

Visible and UV Raman spectra of diamond-like carbon films prepared by a PBII system

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Diamond-like carbon (DLC) films are prepared by a bi-polar-type plasma-based ion implantation (PBII) technique, and the microstructure of the DLC films is examined as a function of a negatively pulsed voltage (V_n), by visible and UV Raman spectroscopy. The visible Raman spectra show typical D and G peaks of DLC films, and the intensity ratio of D peak to G peak and G peak position increase with increasing V_n . On the other hand, in the UV Raman spectra, a sharp peak at $\sim 1580 \text{ cm}^{-1}$ and a broad peak at $\sim 1620 \text{ cm}^{-1}$ appear, and shift to $\sim 1565 \text{ cm}^{-1}$ and $\sim 1580 \text{ cm}^{-1}$ with increasing V_n , respectively. The origin of the former might arise from small cluster of aromatic ring. The latter can be attributed to G peak of finite size graphite structure and sp^2 olefinic chains. The results of the visible and UV Raman measurements suggest that clustering of aromatic ring is enhanced as the V_n increased.

Key words: DLC, visible Raman spectra, UV Raman spectra, PBII

1. INTRODUCTION

Diamond-like carbon (DLC) films have attracted much attention because of its excellent properties, such as high hardness, high wear resistance and chemical inertness. Therefore, many investigations of DLC films [1] have been carried out with various preparation methods, such as ion beam deposition, sputtering, plasma-based ion implantation (PBII) and chemical vapor deposition. In particular, PBII has attracted much interest because of the capability of surface coating for 3 dimensional workpieces [2-4].

DLC films are composed of sp^2 and sp^3 bonded carbon and then show a wide variety of properties as a consequence of different fraction of sp^2 and sp^3 bonds. To obtain proper DLC coating, the control of the microstructure of the DLC films is necessary. In PBII process, the deposition of DLC films should be affected by the behavior of radicals, ions and electron [2,3]. In our laboratory, characterization of DLC films depending on ion bombardment and electron impinging has been carried out using a bi-polar-type PBII system [4].

Electrical resistivity of the films can be varied depending on the microstructure under the different deposition condition [4]. On the other hand, Raman spectroscopy is believed to be a useful tool for the characterization of DLC films. In this study, the microstructure of the DLC films is examined as a function of a negatively pulsed voltage (V_n) by visible and UV Raman spectroscopy.

2. EXPERIMENTAL

DLC films were prepared by the bi-polar-type PBII system [4]. Toluene was used as a source gas. Typical preparation conditions are listed in Table I. A positively pulsed voltage (V_p) was kept a constant of 4 kV, and V_n

was varied from -2.5 to -10 kV. The thickness in each film deposited for 2 h was about $\sim 1 \mu\text{m}$. Temperature of the sample during deposition was less than $250 \text{ }^\circ\text{C}$. Pressure was about 8×10^{-2} Pa. Plasma was firstly produced around the sample by applying V_p , and then ions were accelerated toward the sample by applying V_n after the V_p was turned off. When applying V_n electrons were also accelerated backward the sample, leading to the increase in plasma intensity through the electron collision. Therefore, increasing V_n caused not only increasing ion energy but also ion density. Thus, ion bombardment effect was expected to be enhanced as the V_n increased. Details of equipment and process condition were described elsewhere [4].

Electrical resistivity of the film was measured by Keithley 6517 type electrometer. Ti electrodes of 2 mm in diameter were evaporated on the surface of DLC film deposited on glassy carbon substrate 1 cm wide and 2 cm long. The resistance of the sample without DLC film was also measured and subtracted from the resistance of DLC coated samples to eliminate contact resistance. The electrical resistivities of typical films are also listed in Table I.

Table I. Typical preparation condition, film thickness and electrical resistivity for the sample.

Sample	+ pulse (kV)	- pulse (kV)	Thickness (μm)	Resistivity ($\text{k}\Omega\text{cm}$)
A	4.0	-2.5	0.87	25.0
B	4.0	-5.0	1.08	9.3
C	4.0	-10.0	0.90	7.2

To examine the microstructure, visible and UV Raman spectroscopy were carried out. The visible Raman spectra of DLC films were measured on Renishaw inVia micro-Raman spectrometer with the 514.5 nm line of an Ar ion laser. The power of the laser was 10 mW and the laser was focused to about 1 μm on the surface of the film. Typical data acquisition time was 10 s. The UV Raman spectra were measured on JASCO NRS-1000 spectrometer with 244 nm line. Typical data acquisition time was 60 s. Raman shift was calibrated by the peak of diamond and glassy carbon. To confirm sp^3/sp^2 ratio of DLC films, X-ray photoemission spectroscopy (XPS) is also carried out. XPS spectra were measured on VG sigma probe spectrometer. Al K α line was used for analysis.

