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Study on the Large Area Diamond Film Deposition in a Self-built Overmoded Microwave Power Chemical Vapor Deposition Device

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With a self-built overmoded microwave plasma chemical vapor deposition device, the effect of the gas flow rate variation on the uniform deposition of diamond films on molybdenum of 100 millimeter diameter was studied. The plasma density was $1.0\times10^{19}/m^3$ when the microwave power was 5.0 kW and the gas pressure was 10.0 kPa. The ovemoded MPCVD device presented good stability of the gas flow rate field distribution. The substrate surface can be well covered when the hydrogen flow rate varied from 50 to 800 sccm. The uniform diamond film with good quality was obtained at an intermediate gas flow rate, 300 sccm. The diamond film with good quality, 5.74 cm^{-1} as FWHM value and high growth rate, 5.8 μm/h was deposited when the gas flow rate was 300 sccm.

1. Introduction

Microwave plasma chemical vapor deposition (MPCVD) technique was widely used to deposit high quality diamond films due to its prominent properties. It has been continuously studied and developed in the last decades as a most potential method to deposit defect free and transparent diamond films for optical usage. Parameters such as microwave power, gas pressure, and substrate temperature are all critical to the deposition of high quality diamond films. Apart from the parameters mentioned above, the gas flow rate is another critical parameter which had already been proved would affect the growth of diamond films. But less attention was focused on the uniformity change caused by variation of gas flow rate. (Su et al., 2016) investigated the effect of the flow rate by using a new dome-shaped cavity type MPCVD reactor and demonstrated a two-folded mechanism to explain the different experimental results (Su et al, 2013). The different results of the effect of variation of gas flow rate on the diamond growth may due to the different MPCVD device that had been used.

The size and uniformity of activated plasma will be affected by the type of resonant chamber. A resonant chamber with larger diameter can tolerate activated plasma with larger size, but simply increasing the chamber size will lead to the change of the microwave mode, and the electric field can no longer concentrate on the substrate surface and finally lead to the ineffectively activated of plasma. MPCVD devices with complex structures such as a dome-shaped cavity or a overmoded resonant chamber with a con-shaped inner conductor was designed to enlarge the plasma dimension and eventually fulfilled the deposition of large-area diamond films (Li, 2011). By guaranteeing the input microwave power, combing mode-complemented electric field and adopting a proper resonant chamber design, MPCVD device with a large size activated plasma can be obtained (Hideaki et al., 2016).

In this paper a new overmode MPCVD device was built. Computer simulation was applied to investigate the electric field distribution, the plasma density and the gas flow field distribution of the overmoded MPCVD device. The surface morphology, quality, and uniformity of large area diamond films deposited with different gas flow rates were investigated and the experimental results were discussed.

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2. Simulation

2.1 Description of the microwave plasma chemical vapor deposition device

Figure 1 is the cross-section view of the self-built overmoded MPCVD device used in this experiment. A ring-shaped quartz was set under the cooling substrate holder which played as the microwave dielectric window. The location of the quartz window made it avoid be overheating and etching from the activated plasma. The chamber was an overmoded resonant cavity which allowed two primary microwave modes of TM_{01} and TM_{02} overlapping on the top of the substrate to activate a large size plasma ball. The detailed geometry of this overmoded MPCVD device is presented in Figure 1.

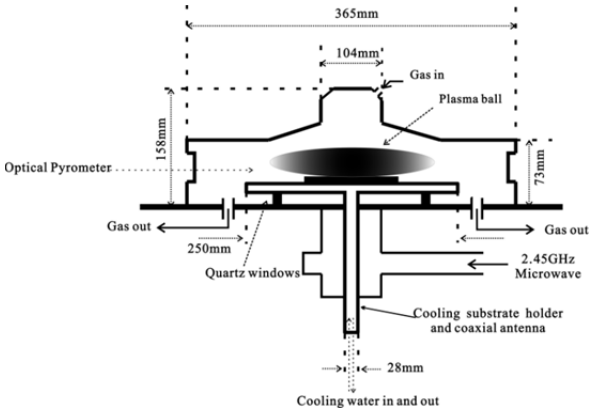

Figure 1: The cross-sectional sketch of the self-build MPCVD device

2.2 Module for microwave electric field simulation

Maxwell's equation, Eq (1), was solved to obtain the microwave electric field of the MPCVD device:

$$\nabla \times \mu_r^{-1}(\nabla \times E) - k_0^2\left(\varepsilon_r - \frac{j\sigma}{\omega\varepsilon_0}\right)E = 0 \tag{1}$$

