

# Diagnostic Technique for Diamond Thin Film Quality Using Infrared Transmission Spectroscopy

Zhang Binglin H. M. Phillips

(Henan Fundamental and Applied Science Research Institute and Physics Department,  
Zhengzhou University, Zhengzhou 450052)

**Abstract** A diagnostic technique utilizing infrared transmission spectroscopy for calculating the ratio of  $SP^2/SP^3$  bonds in diamond thin films is presented. This method allows a quantitative assessment of the quality of films, even when analysis of Raman spectra would give ambiguous results because of sensitivity limitations. Sample calculations comparing two diamond films and amorphous carbon are presented.

**Key words** thin films, optical properties.

Diamond thin films have attracted considerable interest in the last few years because of their excellent properties, such as hardness, chemical inertness, optical transparency, and thermal conductivity. In particular, numerous applications within the microelectronics industry are now feasible due to the success of several different chemical vapor deposition (CVD) methods in depositing polycrystalline diamond films. Development of these applications for these films, though, will require accurate and reliable diagnostic techniques. In some cases, adequate methods already exist. The surface morphology of diamond thin films can be characterized by scanning electron microscopy (SEM) and scanning tunneling microscopy (STM). The face orientation of the polycrystalline films can be diagnosed by X-ray diffraction measurements. One key diagnostic, however, remains problematic, namely the quantitative analysis of diamond film quality.

While the microstructure of diamond films is predominantly a  $SP^3$  bond structure, diamond thin films deposited by CVD also contain some  $SP^2$  structure. This graphitic and/or amorphous  $SP^2$  structure has a detrimental effect on the quality of the diamond films, especially for electronic device applications. Measurement of the ratio of  $SP^2/SP^3$ , then, is essential for evaluating diamond films.

Raman spectroscopy is the most frequently used tool in characterizing diamond film quality. Raman spectra of diamond films have been measured by many authors<sup>[1-6]</sup>. A single peak in Raman spectra is observed at  $1332\text{ cm}^{-1}$  for diamond and at  $1581\text{ cm}^{-1}$  for crystalline graphite. In glassy carbon and pyrolytic graphite, which consists mainly of the  $SP^2$  struc-

ture, two broad bands are observed at  $1360$  and  $1590\text{ cm}^{-1}$ . Accurate determination of the relative contribution of these peaks to the observed Raman signal, however, is difficult. Even if the relative contributions were precisely determined, the respective scattering efficiencies of the various peaks is not well known, making quantitative assessment of the  $SP^2/SP^3$  ratio complex. In addition, even if the broad bands cannot be observed in a Raman spectrum because of sensitivity limitation, the  $SP^2$  structure could still be present. Another factor complicating the determination of the ratio of  $SP^2/SP^3$  is resonance effects in Raman scattering. Excitation in the infrared range is known to be highly sensitive to scattering from  $SP^2$  carbon bonds, whereas ultraviolet excitation enhances the  $1332\text{ cm}^{-1}$  signal from crystalline diamond. A different ratio of  $SP^2/SP^3$  bonds in a diamond thin film, therefore, can be obtained from the same sample by using different laser wavelengths. Raman spectroscopy is thus less than ideal for quantitative analysis for diamond thin film quality.

In this work, the ratio of  $SP^2/SP^3$  bonds in a diamond thin film is calculated using the infrared transmission spectrum. The initial step is the calculation of the real and imaginary parts of the complex refractive index from the infrared transmission spectrum of the diamond film according to Manifacier's method<sup>[7]</sup>. The concentration of  $SP^2$  bonds and the ratio of  $SP^2/SP^3$  is then calculated using the sum rule.

