

THICK DIAMOND FILMS GROWN BY DC DISCHARGE PLASMA CHEMICAL VAPOR DEPOSITION AND THEIR CHARACTERISTICS

Masato KAMADA¹, Shinji ARAI¹, Atsuhito SAWABE¹, Tomoko MURAKAMI², and Tadao INUZUKA²

¹*Toshiba R&D Center, Toshiba Corp., 1 Komukai, Toshiba-cho, Saiwai-ku, Kawasaki 210, Japan*

²*Aoyama Gakuin University, 6-16-1 Chitosedai, Setagaya-ku, Tokyo 157, Japan*

Diamond films, over a hundred microns thick, have been formed on Si substrates by DC plasma chemical vapor deposition. Thick films obtained have good crystallinity in the sense of X-ray diffraction. Micro-Raman spectra, which were measured at several portions in a vertical sectional direction on a film about 120 μm thick, exhibited a sharp peak near 1333 cm^{-1} for diamond, in addition to a broad peak near 1500 cm^{-1} due to non-diamond species. The diamond peaks show significant differences in the full width at half maximum (FWHM), depending on the measured portions. Moreover, the FWHM value for the diamond peak decreases with decreasing the ratio by the peak height of the 1500 cm^{-1} peak to the diamond peak. Fluctuation in the film structure in terms of Raman spectra may be attributed to variation in the substrate surface temperature during deposition.

1. Introduction

Much progress in diamond synthesis from the vapor phase has been made, mainly aimed at developing new growth methods. Especially, forming thick diamond films or plates at a high growth rate has attracted major interest lately. For diamond applications, one of the most interesting subjects is to obtain thicker diamond films or plates without including graphitic or amorphous carbon. There have been a few reports made on forming diamond thick films¹⁾. However, characteristics of the thick films formed seem to be poorly defined. It has been reported that the DC plasma chemical vapor deposition (CVD) method is markedly effective for high rate diamond synthesis, because the DC discharge condition is favorable for generating activated species of high density and there is a large number of initial nuclei²⁾. Therefore, it is interesting to use the DC plasma CVD method for obtaining thicker diamond films.

In this study, attempts have been made to understand the structural properties of thick diamond films formed by DC plasma CVD. Characterization of thick films grown over a hundred microns thick have been carried out by X-ray

diffraction and Raman scattering. The film structure in a vertical sectional direction will be discussed in terms of scanning micrographs and micro-Raman spectra. The present study is the first attempt to form thicker diamond films by DC plasma CVD.

2. Experimental

The apparatus used in DC plasma CVD experiments is shown diagrammatically in Fig. 1. The reaction gas is a mixture of CH_4 (5 vol%), O_2 (1 vol%) and H_2 (94 vol%). A mirror-polished Si (111) substrate ($4 \times 4 \times 1$ mm) is mounted on the anode. After evacuation to 10^{-6} Torr, H_2 gas is introduced to a predetermined pressure and DC discharge is started to preheat and clean the substrate surface by electron bombardment. Then, CH_4 , O_2 and H_2 mixture gas is fed in and the pressure in the reaction chamber is maintained at about 200 Torr during deposition. The flow rate for the mixed gas is typically 400 sccm. The substrate surface temperature during deposition is measured with a pyrometer. Concerning DC discharge conditions for 1 kV and 3.5 A/cm^2 , the substrate temperature rises to about 800~900°C

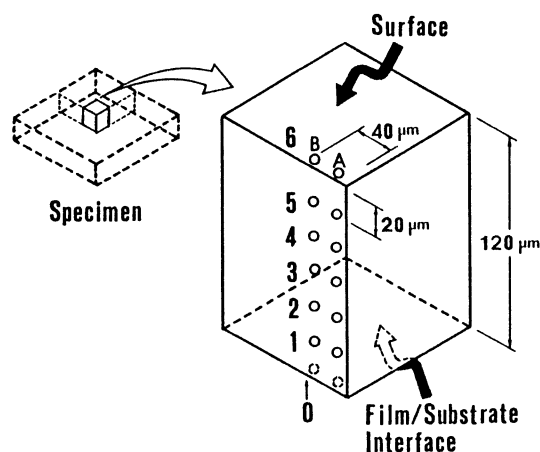


Fig. 4. Diagram indicating measured portions of the thick diamond film for micro-Raman spectrum measurements.

