

Raman Spectra of DLC Films Prepared by Bipolar-type Plasma Based Ion Implantation

Setsuo Nakao, Jongduk Kim, Junho Choi, Soji Miyagawa, Yoshiko Miyagawa and Masami Ikeyama

National Institute of Advanced Industrial Science and Technology (AIST), 2266-98 Anagahora, Moriyama, Nagoya 463-8560
Fax: 81-52-736-7406, e-mail: nakao.s@aist.go.jp

Examination of Raman spectroscopy on the microstructure of diamond like carbon (DLC) films prepared by the bipolar-type plasma based ion implantation as a function of positively and negatively pulsed voltages (V_p and V_n) were carried out. Raman spectra were fitted by 4 peaks (D1: 1190 cm^{-1} , D2: 1380 cm^{-1} , G1: around $1530 - 1555\text{ cm}^{-1}$ and G2: 1590 cm^{-1}). The G1 peak shifted to higher wavenumbers and the intensity of G2 peak was increased with increasing V_p . In addition, the intensity ratio of D (D1 + D2) to G (G1 + G2) peaks was also increased. These results suggested that graphite structure was formed as V_p increased. With increasing V_n , on the other hand, the G1 peak did not shift so much and the intensity of G2 peak was decreased. This corresponds to the development of the turbostratic form (t-DLC).

Key words: Raman spectra, bipolar plasma, PBII, DLC, turbostratic form

1. INTRODUCTION

Raman spectroscopy has usually been used for the characterization of diamond like carbon (DLC) films. Analysis of Raman spectra is brought out by curve fitting using 2 peaks, as well known, disorder (D) and graphite (G) peaks [1]. However, in our experiments, at least 3 or 4 peaks are observed, as shown in Fig. 1, so that the good curve fitting results is not always obtained when the curve fitting was done with only 2 peaks. Some researchers [2-5] try to analyze Raman spectra using 4 or more peaks. In this study, Raman analysis is carried out through 4 peak-curve fitting to obtain well fit results.

On the other hand, many investigations of DLC films have been carried out with various preparation methods, such as ion beam deposition, sputtering, plasma-based ion implantation (PBII) and chemical vapor deposition because of their excellent properties, such as high hardness, high wear resistance and chemical inertness [1]. In particular, PBII has attracted much interest because of the capability of surface coating for 3 dimensional workpieces [6-8].

DLC films are composed of sp^2 and sp^3 bonded carbons and then show a wide variety of properties as a consequence of different fraction of sp^2 and sp^3 bonds. In addition, DLC films incorporated with other elements, such as N, Si and metals [9-12], are studied to get good adhesion and high electrical conductivity. To obtain proper DLC coating, in addition to the above incorporation method, it is also necessary to control the microstructure of the DLC films. In plasma process, the deposition of DLC films should be affected by the behavior of radicals, ions and electrons. In our laboratory, the characterization of DLC films depending on ion bombardment and electron impinging has been carried out using a bipolar type PBII system [8]. When positively and negatively pulsed voltages (V_p and V_n) are varied, the microstructure of DLC films are changed. The changes in Raman spectra are discussed.

2. EXPERIMENTAL

DLC films were prepared on Si(100) substrates by the bipolar-type PBII system. Preparation conditions are listed in Table I. The substrate was held on the center of the cylindrical vacuum chamber. Positively and negatively pulsed voltages (V_p and V_n) were applied to the substrate through a high-voltage feed-through in the range of +2 to +4 kV and of -5 to -15 kV, respectively. The chamber was evacuated to less than 10^{-4} Pa by a turbomolecular pump. Toluene gas was inlet to the chamber at the flow rate of 2 sccm. Plasma was produced around the substrate by alternately applying V_p and V_n at pulse frequency of 2 kHz. The change of V_p and V_n caused the change of deposition pressure in the range of 1 to 6×10^{-2} Pa. Deposition time was kept 30 min for all samples. Film thickness was measured using a surface profilometer (Kosaka Laboratory Ltd., ET350). The thickness of DLC films was changed by the preparation condition in the range of 90 to 200 nm. Temperature during deposition was measured by a chromel-alumel thermocouple insulated from the ground. The temperature is changed in the range of 40 to 200°C .

