Comparative Analysis of Trends Resulting from the Use of a Multi-Gaussian Curve Fitting Method Applied to the Visible Raman Spectra of Sputtered Amorphous Carbon

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This paper discusses the application of a direct integral area method and a multi-Gaussian curve fitting method to the interpretation of visible Raman spectra. A data analysis study was performed on three amorphous carbon films prepared by magnetron sputtering. Application of XPS, AES and the direct integration of the areas under the curves generated by visible Raman spectra, gave results that represented the diamond-like qualities of three amorphous carbon films in a similar manner, but the representation of data-trends using the multi-Gaussian curve fitting method was irregular. More specifically, we discovered that both the number of Gaussian curves applied, and the analytic regions chosen for analyzing the spectra affected the interpretation of the data obtained; our results indicate that the multi-Gaussian curve fitting method may give rise to inconsistent results when applied to the analysis of the visible Raman spectra of diamond-like (amorphous) carbon films.


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Keywords: the multi-Gaussian curve fitting method, visible Raman spectra, amorphous carbon, analytic region, I_D/I_G ratio

1. Introduction

The multi-Gaussian curve fitting method is used by many researchers to elucidate the data trends derived from the Raman spectra of diamond-like (amorphous) carbon films. The ratio of sp³% to sp²% can affect the physical properties of diamond-like (amorphous) carbon films. The multi-Gaussian curve fitting method is generally used to analyze the spectra of diamond-like carbon (DLC) generated by such methods as: near-edge X-ray absorption fine structure (NEXAFS),¹ infrared (IR) absorption,²,³ X-ray photoelectron spectroscopy (XPS),⁴,⁶ and visible Raman spectroscopy.⁴,⁶⁻¹⁷ Visible Raman spectroscopy is applied to the structural characterization of DLC films as a speedy and less destructive technique. A two-Gaussian curve fitting method³,⁴,⁶⁻¹² is usually applied to the visible Raman spectra of these films, to define the D (disordered) and G (graphite) peaks, located at approximately 1350 cm⁻¹ and 1580 cm⁻¹ respectively.⁴³ Some researchers also use three¹³⁻¹⁶ or more Gaussian curves,¹⁷ to fit the visible Raman spectra of DLC and obtain the I_D/I_G ratios. However, some contradictory conclusions have been drawn for amorphous carbon (or diamond-like) films analyzed by applying multi-Gaussian curve fitting methods to Raman spectra.⁵

It is known that determinations of DLC sp³/sp² ratios by XPS using different Gaussian curves, derived from a multi-Gaussian curve fitting method, can result in the generation of different trends in the diamond to graphite ratios;⁴ similar problems occur when the data is derived from visible Raman spectra. In our previous research, we found inconsistent trends for different regions when analyzed using a two-Gaussian curve fitting method.⁷ Therefore, analytic methods, especially multi-Gaussian curve fitting methods, which have been widely used by numerous researchers, should be critically evaluated.

In this study, three amorphous carbon (a-C) films were prepared by magnetron sputtering²⁷,⁹,¹⁰,¹⁶⁻¹⁸ and the visible Raman spectra of each film was measured three times (n = 3), under constant conditions. This study used XPS and Auger electron spectroscopy¹⁸⁻²⁰ (AES) to confirm the qualities of the three films. These Raman spectra were then analyzed by creating nine analytic regions that were defined by their boundary conditions and separated by the wave-number 1450 cm⁻¹ into D and G partitions. This allowed the data to be analyzed directly by area integration (generating nine A_D/A_G ratios); alternatively, the data was analyzed by using a multi-Gaussian curve fitting method that applies two, three or four Gaussian curves. We believe that this paper contains the first direct comparison of results derived from the multi-Gaussian curve fitting and direct integral area methods.

2. Experimental Section

This study used commercial alumina (thicknesses 1 mm) as a substrate. Amorphous carbon/Al_2O_3, amorphous carbon/Au/Al_2O_3, and amorphous carbon/Pt/Al_2O_3 films were produced with high purity Ar gas and a pure C target (SDIC 99.99%), using a previously published radio frequency magnetron sputtering method.⁷ This study was undertaken with a reduced chamber’s pressure, i.e. lower than 4 × 10⁻³ Pa to remove residual gas. The sputtering conditions used to make the amorphous carbon films and the thicknesses of the three samples are given in Table 1.