Micro-Raman spectra were measured at several portions in a vertical sectional direction on the film, as shown in Fig. 4. Each spectrum exhibited a sharp peak near 1333 cm^{-1} assigned to diamond, and a broad peak centered at about 1500 cm^{-1} , due to non-diamond species. No peak due to crystalline graphite, which appears at about 1580 cm^{-1} , was observed. This suggests that little or no crystalline graphite was formed in this film, since the Raman scattering efficiency for crystalline graphite is much larger than that for diamond. The broad peak near 1500 cm^{-1} , which has often been observed for “diamond-like” carbon films, is assumed to be attributable to amorphous carbon with sp^2 bonds. Concerning measured Raman spectra, the full width at half maximum (FWHM) for the diamond peak (1333 cm^{-1}) and the ratio by peak height of the 1500 cm^{-1} peak to the diamond peak were measured and are summarized in Table 2, including FWHM values determined for natural diamond (IIa). Numbers in Table 2 indicate the measured portions shown in Fig. 4. FWHM values for these portions are about 2 to 3 times as large as these for natural diamond. It has been found that the FWHM and the peak height ratio are different, depending on the portion measured. That is, the values for the intermediate region (40 and $60\text{ }\mu\text{m}$ distance from the film/ substrate interface) are smaller than those for other regions. It has also been found that the FWHM values decrease with

Table 2. FWHM values for the diamond peak (1333 cm^{-1}) and peak height ratio of the 1500 cm^{-1} peak to the diamond peak in micro-Raman spectra of the film

	FWHM (cm^{-1})		Ratio (A)
	(A)	(B)	
0 (Interface)	8.2	8.4	2.14
1 ($20\text{ }\mu\text{m}$)	7.6	6.8	0.73
2 ($40\text{ }\mu\text{m}$)	6.5	7.4	0.41
3 ($60\text{ }\mu\text{m}$)	6.1	7.7	0.47
4 ($80\text{ }\mu\text{m}$)	7.8	9.6	0.68
5 ($100\text{ }\mu\text{m}$)	7.9	8.5	1.06
6 (Surface)	7.8	7.9	1.68
Diamond (IIa)	2.9		0

Numbers indicate measured portions in A and B directions, as shown in Fig. 4.

decreasing the peak height ratio.

These differences in Raman spectrum features suggest that structural properties of this film are not homogeneous in the film growth direction. Not enough information has yet been obtained to explain the causes of fluctuation in the film structure. However, it is inferred that this structural fluctuation can be attributed to variation in the substrate surface temperature during deposition, considering the fact that the substrate temperatures measured are about 900°C for 1 hour at the early stage of film formation, about 850°C for 9 hours at the middle stage and about 900°C for 6 hours at the late stage. It seems likely that the substrate surface temperature during deposition is one of the important factors in forming thicker diamond films without including graphitic or amorphous carbon in the DC plasma CVD process.

The authors have attempted to form much thicker diamond films by carefully controlling the substrate surface temperature in the DC plasma CVD process. The thickness of the film, over a range from about a hundred to several hundred microns, has been found to increase proportionately with the duration of deposition. It is expected that a constant film growth rate could be maintained during deposition of longer duration in the DC plasma CVD process. A study of factors influencing the thick film formation at a high growth rate is now in progress.

4. Summary

Diamond films over a hundred microns thick have been formed from $\text{CH}_4/\text{O}_2/\text{H}_2$ mixed gases by the DC plasma CVD method. The obtained diamond films have good crystallinity in the sense of X-ray diffraction. Micro-Raman analysis suggests that the thick films have structural fluctuation, related to partial formation of “diamond-like” carbon with sp^2 bonds. It is inferred that the structural fluctuation may be caused by temperature variation in the substrate surface temperature during deposition. It seems that the substrate temperature plays an important role in the determi-

nation of the structural properties of thick diamond films.

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