Where E is the microwave electric field, ω is microwave angular frequency, σ is plasma conductivity, k_0 is wave number of the microwave in free space, ε_0 is electric permittivity, ε_r is relative permittivity and μ_r is relative permeability. Several boundary conditions were set. Firstly, the chamber wall was assumed as a perfect electric conductor to fulfill the condition that the tangent component of the electric field of the metal chamber was zero. Secondly, ε_r and σ value of quartz were 4.2 and $1e^{-14}S{\cdot}m^{-1}$, respectively. The rest part of the chamber was vacuum therefore the ε_r and σ value were 1 and $0S{\cdot}m^{-1}$, respectively.

2.3 Module for plasma simulation

Simulation of plasma is much more complicated than that of microwave electric field distribution. Pleuler proposed a simplified mode to describe the plasma density: plasma density can be assumed as a result of the balance between electron generating and losing (Pleuler et al., 2002). So by solving Eq (2), the plasma density can be obtained.

$$\nabla \cdot (-D_e \nabla n_e) + R_{vr} \cdot n_e^2 + R_a \cdot n_e = R_i \cdot E^2 \cdot n_e \tag{2}$$

Where n_e is the electron density, D_e is the ambipolar diffusion coefficient of electrons, R_i is the ionization coefficient of gas molecular collisions with electrons, Ra is the coefficient of attachment of electrons to neutral particles. In the simulation, the use of pure hydrogen as a simulated gas, which is due to the traditional methane hydrogen in the volume of hydrogen is much larger than the volume of methane. According to this, D_e can be replaced by D_i (diffusion coefficient of hydrogen ions) (Su, 2014). $R_a{\cdot}n_e$, the attachment term can be ignored. R_{vr}, the recombination coefficient, and R_i, the ionization coefficient can be taken from Su (2014).

2.4 Module for the simulation of gas flow field

Navier-Stokes equations were solved to get the gas flow field distribution in the MPCVD device.

$$\rho(u \cdot \nabla) = \nabla \cdot \left[-pI + \mu(\nabla u + (\nabla u)^T) - \frac{2}{3}\mu(\nabla \cdot u)I\right] + F \tag{3}$$

$$\nabla \cdot (\rho u) = 0 \quad (4)$$

Where μ is fluid viscosity, u is fluid velocity, ρ is fluid density and p is gas pressure.

2.5 Simulation results

Figure 2 is the simulation result of the electric field distribution of the overmoded resonant chamber. Figure 2(a) is the side view of the electric field distribution. A strong electric field only existed on the substrate surface and there was no obvious electric field appeared near the ring-shaped quartz or the coupled antenna. The contamination from the etching quartz and the spark of the coupled antenna can be avoided. The electric field distributed like a circle from the top view as it was presented in the Figure 2(b). It can be told that strong electric field can be obtained and symmetrically distributed on the substrate and the maximum value was 1.7×10^5 V·m^{-1}. With 100 W of the input microwave power, the valid diameter of the electric field was around 70 mm.

