The Korean Journal of Ceramics, 3 [1] 24 - 28 (1997)

Diamond Deposition by Multi-cathode DC PACVD

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(Received November 1996)

Diamond deposition by muti-cathode DC PACVD has been investigated. Five cathodes were independently connected to their own DC power supplies. The voltage and current of each cathode were varied up to 700 V and 3.5 A, respectively. The plasma formation and the diamond deposition behaviour on a substrate of 3 inch in diameter were investigated by optical emission spectroscopy, SEM and Raman spectroscopy. The plasma formed by five cathodes was non-uniform, which was depended on the geometry of cathode array. The growth rate and the quality of diamond film were closely related to the spatial distribution of the plasma.

Key sords : Diamond, DC plasma, Multi-cathode, OES, Raman

I. Introduction

DC PACVD is simple and economic process of CVD diamond deposition.[1,2] The growth rate is higher than that of hot filament and microwave CVD[3,4] and high-quality, white diamond can be synthesized.[3] General DC PACVD system uses single cathode[1,2] and the deposition area depends on the dimension of the plasma, which, in turn, is proportional to the diameter of the electrodes. Therefore, the cathode diameter should be increased for large-area deposition. On the other hand, a cathode temperature higher than 2000°C is desirable for the stability of the plasma in this system.[5] However, for such a hot-cathode system, maintaing a uniform temperature distribution on the large-diameter cathode is not easy, because it is very difficult to increase the power density without arc generation. Therefore the deposition area of a uniform diamond film is limited.[5]

At a optimum condition of the single cathode system, it is possible to deposit a uniform white diamond film with growth rate of 5 μm/h on a substrate of 20 mm in diameter at 2%CH_4. The white diamond film can also be deposited on a substrate of 30 mm in diameter at 2%CH_4. However, the thickness is non-uniform in this case. The growth rate is 3 μm/h at center while it is 5 μm/h at the periphery. An uniform thickness is attained for higher methane concentration, where the growth rate increase up to 30 μm/h at 5%CH_4, but the quality of the film is deteriorated. The radial thickness non-uniformity at low methane concentration is attributed to the smaller plasma size, since the plasma size increases with methane concentration for a given diameter of the cathode and power density.[6] To overcome this limitation we have designed a multi-cathode system in which the number and the arrangement of the cathodes can be easily modifiable. In this study, we employed five cathodes, each of which is connected to independent DC power supplies.[5] The plasma formation and the diamond deposition behaviors on a 3 inch-substrate were investigated by OES, SEM and Raman spectroscopy.

II. Expermental

Figure 1(a) shows the schematic diagram of the deposition system. Five cathodes are suspended at the top plate. The cathode temperature is kept higher than 2000°C to prevent solid carbon formation on the cathode surface. Power is supplied to each cathode by the five independent DC power supplies. Figure 1(b) shows the plane view of the cathode array projected on a substrate of 3 inch in diameter. The distances between the central and the peripheral cathodes, and between two peripheral cathodes, are 33 mm and 47 mm, respectively. The distance between cathodes and substrate was 40 mm. Methane and hydrogen were used as a precursor gas. The morphology and quality of diamond films were studied by SEM and Raman spectroscopy, respectively. The other experimental detail of deposition procedure was reported elsewhere.[4]

The plasma was characterized by optical emission spectroscopy (OES) using the monochrometer system of SOFIE Instrument (DIGISEM) with the spectral resolution of 0.14 nm. The plasma emission was transferred to the monochrometer through a optical fiber. Emission spectra were systematically obtained by moving the focus at an interval of 2 mm, from the plasma center to periphery along a horizontal line 15 mm below the cathode surface. The measured wavelength range was between 400 and 700 nm. The major plasma species identifiable by OES are atomic hydrogen (H_α, H_β), C_2 and CH.[1,7] We observed

