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DETERMINATION OF CHIRALITY (n,m) OF SINGLE-WALLED CARBON NANOTUBES FROM ABSORPTION SPECTRA

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ABSTRACT

Carbon nanotube sample-produced by alcoholic catalytic chemical vapor deposition (CVD) method on quartz substrate is analyzed using absorption spectroscopy. The sample on quartz substrate is in bundle state and the peak separation in the absorption spectrum is not much clear. However, the absorption spectrum of the sample is examined and a series of optical absorptions are identified. For this sample's spectrum, elemental Gaussian shape tends to dominate in the best curve fitting. On the basis of the electronic band theory, the spectral features are systematically assigned to the electronic transitions between pairs of van Hove singularities of semiconducting and/or metallic single wall nanotubes (SWNTs) and corresponding chiralities (n,m) and diameter distribution are determined.

Keywords: Single-walled Nanotubes (SWNTs), Alcohol Catalytic Chemical Vapor Deposition (ACCVD), Chirality (n,m).

1. INTRODUCTION

Carbon nanotube has become a promising material in various fields since its discovery due to its extraordinary electronic, mechanical, optical characteristics [1]. The most eye-catching features of these structures are their electronic, mechanical, thermal, optical and chemical characteristics, which has opened a way to future applications. For example, metallic nanotubes can carry an electrical current density of 4×10^9 A/cm^2 which is more than 1,000 times greater than metals such as copper [2]. In terms of mechanical properties, nanotubes are among the stiffest (Young's modulus) and strongest (yield strength) materials yet measured. Their Young's modulus is 0.64 TPa [3–5], roughly five times greater than steel, which matches theoretical predictions [6]. Specially, its tunability in the wide range from soft to hard, semiconducting to metallic attracts the scientist in various fields of applications. However, electro-optical or mechanical properties are interrelated. Nanotubes can be single walled or multi walled, isolated or bundled. The properties of nanotubes strongly depend on chirality (n,m). Fundamental and practical nanotube researches have shown possible applications in the fields of energy storage, molecular electronics, nanomechanic devices, and composite materials. But before any research in any field, it is necessary to determine the type of carbon nanotubes, i.e. chirality. Carbon nanotubes are determined by the resonant Raman spectroscopy (RRS), photoluminescence spectroscopy (Spectrofluorometry), etc. RRS can give reliable results [7], but high resolution of laser energy makes it difficult for use. And, photoluminescence can detect only semiconducting types and also cannot detect quenched, damaged or defective nanotubes. Absorption spectroscopy is a unique tool to characterize carbon nanotubes, to analyze its structure etc. Kataura et al. [8] first applied absorption spectroscopy to SWNTs and observed three absorption bands, originating from the overlapping van Hove transitions of varying size SWNTs. They also confirmed the inversely proportional relationship between the nanotube diameter and the energy of the absorption features, just as was predicted by theoretical calculation [9]. Here, we have determined the chirality (n,m) of carbon nanotubes in the sample produced by alcohol catalytic CVD method on quartz substrate using the optical absorption spectra of the sample. Estimated chirality of the nanotubes observed to be dependent on method of the synthesis and substrates. The investigation reveals interesting method of chirality estimation. Detailed analyses to obtain chirality of the nanotubes from absorption spectra will be reported in this paper.

2. EXPERIMENTAL DETAILS

This experimental section has been performed by the research group of Professor Shigeo Maruyama (Department of Mechanical Engineering, The University of Tokyo). A catalytic powder was prepared by impregnating iron acetate $(CH_3CO_2)_2Fe$ and cobalt acetate $(CH_3CO_2)_2Co$–$4H_2O$ on to USY-zeolite powder (HSZ-390HUA, over 99% SiO_2) [10-11]. The weight concentration of Fe and Co was chosen to be 2.5 wt% each over the catalytic powder. Molybdenum acetate and cobalt acetate were employed for the catalytic loading on to the quartz substrate using a dip-coat technique. The adoption of Mo instead of Fe in the case of quartz is based on knowledge obtained by preliminary experiments. The schematic of the CVD apparatus and the procedure of the CVD are reported in elsewhere [12].

