Effect of the Analytic Regions on the Quality Trend of Diamond-like/Graphitic Carbon Ratios in Raman Spectra

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Raman spectroscopy is a useful and non-destructive tool for the structural characterization of diamond-like carbon (DLC) films. Even though Raman spectroscopy is not a quantitative technique, the area integral intensity ratio of D and G peaks (I_D/I_G) derived by the fitting of separate Gaussian curves usually serves as an indicator of the quality trend of diamond-like material. However, conflicting reports still exist on the diamond-like films analyzed by the fitting method of Raman spectra. In this work we show that the quality trend of the diamond-like/graphitic carbon ratio is critically dependent upon the boundary conditions of the analytic regions. We also examine the possibility of directly applying the peak height ratio H_D/H_G as an alternative method to analyze Raman spectra. The method based on peak height ratios (H_D/H_G), and an established method using I_D/I_G ratios can give similar results depending on the choice, in the latter method, of the boundary conditions used for integration. However, the method based on the determination of peak heights avoids the arbitrary assignment of integral boundary conditions while additionally generating a data set that shows statistically smaller standard deviations than the commonly used integration method.

Key words: Raman Spectroscopy, Analytic Regions, Diamond-like Carbon, D Peak, G Peak, Peak Position, Deposition Time

Introduction

Although more commonly used for qualitative rather than quantitative determinations, Raman spectroscopy is a useful and non-destructive technique for the structural characterization of diamond-like carbon (DLC) films [1 – 11]. The DLC Raman lines normally have wavelengths from 1320 to 1386 cm^{-1} for the D peak (due to disorder) and from 1550 to 1580 cm^{-1} for the G peak (due to sp^2 sites) [5].

DLC contains both sp^2- and sp^3-hybridized carbon atoms, however DLC films formed with a higher sp^3 content have more diamond-like characteristics. Even though Raman spectroscopy is not a quantitative technique, numerous researchers take the ratios of the integrated intensities of the D and G peaks (I_D/I_G) to represent the sp^3/sp^2 ratio trends. As the fitting parameters in Raman spectrometry are not standardized, different conclusions have been drawn regarding the relationship between the sp^3/sp^2 ratio and the integral intensity ratio I_D/I_G. For example, some researchers have reached the opposite conclusion for amorphous carbon (or diamond-like) films analyzed by the Gaussian fitting method of Raman spectra [8]. Parallel problems also may exist in other spectroscopic techniques, *e. g.* XPS [9, 11] and NMR [12]. These contradictions highlight the problem of defining the I_D/I_G ratio.

In this study, DLC/Ti/Al_2O_3 films were prepared by magnetron sputtering using different deposition times. To find reasonable explanations to address contradictions, the integral intensity ratio I_D/I_G derived by the fitting method of separate Gaussian curves was carefully examined under different boundary conditions of the analytic regions. We also propose a new method to analyze Raman spectra based on the peak height ratio H_D/H_G, which does not use the height ratios from the two peak curve fitting, but depends on the distance from the peak to the baseline. For comparative purposes we have applied different analytical methods to our data to enable us to show how the deposition time affects the DLC's properties.

Experimental Section

Diamond-like carbon film preparation

The DLC/Ti/Al_2O_3 films were prepared using a magnetron sputtering method. In brief, the sputtering targets (Ti or graphite) were 5 cm in diameter, and the target-to-substrate distance was 5 cm. The Ti film was first deposited on the alumina substrate, and then the diamond-like carbon was deposited on the Ti/Al_2O_3 film. To sputter the Ti film, the deposition chamber was evacuated to 3×10^{-5} Torr. The Ti and graphite targets were pre-sputtered for approximately 3 and 5 min, respectively, before deposition, to remove any surface impurities that may have been present. A Ti film was first deposited on the A_2O_3 substrate with the sputtering power set at 50 W for a duration of 5 min with an Ar pressure of 5×10^{-3} Torr. Before sputtering the diamond-like carbon film, we reduced the chamber's pressure again to remove impurities. The system power was 80 W, the bias voltage was set at -80 V, and the Ar pressure during deposition was 5×10^{-3} Torr. The diamond-like carbon film was deposited on the Ti film by a magnetron rf sputtering device using a graphite disk target from 2 to 12 h. Raman spectra, representative of various sputtering durations, derived using an Ulvac, Labram HR spectrophotometer with a 532 nm laser source, were recorded over the range from 500 to 2500 cm^{-1}.