3. RESULTS AND DISCUSSION

The electrical resistivity of DLC film decreased with increasing V_n , as shown in Table I. It seems that the decrease of the electrical resistivity may arise from the increase of the fraction of sp^2 bond in the film by ion bombardment in the deposition process. However, the results of XPS measurements (not shown) showed that there was no significant difference of sp^2 fraction among the samples. In order to check the differences, visible and UV Raman spectra were measured.

Figure 1 shows visible Raman spectra of DLC films deposited on Si substrates. For the sample A, a broad peak at $\sim 1550\text{ cm}^{-1}$ appears. In addition, two shoulder peaks are observed at $\sim 1380\text{ cm}^{-1}$ and $\sim 1190\text{ cm}^{-1}$. As well-known, the dominant peak at $\sim 1550\text{ cm}^{-1}$ is assigned to G (graphite) peak, and the shoulder peak at $\sim 1380\text{ cm}^{-1}$ is assigned to D (disorder) peak. On the other hand, the assignment of the peak at $\sim 1190\text{ cm}^{-1}$ is unclear but a possible origin is CH bending and rocking mode. With increasing V_n , for the sample B, G peak slightly shifts to larger wavenumber and decreases in intensity. Further increase of the V_n causes a similar trend. For the sample C, G peak shifts to $\sim 1560\text{ cm}^{-1}$.

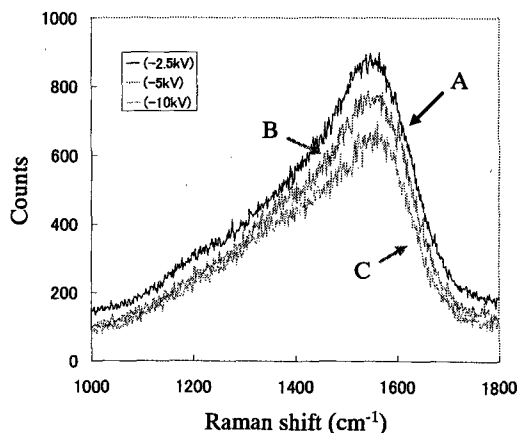


Fig.1. Visible Raman spectra of the samples prepared at different negatively pulsed voltages (V_n).

Figure 2 shows UV Raman spectra of the same DLC films of Fig. 1. D peak as apparently observed in the visible Raman spectra is reduced significantly in intensity because of off-resonant condition. This is also confirmed from the UV Raman spectrum on glassy carbon sample. For the sample A, a sharp peak at $\sim 1580\text{ cm}^{-1}$ is observed. Broad peaks are also observed centered at $\sim 1620\text{ cm}^{-1}$ and $\sim 1050\text{ cm}^{-1}$, respectively. The peak at $\sim 1620\text{ cm}^{-1}$ should be assigned to G peak. With increasing V_n , the sharp peak and the G peak shift to lower wavenumber. For the sample C, the sharp peak at $\sim 1565\text{ cm}^{-1}$, and G peak at $\sim 1580\text{ cm}^{-1}$ are observed. On the other hand, the broad peak at $\sim 1050\text{ cm}^{-1}$ shifts to higher wavenumber as V_n increases and it is observed at $\sim 1240\text{ cm}^{-1}$ for the sample C.

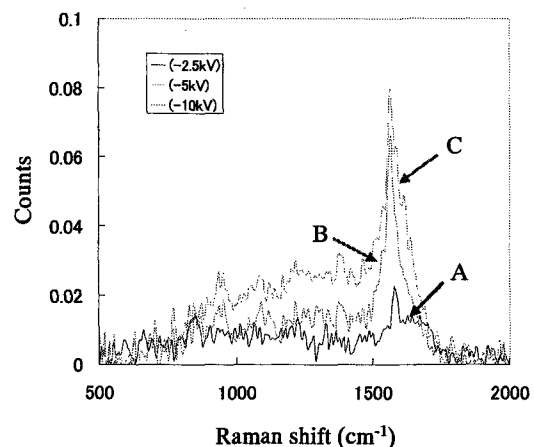


Fig.2. UV Raman spectra of the samples of Fig. 1.

