Multi-Peak Fitting Analysis of Visible Raman Spectra on DLC Coatings Deposited by Vacuum Arc

Ying REN¹,*, Hai-Kuo WANG¹ and Friederike DEUERLER²

¹Faculty of Material Science and Engineering, Henan University of Technology, 450000 Zhengzhou, China
²Faculty D-Department of Mechanical Engineering, University of Wuppertal, 42119 Wuppertal, Germany

*Corresponding author

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Abstract. The typical two-Gaussian fitting of Raman spectra is widely used in disordered and amorphous carbon. However, two-peak fitting method was not always suitable for all amorphous carbons, which made it important to choose appropriate fitting method for different carbon coatings. In this study the diamond-like carbon (DLC) coatings were deposited on steel (P2000) by a vacuum arc adjustable from anodic to cathodic operation mode. The $I_D/I_G$ ratios of DLC coatings were investigated by visible Raman spectroscopy with multi-peak fitting analysis. It is found that for Raman spectra of DLC coatings deposited by vacuum arc four-peak Gaussian fitting is the most suitable method which is conducive to revealing fine structure of DLC films. Furthermore, by comparing with two-peak and three-peak fitting methods, the four-peak fitting method have lower $I_D/I_G$ ratio. It is shown that the values of $I_{D1}/I_{G1}$ and $I_{(D1+D2)}/I_{(G1+G2)}$ of four-peak Gaussian function are consistent nearly.

Introduction

The Raman features resulting from the photophysical and mostly resonant scattering process in amorphous carbon materials. Diamond-like carbon (DLC), as one kind of amorphous carbon material, contains mainly sp³ and sp² both types of bonding.

Although the visible Raman spectra of DLC films mainly come from the ordering of the sp² boned carbon in the films and only indirect from the sp³ fraction in the films, it can be applied a restricted range of film properties to derive information about the sp³/sp² ratio[1]. By comparing with other analysis methods which can directly decide the sp³/sp² ratio, e.g. electron energy loss and NMR spectroscopy, G. Irmer and A. Dorner have also demonstrated the applicability of the Raman spectroscopy[2]. Raman peaks located at ~1350 cm⁻¹ and ~1580 cm⁻¹ are the well-known D and G bands, respectively. Usually the sp³/sp² ratio was considered to be inversely proportional to the intensity ratio of the D and G bands ($I_D/I_G$).

Raman spectrum fitting is used to get the intensity ratio of the D and G bands in the analyzed diamond-like carbon (DLC). As reference[3] shows, for the same carbon coatings, different Raman spectra can be obtained with different excitation wavelengths. This paper is referred to Raman data at 514 nm.

Usually there are two fits: a Lorentzian fit and a Gaussian fit. The simplest fit for Raman spectra of DLC: two Gaussians[4-6], two Lorentzians or a fit with a Breit-Wigner-Fano (BWF) line for the G peak and a Lorentzian for the D peak (BWF + Lorentzian fits)[7-11], in which two Gaussians fitting is widely used in Raman spectra as reference[12] shows. Most papers focus on the G and D peaks as two prominent features, neglecting other features that sometimes are present, such as those at 1100~1200 and 1400~1500 cm⁻¹. Therefore, in order to be fitted very well on a linear background, other peaks must be considered. For example, “T” peak at around 1060 cm⁻¹ is due to CC sp³ bonding and appears only for UV excitation[7-8,13-14], which can’t be observed in visible excitation. However, a simple two symmetric-line fit for different kinds of carbon films is not always suitable.
in visible Raman spectra. In addition, because the D band and the G band often overlap to some extent, in these cases multiple peaks have to be fitted by a peak deconvolution algorithm.

