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# Generation of Microwave Plasma under High Pressure and Synthesis of Diamond

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A microwave plasma generator, which functions under high pressure, has been developed and used in synthesizing diamond. The plasma generator consists of a semi-coaxial-type resonator and an adjustable circuit, which are coupled in series for torching plasma and keeping it stable under high pressure. The circuit has the component of variable inductance. The plasma can be torched at the pressure of 2000 hPa by tuning the dimensions of apparatus elements. Diamond films are obtained using a mixture of hydrogen and methane gas. The maximum growth rate is 125 μm/hour in the flow of $CH_4$ (5.6 sccm) and $H_2$ (100 sccm) under the pressure of 1500 hPa. The concentration of methane used in this synthesis is relatively higher than the concentration used in the conventional CVD diamond synthesis methods.
Key words: high pressure, microwave, plasma, diamond

## 1. INTRODUCTION

In recent years there has been an interest in research on microwave plasma, which is one way to obtain clean plasma[1]. The advantage of this process is that it is free from contamination from discharging electrodes and the processing chamber. Material with a low level of contaminants can be fabricated by applying this plasma to chemical vapor deposition. The microwave plasma is usually torched under low pressure below ~100 hPa. In our study, we attempted to torch the microwave plasma under higher pressures than those used for conventional chemical vapor deposition. Under high pressure, gas molecules are present at high density, and the mean free pass of gas molecules is very short as determined from the kinetic theory of gases. Since the specific energy required to keep torching the plasma is proportional to the concentration of gas molecules, the plasma under high pressure has a high density of energy. The plasma energy under high pressure decreases due to successive collision of gas molecules in the short range. Thus the plasma exists locally according to the form the energy supplied. The following advantages are expected as a result of carrying out the chemical vapor deposition under high pressure. One is a high growth rate of material due to the high density of source gas molecules. A new production method for contaminant-free material is expected to be developed using microwave plasma in high pressure. Many advantages are expected compared with using the conventional microwave plasma in chemical vapor deposition. However, there are many problems associated with torching the microwave plasma under high pressure. In order to apply a high electric field to obtain plasma under high pressure, it is necessary to design a resonator for stable torching of the plasma. There are some reports of torching plasma at atmospheric pressure[2-6] and of chemical vapor deposition for fabricating diamond[7] carried out under atmospheric pressure. In this study, we tried to generate plasma at a pressure about three times higher than atmospheric pressure. We developed a high pressure microwave plasma device and synthesized the diamond using this device.

## 2. EXPERIMENTAL APPARATUS

Some problems exist in torching the plasma in the high pressure. A high electric field is necessary to break down the plasma in the high pressure by using the microwave as a power source. The semi-coaxial type resonator is adopted to realize high electric field in the specific location. The resonator of this type generates high electric field near the central conductor so that the location of the plasma is easier to be controlled than the rectangular type resonator. And this type of resonator is easy to be adjusted to high degree of resonation. The high electric field is required to break down in high pressure, which is known as the Paschen's law of discharge. After torching the plasma, the plasma impedance changes with the supplied power, pressure and the kind of gas mixture. The impedance of torching system is necessary to match with that of plasma. Otherwise, the energy to sustain the plasma is not sufficiently supplied for it and finally the plasma will be vanished.

A schematic drawing of the plasma torch is show in Fig.1, and its equivalent circuit is also shown in Fig.2. The plasma is torched on the top of the electrode. The microwave power is supplied from the lower end of the resonator ( cavity ). Gallium, which is liquid in the room temperature, is filled in the cavity. $r_p$ and $C_1$ are the

