(100) poly</td>
<td>single</td>
<td>single</td>
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<td>poly</td>
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Diamond depositions have been confirmed on following substrates, molybdenum, tungsten, tantalum, copper, gold, zirconium, silicon, graphite, silica glass, sapphire, magnesium oxide, silicon carbide, boron carbide, tungsten carbide, titanium carbide, boron nitride, silicone nitride and aluminum nitride. Features of deposits like shape tend to slightly differ among each substrate.

Single crystalline growth layers have been obtained on (100), (110) and (111) planes of diamond [12]. Substrate temperature is one of the factors which determine the structure of the deposit. Table 1 shows the relations between crystallinity of films grown on diamond substrates and substrate temperatures. Epitaxially grown layers on the (111) and (110) have been obtained in the temperature range from 820°C to 950°C. On the other hand, the layer on the (100) plane was only observed at 820°C. The growth rates on the (111) and (110) planes are 0.3 µm/h at 900°C for 0.3% methane concentration. However, that on the (100) plane is smaller than those on (110) and (111), and was 0.1 µm/h under the same conditions.

4. Characterization of CVD Diamond

Fig. 3 shows scanning electron microscope images of diamond films obtained in the range of methane concentration from 0.3 to 3% at 910°C. Fig. 4 and 5 show cathodoluminescence and Raman spectra of diamond films shown in Fig. 3, respectively [13]. The bright blue emission has been observed in the cathodoluminescence spectrum of the film obtained at 0.3% methane. The emission is attributed to donor-acceptor pair recombination, and is identical to that observed for type IIa natural diamond. The features detected at around 2.33eV, 2.47eV and 2.57eV (Fig. 4a) are characteristic of CVD diamond, and are not observed in natural diamond or diamond produced by high-pressure synthesis. As Raman line features observed at low energies in Fig. 4a become relatively stronger, and additional lines are observed in the spectra.

Polycrystalline diamond film with (100) pre-
ferred orientation, obtained at 850°C and 3% methane, exhibits the emissions at 2.156 eV, 3.188 eV and 4.582 eV (Fig. 6). These emissions are associated with a single nitrogen atom and vacancy, a nitrogen atom in association with a carbon interstitial and an interstitial carbon atom, respectively. The 5RL band with a zero-phonon line at 4.582eV, and phonon replicas spaced at approximately 235 meV, is observed in the films produced with methane concentrations higher than 1%. The band was typically detected for the film obtained at 3% methane. The results indicate that diamond may be contaminated with free carbon atoms at higher methane concentration, that is, at higher growth rate.

Fig. 7 [14] show the absorption spectra for a single crystal shown in Fig. 8, grown using a methane concentration of 1% with a small quantity of water vapor at 850°C, and three polycrystalline films grown using methane concentrations of 0.3%, 0.5% and 1.5%. It can be seen that all samples exhibit an almost monotonically increasing absorption with increasing photon energy. For the single crystal and the film grown using 0.3% methane the absorption edge at 5.5 eV is clearly visible, but the other samples are too strongly absorbing to extend the measurements this far into the ultraviolet regions. It is known from Raman scattering measurements on similar samples that the films grown at higher methane concentrations contain significant amounts of carbon double bonds, and it is probable that the absorption evident in Fig. 7 is associated with this non-diamond carbon.

Fig. 9 shows intrinsic edge emission from diamond particles (Fig. 8) obtained at 1% methane

Fig. 3 SEM images of diamond films obtained using methane concentrations of a) 0.3%, b) 0.5%, c) 1%, d) 1.5%, e) 2% and f) 3% at 910°C
containing water vapor [15]. The features are due to the recombination of a free excitation with momentum-conserving phonons. The emissions indicate that the diamond particles are pure with few structural defects. The edge emission is strong in particles grown at lower methane concentration.
than 1%, and becomes relatively weak with increasing concentrations. The emission is only observed in type IIa diamond that is relatively free from defects.

No intrinsic edge emission is observed in the polycrystalline diamond films prepared under the same conditions as those for the particles exhibiting the edge emission. The results imply that the growth and aggregation of particles with few structural defects result in films being heavily strained, and that it is hard to get the polycrystalline film free from strain. This tendency is supported by the Raman spectra of particles and a film.

Fig. 10 shows the Raman spectra of particles and a film obtained at 1% methane concentration and 850°C, with a small amount of water vapor [16]. The line width of the Raman spectrum of the film is broadened to more than two times that of the particles, which may be caused by strain with the aggregation of the particles. Particles obtained at 0.5% methane containing water vapor exhibit a line width of ca 2.3cm⁻¹ which is similar to 2.0-3.0cm⁻¹ of natural single crystals we have used.

Deposition layers were qualitatively analyzed by SIMS [12]. When hexagonal boron nitride was used as a substrate holder, boron impurity was detected in the growth layer (Fig. II). On the other hand, aluminum was detected as impurity in the layer obtained on an aluminum oxide holder (Fig. 12). These results suggest that the contamination by the elements constituting the substrate holder...
cannot be neglected. The contamination may be attributed to the sputtering of the holder by impacts of plasma. Other impurity content was found to be approximately the same as in natural diamond. Hydrogen content, which is abundantly contained in a starting gas mixture, also seem to be the same as in natural diamond, because even the growth layer with lower hydrogen content than that in a natural diamond has been obtained (Fig. 12).

5. Summary

Preparation methods and optical properties of CVD diamond were reviewed in this paper. Raman and cathodoluminescence spectra of particles obtained at lower methane concentrations than 1% have indicated that the particles are high quality diamond similar to type IIa diamond, the purest form of natural diamond. The results indicate that it is possible to get pure diamond similar to natural diamond using CVD method. Since diamond exhibits some unique properties such as great hardness, high thermal conductivity, high electrical resistivity, optical transparency and semiconductivity induced by impurity doping, many efforts for applications have been attempted. Now, cutting tool coated with CVD diamond and diaphragm for speaker can be commercially available. The structure and properties of CVD diamond do not seem to be sufficiently understood. After the advance of preparation techniques and comprehensive understanding of the properties of CVD diamond, the diamond is further expected to be widely used.

References