In the year 2009, F.C. Tai used three-peak fitting of visible Raman spectra of as-deposited hydrogenated diamond-like carbon (DLCH) film under Gaussian function for D1 (~1450 cm⁻¹), D2 (~1280 cm⁻¹) and G peaks or D, G1 (~1530 cm⁻¹) and G2 (~1600 cm⁻¹) peaks [15], and found that the \( \frac{I_D}{I_G} \) ratio was inconsistent. In one doctoral thesis, A.L. Shen discussed the visible Raman spectra of amorphous carbon by using two-Gaussian, three-Gaussian, two-Lorentzian and three-Lorentzian fitting. More three-peak fitting can be seen from references [16-20] with full Gaussian function, in which the peak position consisted of two peaks (D2, D1) for D peaks and two peaks (G1, G2) for G peaks, ~1180 cm⁻¹ (nanocrystalline diamond), ~1350 cm⁻¹ (microcrystalline or nanocrystalline graphite), ~1490 cm⁻¹ (disordered graphite) and ~1580 cm⁻¹ (ordered graphite), respectively. However, according to the Raman curve fitting made by Nakao [19] and F.C. Tai et al. [15], several assumptions have been made on the multi-peak intensity calculations: D=D1+D2, G=G1+G2, D2<D1 and G2<G1. So it is very important to choose appropriate numbers and positions of peak before fitting the Raman spectrum. Because of the different values, for example the peak position, the ratio of \( \frac{I_D}{I_G} \) and so on, can be obtained using different numbers and positions of peak, which will reflect the characterization of coatings’ structure.

**Materials and Methods**

In this paper, the DLC coatings were deposited on steel (P2000) by a vacuum arc adjustable from anodic to cathodic operation mode, with an anode-cathode diameter ratio of \( d_a/d_c = 1/1 \) at a DC bias of ~250 V to ~1000 V and the corresponding schematic diagram of deposition system was shown in the reference [21]. Ti as interface layer was prepared on P2000 before DLC coatings for improving the adhesion between the substrate and DLC coatings like the previous works [1, 21]. About the details of deposition processing and parameters were shown in the reference [1]. A micro-Raman system of HORIBA Jobin Yvon with the visible excitation of the 514.5 nm Ar⁺ laser line was used.

Raman spectra were fitted by Gaussian curves using two general peaks (D peak and G peak), three peaks (D2, D1 and G peaks) and four peaks (D2, D1, G2 and G1 peaks). For D1, D2 and G three-peak model, the peak positions are ~1100 cm⁻¹, ~1350 cm⁻¹ and ~1580 cm⁻¹, respectively. A linear background was subtracted before fitting the spectra. A four-peak fitting of the Raman spectrum has two peaks for D peaks: D2 (~1100 cm⁻¹), D1 (~1350 cm⁻¹) and two peaks for G peaks: G2 (~1400 cm⁻¹), G1 (~1580 cm⁻¹).

\( \frac{I_D}{I_G} \) is the ratio of peak heights. Usually the intensities of D and G peaks refer to the intensities of these two peaks: “~1350 cm⁻¹” and “~1580 cm⁻¹”, which mean, the ratio of \( I_D/I_G \) stands for \( \frac{I_D}{I_G} \). So there will be two different \( \frac{I_D}{I_G} \) values needed to be discussed. For three-peak fitting, there are \( I_{D1}/I_G \), \( I_{D1+D2}/I_G \) and \( I_{D1}/I_G \). The values of \( I_D/I_G \) and \( I_{D1+D2}/I_G \) are considered in four-peak fitting.

**Results and Discussion**

![Figure 1. Raman spectra fitted with two-Gaussian of DLC synthesized at a DC bias of –250 V to –1000V.](image)
Figure 1-3 shows that the Raman spectra of DLC coatings deposited at –250 V, –500 V, –750 V and –1000 V were fitted with two-Gaussian, three-Gaussian and four-Gaussian, respectively. Most coatings deposited by arc showed weak peaks at ~1100 cm\(^{-1}\) in visible Raman spectra. The red line represents the fitted curve.

Figure 1 shows that Raman spectra were fitted by Gaussian curves using two general peaks (D peak and G peak). It was found that there was no match at the lower frequency (<1200 cm\(^{-1}\)) with original Raman spectrum when fitting spectrum with two Gaussian functions. The fitted curves (red lines in Figure 1) were a little bit higher than the measured data at the highest peak, because a weak peak at ~1400 cm\(^{-1}\) appeared between D peak (1350 cm\(^{-1}\)) and G peak (1570 cm\(^{-1}\)). When D peak and G peak were matched well, the fitted curves about 1400 cm\(^{-1}\) were lower than the original curve. So two-Gaussian fitting was not suitable to characterize the structure of our samples.

Figure 2. Raman spectra fitted with three-Gaussian of DLC synthesized at a DC bias of –250 V to –1000 V.