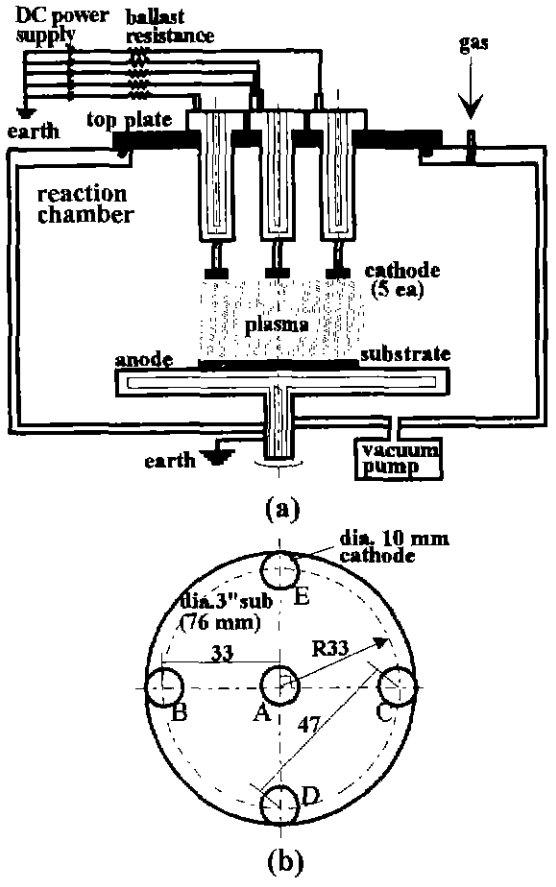

Fig. 1. Schematic diagram for Multi(5)-cathode system (a) and the array of the cathodes (b).

only the variation of H_α and C_2, because the emission intensity variation of two atomic hydrogen species (H_α, H_β) and two carbon containing species (C_2, CH) shows a similar behavior, respectively.

III. Results and Discussion

Figure 2 shows the plasma generated on a substrate of 3 inch in diameter. The plasma was formed continuously between the substrate and the cathodes. However, the boundaries of the plasmas generated from each cathodes were discernible. This shows the plasma is not uniform. So we analyzed the plasma systematically with OES, to estimate its three dimensional shape changing the number of the operating cathodes, as will be shown in Figs. 3~5.

Figure 3 shows the variation of H_α (a) and C_2 (b) peak intensities with the radial distance from the plasma center, in single (A in Fig. 1(b)) and three operating cathodes (A, B, C in Fig. 1(b)). In this graph, the origin is the center of the cathode A. The distance between the centers of cathode A and C on the monitor screen was 30 mm (the real distance is 33 mm, as shown in Fig. 1(b)).

When operating single cathode, the intensity decreased rapidly to zero at the radial distance of 14 mm. When operating three cathodes, a peak c appeared at

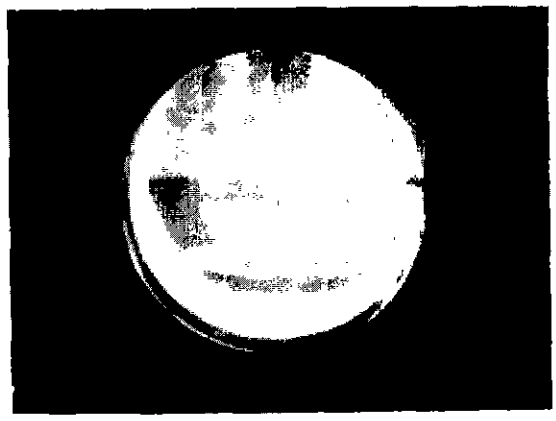

Fig. 2. Plasma shape formed on a substrate of 3 inch in diameter at the condition of 700 V, 3.5 A, 3%CH_4, 120 Torr, 150 sccm.

