Appl Phys A (2009) 97: 341–344
DOI 10.1007/s00339-009-5330-z

Applied Physics A
Materials Science & Processing

Determination of band gaps of self-assembled carbon nanotube films using Tauc/Davis–Mott model

**Xinming Li · Hongwei Zhu · Jinquan Wei ·
Kunlin Wang · Eryang Xu · Zhen Li · Dehai Wu**

Received: 12 February 2009 / Accepted: 1 July 2009 / Published online: 15 July 2009

Abstract The band gaps of self-assembled single-walled carbon nanotube (SWNT) films have been determined through curve fitting using the semi-empirical Tauc and Davis–Mott model, based on the measurement of optical absorption at the visible and near infrared range. This study provides a practicable option for the determination of band gaps for ultra-thin SWNT films or multi-walled carbon nanotube films whose vHs peaks cannot be well resolved in absorption spectra.

PACS 61.46.Fg · 78.67.Ch · 81.07.De · 42.70.Qs · 71.20.Tx

1 Introduction

The band gap is the most important parameter in the physics of semiconductors, especially for those widely used in optoelectronic applications. Single-walled carbon nanotubes (SWNTs) have been proved to be a promising material for short-wavelength photovoltaic devices [1, 2]. For individual nanotubes, theoretical calculations as well as experimental results have shown that the fundamental energy gap is zero in the metallic nanotubes and on the order of about 0.5 eV in semiconducting nanotubes [3]. The gap in the semiconducting nanotubes varies as a function of the tube's chirality. Scanning tunneling microscopy (STM) studies have revealed that well-spaced and symmetric structures, called van Hove singularities (vHs), appear in the local density of states of SWNTs due to their one-dimensional (1D) nature of the conduction electron states [4, 5]. All of the bands have a direct band gap, which allows electronic transitions between the valence and conduction band to proceed without the intervention of phonons. Thus, for a single nanotube, there are multiple bands that could participate in optoelectronic processes, spanning a wide range of energies. Hence, when forming in macroscopic structures, it should be possible to obtain a continuous response over a broad spectral range by combining multiple nanotubes of different bands gaps.

A bulk SWNT sample consists of a mixture of metallic and semiconducting nanotubes [6]. The band gaps of nanotube macrostructures differ from that of individual nanotubes. For example, a super-small energy gap of 1–3 meV has been identified in nanotube bundles in long SWNT strands [7]. As two-dimensional nanotube structures, initial advances [8–12] indicate that CNT films could emerge as new building blocks in macroscale transparent and flexible electronics [13]. For example, photovoltaic effects of bulk heterojunctions of nanotube films over silicon wafers have been reported [14–17], showing great potential for future high-efficiency and light-weight solar cells. Hence, the determination of band gaps for these nanotube structures is of utmost importance.

The band gap is usually deduced from the ultraviolet/visible/near infrared (UV/vis/NIR) absorption spectrum of the material at the absorption edge. For CNTs, it has been found that the optically excited states of SWNTs are excitonic in nature due to the many-body interactions in the excited-state properties of one-dimensional systems and the exciton binding energies represent a large fraction of the band gap [18]. The well-resolved optical absorption peaks can be associated with the vHs in the density of states for SWNTs if the energy of the incoming photon matched a

---

X. Li · H. Zhu (✉) · J. Wei · K. Wang · E. Xu · Z. Li · D. Wu
Key Laboratory for Advanced Manufacturing by Material Processing Technology and Department of Mechanical Engineering, Tsinghua University, Beijing 100084, P.R. China
e-mail: hongweizhu@tsinghua.edu.cn
Fax: +86-10-62770190

