A NEW RF+DC PLASMA CVD METHOD FOR DIAMOND DEPOSITION

S. Matsumoto and K.K. Chattopadhyay

National Institute for Research in Inorganic Materials

1-1 Namiki, Tsukuba-city 305, Japan

Diamond films were synthesized in parallel plate electrode configuration by applying RF and DC powers simultaneously. This new method is superior than DC plasma CVD for diamond deposition in the sense that the discharge is very stable and scale up seems to be easier. The effect of RF and DC parameters on the appearance of the discharge and on the quality of the deposited films were investigated.

1. Introduction

Diamond synthesis from a mixture of activated hydrocarbon and hydrogen is now well established technology. Many methods have been developed so far for diamond film deposition such as hot-filament CVD[1], microwave plasma CVD[2], DC plasma CVD[3], thermal plasma CVD[4] and combustion flame method[5]. Still there are problems to be solved for large scale commercial production of diamond films. For this purpose, plasma CVD with parallel electrode geometry is most attractive. DC plasma CVD is the only one method that has such geometry and gives diamond with high growth rate. However, in DC plasma CVD of diamond relatively higher current density of >2 A/cm^2 is generally used and the pressure around 200 Torr is maintained. At such high current density plasma often forms arc and becomes unstable and it seems unsuitable for large area deposition. Capacitively coupled radio frequency plasmas (CCP) in parallel plate geometry mode are widely used for commercial production of various films such as amorphous silicon but they have not been generally useful for diamond growth. There is only one paper which reports very low growth rate of diamond, i.e., 0.003-0.04 μm/h in CCP mode[6]. It is thought that these unfavorable fact is due to the low plasma density in such plasmas and the presence of relatively high seath potential which breaks the surface bonds and prevent the growth of good quality crystals[7].

To overcome these difficulties in capacitively coupled plasma in parallel electrode geometry for diamond deposition we have developed a new technique using RF+DC power. By applying positive DC power to the substrate the seath structure seems to be changeable and plasma looks more uniform. This RF+DC plasma is superior than only DC plasma in the sense that it is stable and homogeneous, and scale up seems more easier. Diamond films were synthesized using this modified plasma method in the pressure range from 60 - 200 Torr. The results of SEM and Raman study of these films will be reported.

2. Experimental

The CVD apparatus used in this study is shown schematically in Fig. 1. It is made of a conventional vacuum chamber with parallel plate electrodes and the distance between the electrode is 25 mm. The diameter of the upper electrode is 10 mm and it is connected to the power supply. A matching box was designed so that the output of the low frequency RF generator (400 KHz) and negative terminal of the DC power generator were fed to the input of the matching box. The output of the matching box is connected to the upper electrode so that both RF and DC can be applied simultaneously. Deposition pressure was varied in the range of 60 - 200 Torr and the RF or DC power parameters were also varied. The pressure was measured by a Baratron absolute pressure gauge connected to the bottom of the deposition chamber. Prior to introduction of gas mixture the deposition chamber was evacuated to a pressure ~ 10^{-6} Torr. Both diamond paste scratched and unscratched Mo were used as substrate. 4.8% CH_4 diluted in hydrogen was used as diamond precursor. The substrate was placed on the grounded lower electrode whose diameter was 50 mm and the upper electrode was water cooled. No external heater was employed for heating the substrate because by the plasma the substrate was heated up to ~ 1100-1200 K at higher pressures. The substrate temperature was measured by a disappearing filament type optical pyrometer. The deposition time was usually ~ 1 h. The wave form of the input power (RF+DC) was measured by connecting the powered electrode to an oscilloscope through a voltage divider.

3. Results and discussion

Diamond was obtained when in addition to RF, negative DC voltage was added to the upper electrode (i.e., the substrate is positive with respect to the upper electrode). Deposition of diamond was not observed by using