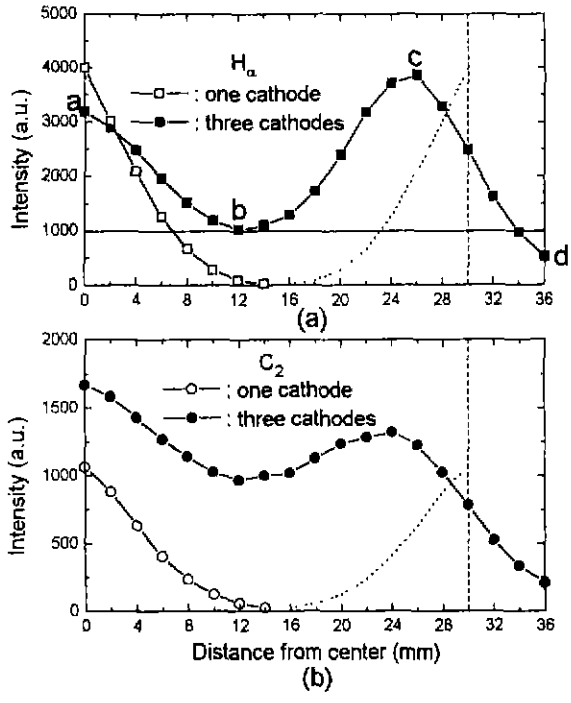

Fig. 3. Variation of H_α (a) and C_2 (b) with the distance from the plasma center in single and three operating cathodes at 3%CH_4, 120 Torr, 150 sccm.

the radial distance of 26 mm, probably due to the emission from the plasma of the peripheral cathode C. However, the distance between cathode A and C is 30 mm on the monitor screen. This shows the center of plasma from the cathode C is shifted toward the cathode A by 4 mm. Moreover, between the two cathodes, the plasma intensity at point b is considerably higher than the case of single cathode. This suggests that the two individual plasmas from cathode A and C interact with each other. In contrast to the plasma from the cathode C, the peak position of the plasma from center cathode A did not shift, probably due to the symmetrical interactions from cathode B and C. The effective plasma di-

ameter was estimated by drawing a horizontal tangent line at the nadir b of H_α curve. The effective plasma diameter of the cathode A and C displayed on the monitor, were about 28 mm and 26 mm, respectively.

To estimate the whole plasma shape, it is necessary to know the interaction between two peripheral cathodes, where the real distance is 47 mm which is projected on the monitor screen as 40 mm. Figure 4 shows the variation of the emissions intensities with the distance between the two operating cathodes for two cases: (i) between cathode A and C and (ii) between cathode D and C. The distances between the cathodes for these two cases are 33 mm and 47 mm, respectively. In both cases the center of each plasma moved toward each other. The shift distances are 4 mm for case (i) and 2 mm for case (ii). In case (i), the emission intensities of H_α and C_2 from the region between two cathodes were much lower than those in case (ii). This indicates that interaction between the plasma is strongly dependent on the distance between cathodes.

The OES results of five operating cathodes (cathode D and E added to cathodes A, B and C in Fig. 1(b)) is shown in Fig. 5. The intensities at the origin increased much more than that in Fig. 3. It is not due to the increase in the intensity of center plasma, but due to the additional emissions of the plasmas from cathodes D and E. The plasma from cathode C moved toward the center by 6 mm, which is larger than 4 mm for the case of three operating cathodes. This shows that the two additional cathodes D and E bear a further effect on the plasma. C_2 intensity did not show any peak.

From the results shown in Figs. 3~5, we can draw the cross-sectional view of the effective plasma shape for five operating cathodes projected on a substrate of 3 inch in diameter, as shown in Fig. 6. The plasma does not fully cover the substrate. Figure 6 is drown from analysis along a horizontal line 15 mm below the cathodes. However, analysis along a horizontal line 25 mm below cathode gave curves similar to those in Fig. 5, except for the low absolute intensities of H_α and C_2. Furthermore, diamond deposition on the 3-inch substrate made a pattern similar to that in Fig. 6, Therefore, the cross-sectional view of the effective plasma shape in the immediate vicinity of the substrate surfac should be similar to that shown in Fig. 6. Figure 7 shows the spatial vari-