Table I. Typical preparation condition and film thickness for each sample.

Sample	V_p (+kV)	V_n (-kV)	Thickness (nm)	Temperature ($^\circ\text{C}$)
A	2	5	147	42
B	2	10	173	52.3
C	2	15	193	79.1
D	3	5	119	66.6
E	3	10	141	96.7
F	3	15	161	135
G	4	5	77	136
H	4	10	95	163
I	4	15	95	202

Raman spectra of DLC films were measured on micro-Raman spectrometer (Renishaw inVia) with 514.5 nm line of an Ar ion laser. The power of the laser was 10 mW and the laser was focused to a diameter of about 1 μm on the surface of the film. Typical acquisition time was 10 s.

In our experiments, good curve fitting result is not always obtained by only 2 peaks. Sometimes it happens that the intensity of fitted D band becomes enormously larger than that of the fitted G band in spite of the apparently dominant G peak. To prevent such mistake on curve fitting, the additional band is necessary. Figure 1 shows typical Raman spectra of DLC films prepared by the bipolar type PBII. In the (a) case 1 (sample A in Table I), 3 peaks are apparently observed at ~ 1190 (D1), ~ 1380 (D2) and ~ 1550 (G) cm^{-1} . In a previous study [13], therefore, visible Raman spectra were fitted by these 3 peaks. In the (b) case 2 (graphitized sample after scratch test), however, another peak at ~ 1590 cm^{-1} clearly appeared. This fact suggests that G peak is probably composed of 2 peaks (G1 and G2). Thus, in this study, 4 peak curve fitting technique is adopted to unify the curve fitting way for all spectra. The analysis of Raman spectra using 4 peaks was carried out by several researchers [2-5]. Iwaki et al. [3] pointed out at least 4 peaks are necessary to obtain the best curve fitting. Referring to their studies [2-5], an assumption is made as follows: (1) the spectrum is composed of 4 peaks at 1190 cm^{-1} (D1 peak), 1380 cm^{-1} (D2 peak), $\sim 1500 - 1560$ cm^{-1} (G1 peak) and 1590 cm^{-1} (G2 peak) (2) the peak is fitted by Gaussian line shape, (3) D1, D2 and G2 peaks do not shift, i.e., 3 peak positions are fixed except for G1 peak. The G1 peak shifts to lower wavenumbers as force constant is reduced due to disordering. The Gaussian line shape is assumed because DLC films show the lost of long range order in structure so that Lorenz component is almost negligible. Possible interpretation of Raman bands used in peak separation is listed in Table II.

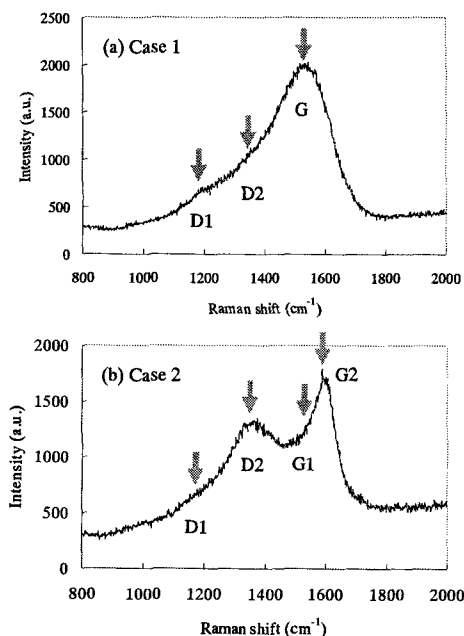


Fig. 1. Typical Raman spectra of DLC films: (a) 3 peaks (case 1) and (b) 4 peaks (case 2) are recognized.

Table II. Possible interpretation of Raman bands used in peak separation in our study.