In brief, the specimen was placed on a quartz boat and the boat was set in the centre of a quartz tube (internal diameter = 26 mm, length = 1 m). One end of the quartz tube was connected to a rotary pump by two different paths, a 25 mm and a 6 mm diameter tube, to select the pumping power. The central 30 cm of the quartz tube was surrounded with an electric furnace. As the furnace was heated up from room temperature, a flow of about 300 sccm of Ar/H_2 (3% H_2) was used, with only the smaller evacuation path open, to maintain the inside of the quartz tube at 300 ± 20 Torr. After the electric furnace reached the desired temperature, the Ar/H_2 flow was stopped and the larger evacuation path was opened to bring the inside of the quartz tube to vacuum. Subsequently, ethanol vapor was supplied from an ethanol reservoir at a constant pressure of 10 Torr into the quartz tube. After the CVD reaction, the electric furnace was turned off and brought back to room temperature with a 100 sccm flow of Ar/H_2.CVD temperatures of 800°C was employed for the quartz substrate because this is the optimum temperature when ethanol vapor pressure is 10 Torr [12-14].

The VIS–NIR absorption spectra were measured with a HITACHI U-4000. Fig. 1 shows the absorption spectra of the sample in the visible and near-infrared ranges.

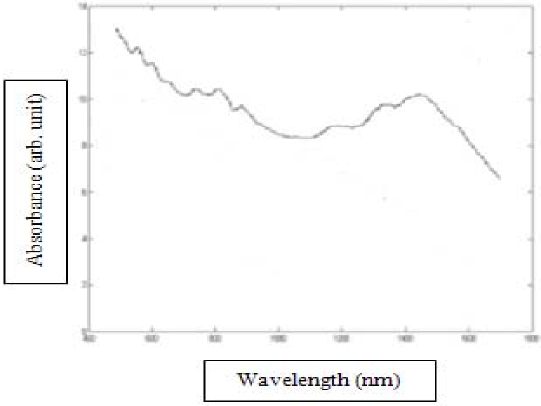

Fig 1. Optical absorption spectrum of alcohol catalytic chemical vapor deposition (ACCVD) single-walled nanotubes directly synthesized on a quartz substrate.

3. RESULTS AND DISCUSSIONS

In the optical spectra of SWNTs sample, three characteristic absorption bands are usually observed, superimposed on a broad background [15]. The first two bands are attributed to electronic transitions between the first and second pairs of VHSs in sem-SWNTs, and the last one to the first pair of singularity in *met*-SWNTs.

Demonstrated in Fig. 2 is the UV-VIS-NIR spectrum of ACCVD SWNTs directly synthesized on a quartz substrate in the range of 400-1700 nm after baseline correction. The base line corrected absorption spectra are fitted with elemental Gaussian and Lorentzian shapes using our own matlab program. Sub peaks or shoulders are resolved here and these features could be correlated with a series of distinct electronic transitions between the pairs of VHSs of sem- and met-SWNTs.

According to the electronic band theory [16], the vertical interband transition energy between the i^{th} pair of VHSs in both the valence and the conduction bands of a semiconducting (S) or metallic (M) nanotube (${}^{S,M}E_{ii}$) are correlated with the diameter of the SWNT (d_t) by

$$ {}^{S,M}E_{ii} = 2na_{C\text{-}C}\,\gamma_0/d_t \qquad (1) $$

Where $a_{C\text{-}C}$ is the nearest-neighbor carbon-carbon distance (~0.144 nm), γ_0 is the nearest-neighbor carbon-carbon interaction energy (~2.9 eV), and n is an integer. ${}^{S,M}E_{ii}$ corresponds to the first, second, third, fourth, and fifth interband transition of semiconducting SWNTs when $n = 1, 2, 4, 5$, and 7, and to the first and