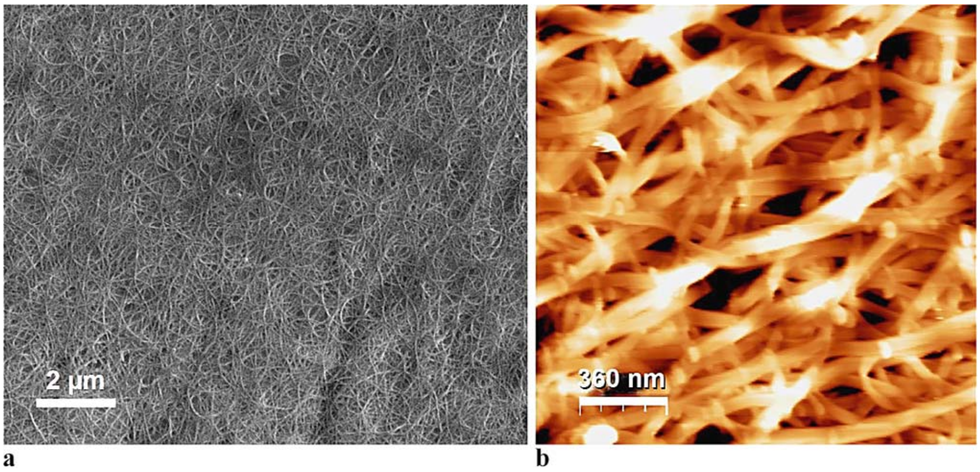

Fig. 1 (**a**) SEM and (**b**) AFM images of SWNT film 145 nm thick

vHs [19]. The band gaps E_S^{ii} (i^{th} vHs with $i = 1, 2, \ldots$) can also be estimated according to $E_S^{ii} = 2ia_{C-C}\gamma/d$ [20], where a_{C-C} is the carbon-carbon bond length, γ is the nearest neighbor Hamiltonian overlap integral, d is the diameter of nanotubes, which can be obtained from electron microscopy and Raman spectra analysis. In this work, optical absorption spectra of self-assembled SWNT films [12] were measured at visible and near infrared range (400–2500 nm). We treat SWNT films as amorphous semiconductors and re-evaluate the semi-empirical Tauc and Davis–Mott model, which could well interpret optical absorption data at the absorption edge for amorphous materials. The band gaps have been determined by comparing E_S^{11} with the values deduced from the model. This study provides a general approach to estimate the band gaps for thin films of CNTs and other nanomaterials.

2 Experimental

Self-assembled SWNT films were prepared directly using a floating chemical vapor deposition method [12]. Free standing transparent films were obtained by post treatment employing a combination of air oxidation and acid purification. The films have a continuous matrix and perfect uniformity (as shown in Fig. 1) thanks to the direct synthesis and deposition technique. The films with high surface area and electrical conductivity have been used as counter electrodes in dye-sensitized solar cells to improve the energy conversion efficiency [21]. Purified SWNT film was transferred to a highly polished quartz substrate to make a conformal and uniform coating. Optical absorption spectra of the films were taken by spectral transmittance measurements using a Perkin Elmer, precisely Lambda 950 UV/vis/NIR optical spectrometer. Film morphology and thickness were investigated by scanning electron microscopy (SEM, Hitachi S3600N) and atomic force microscopy (AFM, 5100 SPM, Agilent Technologies).

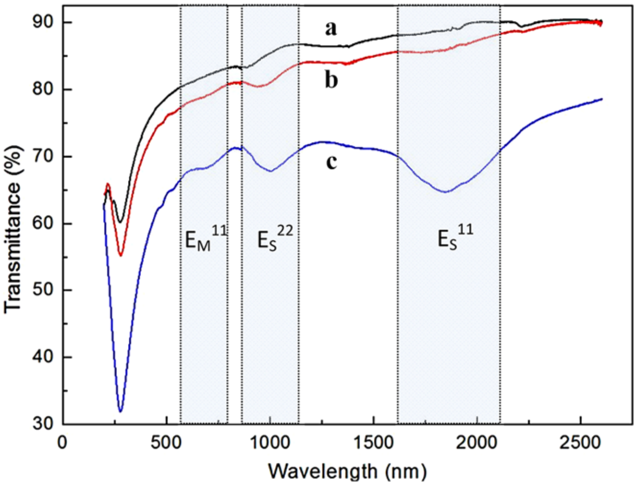

Fig. 2 Typical UV/vis/NIR transmission spectra of SWNT films, (**a**) $t = 35$ nm, (**b**) $t = 55$ nm, (**c**) $t = 145$ nm

3 Results and discussion

Figure 2 shows the optical transmittance curves as a function of wavelength for SWNT films of different thicknesses. The vHs associated optical absorption peaks could be detectable even if the film thickness is down to 35 nm. For a 145 nm thick film, it can be seen that the high transmission ($T > 65\%$) occurs in the wavelength range of 500–1500 nm. The strong UV absorption centered on ~280 nm is due to π-plasmon absorption. Three prominent peaks, at 1852 nm (0.67 eV), 1001 nm (1.24 eV) and 680 nm (1.82 eV), originate from the first (E_S^{11}) and second (E_S^{22}) vHs transitions of semiconducting SWNTs and the first vHs transitions of metallic SWNTs (E_M^{11}), respectively [3].

