physica status solidi b
www.pss-b.com
basic solid state physics

Calculation of optical constants from carbon nanotube transmission spectra

Á. Pekker[1], **F. Borondics**[1], **K. Kamarás**[1], **A. G. Rinzler**[2], and **D. B. Tanner**[2]

[1] Research Institute for Solid State Physics and Optics, Hungarian Academy of Sciences, P.O. Box 49, 1525 Budapest, Hungary
[2] Department of Physics, University of Florida, Gainesville, FL 32611, USA

Received 8 May 2006, revised 15 June 2006, accepted 1 August 2006
Published online 2 October 2006

PACS 78.67.Ch, 81.07.De

We want to clarify a few issues about using optical absorption spectra for characterizing carbon nanotubes. The common method of using optical density for nanotube counting is reasonable in the near-infrared and visible spectral region, but fails for the mid and far infrared, where metallic tubes can be unambigously detected. By performing Kramers–Kronig transformation on wide-range transmittance spectra of free-standing films, the far-infrared spectral region creates a unique possibility for estimating the amount of metallic tubes in different nanotube networks.

phys. stat. sol. (b) **243**, No. 13, 3485–3488 (2006) / **DOI** 10.1002/pssb.200669141

WILEY-VCH

Original Paper

phys. stat. sol. (b) **243**, No. 13, 3485–3488 (2006) / **DOI** 10.1002/pssb.200669141

Calculation of optical constants from carbon nanotube transmission spectra

Á. Pekker[*, 1], **F. Borondics**[1], **K. Kamarás**[1], **A. G. Rinzler**[2], and **D. B. Tanner**[2]

[1] Research Institute for Solid State Physics and Optics, Hungarian Academy of Sciences, P.O. Box 49, 1525 Budapest, Hungary
[2] Department of Physics, University of Florida, Gainesville, FL 32611, USA

Received 8 May 2006, revised 15 June 2006, accepted 1 August 2006
Published online 2 October 2006

PACS 78.67.Ch, 81.07.De

We want to clarify a few issues about using optical absorption spectra for characterizing carbon nanotubes. The common method of using optical density for nanotube counting is reasonable in the near-infrared and visible spectral region, but fails for the mid and far infrared, where metallic tubes can be unambigously detected. By performing Kramers–Kronig transformation on wide-range transmittance spectra of free-standing films, the far-infrared spectral region creates a unique possibility for estimating the amount of metallic tubes in different nanotube networks.

1 Introduction

The use of optical absorption is one of the most widespread methods of characterization of carbon nanotubes. In the first approximation, the characteristic near infrared – visible (NIR/VIS) peaks correspond to transitions between the Van Hove singularities in the one-dimensional density of states [1] and their position gives qualitative information about the chirality of tubes in a network. Individual semiconducting nanotubes can be identified by combination of absorption and fluorescence insuspensions [2, 3], but quantitative information on the composition of a given sample from spectroscopic results ("nanotube counting") is still an open question. For metallic tubes, information from Raman excitation profiles [4] or absorption at the first metallic interband transition around 2 eV [5] has been used. The selective decrease in absorption of these peaks proved the chirality-selective character of certain sidewall reactions [5]. However, this is not the only peak to indicate the presence of metallic tubes. The far-infrared absorption, characteristic of metallic nanotubes in pristine, non-doped samples [6, 7] also decreases significantly when adding covalent bonds to the sidewalls [8]. Quantification of these results is difficult, however, for several reasons: purity of the nanotube samples [9], determination of concentration and density [10], and, first and foremost, the mixed nature of all macroscopic nanotube networks.

In this paper, we address a fundamental issue regarding evaluation of wide-range nanotube spectra: the determination of optical constants from transmission. A carefully established procedure has been presented by Itkis et al. [9–11] to determine semiconducting tube concentration from optical density in dilute suspensions and thin films. We find that this method cannot be extended to metals, based on far-infrared transmission; instead, the application of the Kramers–Kronig transformation is unavoidable.