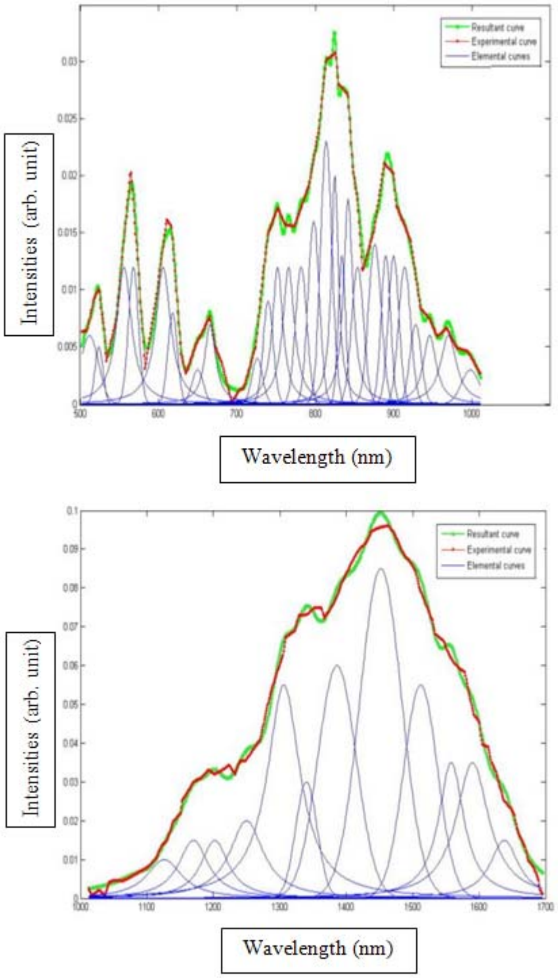

Fig 2. Optical absorption spectrum of alcohol catalytic chemical vapor deposition (ACCVD) single-walled nanotubes directly synthesized on a quartz substrate after background correction (the bold dot lines-experimental data) with Gauss-Lorentz fitting (the light solid and bold cross lines).Upper figure is for 500-1000nm and lower figure is for 1000-1700nm range.

second interband transition of metallic SWNTs when *n* = 3 and 6, respectively.

The diameter distribution and mean diameter can be obtained from the width and absorption maximum of this absorption band. After an energy calibration owing to Coulomb effects [17-18], mean diameter and diameter distributions are achieved (Table 1) for the SWNTs in the sample.

The sample grown on quartz substrate is in bundled state and the absorption peaks are not much clear. This has absorption peaks of slightly smaller energy. Observed in Fig 2 are fine structures, originating from the first inter band transitions of met-SWNTs and the first, second and third counterparts of sem-SWNTs. Analysis of them in details leads us to determine the diameter and chirality distributions and hence the chiral indices (*n*, *m*) of SWNTs presented in the sample and the results are tabulated in Table 1.

Table 1: Spectral Data and Assignment of the Inter band Transitions and Chiral Indices of ACCVD SWNTs (grown on quartz substrate)

Abs. Wavelength (nm)	Inter band Transitions	Calculated Diameter (nm)	(n,m)
524	M_{11}	1.057	(9,6)
556	M_{11}	1.122	(8,8)
568	M_{11}	1.146	(11,5)
604	M_{11}	1.218	(10,7)
650	M_{11}	1.311	(11,8)
724	S_{22}	0.973	(9,5)
738	S_{22}	0.99	(8,6)
774	S_{22}	1.041	(8,7)
812	S_{22}	1.092	(11,3)
892	S_{22}	1.199	(11,6)
1176	S_{11}	0.89	(7,6)
1216	S_{11}	0.92	(11,1), (9,4)
1264	S_{11}	0.956	(10,3), (8,6)
1310	S_{11}	0.991	(9,5), (11,3)
1350	S_{11}	1.021	(8,7), (12,1)
1398	S_{11}	1.057	(10,5),(12,2)
1456	S_{11}	1.102	(10,6),(13,2)
1508	S_{11}	1.141	(12,4)
1548	S_{11}	1.171	(13,3)
1580	S_{11}	1.195	(12,5)

The average diameter for the sample grown on quartz substrate is found to be around 1.1nm with diameter distribution from 0.85nm to 1.35nm. For this sample's spectrum, elemental Gaussian shape tends to dominate in the best fitting. The (n,m) assignment for both the sample have been calculated from the absorption spectra considering Coulomb effect for the first semi-conducting transition band (S_{11}).

The relative abundance of the nanotubes with respect to diameters is shown in Fig 3. We have utilized the elemental curve areas in Fig 2 to find the relative distribution in Fig 3. We have also found that, semiconducting nanotubes are produced in much proportion than metallic nanotubes for the sample.

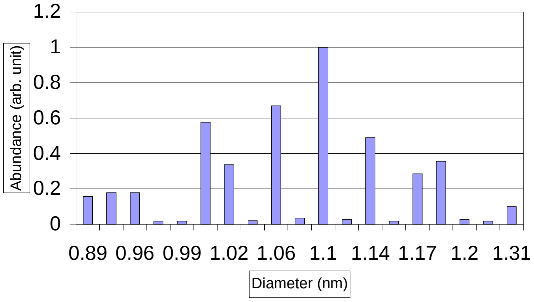

Fig 3. Abundance of nanotubes with respect to diameter in the sample grown on quartz substrate.

4. CONCLUSIONS

There are different direct methods for characterization such as scanning electron microscopy (SEM), transmission electron microscopy (TEM), transmission electron diffraction, scanning tunneling microscope (STM) which are very delicate and can be destructive. On the other hand, there are quick and non-destructive methods using the optical properties of carbon nanotubes such as resonant Raman spectroscopy (RRS), photoluminescence and absorption spectroscopy. Here, we have worked with absorption spectroscopy and a detailed analysis of the optical properties of SWNT's of the sample produced on quartz substrate was presented.