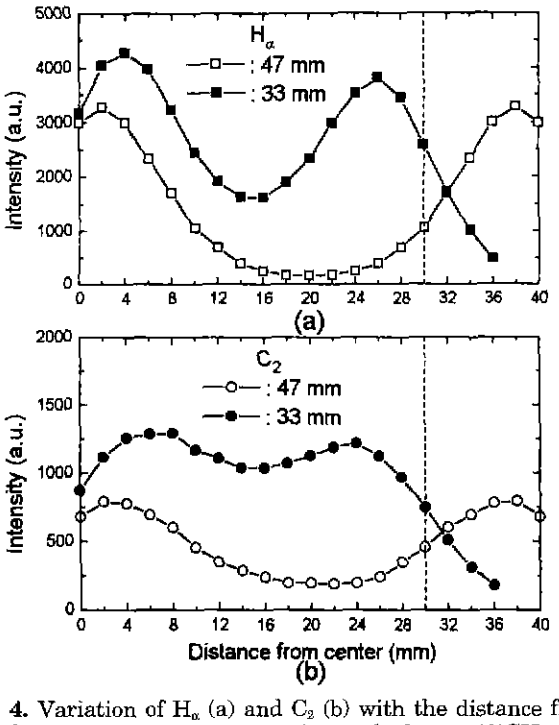

Fig. 4. Variation of H_α (a) and C_2 (b) with the distance from the plasma center in two operating cathodes at 3%CH_4, 120 Torr, 150 sccm.

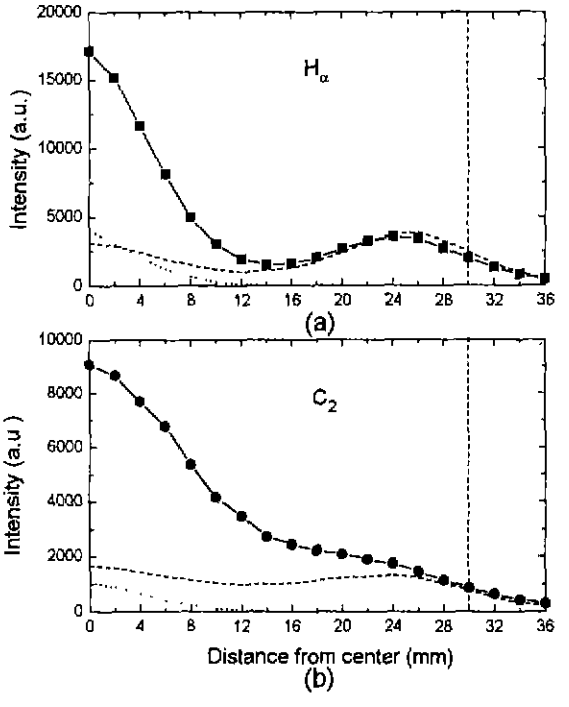

Fig. 5. Variation of H_α (a) and C_2 (b) with the distance from the plasma center in five operating cathodes at 3%CH_4, 120 Torr, 150 sccm

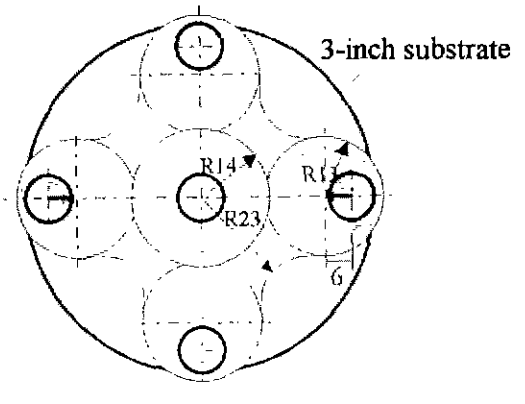

Fig. 6. The cross sectional view of the effective plasma shape expected from Figs. 3~5.

ation of the surface morphology in the diamond film deposited on the 3-inch substrate. The morphology showed a wide variation with the position on the substrate surface. The diamond film at region A and B showed a typical mixed-habit morphology and were white and transluscent. In region C in contact with the peripheral plasma, the hexagonal (111) facets were predominant and the color was grey. The diamond film in region D, not in contact with plasma, showed a typical low-temperature octahedral morphology with prominent secondary nucleations[6,8] and it was black and opaque. The growth rate also changed with the position. The growth rates of the region A, B, C and D were 1~2 μm/h, 3~5 μm/h, 5~8 μm/h and 4~5 μm/h, respectively.