Here, E_S^{11} can be considered as the band gap (E_g) of the SWNT film, which is very crucial to the optoelectronic applications of SWNTs. Since SWNTs have direct transitions, we further apply two models for the determination of band gaps for crystalline or amorphous materials on the self-

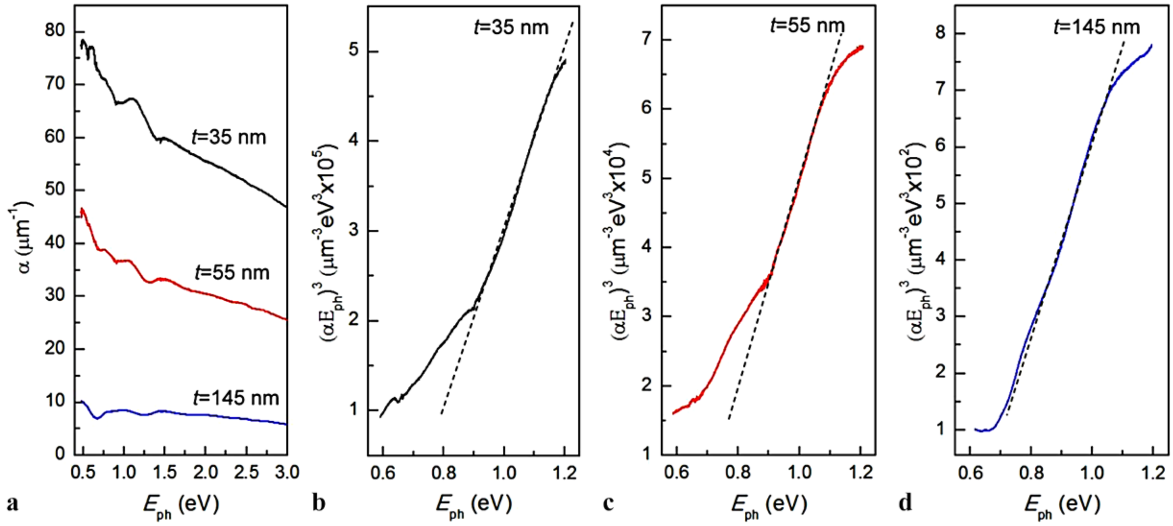

Fig. 3 (**a**) The absorption coefficient (α) as a function of photon energy (E_{ph}). (**b–d**) Tauc and Davis–Mott plots: $(\alpha E_{ph})^3$ as a function of E_{ph}

assembled SWNT films. The relation between the optical absorption and E_g for a direct transition can be expressed by (1) or (2).

For a crystalline material [22], we have

$$(\alpha)^n = A(E_{ph} - E_g) \tag{1}$$

For an amorphous material (Tauc and Davis–Mott model) [23–25],

$$(\alpha E_{ph})^n = B(E_{ph} - E_g) \tag{2}$$

where E_g is the optical band gap, A and B are two constants, E_{ph} is the photon energy ($E_{ph} = h\nu$) of the incident light. n is an index characterizing the type of optical transition. The absorption coefficient (α) is defined by the Lambert-Beer law and can be calculated from the optical transmittance.

$$\alpha = -\ln A/t \tag{3}$$

where A is the absorbance, $A = -\lg T$; T is the transmittance, t is the film thickness. The optical band gaps can be obtained from the extrapolation of the best linear parts of the curves at $\alpha = 0$ near the band edge region.