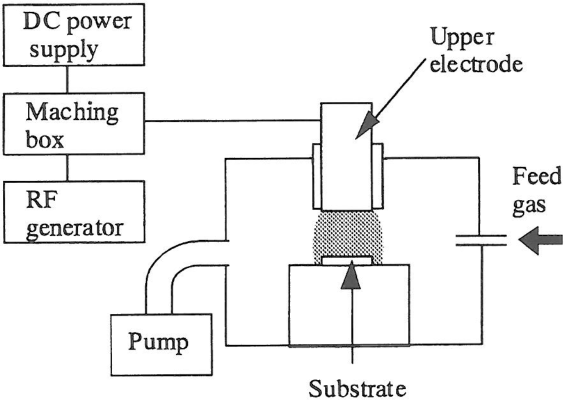

Fig. 1. Schematic illustration of the apparatus

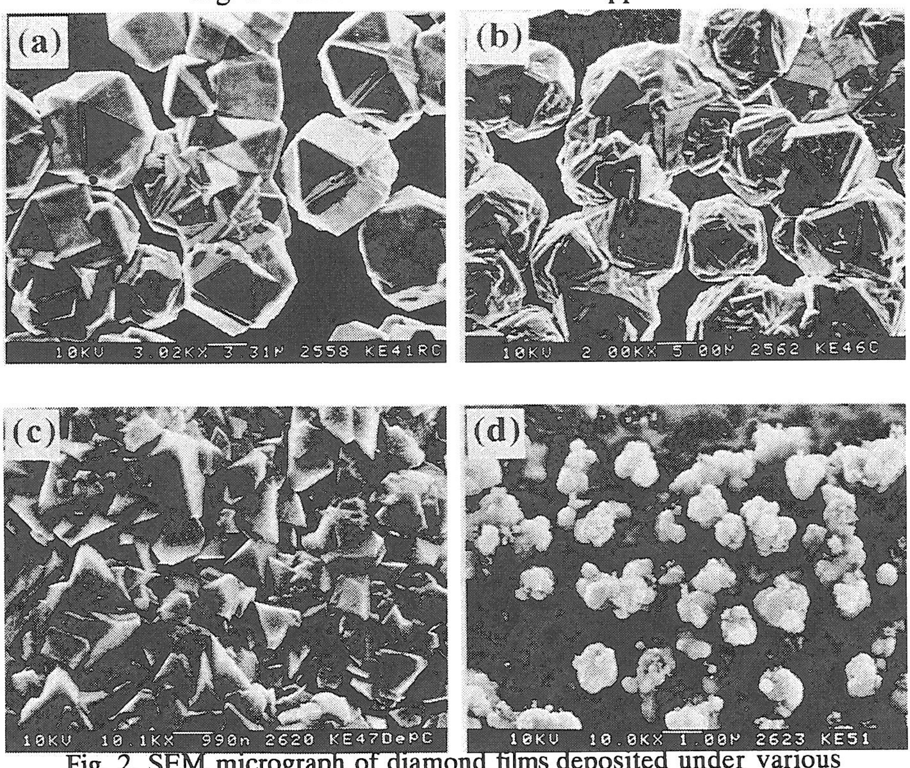

Fig. 2. SEM micrograph of diamond films deposited under various conditions: (a) RF (350W) + DC (340W), Vpp= 0 ~ -860V; (b) RF (390W) + DC (310W), Vpp= +80 ~ -880V; (c) RF (530W) + DC (160W), Vpp= +320V ~ -880V; (d) Only RF (700W), Vpp= +840 ~ -840V.

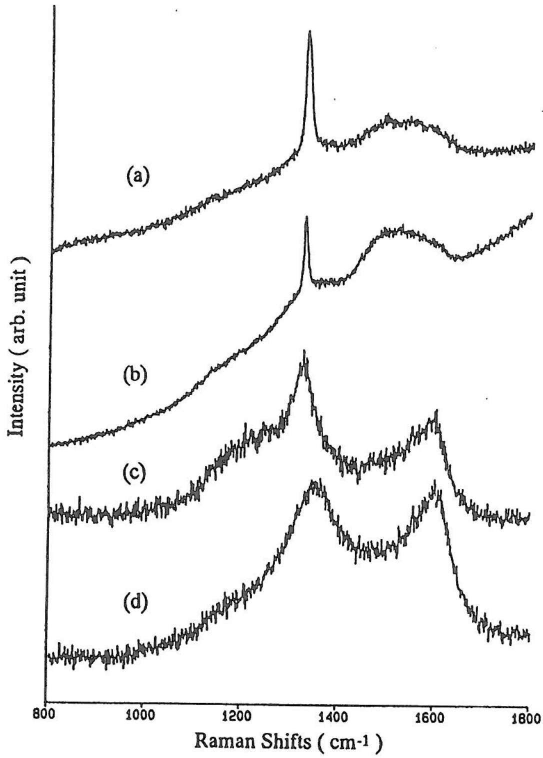

Fig. 3. Raman Spectra of the films made under different conditions as given in Fig. 2.

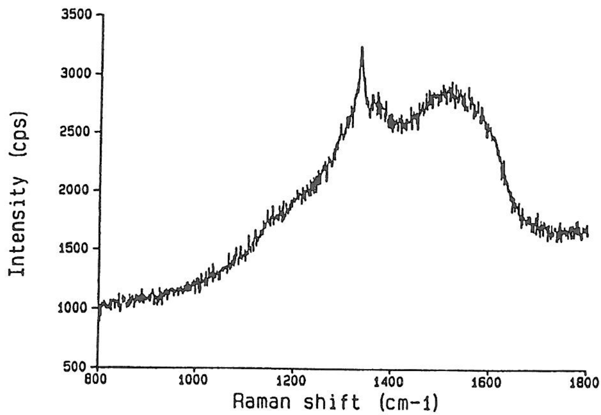

Fig. 4. Raman spectrum of a film deposited at 70 Torr.

only RF. Figure 2 shows SEM pictures of deposits made by RF+DC power with different conditions (a-c) and by only RF (d). Figure 3 shows corresponding Raman spectra of the specimens in Fig. 2. The methane concentration, the pressure, and the total power of RF+DC during deposition were 4.8 %, 200 Torr, and ~ 700 W, respectively. Deposition time was 1 hr. The deposition rate was found to be ~ 6 μm/h from SEM measurement but it is not optimized value because the chamber volume was large as compared to the flow rate of the feed stock gas and it took more than 40 min for the methane concentration in the chamber to reach the value determined by the flow rate of the gases.