Two Gaussian curves fitting method

The Raman spectra of DLC formed with different deposition times are shown in Fig. 1. As the Raman peaks were reasonably well defined after 2 h sputtering time, we chose this as our minimum time for DLC formation. Additional measurements were made on materials formed in up to 12 h. The two Gaussian curves were fitted using commercially available software (OriginLab® corporation) to identify peak positions and intensities. For the analysis, different Raman spectral regions, as defined in Table 1, between 500 and 2500 cm^{-1} were fitted with separate Gaussian curves. Fig. 2 shows the fitting of both the D and G peak positions to the individual curves at analytic region A. Peak integral areas, derived from the fitted curves, were then used to calculate the integral intensity ratio I_D/I_G.

Table 1. A series of analytic regions defined and designated A to I.

Designated symbol	Analytic regions in Raman spectra (cm^{-1})
A	500 ~ 2500
B	600 ~ 2400
C	700 ~ 2300
D	800 ~ 2200
E	800 ~ 2100
F	800 ~ 2000
G	800 ~ 1900
H	900 ~ 2000
I	900 ~ 1900

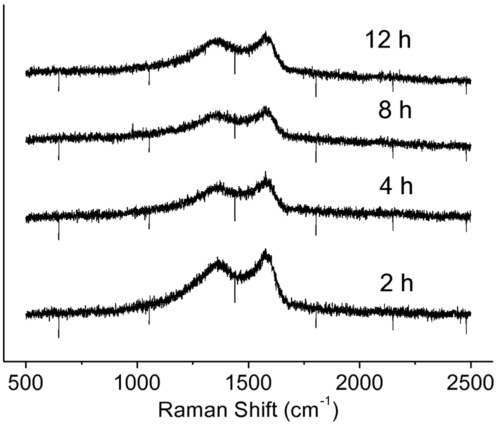

Fig. 1. Change in Raman spectra of DLC films after different sputtering deposition times.

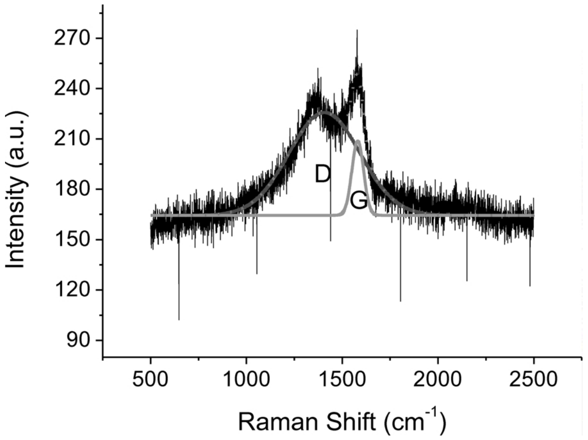

Fig. 2. Gaussian curve fitting to the D and G peak positions. Shown is the Raman spectrum analytic region, designated as A in Table 1 (500 ~ 2500 cm^{-1}).

Results and Discussion

Effect of the analytic regions on D and G peaks in the Raman spectra

The effect of the analytic region on the D and G peaks in the Raman spectra after various sputtering times of DLC films was studied as shown in Fig. 3. Fig. 3a shows that the D peaks can change depending upon how the boundary conditions of the analytic regions are defined. For the DLC films prepared by 2 h sputtering time, the position of the D peak shifts from 1390 to 1374 cm^{-1} when the boundary conditions of

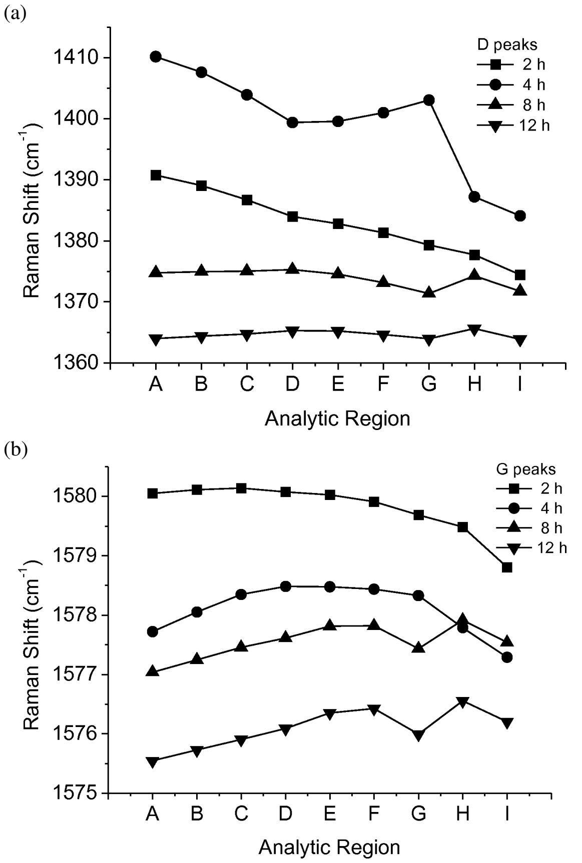

Fig. 3. The correlation between Raman shift and analytic region at different sputtering times of DLC films: (a) D, (b) G peaks.