Peak	Peak position (cm^{-1})	Tentative assignment	Reference
D1	1190	"D peak" due to high phonon density of graphite	[2]
D2	1380	"D peak" due to nanocrystalline graphite and aromatic ring cluster	[2-5]
G1	1500-1560	"G peak" due to disordered graphite	[2,5]
G2	1590	"G peak" due to ordered graphite	[2-5]

3. RESULTS AND DISCUSSION

To deduce the V_p and V_n dependence, Raman spectra were measured and curve fittings with 4 peaks as listed in Table II are carried out for the samples prepared under the different V_p and V_n . Figure 2 shows Raman spectra of DLC films deposited at $V_p =$ (a) +2 and (b) +4 kV when $V_n = -10$ kV. On the other hand, Fig. 3 shows Raman spectra of DLC films deposited at $V_n =$ (a) -5 and (b) -15 kV when $V_p = +3$ kV. Curve fitting results are also shown. In Fig. 2(a), a broad peak appears at ~ 1530 cm^{-1} , which corresponds to G1 peak. In addition, two shoulder peaks are observed at 1190 cm^{-1} (D1) and 1380 cm^{-1} (D2), respectively. A small fraction of G2 peak is also obtained at 1590 cm^{-1} by peak separation. With increasing V_p , in Fig. 2(b), the G1 peak slightly shifts to higher wavenumber of ~ 1555 cm^{-1} and is decreased in intensity as compared with whole intensity (D1 + D2 + G1 + G2). In contrast, the intensity of the two shoulder peaks, D1 and D2, are increased and the G2 peak is also increased in intensity. In Fig. 3(a), a dominant G1 peak appears at ~ 1545 cm^{-1} , and shoulder D1 and D2 peaks are also observed and G2 peak is clearly obtained by peak separation. With increasing V_n , in Fig. 3(b), the G1 peak does not shift significantly. However, the intensity of G1 peak is decreased as compared with whole intensity. It is noted that the G2 peak is also decreased in intensity with increasing V_n .

Comparing Figs. 2(a) with 2(b), it is found that G1 peak slightly shifts to higher wavenumber at high V_p and the intensity of G2 peak is increased as compared with whole intensity. The origins of G1 and G2 peaks should be assigned to disordered graphite and ordered graphite, respectively, as listed in Table II. Therefore, these results suggest that the formation and ordering of graphite structure is enhanced at high V_p . Comparing Figs. 3(a) with 3(b), however, G1 peak does not shift at high V_n but the intensity of G2 peak is reduced as compared with whole intensity. These results suggest that the ordering of graphite structure is reduced at high V_n . To estimate the intensity ratio of D peak and G peak (I_D/I_G) that is a useful parameter and usually used for characterization of DLC films, it is presumed that the summation of G1 and G2 peaks is equal to the intensity of G peak. As well known, G band is Raman active E_{2g} mode in graphite. Therefore, the intensity ratio of G2 to G peak (I_{G2}/I_G) may also be useful for the evaluation of the magnitude of ordered graphite structure.

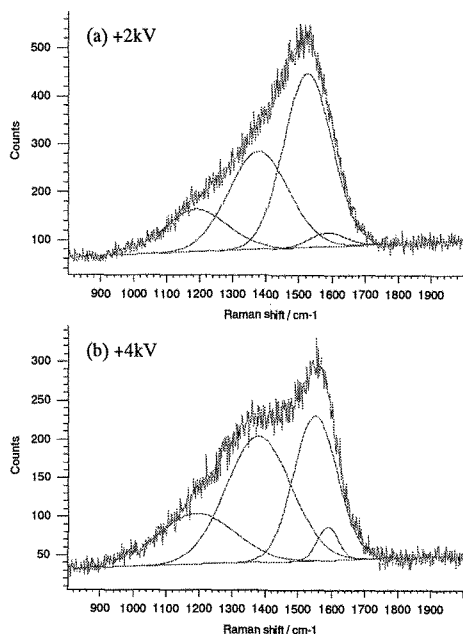


Fig. 2. Raman spectra of DLC films prepared at V_p of (a) +2 kV and (b) +4 kV under the same V_n of -10 kV. Curve fitting results are also shown.