Starting from the transmittance of SWNT films (Fig. 2), the dependence of α on E_{ph} is drawn in Fig. 3(a). In the two models mentioned above, n is the most important parameter for the determination of E_g. For crystals, $n = 2$ for a direct allowed transition [22]. For amorphous materials, it has been suggested that $n = 2$ or $3/2$, depending on whether the direct transition is allowed or forbidden [25]. We first plot α^2 vs. E_{ph} based on (1) and find no obvious linear part near the absorption edge. All vHs peaks are intensified in the range of 0.4–2 eV and can be read unambiguously from the plot.

Table 1 E_S^{11} and E_g obtained from the vis/NIR spectra and the Tauc and Davis–Mott model

t (nm)	E_S^{11} (eV)	E_g (eV)		
		$n = 3/2$	$n = 2$	$n = 3$
35	0.73	0.38	0.56	0.70
55	0.71	0.35	0.54	0.68
145	0.67	0.34	0.51	0.65

We then plot $(\alpha E_{ph})^n$ vs. E_{ph} based on (2) with different index values: $n = 1/2, 3/2, 2$ and 3. $n = 1/2$ gives negative values of E_g, while $n = 3/2$ and 2 yield smaller E_g compared with E_S^{11}, indicating they are not suitable in the case of SWNT films. The presence of metallic tubes will modify the electronic states and optical transitions of the films and result in allowed transitions rather than forbidden transitions of sole semiconducting tubes. Hence, a larger index n (>2) is expected. The best fit was obtained for $n = 3$, as it gives the near-perfect linear curves for three samples in the band edge region (Fig. 3(b–d)) and an E_g comparable to E_S^{11} (Table 1). Equation (2) is a semi-empirical equation and has been applied to amorphous and polycrystalline semiconductors, e.g. diamond-like carbon films [26] and ZnO thin films [27]. It is not based on a firm theoretical model; E_g deduced here only provides a reference for the band gap of the SWNT film. The variations between E_g to E_S^{11} (~0.03 eV) suggest that the index n needs to be optimized further (even to a fractional value) and might be varied for nanotube films obtained by other methods. The likelihood of applying the Tauc and Davis–Mott model on SWNT films provides a practicable option for the determination of band gaps for ultra-thin SWNT films or MWNT films [14] whose vHs peaks cannot be well resolved in absorption spectra.

It is worth noting that the band gaps (both E_S^{11} and E_g) show a thickness dependence and increase inversely with film thickness (Table 1). In general, the thickness dependence of the band gap can be associated with two major factors: the density of dislocations (or disorder) and the change in barrier height [28]. In the present case, thinner films are likely to introduce some amount of disorder in the films due to the low tube coverage and subsequently enlarge the band gaps. On the other hand, the increasing band gap with decreasing film thickness is similar to its length dependence [29], indicating an increasing barrier height in thinner films. This dependence suggests that the band gaps of CNT films could be tailored to some extent by controlling their thicknesses.

4 Conclusion

In summary, the Tauc and Davis–Mott model has been applied to SWNT films to estimate their band gaps. An index $n = 3$ is obtained by comparing the optical gaps obtained from the vHs peaks with the band gaps deduced from the model. This method is only based on measurements of the vis/NIR absorption and provides an alternative approach to study the optical and electrical properties of the macrostructures of nanotubes and other nanomaterials.

Acknowledgements This work is sponsored by the Program for New Century Excellent Talents in University (NCET-08-0322) and the Scientific Research Foundation for the Returned Overseas Chinese Scholars (20091020304), State Education Ministry of China.