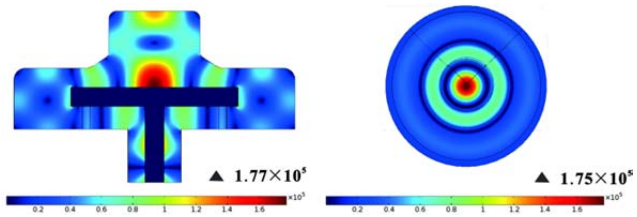

Figure 2: Simulation images of the electric field distribution: (a) side view, (b) top view

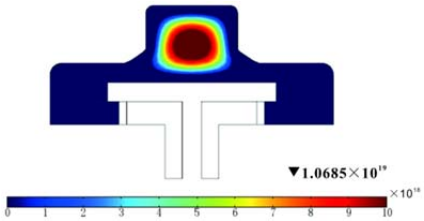

Figure 3: Simulation image of plasma density

Figure 3 presents the simulation result of the plasma density distribution in the resonant chamber with 5.0 kW of microwave power and 10.0 kPa of gas pressure. The plasma concentrated on the substrate surface and the maximum plasma density was about 1.0×10^{19} /m^3, which was three magnitudes higher than other new type MPCVD device with lower input microwave power and gas pressure (Su, et al., 2013).

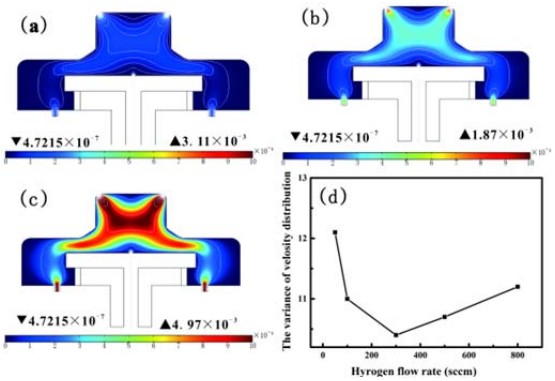

Figure 4: Simulation images of gas flow rate field distribution with different hydrogen flow rate: (a) 50 sccm, (b) 300 sccm, (c) 800 sccm, (d) the variance of velocity distribution as a function of hydrogen flow rate

In the deposition process, gas flow stayed in the form of viscous flow state. The simulation result of gas flow field distribution was displayed in the Figure 4. Pure hydrogen was chosen to represent the working gas during the simulation and gas flow rate of the hydrogen varied from 50 sccm to 800 sccm. As it was presented in

Figure 4, the substrate can be well covered at various hydrogen flow rate. The maximum flow velocity elevated from 3.1×10^{-3} m/s to 4.9×10^{-3} m/s when the hydrogen flow rate increased from 50 sccm to 800 sccm, in the meanwhile the distribution of the gas flow filed was not obviously changed. This indicated that the overmoded MPCVD device was equipped with a good stability of the gas flow field distribution which can benefit the uniform deposition of large area diamond films. The variance of velocity distribution was presented in Figure 4(d) as a function of hydrogen flow rate. The variation demonstrated that by increasing the hydrogen flow rate the variance first decreased and got to the lowest value when the hydrogen flow rate was 300 sccm and then increased with the keeping increasing of the hydrogen flow rate.

3. Experiment and characterization

Molybdenum plate, 100mm in diameter, 3mm in thickness and 0.2μm for roughness, was used as the substrate. High purity H_2 (99.999%) and CH_4 (99.99%) were used as the reactive gas. Before putting into the resonant chamber, Mo plate was firstly ultrasonically cleaned with acetone and ethyl alcohol for 15 minutes to remove the organic contaminants from the machining operation respectively. Diamond powders, 0.5 μm in diameter, were used to pre-scratch the Mo plate surface for 1 hour to form uniform scratches which would benefit the deposition of the diamond film. And Mo plate was ultrasonically cleaned with acetone and deionized water for 10 minutes respectively. Finally, after being dried in nitrogen flow, Mo plate was placed into the resonant chamber and the pump was turned on to maintain that the Mo plate stayed in the vacuum environment. The detailed parameters for diamond film deposition were listed in Table 1.
After deposition the surface morphology was characterized by the scanning electron microscopy (SEM, JSM-5510LV, Japan), diamond film quality was tested by Raman spectroscopy (Raman, DXR, USA) and 633nm as the excitation wavelength was applied in this study.