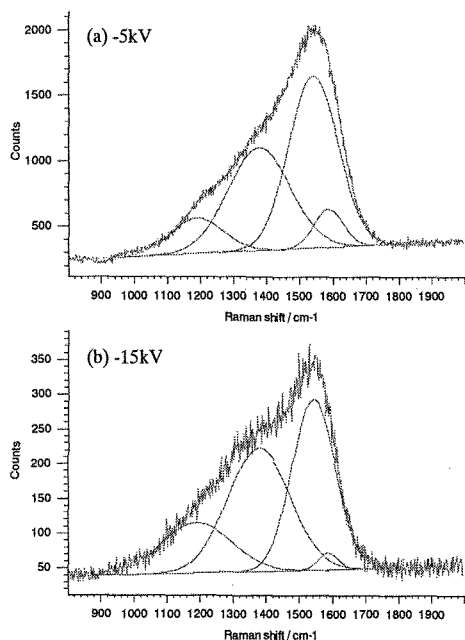


Fig. 3. Raman spectra of DLC films prepared at V_n of (a) -5 kV and (b) -15 kV under the same V_p of +3 kV. Curve fitting results are also shown.

On the other hand, the origin of D1 peak is still uncertified. Possible candidates are (1) sp^3 C-C stretching vibration, (2) C-H rocking and bending vibration and (3) D band due to high phonon density of graphite [2]. In the previous study [13], it was conjectured that D1 peak possibly originated from C-H vibration since the films contain about 20 at% hydrogen. However, the D1 peak is also observed for DLC films prepared by a conventional Ar sputtering with graphite target, which contain less sp^3 bonded carbon and no hydrogen (not shown). From this fact, as of the present time, it is believed that the D1 peak can be assigned to D band due to high phonon density.

The origin of D2 peak also should be assigned to D band due to nanocrystalline (nc-) graphite and/or stretching vibration in aromatic rings. It is well known that D band is Raman inactive mode of graphite, but the peak appears when the selection rule is broken out due to microcrystallization. Thus, D peak is different from G peak and the total intensity of D peak is obtained by the summation of D1 and D2 peaks.

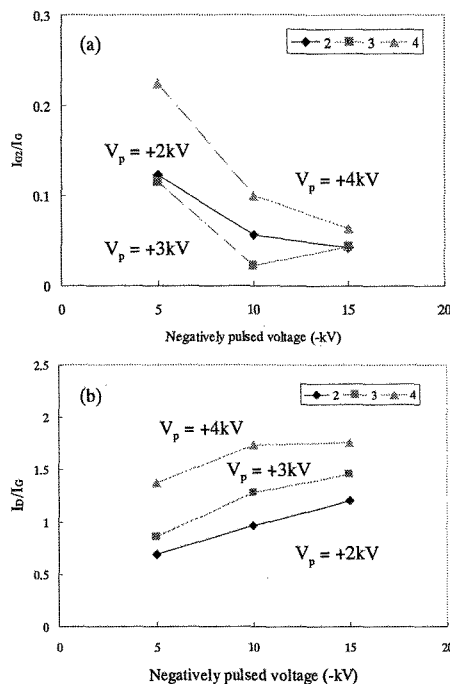


Fig. 4. The intensity ratio of (a) G2 peak to G peak (I_{G2}/I_G) and (b) D peak to G peak (I_D/I_G) as a function of V_n , where $I_D = I_{D1} + I_{D2}$ and $I_G = I_{G1} + I_{G2}$. Different symbols indicate different V_p as inserted in figures.