Fig. 4 shows the Raman spectrum of the specimen made with 500 W RF + 160 W DC power at 70 Torr. The SEM figure of this sample did not show faceted crystals but Fig. 4 clearly shows that diamond can be obtained at this low pressure also. The low quality of this diamond may be partly due to the low substrate temperature (<900 K) during deposition; the substrate was heated only by the plasma. Independent heating of the substrate seems to be necessary to get diamond at a pressure lower than 60 Torr.

Figure 5 shows the appearances of plasma in CH_4(4.8%)+ H_2 atmosphere at 190 Torr in different RF+DC conditions. The total power of RF+DC was kept nearly the same, i.e., 700 W. Fig. 5a shows a plasma generated by only DC power and Fig. 5d shows the one by only RF, in which one can notice dark sheath region just above the substrate. When RF+DC was applied (Fig. 5(b),(c)), visible seath disappeared and the plasma became more homogenous. Also it was more stable than by DC only and arcing did not take place even for long operation. Although the electrode used in these experiments is small, the homogeneity and stability of the plasma suggest the possibility of scaling up in parallel electrode geometry by this new technique. It is not certain at present that this dark region above the substrate observed is responsible for deterioration of diamond deposition, but the change of the appearance of the plasma suggests that electric field above the substrate changes when DC power is added to the RF. To understand the mechanism of these effect of using RF and DC simultaneously for diamond deposition, detailed analysis and diagnostics of the plasma will be necessary. To investigate the effect of RF frequency, experiments with 13.56 MHz RF is also now under going.

In conclusion, by using RF+DC power in parallel electrode geometry, we can obtain good quality diamond with relatively high growth rate. In this method the discharge is very stable and there is a possibility of scaling up to large area deposition.

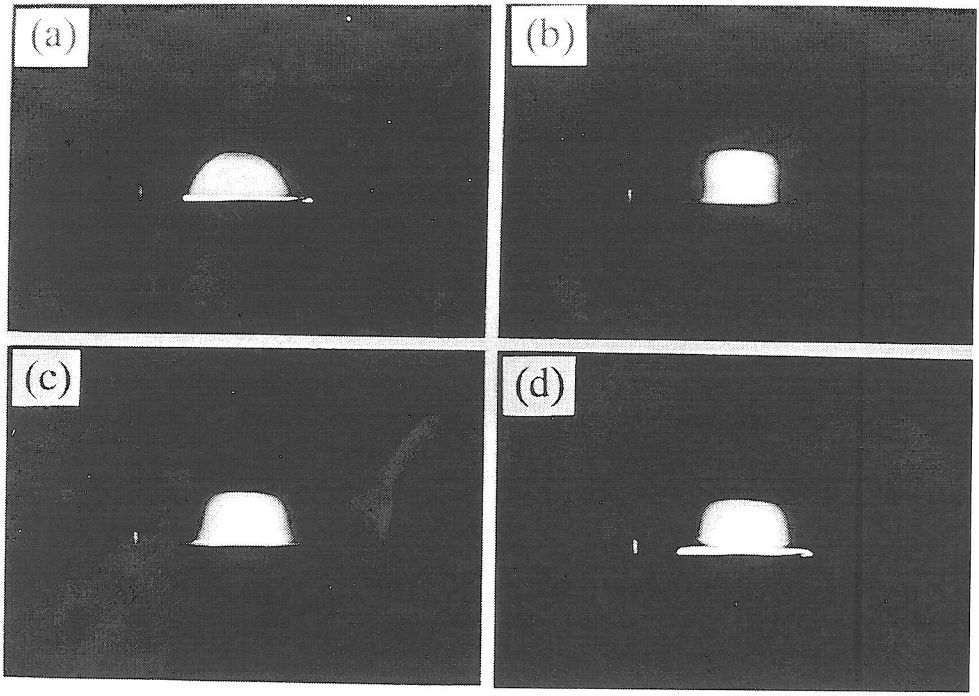

Fig. 5. Photographs of plasmas in 190 Torr hydrogen + methane (100 and 5 ccm, respectively) under different conditions. (a) Only DC (610V - 1.1A); (b) RF (465W) + DC (235V - .52A); (c) RF (610W) +DC (240V - .38A); (d) Only RF (700W).

References

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