It is believed that Raman spectroscopy is very sensitive for the microstructure of carbon materials although its quantitative analysis is difficult. As an attempt of qualitative analysis, an assumption was made as follows: For the visible Raman spectra, (1) the spectrum is composed of 3 peaks at $\sim 1550\text{ cm}^{-1}$ (G peak), 1380 cm^{-1} (D peak) and 1190 cm^{-1} , (2) the peak is fitted by Gaussian line shape, (3) 2 shoulder peaks at 1380 cm^{-1} and 1190 cm^{-1} do not shift, i.e., both peak positions are fixed except for G peak. For the UV Raman spectra, (1) the spectrum is composed of 3 peaks: the sharp peak at 1565 cm^{-1} (or at 1580 cm^{-1} for the sample A), the broad peaks at 1580 cm^{-1} and at $1050 - 1250\text{ cm}^{-1}$, (2) the peak is also fitted by Gaussian line shape, (3) in the case of sample A, the peak at 1640 cm^{-1} is added to get the better fitting. The results of curve fitting are shown in Figs. 3 and 4, respectively.

Figure 5 shows intensity ratio of D peak to G peak (I_D/I_G) and G peak position obtained from the curve fitting results of the visible Raman spectra as a function of V_n . It is clearly seen that the I_D/I_G ratio and G peak position increase with increasing V_n . Since the results of XPS analysis indicated that all the films contain the most sp^2 and fraction ($\sim 10\%$) sp^3 bonds, this trend can be explained by stage 2 in 3-stage model [1] which shows that DLC film contains $\sim 100\%$ sp^2 (stage 1:

graphite to nanocrystalline (nc-) graphite), the most sp^2 and $\sim 10\%$ of sp^3 (stage 2: nc-graphite to amorphous carbon (a-C)), and a fraction of sp^2 and the most sp^3 (stage 3: a-C to tetrahedral a-C). According to J. Robertson [1], the increase of I_D/I_G ratio and G peak position in stage 2 means the enhancement of the clustering of aromatic ring.

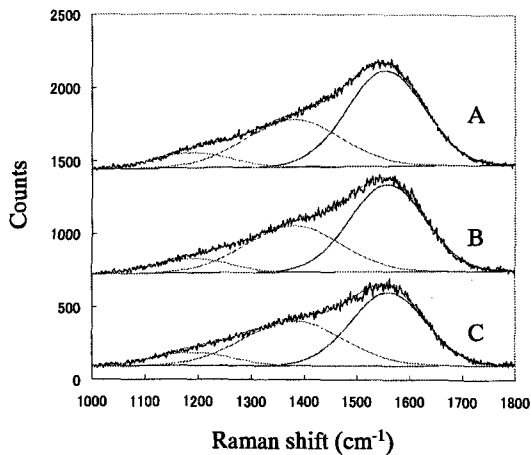


Fig.3. Curve fitting results of the visible Raman spectra.

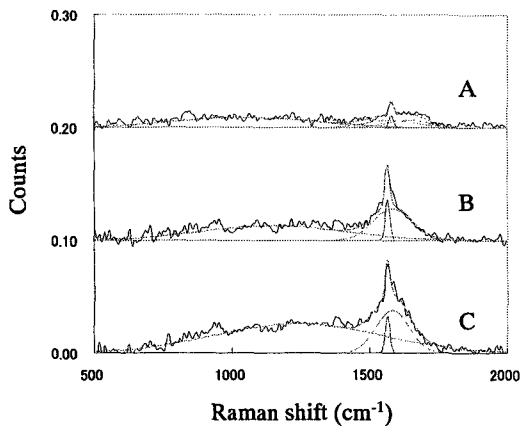


Fig.4. Curve fitting results of the UV Raman spectra.

The some differences on the curve fitting results between the UV Raman spectra of the samples are shown. However, the origin of the peaks has not been always completely understood yet. Possible interpretation is attempted. The appearance of the sharp peak at 1565 or 1580 cm^{-1} suggests that there is some resonant reaction by high photon energy. M. Ramsteiner and J. Wagner [5] pointed out that high incident photon energy would probe small sp^2 carbon clusters because the energy gap of the cluster depends on the cluster size. It is noted that the results of the visible Raman