The absorption properties of SWNTs is measured by using a technique of synthesizing a SWNT directly on to the surface of quartz substrates , by which any effects of post-treatments are excluded. From the absorption peaks in the spectra, the electronic state of the produced SWNTs is characterized since each peak corresponds to a band gap of the obtained SWNTs. Since the SWNTs on quartz are in the bundled state and not sonicated or dispersed in liquid at all, the peak separation is ambiguous.

Further study can be made using roughly estimates of the mixture ratio between semiconducting and metallic tubes from the intensities of absorption peaks in different samples as well as using abundance of produced nanotubes in different samples by analyzing the area of the elemental curves in the fitted resultant curve and all this estimation can be useful to establish a production technique with preferred and pre-selected chirality distribution.

5. ACKNOWLEDGEMENT

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6. REFERENCES

1. Saito R, Dresselhaus G and Dresselhaus M S 1998 Physical Properties of Carbon Nanotubes (London: Imperial College Press).
2. Hong, Seunghun; Sung Myung (2007). "Nanotube Electronics: A flexible approach to mobility". Nature Nanotechnology 2: 207–208.
3. Treacy, M. M. J., Ebbesen, T. W., and Gibson, J. M.,

Exceptionally high Young's modulus observed for individual carbon nanotubes, Nature 381, 678–680,1996.
4. Krishnan, A., Dujardin, E., Ebbesen, T. W., Yianilos, P. N., and Treacy, M. M.J., Young's modulus of single-walled nanotubes, Physical Review B 58, 14013–14019, 1998.
5. Yu, M.-F., Files, B. S., Arepalli, S., and Ruoff, R. S., Tensile loading of ropes of single-wall nanotubes and their mechanical properties, Physical Review Letters 84, 5552, 2000.
6. Gao, G., Agin, T., and III, Goddard, W. A., Energetics, structure, mechanical and vibrational properties of single-walled carbon nanotubes, Nanotechnolog*y* 3, 184, 1998.
7. Jorio, A.; Saito, R.; Hafner, J. H.; Lieber, C. M.; Hunter, M.; McClure, T.; Dresselhaus, G.; Dresselhaus, M. S. Phys. ReV. Lett. 2001, 86, 1118.
8. Kataura, H.; Kumazawa, Y.; Maniwa, Y.; Umezu, I.; Suzuki, S.; Ohtsuka, Y. Achiba, Y. Synth. Met. 1999, 103, 2555.
9. Hamada, N.; Sawada, S. I.; Oshiyama, A. Phys. ReV. Lett. 1992, 68, 1579.
10. Mukhopadhyay K, Koshio A, Tanaka N and Shinohara H 1998 Japan. J. Appl. Phys. 37 L1257
11. MukhopadhyayK, Koshio A, Sugai T, Tanaka N, Shinohara H, Konya Z and Nagy J B 1999 Chem. Phys. Lett. 303 117
12. Murakami Y, Miyauchi Y, Chiashi S and Maruyama S 2003 Chem. Phys. Lett. 374 53.
13. Murakami Y, Yamakita S, Okubo T and Maruyama S 2003 Chem. Phys. Lett. 375 393.
14. Murakami Y, Miyauchi Y, Chiashi S and Maruyama S 2003 Chem. Phys. Lett. 377 49.
15. Kataura, H.; Kumazawa, Y.; Maniwa, Y.; Umezu, I.; Suzuki, S.; Ohtsuka, Y. Achiba, Y. Synth. Met. 1999, *103*, 2555.
16. Charlier, J. C.; Lambin, Ph. *Phys. Re*V. *B* 1998, *57*, R15 037.
17. Ichida, M.; Mizuno, S.; Saito, Y.; Kataura, H.; Achiba, Y.; Nakamura, A. *Phys. Re*V. *B* 2002, *65*, 241407.
18. Pichler, T.; Knupfer, M.; Golden, M. S.; Fink, J.; Rinzler, A.; Smalley, R. E. Phys. ReV. Lett. 1998, 80, 4729.

7. NOMENCLATURE

Symbol	Meaning	Unit
${}^{S,M}E_{ii}$	The vertical interband transition energy between the i^{th} pair of VHSs in both the valence and the conduction bands of a semiconducting or metallic nanotube	(eV)
n	An integer	dimensionless
a_{C-C}	Nearest-neighbor carbon-carbon distance	(nm)
γ_0	Nearest-neighbor carbon-carbon interaction energy	(eV)
d_t	Diameter	(nm)

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