Table 1: Experiment parameters for the diamond film deposition

Microwave Power (kW)	Pressure (kPa)	Temperature (□)	CH_4/H_2 ratio	H_2 flow rate (sccm)	Deposition time (h)
5.0	15.0	980	2%	50 ~ 800	10

4. Result and discussion

4.1 Surface morphology

The surface morphology of the deposited diamond films was presented in Figure 5.

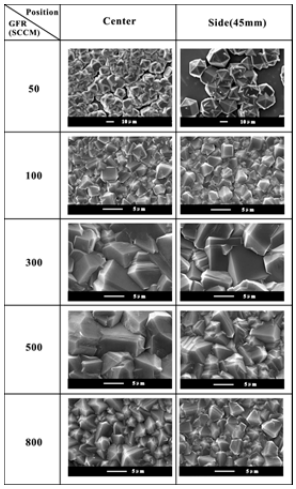

Figure 5: SEM images at center (00 mm) and side (45 mm away from the center) of diamond films deposited at different hydrogen flow rate. (GFR is short for gas flow rate)

The SEM images of center places and side places, 45mm away from the center, are both displayed. The varied gas flow rate not only obviously affected the appearance but also the grain size, differed from the recent report of Su et al. (Su et al, 2013). After 10 hours deposition, the substrate surface could not be fully covered when the hydrogen flow rate was 50 sccm. Massive twin diamond crystals were presented when the

flow rate was 50 sccm. The low gas flow rate indicated the low volume of CH_4 in the chamber. Without insufficient carbon groups, diamond films could not effectively be deposited. Increased the hydrogen flow rate to 100 sccm, the substrate surface could be well covered and there was no obvious differences between the center and side images. The average size was 2 μm and the number of the twin crystals decreased. Increased the gas flow rate to 300 sccm the average grain size increased to 4 μm and there was no twin crystal shown neither in the center or the side images. The average size was 5 μm when the flow rate was 400 sccm, but the grain surfaces were rougher than the grain surfaces when the gas flow rate was 300sccm. The side SEM image was quite different from the center one as it was presented when the flow rate was 400 sccm. The grain size decreased and the parallel lamellad twin showed up. When the flow rate was 800 sccm, the average grain size dropped to 1 μm and the orientation of crystals was obviously changed. The change of surface morphology at various gas flow rate was also observed and may be caused by the asymmetrical distribution of the active carbon groups in plasma. The deposition of diamond film was mainly affected by the concentration and energy of the carbon radicals and hydrogen atoms. The variation of the gas flow rate would affect the distribution of the chemical radicals. The variance value of the gas velocity distribution was higher when the gas flow rate was too low or too high. This indicated that the uniformity of the gas velocity was worse when the gas flow rate was too low or too high. The effect of the changing gas velocity was more obvious on the heavier carbon radical than the lighter hydrogen atoms. Therefore, lager variance value indicated worse distribution of carbon radicals which lead to the nonuniform deposition of diamond films.

4.2 Raman spectra

Raman spectra of deposited diamond were presented in Figure 6(a).

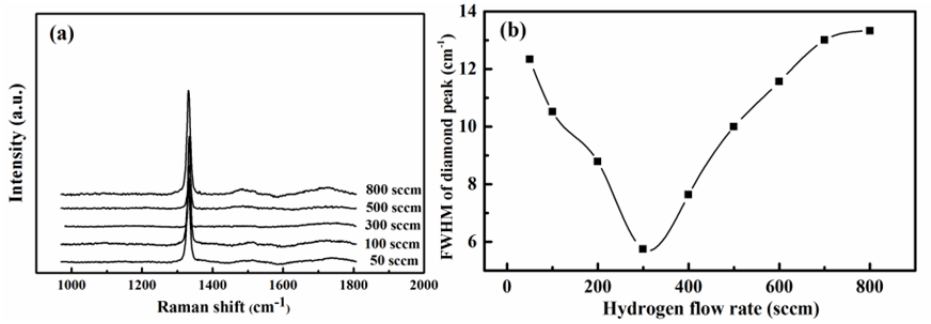

Figure 6: (a) raman spectra of diamond films deposited with different hydrogen flow rate; (b) FWHM value of diamond peaks from raman spectra as a function of hydrogen flow rate