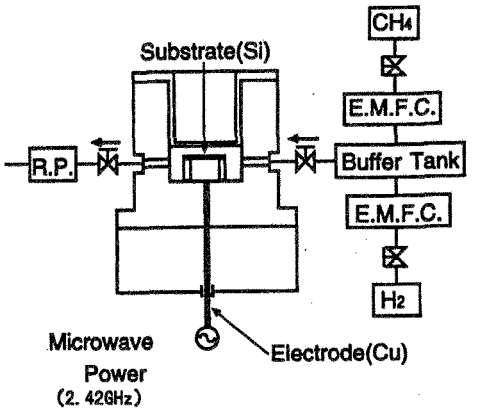



Fig. 1 Schematic drawing of apparatus

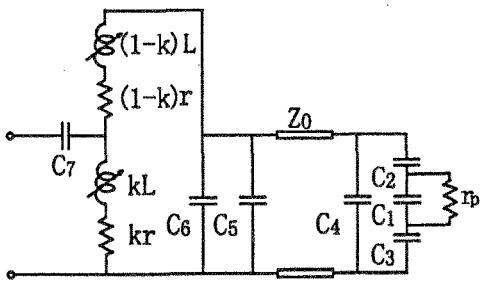



Fig. 2 Equivalent circuit of apparatus

resistance and the capacitance of plasma, respectively in the equivalent circuit. $Z_0$ is the impedance of the co-axial line between the cavity and the chamber. $C_2$ and $C_3$ are the stray capacitance. $C_4$ is the capacitance on the top of the cavity. $L$ is the inductance of the cavity, which is varied with the inner surface area of the cavity. $r$ is the bark resistance in the cavity. $k$ is the dividing ratio of the microwave power inlet. The impedance between the resonator and the chamber, where the plasma is generated, is matched by controlling the level of the surface of Gallium and the length of the coupling wire. We can torch the plasma under the pressure up to twice the atmospheric pressure using this device.

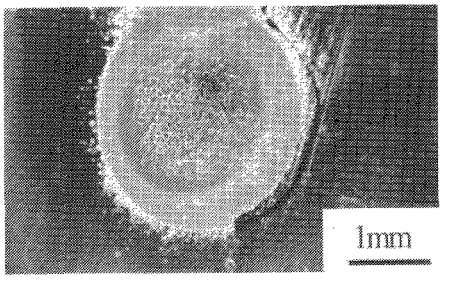
## 3. EXPERIMENTS

In order to confirm the effectiveness of the microwave plasma torching device, it was applied to the synthesis of diamond films from $H_2$-$CH_4$ system same as the conventional CVD process. The total pressure was increased up to 1.5 times of atmospheric pressure. Mixed gas of methane and hydrogen, whose flow rate were controlled by mass flow controllers, was injected in the chamber just beside the top of electrode. A silicon plate was used as a substrate. Diamond particles or films were deposited on the Si substrate above the torch held by the substrate holder. The Si substrate was prepared by the mechanical vibration method with diamond powder (2-4 μm) for the high density nucleation of growing site. The substrate temperature was measured by the radiation pyrometer through the quartz windows of the chamber.

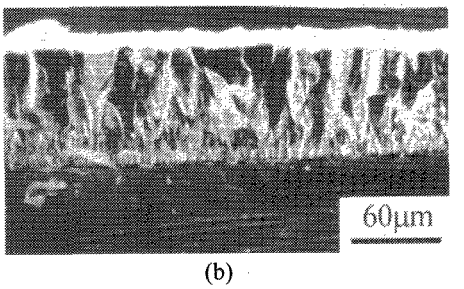
The samples obtained were analyzed by Raman spectroscopy and scanning electron microscopy.

## 4. RESULTS

Diamond films were deposited under atmospheric pressure on Si substrates for two hours, which were treated by diamond powder, as shown in Fig. 3. The




(a)




(b)

Fig. 3 A scanning electron microscope of the deposited film. (a) top view, (b) cross section. Experimental conditions: pressure 800 hPa, flow rate $H_2$ 100 sccm, $CH_4$ 2.8 sccm, microwave power 300 W, processing time 2 hours.

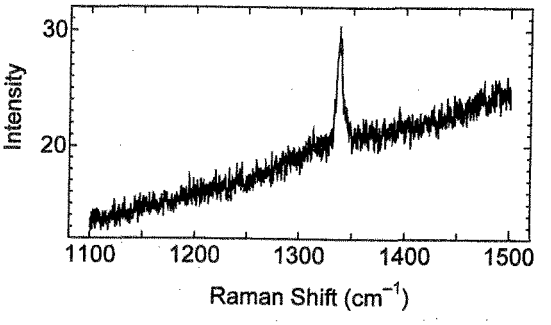



Fig. 4 Raman spectrum of the deposited film. Experimental conditions: pressure 800 hPa, flow rate $H_2$ 100 sccm, $CH_4$ 2.8 sccm, microwave power 300 W, processing time 2 hours.

cross section of this film is also shown in Fig. 3 (b). Table 1 shows the experimental conditions for this synthesis.

