RAMAN AND PEELS STUDIES OF MAGNETRON SPUTTERED a-C

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Amorphous carbon coatings (a-C, a-C:H) of less than 100 nm thick were deposited on KBr pellets and silicon wafer substrate via magnetron sputtering of graphite target in argon, argon/hydrogen and argon/nitrogen atmosphere. Parallel electron energy loss spectroscopy (PEELS) analysis was used to quantify the sp² / sp³ bonding in carbon films. Stand-alone films of amorphous carbon were produced by sputtering onto compressed KBr pellets and then floating off in distilled water for PEELS study. Raman spectroscopy was used to measure the peak intensity ratio of D-band to that of the G-band (I_D/I_G). It shows that higher sp³ fraction often associates with lower Raman peak ratio I_D/I_G. At the same time, G-band peak position P_g decreases while sp³ fraction increases.

1. Introduction

Raman spectroscopy, electron energy loss spectroscopy and nano indentation are some most commonly used techniques in characterizing of thin solid films of diamond, amorphous diamond-like carbon (DLC) or amorphous carbon. In Raman spectra, amorphous DLC films are characteristic of a broad single peak centered around 1530 cm⁻¹ (G-band) with a “shoulder” at around 1350 cm⁻¹ (D-band). The “shoulder” is the signature of the DLC film (otherwise a sharp peak at around 1580 cm⁻¹ would be that for a highly oriented pyrolytic graphite). The peak intensity ratio and peak position have been commonly used in the characterization of diamond-like carbon or amorphous carbon films[1, 2, 3]. The peak position and the intensity vary from film to film. This variation comes from the structural change or disturbance of otherwise full three-fold coordination of carbon network (sp²) as four-fold coordinated structures (sp³) are introduced through vapor deposition. Electron energy loss spectroscopy (EELS) analysis can distinguish atomic elements and differentiate between graphite, amorphous carbon, diamond and the variety of diamond-like carbon materials and enables quantification of the sp² and sp³ bonding in carbon films [4, 5, 6]. The aim of this paper is to clarify for DLC or amorphous films the relationship between the Raman peak intensity ratio (I_D/I_G) and four-fold coordination fraction (sp³) through EELS studies.

2. Experimental Procedure

There are a number of techniques to deposit amorphous carbon coatings[7]. In this study, the unbalanced magnetron sputtering [8, 9] was used to deposit a-C coatings on silicon wafer and KBr pellets with varying bias and target power. The background pressure in the sputtering chamber was pumped below 5×10⁻² Torr before the sputtering gases were introduced. The substrates were placed in a rotary sample holder facing the rectangular (330 x 133 mm) graphite target (99.9% purity) situated 85 mm above the sample. A standard radio frequency (13.56 MHz) bias power was applied to the substrate. Raman
spectra were obtained with a Raman imaging microscope (Rennishaw Model 127) using a He-Ne laser beam of 632.8 nm as the excitation source.

The samples for PEELS (Parallel Electron Energy Loss Spectrum) were examined in a Philips EM430 electron microscope fitted with a Gatan 666 PEELS Spectrometer operating at 200 keV. The PEELS analysis [10, 11] was performed in two stages, first, the low-loss or plasmon region at 0-50 eV of the energy loss spectrum and then the core loss region at 200-300 eV where the carbon K-edge (281 eV) is located. For the core region, with a focal length of 640 mm, the diffraction mode was used in analyzing the carbon K-edge to determine the sp² fraction. First, glassy carbon K-edge was collected and assumed to be 100% graphitic (sp²=1), then these spectra were analyzed to determine the number of counts in the 1s-π* pre-edge feature. The number of counts in the 1s-π* feature (I_{g*}) were then normalized for the calibration sample using the integral counts under the 1s-σ* peak (I_{d}(dE)). For samples of unknown sp² fraction, the sp² fraction (f) was calculated from the experimentally measured I_{u*} and I_{u}(dE) (where the subscript u stands for the sample of the unknown sp² fraction) through the following relation [12]:

\[ f = \frac{I_{u*}}{I_{g*}} \times \frac{I_{g}(dE)}{I_{u}(dE)} \]  

(2)

Assuming that the amorphous carbon or the DLC film consists only of sp² and sp³ components, then the fraction of sp³ is

\[ sp^3 \text{ fraction} = 1 - f \]  

