LARGE AREA CVD OF DIAMOND FILMS USING MAGNETO-MICROWAVE PLASMA AT LOW PRESSURE

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Large area and uniform diamond film depositions have been studied using magneto-microwave plasma assisted CVD at 0.1–0.01 Torr. Setting ECR condition at the deposition area, high density plasma \( \left( 1 \times 10^{11} \text{ cm}^{-3} \right) \) is obtained around the substrate. The discharge area is quite uniform and diamond films are obtained on positively biased substrates under pressure. As the reaction pressure becomes lower, the substrate temperature for the diamond formation tends to decrease.

1. Introduction

Diamond films have been formed by various deposition techniques, e.g., thermo-filament CVD\(^1\)\(^-\)\(^3\), microwave-plasma CVD\(^4\), DC thermo plasma CVD\(^5\), DC plasma jet CVD\(^6\), etc. These CVD methods are carried out at high pressure, around 20–200 Torr. But these methods have limitations in the uniform expansion of the size of the reaction area. Low pressure deposition is one of the means to overcome these difficulties. By decreasing the pressure, the mean free path of the electrons becomes longer and it is easy to increase the plasma density over a large area by using a magnetic field. We have obtained large area and uniform diamond films at 0.1–0.01 Torr on positively biased substrates using magneto-microwave plasma.

2. Experimental

The substrates used in the experiments were p-type Si(100). Before the deposition, they received supersonic treatment. The substrates were loaded into the magneto-microwave plasma CVD\(^7\), which was evacuated to \( 10^{-6} \) Torr. Then CO diluted with \( \text{H}_2 \)\(^8\) was introduced to the system at a total flow rate of 100 scem. The maximum magnetic field (2.2 kG) was set at around the right end of the round waveguide, the field was decreased along the axis and was applied to set the ECR condition (875 G) at the substrate position. The distribution of the magnetic field is shown in Fig. 1(c). The input microwave power was 800–1200 W. The substrate temperatures were controlled independently of the microwave power by a tungsten heater.

3. Results and discussions

The discharge areas at 0.1 Torr and 10 Torr are shown in Figs. 1(a) and (b). At the lower pressure, the plasma is quite uniform and the discharge area is all over the round waveguide. The plasma at 0.1–0.01 Torr can be explained by the off-resonance plasma formed in the magnetic field higher than the ECR condition\(^9\),\(^10\). In this condition, complete electron gyrations occur, and the plasma density is increased by the microwave absorption. The microwave is effectively absorbed in the magnetic field higher than the ECR condition\(^9\),\(^10\). The plasma density measured by the double probe method\(^11\) was \( 1 \times 10^{11} \text{ cm}^{-3} \) around the substrate at 0.1 Torr. On the other hand, at 10 Torr, the plasma was spherical and located around the substrate. The magnetic field enhances the former and controls discharge in the latter.

Table 1 shows the experimental conditions and products. This table shows two interesting phenomena observed at lower pressure. First, there is a great effect of the potential difference between substrate and plasma at 5–0.01 Torr. At 3 Torr...

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(400 Pa), a relation between the electric field on the substrate and the reaction products using microwave CVD has been reported\textsuperscript{13}. However, at 0.1–0.01 Torr, the effect of the potential of the substrate increases. Diamond was formed only on positively biased substrates. As the voltage becomes higher, the diamond deposition rate tends to increase (Fig. 2). On the contrary, SiC was formed at low negative DC voltage (−10 V) and the substrate was sputtered at high negative DC voltage (−60 V). Based on these facts, we speculate that fast ions or neutrals bombard the substrate under the negative bias. However, under the positive bias, only electrons or slow neutrals reached it.

Second, the temperature for the diamond formation was lowered. 900°C is in the optimum condition for diamond formation at 10–50 Torr. However, at 0.1 Torr, graphite is mainly synthesized at this temperature. At 750°C, diamond films are obtained instead of graphite. The temperature is lowered to 600°C. We speculate that this phenomenon is related to a reaction unique to the low pressure.

Figure 3 shows SEM images of the surface of a polycrystalline diamond film, formed under condition of 0.1 Torr, CO(5%)/H\textsubscript{2}, 650°C. The deposition rates of these films are 700–800 Å/h. Almost all of them have [111] habit planes and are uniform diamond. Figure 4 shows the uniformity of the diamond film formed under the same condition. The average thickness is 5450 Å and its deflection is within ±7%. The electron diffraction pattern of the diamond film deposited at 0.1 Torr is shown in Fig. 5. All of the observed Debye-Scherrer rings are identified as those of diamond and not as those of graphite. Figure 6 shows the Raman spectra of the film formed at 0.1 Torr and 650°C using CO(5%)/H\textsubscript{2}. A peak at 1333 cm\textsuperscript{−1} due to the line of diamond is clearly seen, and the broad peak near 1500 cm\textsuperscript{−1} inherent to amorphous carbon is also observed. We consider there to be two reasons for this. First, amorphous carbon exists on the surface of the diamond film, so the excitation beam which reached the crystal layer becomes weak because of the great absorption in the amorphous carbon layer. The second reason is based on the small grain sizes. Most of the amorphous carbon layer exists in the grain boundary, the ratio of which is

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Fig. 1. Schematic diagram of discharge area of magnetron-microwave plasma deposition system. (a) 0.1 Torr. (b) 10 Torr. (c) Corresponding magnetic field distribution in (a) (b) along the axis of a round waveguide.
Table 1. Experimental conditions and products

<table>
<thead>
<tr>
<th>Pressure (Torr)</th>
<th>CO(%) in H₂</th>
<th>T_{sub} (°C)</th>
<th>Bias (V)</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>10-50</td>
<td>3-20</td>
<td>900</td>
<td>0</td>
<td>D</td>
</tr>
<tr>
<td>800</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5-1</td>
<td>5</td>
<td>900</td>
<td>+40</td>
<td>D</td>
</tr>
<tr>
<td>800</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>3-5</td>
<td>900</td>
<td>+40</td>
<td>G (D)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>750</td>
<td>0</td>
<td>D</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-10</td>
<td>SiC</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-60</td>
<td>(Sputtered)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>650</td>
<td>+40</td>
<td>D [111]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>600</td>
<td>+40</td>
<td>D [111]</td>
</tr>
</tbody>
</table>

D and G mean diamond and graphite respectively. [ ] means a dominant plane of facet. T_{sub} means the substrate temperature.

Fig. 2. Dependence of the deposition rate of diamond films formed at 0.1 Torr on the positive DC bias voltage. The concentration of CO is 5% in H₂. T_{sub} is 750°C. Input microwave power is 800 W.

Fig. 3. SEM image of surface of diamond films on Si substrate formed at 0.1 Torr. The concentration of CO gas is 5% in H₂. T_{sub} is 650°C. Input microwave power is 1200 W.

higher in the small grains shown in Fig. 3. As a result, the broad peak appears relatively large.

4. Conclusions

Using high density plasma of magneto-microwave CVD with a CO/H₂ reaction gas mixture, large size and uniform diamond films have been obtained at 0.1–0.01 Torr. In such low pressure deposition, it is necessary to apply a positive DC bias on the substrate for the diamond formation. As the reaction pressure becomes lower, the substrate temperature tends to decrease.
Fig. 4. Uniformity of the diamond film formed at 0.1 Torr. The concentration of CO gas is 5% in H₂. Tₐsh is 650°C. (a) Position of measuring points of diamond film. (b) Distribution of the thickness of diamond film.

Fig. 5. Electron diffraction pattern of diamond film formed at 0.1 Torr. Tₐsh is 750°C.

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