In order to appraise the diagnostic method presented here, the transmission spectrum of two free-standing diamond films were measured using an infrared Fourier transform spectrophotometer. The transmission versus wavenumber is plotted in Fig. 1. The Raman spectrum for the respective sample is shown as an insert in the graph. The diamond films were deposited by microwave CVD with hydrogen etching. SEM, X-ray diffraction and Raman spectroscopy confirmed the diamond character of the films. A sharp peak at  $1332\text{ cm}^{-1}$  in the Raman spectra was observed. The broad band from  $SP^2$  bonds was greatly reduced in comparison with the  $1332\text{ cm}^{-1}$  peak for the samples. More details of the experimental techniques used have been published elsewhere<sup>[8]</sup>.

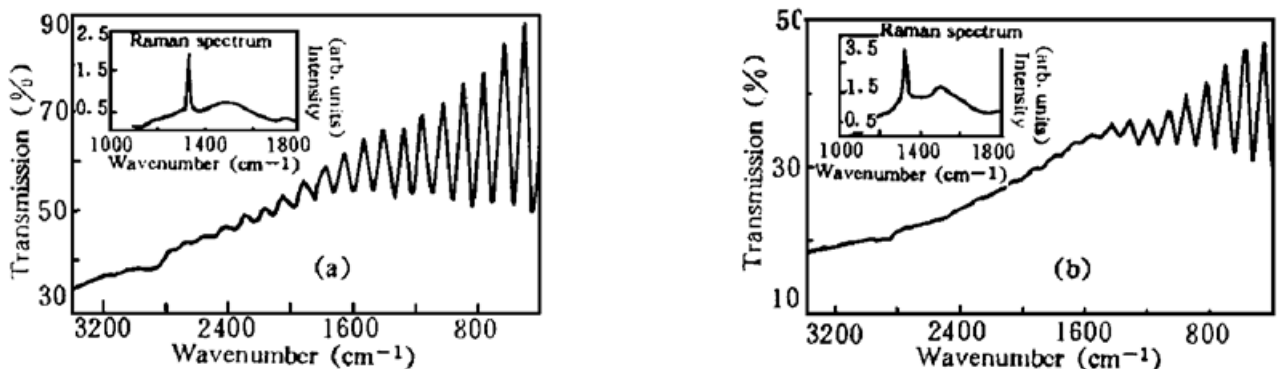


Fig. 1 Infrared transmission spectra for (a) Sample # 1 and (b) Sample # 2, which were used for the calculations given in this paper. The insert in each graph shows the Raman spectrum for the respective sample

Analysis of the samples begins with the calculation of the complex index of refraction  $\eta$  and the complex dielectric function  $\epsilon$  which are given by

$$\begin{aligned}\eta &= n + ik \\ \epsilon &= \epsilon_1 + i\epsilon_2\end{aligned}\quad (1)$$

where the indices  $n$  and  $k$ , and the dielectric constants  $\epsilon_1$  and  $\epsilon_2$  are real. The index of refraction and the dielectric constant are related by

$$\begin{aligned} \epsilon_1 &= n^2 - k^2 \\ \epsilon_2 &= 2nk \end{aligned} \tag{2}$$

From Manifacier's method<sup>[7]</sup>, an expression for  $n$  is obtained:

$$n = [N + (N^2 - n_0^2 n_1^2)^{1/2}]^{1/2} \tag{3}$$

where

$$N = \frac{(n_0)^2 + (n_1)^2}{2} + 2n_0 n_1 \left[ \frac{T_{\max} - T_{\min}}{T_{\max} T_{\min}} \right]$$