Figure 4 shows the intensity ratio of (a) I_{G2}/I_G and (b) I_D/I_G as a function of V_n under the different condition of V_p where $I_D = I_{D1} + I_{D2}$ and $I_G = I_{G1} + I_{G2}$. In Fig. 4(a), the I_{G2}/I_G ratio is not changed or slightly decreased with increasing V_p up to +3 kV. However, the ratio is surely increased at high V_p of +4 kV. On the other hand, the ratio is monotonically decreased with increasing V_n except for that of V_p , +3 kV. As mentioned above, G2 peak should arise from ordered graphite form and G peak is well known as graphite peak. Thus, this parameter is sure to be an indicator for the magnitude of ordered graphite structure. The tendency of I_{G2}/I_G ratio implies that ordered graphite structure is developed at high V_p , but reduced at high V_n . On the other hand, in Fig. 4(b), it is clearly seen that the I_D/I_G ratio is increased with increasing V_p or V_n . J. Robertson [1] reviewed many studies on DLC films and summarized the relationship between the change of I_D/I_G ratio and the microstructure of DLC films, although data on I_D/I_G ratio obtained from different curve fitting by different researchers were included. In the review paper, 3-stage model was proposed and common tendency of I_D/I_G ratio in each stage was found out. According to the model, our DLC films are able to be classified stage 2 in which the microstructure of the films is varied from nc-graphite to amorphous carbon (a-C), and the increase of I_D/I_G ratio means the enhancement of the clustering of aromatic rings.

Interest in the microstructure of DLC film prepared at high V_p and V_n is arising, since the change in the I_{G2}/I_G indicates that ordered graphite structure is formed at high V_p , but reduced with increasing V_n , although the change in the I_D/I_G shows that aromatic ring clustering are enhanced with increasing V_p and V_n . To make clear this point of view, transmission electron microscopy (TEM: JEOL, JEM2000FX) was carried out. Figure 5 shows the TEM micrograph for the film prepared at $V_p = +4$ kV and $V_n = -15$ kV. A turbostratic form of carbon (t-DLC) is clearly seen, which shows the 2-dimensional in-plane order of the hexagonal basal planes is largely retained, but these planes are stacked in a random sequence and with random rotation about the c axis. The basal planes are highly disordered and extend to only a short distance so that the fringe spacing ranges from 0.34 - 0.37 nm. The turbostratic form is most commonly observed in boron nitride thin film which is referred to t-BN [14, 15].

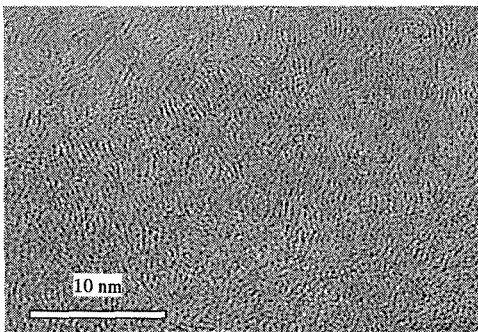


Fig. 5. TEM micrograph for the film prepared at $V_p = +4$ kV and $V_n = -15$ kV.

The results of Raman analysis indicate that the ordered graphite structure is formed at high V_p and the highly disordered graphite (turbostratic) structure is developed at high V_n , as shown in Fig. 5. The effects of V_p and V_n are considered with the results of computer simulation for the bipolar pulse system [16-18] carried out using a simulation software PEGASUS as follows: When V_p is applied to the target, electrons gather in the small area close to the target surface, so, the collision probability between atoms is very high. The increase of V_p , therefore, caused the increase in the number of electrons and collision probability. Then, increasing V_p makes intense plasma and electron bombardment, i.e., electron heating effect increase. Moreover, V_n applied after the plasma being generated by V_p brings about the generation of much more intense plasma. Therefore, increasing V_n caused the increase in not only ion energy but also the number of ions. Thus, higher V_n makes more intense ion bombardment to the target sample. From the above consideration, it can be said that the increase of electron heating with increasing V_p should cause the enhancement of ordered graphite structure formation. In fact, the temperature of the sample is increased with increasing V_p , as listed in Table I. On the other hand, the intense of ion bombardment at high V_n should disturb the ordering of the basal planes in spite of growing graphite crystallites at the same time, resulting in making the turbostratic form (t-DLC).