(3)

3. Results and Discussions

3.1. Ratio of I_d/I_g and Peak Position as Revealed by Raman Spectroscopy

The Raman spectrum can be deconvoluted into two Gaussian peaks (bands) plus a linear background. Schwet et al. has pointed out that carbon films prepared by magnetron sputtering show two additional Raman features at 1180 and 1490 cm⁻¹ in addition to the G and D peaks. However, this paper will concentrate on the G and D peaks because they are the most prominent and less prone to measurement errors. The peak at around 1350 cm⁻¹ is the D-band and the other at around 1530 cm⁻¹ the G-band. The ratio of the peak intensity of D-band over that of the G-band, or I_d/I_g has usually the same trend as the ratio of the area under the D-peak over that under the G-peak. Both of the ratios provide a signature of the atomic bonding structure of the DLC coating. Therefore, in later discussions, we will use only the I_d/I_g ratio.

We plotted the peak intensity ratio (I_d/I_g) and the G-band peak positions (cm⁻¹) for coatings obtained under different deposition conditions in Figure 1.
It can be seen from the plot that initially when the G-band peak position shifts down, the peak intensity ratio also shifts to lower values with increasing sputtering target power density. However, with further increase in power density, both $I_d/I_g$ and G-band peak position increase, indicating more graphitic structure ($sp^2$). This trend was observed also in thick (2–3 µm) titanium-doped hydrogenated carbon (Ti-C:H) sputter-deposited films on WC/Co and high speed steel tool materials (unpublished work). It was confirmed by direct PEELS measurement as discussed in the next section.

3.2. Ratio of $sp^3/sp^2$ as revealed by PEELS

The PEELS core loss profile was used to determine the $sp^2$ fraction (eq (2)) and $sp^3$ (eq(3)). The $sp^3$ values thus determined were plotted as a function of deposition power density in Figure 1, except in a reverse manner: the band intensity ratio $I_d/I_g$ decreases with power density and then increases. Decreasing $I_d/I_g$ indicates a reduction in the total number and/or size of graphitic micro domains, and therefore an increase in the number of four-fold coordinated carbon atoms ($sp^3/sp^2$), as demonstrated by Lee and coworkers [13], Marchon and coworkers [14] and Ager III [15] in hydrogenated amorphous carbon films with increasing hydrogen content. The influence of the target power density is believed to come from the increased degree of ionization and temperature as target power density is increased. However, a high temperature [16] or a high ion energy [17] would promote deposition of higher $sp^2$ than $sp^3$ coordination. This is also demonstrated in Figure 2: while increasing deposition power density increases $sp^3$ formation, when power density becomes excessive, the $sp^3$ formation starts to decrease.
Experiments were also conducted at different bias to assess the effect of bias on sp³ formation. Figure 3 is the resulting plot. A few observations are important: first, the sp³ fraction increases with bias power until around -150 V followed by a decrease at extreme bias power. The effect of bias in this case is similar to that of the target power density, since a high bias power induces a high temperature that in turn hinders the formation of sp³ coordination.

![Graph](image)

**Figure 2.** PEELS sp³ fraction as a function of effective target power density at constant rate of hydrogen flow and substrate bias power.

Also note that in Figure 2 the samples are hydrogenated while in Figure 3 the samples are non-hydrogenated. The similar trends showing sp³ fraction variation with power density and bias power indicate that the effect of power density and bias power on the formation of sp³ or sp² sites are similar with or without hydrogen inclusion.

4. Conclusion

1. \( \text{I}_d/\text{I}_g \) decreased with target power density followed by an increase when power density was further increased. Similar trend was observed for G-band peak position shift with regard to power density variation.
2). Within the conditions examined in this study, qualitatively higher sp³ fraction tends to associate with lower Raman intensity ratio I₆/Iₑ. At the same time, the G-band peak position decreases while sp³ fraction increases.

3). Increase of deposition power density and substrate bias power both bring about increase in sp³ formation to a certain extent. The use of either too high a power density or bias power reduces the formation of sp³ bonded carbon. This is the case for both non-hydrogenated and hydrogenated a-C films studied in this work.

![Graph showing PEELS sp³ fraction as a function of substrate bias.](image)

**Figure 3.** PEELS sp³ fraction as a function of substrate bias for non-hydrogenated (a-C) amorphous carbon.

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References