References

1. D.A. Stewart, F. Leonard, Nano Lett. **5**, 219 (2005)
2. P. Avouris, M. Freitag, V. Perebeinos, Nat. Photonics **2**, 341 (2008)
3. H. Kataura, Y. Kumazawa, Y. Maniwa, I. Umezu, S. Suzuki, Y. Ohtsuka, Y. Achiba, Synth. Met. **103**, 2555 (1999)
4. J.W. Wildoer, L.C. Venema, A.G. Rinzler, R.E. Smalley, C. Dekker, Nature **391**, 59 (1998)
5. T.W. Odom, J.L. Huang, P. Kim, C.M. Lieber, Nature **391**, 62 (1998)
6. M.S. Dresselhaus, G. Dresselhaus, P.C. Eklund, *Science of Fullerenes Carbon Nanotubes* (Academic Prees, San Diego, 1996)
7. H.W. Zhu, G.L. Zhao, C. Masarapu, D.P. Young, B.Q. Wei, Appl. Phys. Lett. **86**, 203107 (2005)
8. Z. Wu, Z. Chen, X. Du, J.M. Logan, J. Sippel, M. Nikolou, K. Kamaras, J.R. Reynolds, D.B. Tanner, A.F. Hebard, A.G. Rinzler, Science **305**, 1273 (2004)
9. M. Endo, H. Muramatsu, T. Hayashi, Y.A. Kim, M. Terrones, M.S. Dresselhaus, Nature **433**, 476 (2005)
10. R. Duggal, F. Hussain, M. Pasquali, Adv. Mater. **18**, 29 (2006)
11. W.J. Ma, L. Song, R. Yang, T.H. Zhang, Y.C. Zhao, L.F. Sun, Y. Ren, D.F. Liu, L.F. Liu, J. Shen, Z.X. Zhang, Y.J. Xiang, W.Y. Zhou, S.S. Xie, Nano Lett. **7**, 2307 (2007)
12. H.W. Zhu, B.Q. Wei, Chem. Commun. **29**, 3042 (2007)
13. G. Gruner, J. Mater. Chem. **16**, 3533 (2006)
14. M.B. Tzolov, T.F. Kuo, D.A. Straus, A.J. Yin, J. Xu, J. Phys. Chem. C **111**, 5800 (2007)
15. J.Q. Wei, Y. Jia, Q.K. Shu, Z.Y. Gu, K.L. Wang, D.M. Zhuang, G. Zhang, Z.C. Wang, J.B. Luo, A.Y. Cao, D.H. Wu, Nano Lett. **7**, 2317 (2007)
16. A. Behnam, J.L. Johnson, Y. Choi, M.G. Ertosun, A.K. Okyay, P. Kapur, K.C. Saraswat, A. Ural, Appl. Phys. Lett. **92**, 243116 (2008)
17. Y. Jia, J.Q. Wei, K.L. Wang, A.Y. Cao, Q.K. Shu, X.C. Gu, Y.Q. Zhu, D.M. Zhuang, G. Zhang, B.B. Ma, L.D. Wang, W.J. Liu, Z.C. Wang, J.B. Luo, D.H. Wu, Adv. Mater. **20**, 4594 (2008)
18. F. Wang, G. Dukovic, L.E. Brus, T.F. Heinz, Science **308**, 838 (2005)
19. I.W. Chiang, B.E. Brinson, R.E. Smalley, J.L. Margrave, R.H. Hauge, J. Phys. Chem. B **105**, 1157 (2001)
20. X. Liu, T. Pichler, M. Knupfer, M.S. Golden, J. Fink, H. Kataura, Y. Achiba, Phys. Rev. B **66**, 45411 (2002)
21. H.W. Zhu, H.F. Zeng, V. Subramanian, C. Masarapu, K.H. Hung, B.Q. Wei, Nanotechnology **19**, 465204 (2008)
22. P.S. Kireev, *Semiconductor Physics*, 2nd edn. (Mir, Moscow, 1978)
23. J. Tauc, *Optical Properties of Solids* (Plenum, New York, 1969)
24. E.A. Davis, N.F. Mott, Philos. Mag. **22**, 903 (1970)
25. N.F. Mott, E.A. Davis, *Electronic Processes in Noncrystalline Materials* (Clarendon, Oxford, 1979)
26. S. Adhikary, X.M. Tian, S. Adhikari, A.M.M. Omer, H. Uchida, M. Umeno, Diam. Relat. Mater. **14**, 1832 (2005)
27. S.T. Tan, B.J. Chen, X.W. Sun, W.J. Fan, H.S. Kwok, X.H. Zhang, S.J. Chua, J. Phys. Appl. **98**, 013505 (2005)
28. P. Tyagi, A.G. Vedeshwar, Bull. Mater. Sci. **24**, 297 (2001)
29. X. Sun, S. Zaric, D. Daranciang, K. Welsher, Y. Lu, X. Li, H. Dai, J. Am. Chem. Soc. **130**, 6551 (2008)