Table 1. Experimental Conditions

| | |
|---|---|
| Gas flow rate $H_2$ | 100 sccm |
| Gas flow rate $CH_4$ | 2.8 sccm |
| Total pressure | 800 hPa |
| MW supplied power | 300 W |
| Substrate Temperature | 1100-1200 K |

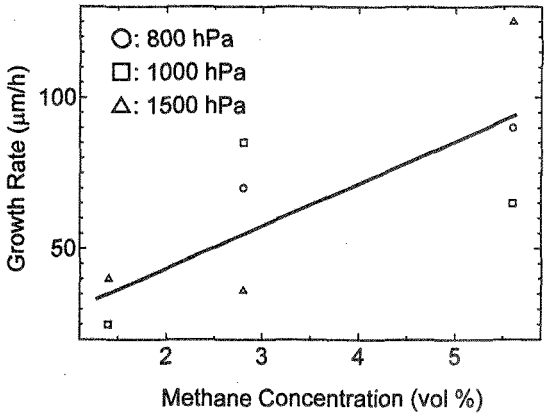



Fig. 5 Dependence of growth rate of the deposited films on the methane concentration.

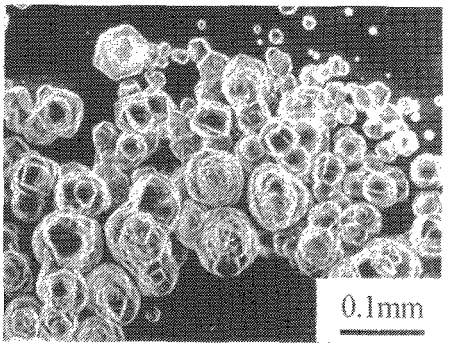



Fig. 6 A scanning electron microscope of the deposited film. Experimental conditions: pressure 1500 hPa, flow rate $H_2$ 100 sccm, $CH_4$ 1.4 sccm, microwave power 300 W, processing time 2 hours.

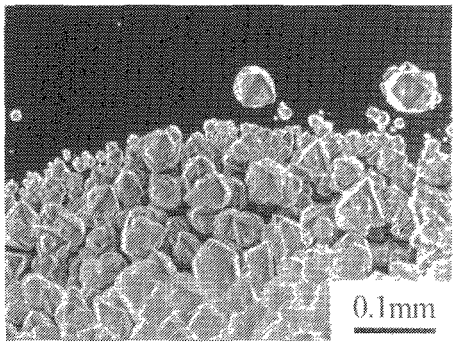



Fig. 7 A scanning electron microscope of the deposited film. Experimental conditions: pressure 1500 hPa, flow rate $H_2$ 100 sccm, $CH_4$ 2.8 sccm, microwave power 300 W, processing time 2 hours.

Diameter of deposited region was about 2 mm, which was almost same size as the diameter of plasma contacted to the substrate. The input microwave power was controlled to hold the temperature T = 1110 K. The thickness of this film was about 140 μm. The Raman spectrum of this film is shown in Fig. 4. The sharp peek of about 1336 $cm^{-1}$ agrees with the value of 1335 $cm^{-1}$ of natural diamond, which we measured. The small hilly peak about 1500 $cm^{-1}$, which was due to the

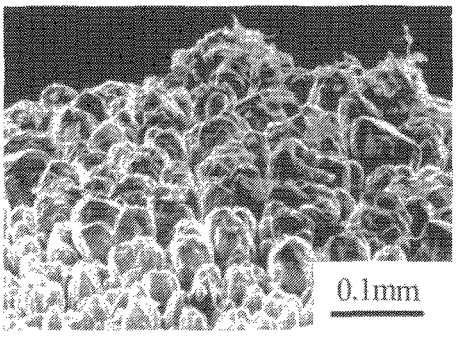



Fig. 8 A scanning electron microscope of the deposited film. Experimental conditions: pressure 1500 hPa, flow rate $H_2$ 100 sccm, $CH_4$ 5.6 sccm, microwave power 300 W, processing time 2 hours.