Figure 8 shows Raman spectra of the diamond films in region A~D. The full width at half maximum (FWHM) value of the diamond peak drastically increased going from region A to D. This shows that the quality of the diamond film is closely related to the local intensity of the plasma in contact. Raman spectra of film in region D, which was not in direct contact with the plasma, showed a broad shoulder in the range of 1350~1600 cm^{-1} due to sp^2 component as shown in Fig. 9, while no such shoulder is found in region A~C.

To decrease such non-uniformity, the 3-inch substrate was rotated during the deposition for 7 days at the same condition as that of Fig. 7. By substrate rotation, the film became unifrom in the azimuthal direction but not in radial direction. The growth rate monotonically increased from 1 μm/h at the center to 8 μm/h at the periphery. The diamond film within the diameter of 40 mm was white and transluscent while the film at the outside was dark and opaque.

On the other hand, decreasing the substrate diameter improved the radial uniformity. Figure 10 shows the spatial distribution of film thickness, FWHM and I_d/I_b

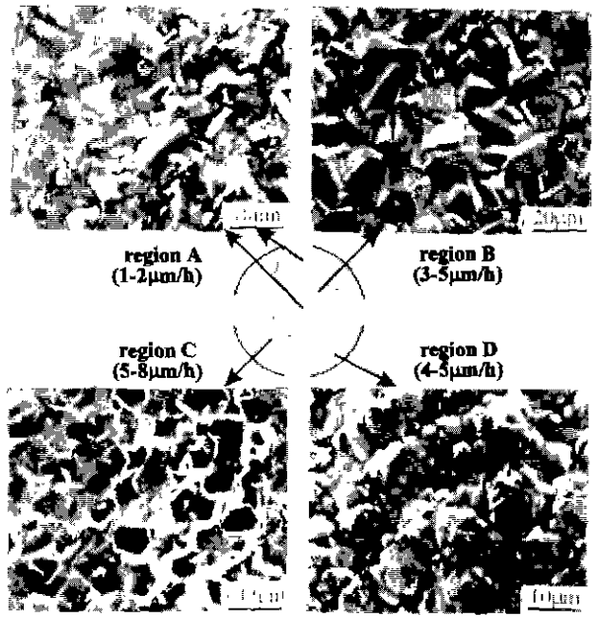

Fig. 7. Surface morphologies with the position of Fig. 6(b) at the condition of 700 V, 3.5 A, 3%CH_4, 1200~1300°C, 120 Torr, 150 sccm.

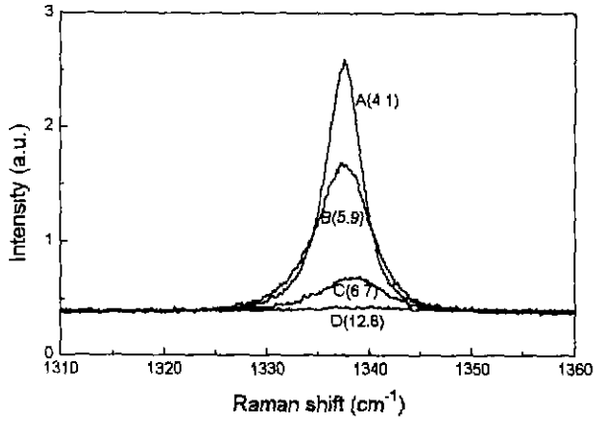

Fig. 8. Raman spectra of the diamond films in region A~D of Fig. 7.

