THICK DIAMOND FILM SYNTHESIS BY DC PLASMA JET CVD

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We obtained a high growth rate for diamond film using DC plasma jet CVD. The polycrystalline cubic diamond film we grew is 2 mm thick and 10 mm square with a hardness of 10,000 kg/mm² and a thermal conductivity of 800 W/mK. We used the film as a heat sink for a laser diode. The laser output intensity was the same as that of a laser diode using a natural diamond heat sink.

1. Introduction

Diamond films will soon be used in a wide range of applications. Diamonds are hard, and the lifetime and performance of grinding tools can be improved by a diamond coating. Diamonds are also transparent over a wide range of wavelengths and thus are excellent optical materials. Diamonds have the largest thermal conductivity, and diamond film can be used as a large-area heat sink. Making such a diamond film by CVD is less expensive than using natural diamonds or those synthesized under high pressure. Film made by conventional CVD has a low growth rate \(^{1,2}\) and is not thick enough for such applications, however. We developed a DC plasma jet CVD which has a high growth rate \(^{3}\) and named it DIA-JET. It can make the thick diamond films required for such applications.

2. Experiment

We prepared a thick diamond film sample with our new CVD method (Fig. 1). The conventional, nontransfer plasma torch has a cylindrical anode and a cathode rod. The anode nozzle is between 1 and 3 mm in diameter. The copper substrate holder is welded to a coaxial stainless steel tube, which contains cooling water. The plasma torch and the substrate holder are in a vacuum chamber. The distance between the nozzle and the substrate is changed by adjusting the steel tube. The plasma jet is formed by forcing the source gas through the narrow gap between the two electrodes, across which an arc discharge is generated by a constant DC current power supply. High-density carbon and hydrogen plasmas are obtained. The diamond film is synthesized by spraying high-velocity plasma, in the form of a plasma jet, onto a water-cooled substrate. Table I shows the preparation conditions. The synthesized diamonds were examined by optical microscopy, scanning electron microscopy (SEM), X-ray diffraction, and Raman spectroscopy. Vicker's hardness was measured by

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Fig. 1. DC plasma jet CVD apparatus (DIA-JET).
Table 1. Preparation conditions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>Voltage (V)</td>
<td>80–150</td>
</tr>
<tr>
<td>Current (A)</td>
<td>10–50</td>
</tr>
<tr>
<td>Gas (l/min)</td>
<td></td>
</tr>
<tr>
<td>CH₄</td>
<td>0.01–0.2</td>
</tr>
<tr>
<td>H₂</td>
<td>10–50</td>
</tr>
<tr>
<td>added gas</td>
<td>0–20</td>
</tr>
<tr>
<td>Pressure (Torr)</td>
<td>30–300</td>
</tr>
</tbody>
</table>

the micro-Vicker's method. We also analyzed the plasma jet by optical emission spectroscopy. The diamond film was cut with a YAG laser to fit the chip. The surface of the chip was metallized with Ti, Pt, and Au for use as a heat sink.

3. Results and discussions

The temperature of the DC plasma jet is above 5000°C. The diamond is synthesized at substrate temperatures between 800°C and 1200°C; when the substrate temperature is more than 1200°C, diamond changes to graphite. The discharge voltage of hydrogen is higher than that of the argon or nitrogen used in conventional arc discharge. Figure 2 shows the dependence of the substrate temperature and discharge voltage on time; increasing the discharge voltage increases the substrate temperature. If the discharge voltage is not carefully controlled, the film temperature may increase and the diamond may change to graphite. Figure 3 shows micrographs of our diamond film and a graphite film changed from diamond by overheating. Thus, the discharge voltage must be controlled to synthesize thick diamond film. Figure 4 shows the discharge voltage for different pressures. At high pressures above 200 Torr, the discharge voltage fluctuates greatly. However, at low pressures below 100 Torr, the discharge voltage becomes more stable. Figure 5 shows the shapes of the plasma jets and their emission spectra at different pressures. At low pressure, the plasma jet becomes longer and the emission intensity of the CH radical becomes larger than that for hydrogen. The effect of pressure on stability is considered as follows. At high pressures, methane decomposes mainly in the narrow space inside the nozzle and the pressure or temperature change caused by the decomposition is large, making the discharge voltage unstable. However, at low pressures below 100 Torr, the arc discharge occurs in the large outside space and the effects of methane decomposition are less, making the discharge voltage stable.

We obtained a 10×10×2 mm diamond film (Fig. 6). This is the thickest diamond film to reported. X-ray diffraction indicates that this film is a polycrystalline cubic diamond (Fig. 7). Figure 8

Fig. 2. The relationship between substrate temperature ($T_s$) and discharge voltage ($V_d$).

Fig. 3. Diamond and graphite films. (A) Diamond, (B) Graphite.
shows the Raman spectrum; only the sharp peak of diamond was observed at 1332 cm⁻¹. Graphite and amorphous carbon were not detected. Figure 9 shows the peak and its half-width of the typical peak for natural diamond and our CVD diamond film. A peak shift to a shorter wavenumber indicates compression and a peak shift to a longer wavenumber corresponds to expansion. The Raman peak shift of CVD diamond to a shorter wavenumber indicates that the sample has expanded. The larger half-width of the CVD sample indicates that the diamond film has internal stress and lattice defects. Table 2 shows the properties of our thick diamond film. The Vicker's hardness and the density of the diamond film are almost the same as those of natural diamond, and the thermal conductivity is nearly equal to that of Ia diamond. The reason why the resistivity is lower than that of natural diamond would be caused by the presence of a small amount of graphite.

We made a heat sink with the CVD diamond film, which is the first time, to our knowledge, that this has been done. The heat sink is 2.5×2.5×0.5 mm. The surface of the heat sink was polished with a diamond disk and diamond powder to a roughness of 2000 Å. Figure 10 shows the InP laser diode package. The diamond heat sink is attached to a copper subcarrier and the laser diode is mounted on the diamond heat sink. We measured the laser output intensity as a function of DC diode current, and found it to be the same as when a natural diamond heat sink was used.
4. Conclusion

We synthesized a 2 mm thick diamond film by DC plasma jet CVD. The most important factor for stability was low pressure. Grown samples were cubic diamond, and the hardness and density were almost the same as natural diamond. Thermal conductivity was nearly equal to that of Ia diamond.

We used the CVD diamond as a heat sink for an InP laser diode. The optical properties were almost the same as when a natural diamond heat sink was used.
Acknowledgements. We would like to thank Mr. Kihara for helping us make the laser diode assembly.

REFERENCES