All spectra of deposited diamond films presented a typical diamond peak at 1332 cm^{-1}. Graphic peak around 1540 cm^{-1} was detected when the hydrogen flow rate was 50 sccm, 100 sccm and 800 sccm. Graphic peak in Raman spectra was arising from the in-plate stretching mode of sp^2-bond carbon at grain boundaries. The existence of the twin crystals provided a lot of grain boundaries. With the decrease of the number of twin crystal the intensity of graphics peak decreased or disappeared. The FWHM (Full Width at Half Maximum) value of Raman spectrum of the deposited diamond film was presented in Figure 6(b) as a function of the hydrogen flow rate. The FWHM value first decreased from 12.33 cm^{-1} to 5.74 $cm^{-1}$when the hydrogen flow rate increased from 50 sccm to 300 sccm and then increased to 13.32 $cm^{-1}$when the hydrogen flow rate increased to 800sccm. Results of the Raman spectra and the FWHM value both indicated the increase of the flow rate firstly enhance the quality of the deposited diamond film and then degrade the quality of diamond film with future increase of the gas flow rate. The increase of gas flow rate at early stage was helpful to the dissociation of the plasma because more gas was introduces into the chamber and the collision frequency of different radicals was enhanced. The quality of the deposited diamond film was improved. The further increasing of gas flow rate made the collision frequency too high, electrical radicals could not obtain enough energy and this was harmful to the dissociation of the plasma, therefore the quality of the deposited diamond film deteriorated (Nistor,et, al, 2007).

4.3 Growth rate

The grow rate of deposited diamond films was presented as a function of the hydrogen flow rate in Figure 7.
The growth rate dramatically increased from 1.5μm/h to 5.8μm/h when the hydrogen flow rate increased from 50 sccm to 300 sccm and was almost constant when the flow rate kept increasing. Minor content leaking nitrogen from the atmosphere could improve the growth rate. The leaking nitrogen can be isolated from the growth area When the flow rate increased and the growth rate dramatically dropped. The MPCVD device in

this experiment also has the leaking problem. It mainly happened at the quartz windows area. Due to its special location the leaking air cannot reach the deposition area. Therefore the two-folded mechanism is not suitable for our experiment.

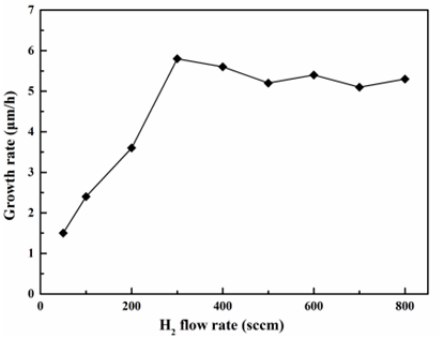

Figure 7: The growth rate of deposited diamond films as a function of the hydrogen flow rate

As discussed before, the increasing gas flow rate was helpful to the disassociation of the plasma which indicated that more activated carbon radicals at the substrate surface and leaded to the increase of the growth rate. The substrate surface was saturated with carbon radicals and the activated plasma had a disassociation limitation (10^{-12})(Bolshalov, et al, 2016), therefore the growth rate was almost constant when the hydrogen flow rate further increased.

5. Conclusion

With the overmoded MPCVD device, the affect of the gas flow rate of the growth and uniformity of the deposited diamond films on molybdenum substrate which is 100 mm in diameter was studied. Simulation result indicated that large area plasma ball can be active by this overmoded MPCVD device and substrate can be well covered with various gas flow rate. The uniform diamond film was obtained when the gas flow rate was 300 sccm. With lower or higher gas flow rate, the uniformity cannot be sustained due to the large variance value of the gas velocity distribution. Uniform diamond film with highest growth rate, 5.8 $\mu m/h$, and lowest FWHM value, 5.74 cm^{-1}, was deposited when the hydrogen flow rate was 300 sccm.

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