The imaginary part of the refractive index  $k$  is expressed as

$$\exp\left(\frac{4\pi kt}{\lambda}\right) = \frac{C_1 \left(1 - \frac{T_{\max}}{T_{\min}}\right)^{1/2}}{C_2 \left(1 + \frac{T_{\max}}{T_{\min}}\right)^{1/2}} \tag{4}$$

where  $C_1 = (n + n_0)(n_1 + n)$ ,  $C_2 = (n - n_0)(n_1 - n)$  with  $n_0$  and  $n_1$  being the refractive indexes of the transparent media in front and behind the diamond film, respectively.  $T_{\min}$  and  $T_{\max}$  are continuous functions of photon energy and are the respective envelopes of the maxima and minima in the transmission spectrum illustrated in Fig. 1. The spectra presented in this paper were taken with free standing films, so  $n_0 = n_1 = 1$ . Equation (3) shows that  $n$  is explicitly determined from  $T_{\max}$ ,  $T_{\min}$ ,  $n_0$  and  $n_1$  at the same photon energy. The calculated results for  $n$  and  $k$  in the photon energy range from 0.065 to 0.4 eV are shown in Fig. 2 and indicate that

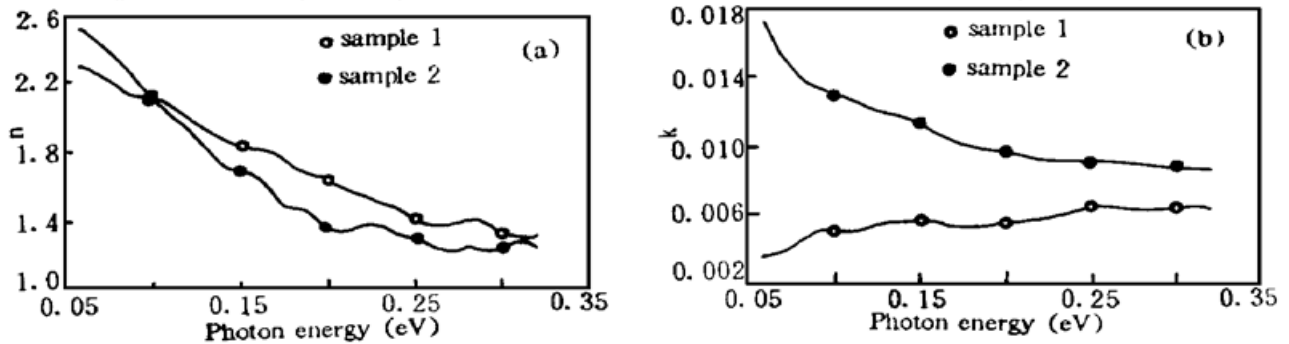


Fig. 2 Calculated results for (a)  $n$  and (b)  $k$  as a function of photon energy for the samples shown in Fig. 1

the diamond films under investigation are weakly absorbing in the infrared region. It can also be seen that the optical constants  $n$  and  $k$ , and especially  $n$ , underwent rapid oscillations in this photon energy range because of inhomogeneities of the films. Inhomogeneity, often due to variations in packing density, is at the root of many anomalies in optical properties<sup>[9]</sup>. The dielectric constant  $\epsilon_2$  can be calculated from Eq. 2 and is shown in Fig. 3.

According to the band structure of graphite, absorption with photon energies below 0.15 eV may be due to the intra-band transitions. An absorption maximum occurs at a photon energy of 0.05 eV due to the passage through the plasma frequency<sup>[10]</sup>. The value of  $k$  and  $\epsilon_2$  for Sample # 2 increased between photon energies of 0.15 eV and

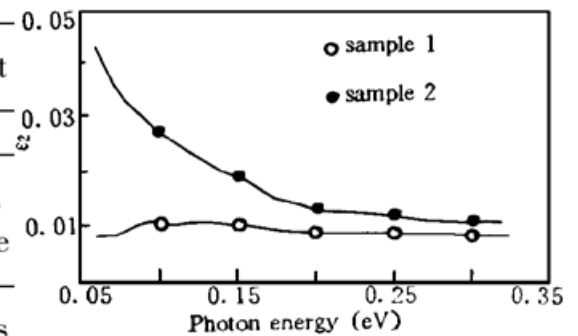


Fig. 3 Calculated results for  $\epsilon_2$  as a function of photon energy for the samples shown in Fig. 1

0.05 eV, as can be seen in Fig. 2 and Fig. 3, respectively. The observed behavior of the Raman spectrum for Sample # 2, shown in Fig. 1(b), indicated that it likely contained more  $SP^2$  graphite phase than Sample # 1.