the analytic regions are set from A (500 ~ 2500 cm^{-1}) to I (900 ~ 1900 cm^{-1}). A similar phenomenon occurs in the material made with 4 h sputtering time. Little obvious change is seen in the Raman shift profiles of the films after 4 h sputtering. Although the effect of the analytic regions on the position of the G peaks for individual samples can be neglected as shown in Fig. 3b, the divergence of trends that show how the sputtering time affects the G peaks positions was observed between analytic region G and H.

Effect of the analytic regions on I_D/I_G ratios in the Raman spectra

The variation of I_D/I_G ratios of DLC films with the sputtering deposition time used for the preparation of DLC films and with the analytic regions is shown in Fig. 4. The profiles of the two fitted Gaussian curves, and with them the I_D/I_G ratios, change in response to changes in the boundaries of the chosen analytic regions. This is shown clearly in Fig. 4 where the application of two Gaussian curves to different analytic regions leads to area integral ratios varying from 3.35 (analytical region I, 900 ~ 1900 cm^{-1}) to 8.50 (analytical region A, 500 ~ 2500 cm^{-1}) for the material made with 4 h sputtering time. In addition, and perhaps more worrying from an analytical perspective, there is a clear divergence of trends seen for measurements made with initial conditions defined as analytical regions D to I (all set within 800 – 1900 cm^{-1}). This wide variation in I_D/I_G ratios means that the quality trend of diamond-like/graphitic carbon ratio is not easily predictable.

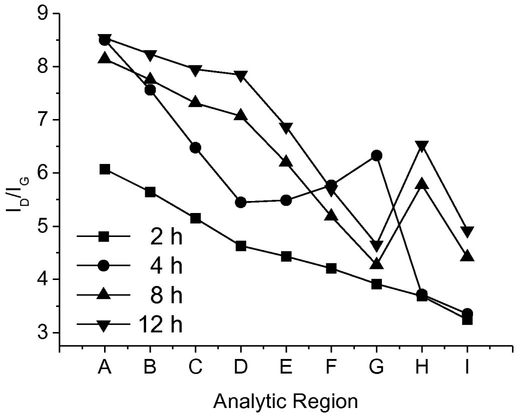

Fig. 4. I_D/I_G ratios of deposited films showing the critical effect exerted by altering the boundary conditions of the measurement system.

The peak height ratio H_D/H_G

Instead of using the two Gaussian curves fitting method to calculate the integral ratio I_D/I_G of the DLC films, an alternative approach based on the measurement of the peak height ratio H_D/H_G was compared in the following work. We applied a localized peak fitting method (OriginLab® corporation) to find both the heights and sites of the D and G peak positions as shown in Fig. 5. From the height differences of the peaks we calculated the peak height ratio H_D/H_G. When comparing these two methods, it is apparent that there is just one H_D/H_G ratio trend that depends on the distance from the peak to the full range baseline in this study, whereas we can have a multitude of different I_D/I_G ratio profiles for the same initial data set depending on how we define our boundary conditions for peak integration.

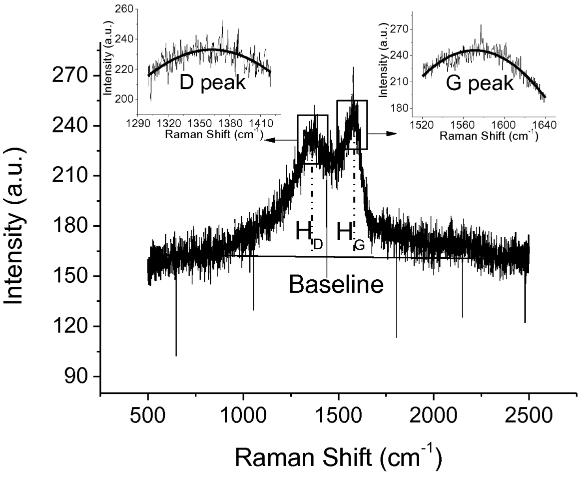

Fig. 5. General profile of the Raman spectra (taken after 4 h sputtering time) showing peak height measurements H_D and H_G together with the use of the peak location to fit the D and G peaks.

