High-Rate Growth of Large Diamonds by Microwave Plasma Chemical Vapor Deposition with Newly Designed Substrate Holders

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(Received 28 October 2005; accepted 24 January 2006)

Key words: diamond growth, microwave plasma chemical vapor deposition (MPCVD), homoepitaxial growth, high growth rate

The epitaxial growth of diamond on type-Ib diamond (100) substrates has been attempted using a 5 kW, 2.45 GHz microwave plasma chemical vapor deposition (MPCVD) system with nitrogen addition in methane and hydrogen source gases. To realize high growth rates, we designed new substrate holders to generate high-density plasma. The effects of nitrogen addition during high-rate microwave plasma CVD of diamond on the growth rate and crystallinity were investigated. Growth rates ranging from 30 to 120 μm/h were achieved. The nitrogen addition enhanced the growth rate by a factor of 2, and was beneficial to the creation of a macroscopically smooth (100) face. The deposited diamond was characterized by optical microscopy, Raman spectroscopy, cathode-luminescence spectroscopy and X-ray diffraction analysis.

1. Introduction

Diamond has many excellent electrical properties and is a promising material for the next-generation semiconducting devices. To use diamond for electronic devices, large-scale substrates, i.e., wafers, will be essential for device fabrication. A diamond substrate is dominantly synthesized by the high-pressure, high-temperature (HPHT) method. Due to the high cost and limited size of HPHT diamond, the applications of diamond have been limited. It is difficult to fabricate diamond with a size over 10 mm and to control impurities...
by the HPHT method. It is needless to say that as the quality and purity control of the synthesized diamond are very important for electronic purposes, the cost is also a very important item for industrial purposes. Thus, we think that the growth rate is one of the key issues for practical uses of diamond.

Chemical vapor deposition (CVD) is one of the most promising technologies for producing low-cost and large single-crystal diamond. It also seems to be easier to control impurities by this method than by the HPHT method. Microwave plasma CVD (MPCVD) is appropriate for large-area synthesis, but the growth rate is known to be lower than that of other CVD methods, which makes cost high. However, it has recently been reported that the growth rate of MPCVD on a (100) surface is improved drastically by adding nitrogen into source gases. A growth rate over 100 μm/h is realized, although the conventional growth rate is 10 μm/h or less. This development is very important for industrial purposes. However, the details such as how to increase plasma density are not clear.

In this paper, we report on high-density plasma generation using newly designed substrate holders to realize high-rate single-crystal diamond growth. The details of the holders are shown. The effects of nitrogen addition into the MPCVD system are also reported. Our trials realized high growth rates over 100 μm/h for homoepitaxial (100) diamond.

2. Experimental Methods

Diamond films were grown in a conventional 5 kW, 2.45 GHz microwave CVD system (Seki-technotron Corp. AX-5250) using gas mixtures of hydrogen (6N), methane (6N) and nitrogen (4N). The chamber was evacuated using a rotary pump. The growth conditions are summarized in Table 1. To obtain high growth rates, we have redesigned the molybdenum substrate holders to generate high-density plasma and to adjust the temperature of the substrates. The substrate temperature was measured using an optical pyrometer. The optical emission of the microwave plasma was monitored using an optical multichannel spectrometer during the diamond growth.

The experimental procedure is summarized in Fig. 1. Substrates were type-Ib (100) single-crystal diamonds grown by the HPHT method provided by Sumitomo Electric. Prior to diamond growth, the substrates were cleaned with isopropanol in an ultrasonic bath. Then plasma etching for 30 min was performed in the MPCVD reactor under a pressure of 21.3

Table 1
Growth conditions in this study.

<table>
<thead>
<tr>
<th>Total gas pressure:</th>
<th>21.3 kPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas flow rate:</td>
<td></td>
</tr>
<tr>
<td>H₂</td>
<td>500 sccm</td>
</tr>
<tr>
<td>CH₄</td>
<td>60 sccm</td>
</tr>
<tr>
<td>N₂</td>
<td>0–3 sccm</td>
</tr>
<tr>
<td>Microwave power:</td>
<td>1600–2600 W</td>
</tr>
<tr>
<td>Substrate:</td>
<td>Type Ib (100)</td>
</tr>
<tr>
<td>Substrate temperature:</td>
<td>1150–1220°C</td>
</tr>
</tbody>
</table>
kPa, H₂ and N₂ flow rates of 500 sccm and 1.8 sccm, respectively, at the same temperature for diamond growth. Then, methane gas was introduced into the chamber to grow diamond. The substrate temperature was around 1200°C. The flow rates of hydrogen and methane were 500 and 60 sccm, respectively, and the range of nitrogen flow rate was 0–3 sccm. The thicknesses of the grown diamonds were estimated from the weight gain measured using a microbalance.

The grown diamonds were characterized by optical microscopy, differential interference-contrast microscopy (DICM), atomic force microscopy (AFM), micro-Raman spectroscopy, cathode luminescence (CL) at room temperature and high-resolution X-ray diffraction (XRD) analysis.

3. Results and Discussion

In Fig. 2, the schematics of the newly designed substrate holder together with corresponding results of the numerical calculation of plasma, the pictures of hydrogen plasma and the observed diamond growth rates are shown. To focus plasma, a small projection is placed on the front surface of the holder. The figure shows the projection radius dependence of hydrogen plasma. We can see the focusing of plasma by adding small projections. The emission from plasma seems to become more intense as the radius decreases. A numerical calculation shows that the magnitude of the electrical field around the projection increases as the radius decreases, which is consistent with the behavior of the emission. The diamond growth rate of the 8 mm holder was 30 µm/h, although that of the 36 mm one was 5 µm/h. After optimizing the 8 mm holder’s shape, we obtained a growth rate of 50 µm/h.