Once the dielectric function has been found, the sum rule is used to obtain  $n_{\text{eff}}$ , which is the effective number of electrons per atom contributing to the optical properties of the material in the photon energy range up to a specific frequency ( $\omega$ ) or energy ( $E_{\text{max}}$ ). The sum rule can be written as<sup>[11, 12]</sup>

$$\begin{aligned} n_{\text{eff}} &= \left( \frac{m}{2\pi^2 N_a e^2} \right) \int_0^{\omega_0} \omega \epsilon_2 d\omega \\ &= (7.66 \times 10^{-1} \frac{A}{\rho}) \int_0^{E_{\text{max}}} E \epsilon_2 dE \end{aligned} \quad (5)$$

where  $N_a$  is the atomic density,  $A$  is the atomic weight,  $\rho$  is the density of the solid in  $\text{kg}/\text{m}^3$ , and  $E$  is expressed in eV.

In the diamond structure, four  $SP^3$  hybrid orbitals form tetrahedral bonds. In the graphitic phase, hybridization of the four outer shell electronic wave functions gives three  $SP^2$  orbitals, with localized  $\sigma$  bonds, and one  $p_z$  orbital forming a  $\pi$  bond. From energy band calculations and detailed optical spectra, it is known that the  $\pi \rightarrow \pi^*$  transitions are exhausted at a photon energy of 9 eV. Since one electron per carbon atom is available for  $\pi$  bonding,  $n_{\text{eff}}$  for the graphitic phase increases with photon energy to a value of 1 at about 9 eV. For photon energies lower than 9 eV, the  $\pi \rightarrow \pi^*$  transition probability decreases with decreasing photon energy. It is therefore possible to determine  $C_{SP^2}$ , the concentration of  $SP^2$  carbon atoms by calculating the ratio of  $n_{\text{eff}}$  for diamond films to  $n_{\text{eff}}$  for graphite at the same photon energy of approximately 9 eV, i. e.,

$$C_{SP^2} = n_{\text{eff}}(\text{diamond})/n_{\text{eff}}(\text{graphite}) \quad (6)$$

In the very low energy region of less than 1 eV, both inter-band and intra-band transitions exist in graphite. According to the band structure of graphite, the Fermi level lies at the corners of the hexagonal Brillouin zone, in a region where there are four  $\pi$  bands with a separation of less than 1 eV. The inter-band transition between any two of these bands will give contribution in the infrared region, and intra-band transitions by free carriers also give contributions in the infrared region for graphite<sup>[10]</sup>. For the  $SP^2$  phase in amorphous carbon and diamond, however, the inter-band transitions give the main contributions in the same region. The intra-band transitions can be neglected because of the scarcity of free carriers in diamond and amorphous carbon. In the infrared region, therefore, Eq. 6 should be modified by a factor of  $\chi$ , i. e.,

$$C_{SP^2} = n_{\text{eff}}(\text{diamond})/[\chi n_{\text{eff}}(\text{graphite})] \quad (7)$$

The ratio of  $SP^2/SP^3$  is then given by

$$R = SP^2/SP^3 = C_{SP^2}/(1 - C_{SP^2}) \quad (8)$$

The effective number  $n_{\text{eff}}$  for the diamond films was calculated as a function of photon energy according to equation 5 and is shown in Fig. 4. For comparison, the effective number  $n_{\text{eff}}$  for graphite and amorphous carbon is also shown in Fig. 4. The calculations for graphite were performed with data taken from the work of Savvides<sup>[12]</sup>, and calculations for amorphous carbon were performed with data taken from the work of Knoll and Geiger<sup>[13]</sup>. To obtain  $R$ ,  $C_{SP^2}$  must be calculated for photon energies above 0.28 eV, because splitting of the  $\pi$  bands at a corner of the Brillouin zone has been set at  $2\Gamma_1 = 0.28$  eV<sup>[10]</sup>. For energies below this value, there will be some contribution from intra-band transitions which will skew the results.