measurements suggest the enhancement of the clustering of aromatic ring with increasing V_n . From this and the fact that the sharp peak increases in intensity as the V_n increased, it is believed that the sharp peak may arise from $\pi-\pi^*$ resonant Raman scattering from aromatic ring cluster in small size. The downward shift of the peak from 1580 to 1565 cm^{-1} with increasing V_n may be caused by decreasing force constant due to the reduction in the amount of sp^2 olefinic chains as mentioned below. On the other hand, the peak at 1580 cm^{-1} presumably originates from finite size graphite structure. The E_{2g} mode of graphite, i.e., infinite size graphite structure, should appear at 1600 cm^{-1} in UV Raman measurement. Thus, the peak from finite size graphite structure is expected to shift to lower wavenumber due to the decrease of the force constant. For the sample A, the peak at 1640 cm^{-1} is necessary to fit the spectrum. J. Robertson [1] asserted that the appearance of the peak beyond 1600 cm^{-1} in UV Raman measurements is direct evidence on the presence of sp^2 olefinic chains since the peak caused by aromatic ring structure does not appear beyond 1600 cm^{-1} . According to him, the peak at 1640 cm^{-1} can be assigned to sp^2 olefinic chains. This suggests that the amount of sp^2 olefinic chains in the film is high at low V_n and is decreased at higher V_n . The broad peak at 1050 - 1240 cm^{-1} is also observed as shown in Fig. 4. This peak seems to be assigned to T (tetrahedral) peak as T peak should appear at ~ 1200 cm^{-1} in the case of UV Raman spectrum. However, it is noted that there is the most sp^2 bonds in the current films. In addition, the visible Raman spectra show the peak at ~ 1190 cm^{-1} . This peak is possible to arise from CH bending and rocking mode, and it is expected that the related peak also appears in the UV Raman measurements. Moreover, D peak shifts to higher wavenumber with increasing incident photon energy [6] and is expected to appear at ~ 1400 cm^{-1} in UV Raman spectrum, although the peak intensity significantly decreased. Therefore, it is assumed that the broad peak is composed of the peaks caused by CH bending and rocking mode, T and D bands. To confirm this assumption, further investigation is necessary.

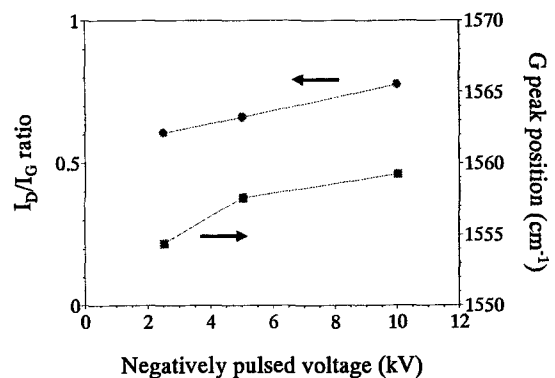


Fig.5. I_D/I_G ratio and G peak position obtained from the visible Raman spectra.

From the results of both visible and UV Raman measurements, the consideration that the clustering of aromatic ring is enhanced and the amount of sp^2 olefinic chains is decreased by the increase of ion energy and ion bombardment with increasing V_n , is deduced. The increase of aromatic ring cluster might seem to cause the graphitization ($\sim 100\% sp^2$). However, XPS analysis with depth profile measurement revealed that the sp^3/sp^2 ratio between the samples does not change significantly. It is noted that XPS analysis is not sensitive for the difference of sp^2 phases, such as aromatic ring cluster and olefinic chains. From XPS and Raman results, it is suggested that ion bombardment with high energy enhances the phase change from sp^2 olefinic chains to sp^2 aromatic ring cluster, but keeps the sp^3/sp^2 ratio. According to the subplantation model [1,3] in which ion bombardment makes densification by carbon penetration leading to the creation of sp^3 bonding, it is considered that ion bombardment keeps the sp^3/sp^2 ratio as consequence of the equilibrium between the creation and reduction of sp^3 bonding. Moreover, it is believed that the film stops short of graphitization since the deposition temperature is as low as 250 °C.

Above consideration is also consistent with the result that the electrical resistivity decreases with increasing V_n . It is noted again that the amount of sp^2 olefinic chains is decreased and the clustering of sp^2 aromatic ring is enhanced with increasing V_n , deduced from the visible and UV Raman analysis. This suggests that π electrons are delocalized with increasing V_n . Thus, the spread of delocalized π electrons to the film should be caused in consequence of the increase of aromatic ring clusters accompanied by the decrease of olefinic chains. This is believed to be responsible for the reduction of the electrical resistivity.

4. SUMMARY

DLC films were prepared by the bi-polar-type PBII technique and the microstructure was examined as a function of V_n by the visible and UV Raman spectroscopy. The visible Raman spectra showed that I_D/I_G and G peak position are increased with increasing V_n . On the other hand, the UV Raman spectra showed that G peak position is decreased from 1620 cm^{-1} to 1580 cm^{-1} as the V_n increased. These results suggested that the clustering of aromatic ring was enhanced and the amount of sp^2 olefinic chains was reduced with increasing V_n . Possible assignment of the peaks obtained from curve fitting on the UV Raman spectra of the samples was attempted. The results of both visible and UV Raman analysis were believed to be consistent with the fact that the electrical resistivity was reduced with increasing V_n .

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