Figure 2 shows that Raman spectra were fitted by Gaussian curves using three peaks (D2, D1 and G peaks). For D2, D1 and G three-peak model, the peak positions are ~1100, ~1350 and ~1580 cm\(^{-1}\), respectively.

To use three-peak fitting was much better than two-peak fitting as shown in Figure 2, but a weak peak at ~1400 cm\(^{-1}\) was not fitted well if using only three peaks, especially the Raman spectra at a bias of –250 V and –1000 V. However, when four-peak fitting was used to deconvolute the Raman spectra (see Figure 3), it was found that the measured data were fitted very well compared with using two-Gaussian (Figure 1) and three-Gaussian (Figure 2).

Figure 3. Raman spectra fitted with four-Gaussian of DLC synthesized at a DC bias of –250 V to –1000 V.

Hence, for the visible Raman spectrum fitting of DLC coating prepared with vacuum arc, the best method was to choose four peaks, D2 (~1100 cm\(^{-1}\)) and D1 (~1350 cm\(^{-1}\)), as well as G2 (~1400 cm\(^{-1}\)) and G1 (~1580 cm\(^{-1}\)). As known, DLC coating as amorphous carbon existed the defects and disorder, as well as pairs of C sp\(^2\) atoms which resulted in the presence of D1 (~1350 cm\(^{-1}\)) and G1 (~1580 cm\(^{-1}\)) or the well-known D band and G band, respectively. D2 peak (~1100 cm\(^{-1}\)) arose from the origin of peak in nanocrystalline diamond which have been proved by Ferrari and Robertson\(^{[22]}\)
Meanwhile, DLC contains mainly sp³ and sp² both types of bonding with sp²-bonded graphite-like clusters embedded in an amorphous sp³-bonded carbon matrix. Therefore, here the presence of G2 (~1400 cm⁻¹) was thought to result from disordered graphite.

However, with different fittings of Raman spectra, different values of D, G position, as well as the \( I_D/I_G \) ratio can be obtained as shown in Figure 4.

![Figure 4. \( I_D/I_G \) ratio of DLC synthesized at a DC bias of −250 V to −1000 V under different fitting function.](image)

Figure 4 shows the corresponding value of \( I_D/I_G \) at the two-peak fitting, three-peak fitting and four-peak fitting, respectively. It was shown that the \( I_D/I_G \) ratio of all fitting function for Raman spectra had the same tendency to change with the biases. According to Raman spectra fittings, the most widely used two-Gaussian function was absolutely not suitable to the Raman spectra on DLC films deposited by vacuum arc adjustable from anodic to cathodic operation mode, so the intensity ratio of D and G peak was not exact and will not be discussed here.

However, by comparing with the ratio of \( I_D/I_G \) of two-peak fitting function, the three-peak Gaussian function had higher \( I_D/I_G \) ratio and the four-peak Gaussian function exhibited lower one, no matter what kind of D and G peak were used in calculation of \( I_D/I_G \). In three-peak fitting function, it was obviously observed the \( I_{D1+D2}/I_G \) value was higher than the ratio of \( I_{D1}/I_G \) due to D2 peak. For four-peak Gaussian function, values of \( I_{D1}/I_{G1} \) and \( I_{D1+D2}/I_{G1+G2} \) were nearly the same. Therefore, the \( I_D/I_G \) ratio in the visible Raman spectra of DLC coating can be calculated directly by \( I_{D1}/I_{G1} \) instead of \( I_{D1+D2}/I_{G1+G2} \).

Conclusions

Raman spectra using four peaks can be fitted very well to analyze DLC films deposited on P2000 steel substrates by vacuum arc adjustable from anodic to cathodic operation mode, instead of the typical two-Gaussian fitting. By comparing with multi-peak Gaussian function, three-peak Gaussian function had the largest \( I_D/I_G \) ratio and four-peak fitting had a smaller \( I_D/I_G \) ratio. In addition, the intensity ratio of D and G bands obtained was almost not affected by the calculation formula. The results of \( I_{D1}/I_{G1} \) and \( I_{D1+D2}/I_{G1+G2} \) of four-peak Gaussian function were consistent nearly. This will be very important for the choice of fitting function for Raman spectra of DLC coatings deposited by vacuum arc.

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