Comparison of data trends derived from peak height ratios and integrated areas

A comparison of the trends, with respect to time, shown by figures plotted as (i) peak height ratios (Fig. 6a), or (ii) as area ratios (Figs. 6b and 6c), shows that in all cases the ratio tends to slowly increase with sputtering time. For measurements based on peak heights there can only be one trend with respect to time in this study. However, in the case of measurements based on area integration (Figs. 6b and 6c) an unlimited number of boundary conditions for the integration can be defined. As the quality trend is often a determinant of the sputtering time allowed for film deposition, we have the quality trends into two groups based on the initial conditions set for integration (Figs. 6b and 6c). It is noteworthy that for the analytic regions set in Fig. 6b the quality trend continuously moves in the direction of an increase in the I_D/I_G ratio. However, with the boundary conditions used for the trend analyses shown in Fig. 6c, between 4 and 8 h the same quality trend ratio appears to decrease.

Conclusions

DLC/Ti/Al_2O_3 films were prepared by magnetron sputtering with deposition times ranging from 2 to 12 h. We found that the Raman I_D/I_G ratios changed significantly depending on the analytic region chosen for integration. The analysis of the peak height data

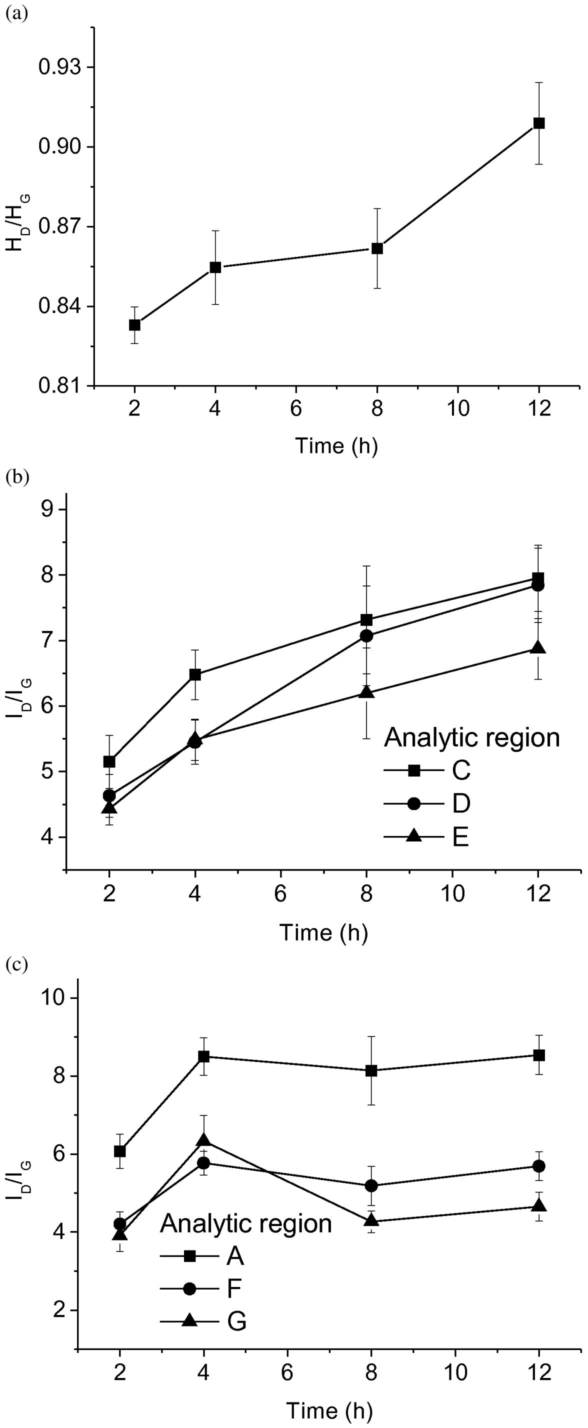

Fig. 6. Use of peak height ratios to show the quality trend of DLC films with respect to sputtering time ($n = 4$) (a), use of Gaussian integrals with varying initial boundary conditions to show the quality trend with respect to sputtering time ($n = 4$) (b, c).

shows that the overall ratio trend is similar to that observed using the method based on the Gaussian integration of the two separate peaks; however, due to the relative ease of baseline fitting the standard deviation of each measured data point was much reduced. The data interpretation method based on peak height measurement is potentially useful as another reference to determine the quality of DLC films. According to our study, it would be prudent for researchers to check their boundary conditions to determine how, if at all, they are affecting the interpretation of their data. If their data interpretations are dependent on extracting information from curves that are only partially separated, it may be an advantage to consider an interpretation based on peak heights as a potential alternative reference for quality or trend assignments.

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