The modification factor  $X$  can be determined by comparing the calculated result of  $C_{SP^2}$  with experimental results of  $C_{SP^2}$  for amorphous carbon films. For various experimental conditions, the value of  $C_{SP^2}$  for amorphous carbon films can vary from about 25% to over 50%<sup>[14, 15]</sup>. Knoll and Geiger estimated  $C_{SP^2}$  for their films which were used in this analysis to be around 50%<sup>[13]</sup>. Using this figure for  $C_{SP^2}$ , the factor  $X$  is equal to approximately 0.015. According to Eq. 7 and Eq. 8, the values of  $C_{SP^2}$  for sample # 1 and sample # 2 are 0.0063 and 0.011, respectively. The corresponding values for  $R$  are 0.00633 and 0.0111. By comparison, the calculated result of  $C_{SP^2}$  from the Raman spectra for sample # 1 and # 2 is 0.066 and 0.111, respectively, and the corresponding values for  $R$  are 0.071 and 0.125. The difference between the two calculated results is approximately one order of magnitude. Two reasons can be given to explain the discrepancy. Firstly, since the data for graphite were taken from a graph, there may be some error in the absolute values, especially at lower photon energies. The other reason is that the respective scattering efficiencies of the various peaks in the Raman spectra are not accurately known. It should be noted, however, that the ratio of  $C_{SP^2}$  for sample # 2 to  $C_{SP^2}$  for sample # 1 is almost identical for these two independent methods. This ratio using the Raman data is 1.68, while the ratio using the calculations presented here asymptotically approaches a value of approximately 1.65 for photon energies above 0.3 eV.

In conclusion, a means for calculating the concentration of  $SP^2$  bonds and the ratio of  $SP^2/SP^3$  bonds for diamond films has been presented. Even if the  $SP^2$  broad band is not seen in Raman spectra for diamond films,  $SP^2$  bonds are still present in the sample. The diagnostic technique outlined above provides a qualitative determination of the ratio of  $SP^2/SP^3$ , even in the case where such a calculation would be impossible with Raman spectroscopy.

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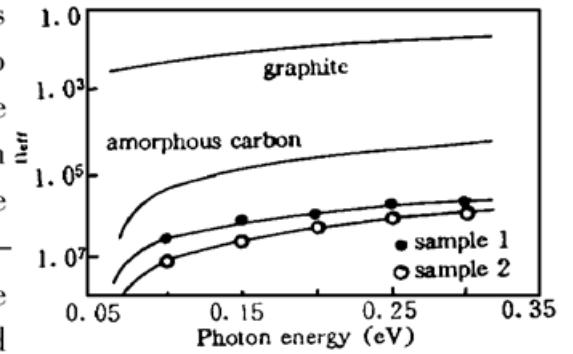


Fig. 4 Calculated results for  $n_{\text{eff}}$  as a function of photon energy for graphite, amorphous carbon and the samples shown in Fig. 1. Data for graphite was taken from Ref. 11 and data for amorphous carbon was taken from Ref. [13]

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## 金刚石薄膜质量的红外光谱判断技术

张兵临 H. M. Phillips

(郑州大学物理系及河南省基础及应用科学研究所, 郑州 450052)

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**摘 要** 给出了利用红外透射光谱计算金刚石薄膜中  $SP^2/SP^3$  键价比, 从而判断金刚石薄膜质量的判断技术。这种方法给出了薄膜质量的定量判断, 甚至当由于灵敏度限制拉曼光谱无法给出判断结果时这种方法仍可使用。文中给出了两个金刚石薄膜样品的计算结果并和非晶碳膜进行了比较。

**关键词** 薄膜, 光学特性。