Measurements of the thin films’ thicknesses in this study was determined by cross-sectional high Resolution Field-Emission Scanning Electron Microscopy [(SEM), JEOL JSM-6700], while the roughness was measured by Atomic force microscopy (DI MIMAFM-2). XPS (PHI 5000 VersaProbe) used Al k-alpha radiation and the fitting of the
C 1s spectra used three peaks (each being a mixture of a Gaussian and a Lorentzian). AES (JEOL, JAMP-9500F) was undertaken using 10 kV to accelerate the electron beam. The visible Raman spectra were obtained by scanning from 500 to 2500 cm\(^{-1}\) using an Ulvac, Labram HR spectrophotometer with a 50 mW laser source (\(\lambda = 532\) nm, spot size 1 mm). The spectra were recorded three times (\(n = 3\), without changing the focus) at similar positions on the surfaces of the three amorphous carbon films. The visible Raman spectra were analyzed with reference to nine regions as defined in Table 2.

### 3. Results and Discussion

After sputtering, three dark-brown uniform amorphous carbon films (each 2 \(\mu m\) thick) were obtained. The roughnesses of samples I, II, and III, were 0.13 \(\mu m\), 0.12 \(\mu m\), and 0.13 \(\mu m\) respectively. Visible Raman spectra, XPS, and AES, representative of each of these three samples, are shown in Fig. 1. The data analysis methods used were in accordance with previously published protocols, the \(\text{sp}^3/\text{sp}^2\) ratios determined from the XPS results were 12.5\% (sample I), 17.2\% (sample II), and 14.4\% (sample III), while the AES results demonstrated differences in the \(D\) values, of the films, as being less than 5\%. Figure 2 shows the respective \(A_D/A_G\) ratios for the visible Raman spectra of the three samples, after applying, either: two, three or four Gaussian curves to the data, within the defined analytic regions. For each sample, all the ratios in the analytic regions changed; they were additionally changed by the number of peaks used to generate the curves. Inspection of the derived data showed that most of the \(I_D/I_G\) ratios were greater than the \(A_D/A_G\) ratios (bottom data set of data points in each of Figs. 2(a)–(c) in the same analytic regions. The absolute values were not meaningful because the real regions of the \(D\) and \(G\) peaks were not clear. However, the pattern and uniformity of the \(A_D/A_G\) ratios of the nine regions (designated A to I in Table 2), which all included the \(D\) and \(G\) peaks, also demonstrated that the quality of the three samples was similar. The data obtained from the multi-Gaussian curve fitting method, shows the \(I_D/I_G\) ratios to be disorderly.

Using a two-Gaussian curve fitting method, the \(I_D/I_G\) ratios in sample II were apparently lower than the results for

### Table 1 Experimental conditions applied for sputtering and the resultant thicknesses of the three samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Film</th>
<th>Power (P/W)</th>
<th>Pressure (P/Pa)</th>
<th>Time (t/min)</th>
<th>Thickness (L/(\mu m))</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>a-C/Al(_2)O(_3)</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>—</td>
</tr>
<tr>
<td>II</td>
<td>a-C/Au/Al(_2)O(_3)</td>
<td>50</td>
<td>4.7</td>
<td>5</td>
<td>1.3</td>
</tr>
<tr>
<td>III</td>
<td>a-C/Pt/Al(_2)O(_3)</td>
<td>50</td>
<td>4.7</td>
<td>5</td>
<td>1.0</td>
</tr>
</tbody>
</table>

### Table 2 A series of analytic regions defined and designated A to I.

<table>
<thead>
<tr>
<th>Designated symbol</th>
<th>Analytic regions in Visible Raman spectra (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>500–2500</td>
</tr>
<tr>
<td>B</td>
<td>600–2400</td>
</tr>
<tr>
<td>C</td>
<td>700–2300</td>
</tr>
<tr>
<td>D</td>
<td>800–2200</td>
</tr>
<tr>
<td>E</td>
<td>800–2100</td>
</tr>
<tr>
<td>F</td>
<td>800–2000</td>
</tr>
<tr>
<td>G</td>
<td>800–1900</td>
</tr>
<tr>
<td>H</td>
<td>900–2000</td>
</tr>
<tr>
<td>I</td>
<td>900–1900</td>
</tr>
</tbody>
</table>

Fig. 1 The spectra of samples I, II, and III: (a) visible Raman, (b) XPS, and (c) AES.
sputtered amorphous carbon films can cause the results to show unexpected trends. The search for the optimum conditions (analytical method) with which to analyze Raman spectra may not yet have been discovered because the resolution of spectral irregularities remains problematic.

In order to avoid the wrong determinations and conclusions being made, we suggest that scholars also use XPS or other spectral techniques, for $sp^3/sp^2$ trend analysis, when working with diamond-like (amorphous) carbon films.

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REFERENCES