[*] Corresponding author: e-mail: pekkera@szfki.hu, Phone: +36 1 392 2222, Fax: +36 1 392 2219

2 Basic considerations

The basic equation for light transmitted through a sample at normal incidence is:

$$I_0 = I_R + I_A + I_T = RI_0 + I_A + (1-R)\,\mathrm{e}^{-\alpha d}\, I_0\,. \tag{1}$$

Using the approximation for a transparent sample ($R \cong 0$, $\alpha d \ll 1$), we obtain Beer's law, the well-known relation between extinction coefficient and transmittance:

$$D = -\log T = \varepsilon x d\,. \tag{2}$$

Here $T = I_T/I_0$ is the transmittance, ε the specific (molar) extinction coefficient, x the concentration (for mixtures) and d the thickness of the sample. $D = \varepsilon x d$ is called optical density. The optical density is proportional to the power absorption coefficient α only when reflection can be neglected and the sample is sufficiently transparent. Unfortunately, the nomenclature is being confused by the majority of today's spectrometer software, where the measured transmissionis automatically converted to optical density and called "absorbance". Nanotube networks always contain metallic tubes, and because of the free carriers, high reflection occurs in the far-infrared region, thus the approximation in Eq. (2) no longer holds. In this case, we have to use the Fresnel equations [12] connecting the complex index of refraction N and the transmission coefficient t:

$$t = \sqrt{T}\,\mathrm{e}^{i\Theta} = \frac{4N}{(N+1)^2\mathrm{e}^{-i\delta} - (N-1)^2\mathrm{e}^{i\delta}}\,, \qquad \delta = \frac{\omega N d}{c}\,, \tag{3}$$

where c is the velocity of light. The measured quantity is the transmittance T, whose square root is the amplitude of the transmission coefficient. The transmission coefficient is an analytical function whose phase and amplitude satisfy a dispersion relation. Therefore, the phase can be analytically calculated from the integral of the amplitude [13], similar to the Kramers–Kronig transformation of single-bounce reflectance:

$$\Theta(\omega) = -\frac{2\omega}{\pi}\int_0^\infty \frac{\ln\left(|t(s)|/|t(\omega)|\right)}{s^2-\omega^2}\,\mathrm{d}s + 2\pi\omega d\,. \tag{4}$$

To circumvent the problem of finite frequency range in a real measurement, standard extrapolations based on metallic or semiconducting dielectric function models are used at high and low frequencies. From T and θ, by numerically solving Eq. (3), the complex index of refraction N and all other optical quantities can be determined.

$$N = n + i\kappa, \qquad \rightarrow \qquad = \frac{2\omega\kappa}{c}, \qquad \varepsilon = N^2. \tag{5}$$

Microscopic theories yield the dielectric function ε, which is directly related to the band structure, whereas the index of refraction and the absorption coefficient are more often derived from measurements on bulk samples.

3 Evaluation of measured transmission spectra

Figure 1 shows the transmittance of a 150 nm thick (thickness measured by atomic force microscopy) self-supporting film [13, 14] and the optical functions derived thereof. The left panel illustrates that the bulk reflectance (that of a hypothetical semi-infinite, non-transparent sample with the same optical properties as the present film) is almost perfect in the low-frequency region, where it is caused by the free carriers of the metallic tubes. Above ~3000 cm^{-1}, the frequency dependence and relative intensities of