In Fig. 3, diamond growth rate as a function of nitrogen flow rate is shown. Upon nitrogen addition, the diamond growth rate increases from 50 µm/h to 100 µm/h and (100) face growth is promoted(2) as in the case reported by Yan et al.(1)
**Fig. 2.** Schematics of newly designed substrate holder together with corresponding results of simulation of plasma, pictures of hydrogen plasma and observed diamond growth rates.

<table>
<thead>
<tr>
<th>Holders</th>
<th>Numerical Results</th>
<th>Hydrogen Plasma (observed)</th>
<th>Diamond Growth Rates (observed)</th>
</tr>
</thead>
<tbody>
<tr>
<td>φ 8mm</td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td>~30 μm/h</td>
</tr>
<tr>
<td>φ 16mm</td>
<td><img src="image3.png" alt="Image" /></td>
<td><img src="image4.png" alt="Image" /></td>
<td>~30 μm/h</td>
</tr>
<tr>
<td>φ 28mm</td>
<td><img src="image5.png" alt="Image" /></td>
<td><img src="image6.png" alt="Image" /></td>
<td>~10 μm/h</td>
</tr>
<tr>
<td>φ 38mm</td>
<td><img src="image7.png" alt="Image" /></td>
<td><img src="image8.png" alt="Image" /></td>
<td>~5 μm/h</td>
</tr>
</tbody>
</table>

**Fig. 3.** Growth rate of homoepitaxial diamond films as measured by weight as a function of nitrogen flow rate.

Growth Temp.: 1220°C  
Microwave Power: 1600~2600 W  
Pressure: 21.3 kPa  
H₂: 500, CH₄: 60 sccm
In Fig. 4, an optical emission spectrum from the microwave-generated plasma is shown. The high intensity of emission from C2 is a feature of the discharge under the conditions of high pressure, a high CH4/H2 ratio and high power density. The spectra under the conditions of Table 1 were similar to each other except for the intensity of the CN bands between 385 and 390 nm. This means that the addition of nitrogen did not significantly affect the reaction. The peak intensity of the CN bands increases in proportion to the flow rate of nitrogen, which indicates that the concentration of CN species is not saturated up to the nitrogen flow rate of 3 sccm.

Figure 5 shows the CL spectra at nitrogen flow rates of 0 and 0.5 sccm. The spectrum
of the sample grown without nitrogen addition shows two peaks well-known as band A and the H3 center, originating from nitrogen atom inclusions and dislocations, respectively.\((5-8)\) A peak near 740 nm is related to Si inclusions during homoepitaxial growth.\((5-7)\) The samples grown with nitrogen addition exhibited intense luminescence from the NV center, but the band A emission was not observed. The intensities of emission from the NV center had no relation with the flow rate of nitrogen, and depended on the measuring spots. Takeuchi et al. reported that the band A emission from homoepitaxial diamond films grown by MVCVD is observed at incoherent grain boundaries and dislocations located inside the nonepitaxial crystallites.\((8)\) According to their results, the disappearance of the band A emission suggests that such grain boundaries and dislocations with nonepitaxial crystallites are reduced by the addition of nitrogen.\((2)\) The Raman spectra of all the samples in this report show a strong diamond peak and no graphitic peak. The background levels of the Raman spectra changed depending on the intensities of CL from the NV center. From the Raman spectra, it is shown that the deposited diamond possesses the same internal stress strength as that of HPHT synthetic diamond.

To measure the (400) rocking curve without the influence of the substrates, samples with a growth thickness of 2.1 mm were grown with nitrogen addition at a flow rate of 0.6 sccm. The X-ray diffraction measurements were performed using a Ge(440) four-crystals monochrometer. The grown samples had a full width at half-maximum (FWHM) of 0.0028 deg in the (400) rocking curves obtained by the X-ray diffraction analysis. This value is close to that of 0.0020 deg for the substrate of Ib-type diamond.

We have succeeded in realizing a synthetic diamond with a weight of 1 carat by MPCVD as shown in Fig. 6. Recently, we have succeeded in synthesizing diamonds with a weight of over 4 carats by MPCVD. The grown crystal was used as a substrate for the next growth and this procedure was repeated for a number of times. The regrowth conditions were optimized mainly by changing the shape of the substrate holder. As a result, a 4.65 carat single-crystal diamond with a thickness of 10 mm has been successfully grown on a 5 x 5 x 0.7 mm³ substrate without any cracking and macroscopic defects on the surface. The details are presented in ref. 9.

![Fig. 6. Synthetic diamond with weight of 1 carat synthesized by MPCVD.](image-url)
4. Summary

Homoepitaxial diamonds were grown at the growth rates ranging from 30 to 120 μm/h with newly designed substrate holders, and the effects of nitrogen addition were shown. The nitrogen addition enhanced the growth rate by a factor of 2. The nitrogen addition was beneficial to the creation of a macroscopically smooth (100) face. The macroscopic smoothing during the growth enabled the long-term stable deposition required to produce large crystals. In future studies, we plan to investigate the content of nitrogen and its relationship with defects and crystallinity. We have succeeded in realizing a synthetic diamond with a weight of over 1 carat by the newly developed method.

References