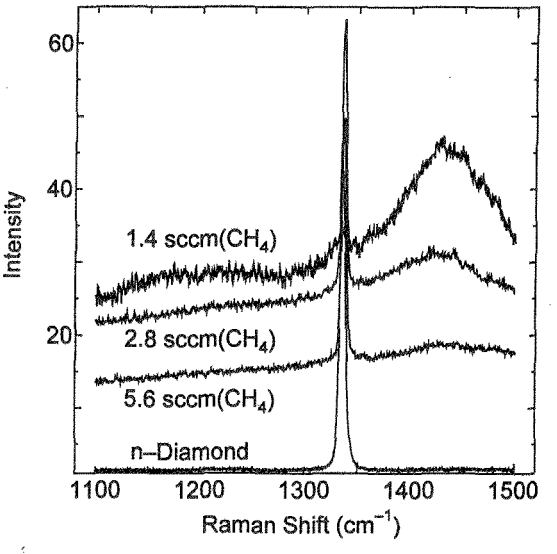



Fig. 9 Raman spectra of the deposited films. Experimental conditions: pressure 1500 hPa, flow rate $H_2$ 100 sccm, $CH_4$ 5.6 sccm, microwave power 300 W, processing time 2 hours.

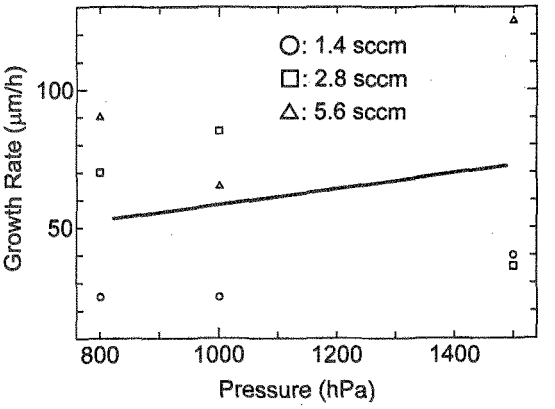



Fig. 10 Dependence of growth rate of the deposited films on the processing pressure.

presence of amorphous carbon, was also observed in the films.

The influence of the concentration of methane on the growth rate of the films is shown in Fig. 5. The

growth rate increases with the methane concentration. The concentration of methane of the process is few times higher than by the conventional low pressure process. The SEM photographs of the deposited films at 1500 hPa are shown in Figs. 6, 7 and 8 at the concentration of methane 1.4 %, 2.8 % and 5.6 %, respectively. At low methane concentration 1.4 %, the particles are not seen in the center of deposited region. The relatively flat surface films were deposited under the middle methane concentration 2.8 %. And the sloping shape of films was observed on the high methane concentration 5.6 %. The morphology of these films tends to have flat face (100) and not so much difference each other. The ballistic shape was observed on the films at the methane concentration 5.6 %. The "Cauliflowers" grown on films was not observed from the SEM images. Raman spectra of these films have the sharp peak at 1336 $cm^{-1}$ as shown Fig. 9. The broad peaks centered at 1450 $cm^{-1}$ were observed in every methane concentration of deposited films. The height of these peaks decreased with the increase in methane concentration.

Figure 10 shows the deposition rate of the diamond films ( thickness ) at the processing pressure 800, 1000 and 1500 hPa, when the volume fraction of methane was 2.8 %. The growth rate increases linearly with the pressure. The diameter of particles was also observed to grow up linearly with the pressure. These processing pressures are more than ten times higher than by the conventional microwave CVD diamond process. The influence of methane concentration on the morphology of films in each pressure was the same.

The diamond was grown at $CH_4$ concentration up to 8 vol % and processing pressure up to 1500 hPa, and the growth rate was more than 100 μm/hour, which was about ten times higher than in the conventional microwave CVD method. These may be caused by the fact that the generated plasma had high density of energy by using this device. The hydrogen gas was activated highly in the plasma so that the diamond was deposited under the high methane concentration and the high processing pressure. By using higher microwave power source and larger electrode, the diamond film will be deposited on larger area.

## 5. CONCLUSIONS

A microwave plasma generator, which functions under high pressure, has been developed and used in synthesizing diamond. The results obtained are as follows:

1) The plasma can be torched at the pressure of 2000 hPa. Diamond films were obtained using a mixture of hydrogen and methane gas,
2) The diamond was grown at $CH_4$ concentration up to 8 vol % and processing pressure up to 1500 hPa, and the growth rate was more than 100 μm/hour, which was about ten times higher than by the conventional microwave CVD method.

These may be caused by the fact that the generated plasma had high density of energy by using this device. The hydrogen gas was activated highly in the plasma so that the diamond was deposited in the high methane concentration and the high processing pressure.

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