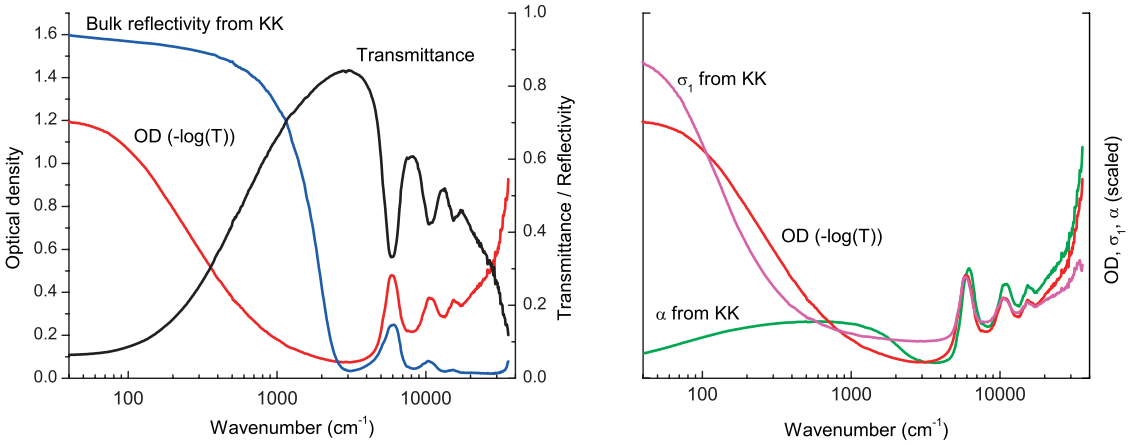

Fig. 1 Left panel: Wide-range transmission of a 150 nm thick nanotube network and the optical density and bulk reflectivity derived thereof (for details, see text). Right panel: Optical density, optical conductivity and power absorption coefficient. It is apparent that the three can be scaled together above 3000 cm^{-1}, but are substantially different below.

the optical density and both the power absorption coefficient α and the optical conductivity σ_1 can be linearly scaled. Although in principle only σ_1 can be compared to the results of microscopic calculations, it is apparent that the correction is negligible for films which are transparent in the whole spectral range.

Another important aspect is the applicability of Beer's law for concentration determination and purity evaluation. Itkis et al. [9] used the S_{22} peak for this purpose and they proved that Beer's law applies to this peak both in suspension [10] and transparent airbrushed films [11] provided it is evaluated properly. For metallic tubes, Strano [5] used the M_{11} transition, but quantitative evaluation is hindered in this case by the relatively low intensity of this peak and the strong $\pi \rightarrow \pi^*$ absorption baseline. Obviously, it would be easier to use the far-infrared absorption instead, but the validity of the approximation in Eq. (2) has to be tested first. Figure 2 shows the result of a simulation for films of different thickness. Using Eq. (3) with N resulting from the data of Fig. 1, we calculated the transmittance T of films with different thicknesses between 10 and 1000 nm, then converted these values to optical density $-\log T$. This step was followed by standard baseline correction, and the resulting optical density values are depicted as a function of thickness. Since we assume uniform thickness, variations in the concentration of nanotubes

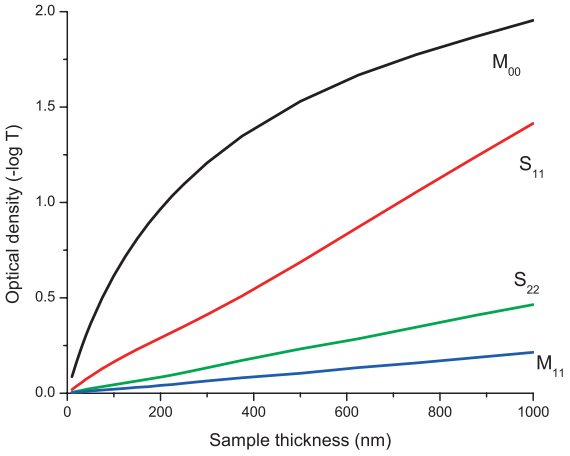

Fig. 2 Thickness dependence of optical density of the low-frequency M_{00}, the NIR S_{11} and the VIS S_{22} and M_{11} peaks calculated as described in the text.