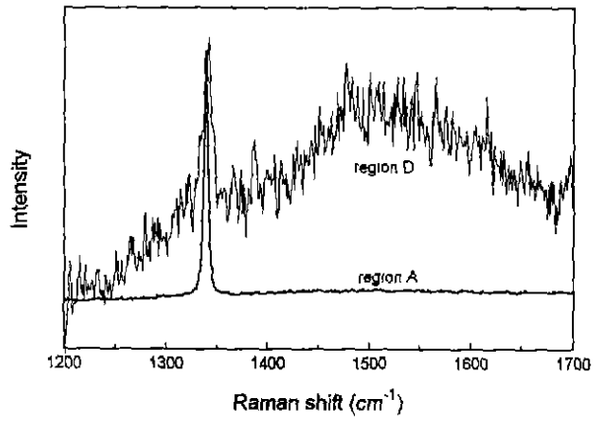

Fig. 9. Raman spectra of the diamond films in region A and D of Fig. 7.

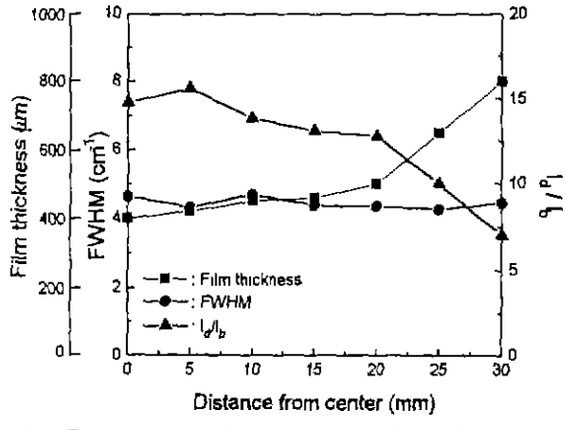

Fig. 10. The spatial distribution of film thickness and, FWHM and I_d/I_b of Raman spectra of the film deposited at the condition of 700 V, 3 5 A, 3%CH_4, 1300°C, 100 Torr, 150 sccm.

(diamond peak intensity/background intensity) of Raman spectra of the film deposited on a rotating substrate of 60 mm in diameter for 7 days. The growth rate at the center increased to 2.5 μm/h, compared to 1 μm/h for rotating 3-inch substrate. It monotonically increased to 5 μm/h at the periphery. Diamond film within diameter of 40 mm was transparent while that in the outer region was opaque. I_d/I_b also radially decreased monotonically while FWHM value was constant. This shows that the uniformity of the deposition is improved by increasing the plasma diameter relative to the substrate diameter.[6] These results suggest that an uniform, high quality diamond film deposition on a large area above 3-inch can be achieved by modifying the arrangement and increasing the number of the cathodes.

In present system, the plasma was stable for a long time. However, the maximum possible current for each cathode was lower than that for the single cathode system. The current limit of each cathode in the 5-cathode system was 3.5~4.0 A at the condition of 100~120 torr, 2~3%CH_4 while it was 6.0~6 5 A for single-cathode system[7] at the same condition. It is probably due to the temperature gradient in the peripheral cathodes induced by the plasma shift as shown in Figs 3~5, since the maximum current is limited by the electric arc bursting when the cathode temperature is excessive. In the peripheral cathode, the temperature at the side facing the central cathode (or plasma) is higher than that at the opposite side by about 200°C. Thus the maximum current is limited by the electric arc bursting when the temperature on the higher-temperature side exceeds a limit.

IV. Conclusion

The five-cathode DC PACVD system was stable enough to deposit diamond for a long time above several days. The plasma formed on a substrate of 3 inch in diameter was non-uniform. The growth rate and the quality of diamond film were closely related to the spatial distribution of the plasma. To deposit an unifrom, high quality diamond film on a large area above 3-inch diameter, it needs to modify the arrangement and increase the number of the cathodes.

Acknowledgement

This research was financially supported by Korea Agency for Defence Development.

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