4. SUMMARY

Raman measurements are carried out to examine the

effects of positively and negatively pulsed voltages (V_p and V_n) on the microstructure of DLC films prepared using the bipolar-type PBII system. Raman spectra are analyzed by the curve fitting with the aid of 4 peaks (D1, D2, G1 and G2). The results suggest that the clustering of aromatic rings is enhanced with increasing V_p and V_n , but the ordering of graphite structure is reduced by the increase of V_n . Considering with the results of computer simulation for bipolar pulse system, it is believed that the growth of graphite is enhanced by electron heating at high V_p , and highly disordered graphite (turbostratic) structure is formed during the growth of graphite crystallites under intense ion bombardment at high V_n .

Acknowledgement

Authors would like to thank to TEM support project of AIST for the use of JEM2000FX and to Mr. T. Yamamoto for the preparation of TEM samples.

References

- [1] J. Robertson, *Materials Science and Engineering*, **R37**, 129-281 (2002).
- [2] B. Oral, R. Hauert, U. Muller and K. -H. Ernst, *Diamond Rel. Mater.*, **4**, 482-487 (1995).
- [3] M. Iwaki and H. Watanabe, *Nucl. Instr. Methods*, **B 141**, 206-210 (1998).
- [4] K. Awazu, N. Sakudo, H. Yasui, E. Saji, K. Okazaki, Y. Hasegawa, N. Ikenaga, K. Kanda, Y. Nambo and K. Saitoh, *Surf. Coat. Technol.*, **136**, 172-175 (2001)
- [5] J. Schwan, S. Ulrich, V. Batori, H. Ehrhardt and S. R. P. Silva, *J. Appl. Phys.*, **80**, 440-447 (1996).
- [6] I. V. Afanasyev-Charkin and M. Nastasi, *Appl. Phys. Lett.*, **85**, 718-720 (2004).
- [7] S. Miyagawa, S. Nakao, K. Saitoh, K. Baba and Y. Miyagawa, *Surf. Coat. Technol.*, **128-129**, 260-264 (2000).
- [8] S. Miyagawa, S. Nakao, M. Ikeyama and Y. Miyagawa, *Surf. Coat. Technol.*, **156**, 322-327 (2002).
- [9] K. Baba and R. Hatada, *Surf. Coat. Technol.*, **136**, 192-196 (2001).
- [10] K. Baba and R. Hatada, *Surf. Coat. Technol.*, **196**, 207-210 (2005).
- [11] M. Ikeyama, S. Nakao, Y. Miyagawa and S. Miyagawa, *Surf. Coat. Technol.*, **191**, 38-42 (2005).
- [12] J. Choi, S. Miyagawa, S. Nakao, M. Ikeyama and Y. Miyagawa, *Trans. Mater. Res. Soc. Japan*, **30**, 781-784 (2005).
- [13] S. Nakao, J. Choi, S. Miyagawa, Y. Miyagawa, M. Ikeyama and K. Tsugawa, *Trans. Mater. Res. Soc. Japan*, **30**, 785-788 (2005).
- [14] K. F. McCarty, P. B. Mirkarimi, D. L. Medlin, T. A. Friedmann and J. C. Barbour, *Diamond Rel. Mater.*, **5**, 1519-1526 (1996).
- [15] P. B. Mirkarimi, K. F. McCarty and D. L. Medlin, *Mater. Sci. Eng.*, **R21**, 47-100 (1997).
- [16] Y. Miyagawa, H. Nakadate, M. Ikeyama, S. Nakao and S. Miyagawa, *Diamond Rel. Mater.*, **12**, 927-930 (2003).
- [17] Y. Miyagawa, H. Nakadate, M. Tanaka, M. Ikeyama and S. Miyagawa, *Surf. Coat. Technol.*, **186**, 2-9 (2004).
- [18] Y. Miyagawa, H. M. Ikeyama, S. Miyagawa and Nakadate, *Nucl. Instr. Methods*, **B 206**, 767-771 (2003).