(metallic or semiconducting) would have similar effect on the spectra. The data show that Beer's law is satisfied for all interband transitions in this thickness range, but fails already at relatively small film thickness (~100 nm) in the free-carrier regime. Therefore if the amount of semiconducting nanotubes changes, it can be safely estimated using the optical density of peaks S_{22} or S_{11}. The same procedure for metallic tubes is equally justified using peak M_{11}, but as the absorption coefficient is small, the results will be less precise. Using the free-carrier absorption for estimation of metallic nanotubes is more sensitive, however, the evaluation has to include a Kramers–Kronig transformation.

4 Conclusion

In conclusion, we demonstrated a method for the estimation of metallic nanotube concentration based on wide-range optical spectroscopy. The far-infrared part of the spectrum is a more sensitive indicator of metallic tubes than the M_{22} peak in the visible and does not require baseline correction. Since, however, optical density ($-\log T$) scales with optical conductivity only in the low-reflection regions, we have to invoke Kramers–Kronig analysis of carefully measured transmission data.

Acknowledgement Work in Hungary was supported by the Hungarian Scientific Research Fund OTKA under grant No. T 049338.

References

[1] H. Kataura, J. Kumazawa, Y. Maniwa, I. Umezu, S. Suzuki, Y. Ohtsuka, and Y. Achiba, Synth. Met. **103**, 2555 (1999).
[2] M. J. O'Connell, S. M. Bachilo, C. B. Huffmann, V. C. Moore, M. S. Strano, E. H. Haroz, K. L. Rialon, P. J. Boul, W. H. Noon, C. Kittrell, J. Ma, R. H. Hauge, R. B. Weissman, and R. E. Smalley, Science **297**, 593 (2002).
[3] S. M. Bachilo, M. S. Strano, C. Kittrell, R. H. Hauge, R. E. Smalley, and R. B. Weissman, Science **298**, 2361 (2002).
[4] M. S. Strano, J. Am. Chem. Soc. **125**, 16148 (2003).
[5] M. S. Strano, C. A. Dyke, M. L. Usrey, P. W. Barone, M. J. Allen, H. Shan, C. Kittrell, R. Hauge, J. M. Tour, and R. E. Smalley, Science **301**, 1519 (2003).
[6] M. E. Itkis, S. Niyogi, M. E. Meng, M. A. Hamon, H. Hu, and R. C. Haddon, Nano Lett. **2**, 155 (2002).
[7] F. Hennrich, R. Wellmann, S. Malik, S. Lebedkin, and M. Kappes, Phys. Chem. Chem. Phys. **5**, 178 (2003).
[8] K. Kamarás, M. E. Itkis, H. Hu, B. Zhao, and R. C. Haddon, Science **301**, 1501 (2003).
[9] M. E. Itkis, D. Perea, S. Niyogi, S. M. Rickard, M. A. Hamon, H. Hu, B. Zhao, and R. C. Haddon, Nano Lett. **3**, 309 (2003).
[10] B. Zhao, M. E. Itkis, S. Niyogi, H. Hu, J. Zhang, and R. C. Haddon, J. Phys. Chem. B **108**, 8136 (2004).
[11] E. Bekyarova, M. E. Itkis, N. Cabrera, B. Zhao, A. Yu, J. Gao, and R. C. Haddon, J. Am. Chem. Soc. **127**, 5990 (2005).
[12] M. Dressel and G. Grüner, Electrodynamics of Solids (Cambridge University Press, 2002).
[13] F. Borondics, K. Kamarás, M. Nikolou, D. B. Tanner, Z. H. Chen, and A. G. Rinzler, cond-mat/0512667.
[14] Z. Wu, Z. Chen, X. Du, J. Logan, J. Sippel, M. Nikolou, K. Kamarás, J. R. Reynolds, D. B. Tanner, A. F. Hebard, and A. G. Rinzler, Science **305**, 1273 (2004).

