

Metallic/semiconducting ratio of carbon nanotubes in a bundle prepared using CVD technique

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Abstract. We present an investigation of the nature of single-walled carbon nanotubes (SWCNTs) in a bundle by resonant Raman spectroscopy. The calculation has been done for the three peak positions in radial breathing mode (RBM) spectra obtained by using a laser excitation wavelength (λ) of 633 nm from He–Ne laser on SWNT bundle sample prepared by chemical vapor deposition (CVD) technique using iron catalyst at 800°C. The detailed analysis in the present study is focused on peak positions 162 cm⁻¹, 186 cm⁻¹, and 216 cm⁻¹. The first step of the analysis is to construct a list of possible (n, m) pairs from the diameters calculated from the RBM peak positions. The parameters of SWNTs studied gives in-depth understanding of many symmetry, resonance and characteristic properties of SWNT bundles. Our results indicate that the contribution of metallic SWNTs in the bundle is small at RBM peak positions 162 cm⁻¹, 186 cm⁻¹ and in agreement with pervious results at peak position 216 cm⁻¹.

Keywords. Raman spectroscopy; metallic/semiconducting ratio; chirality.

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1. Introduction

Carbon nanotubes have attracted the scientific community throughout the world during the last decade because of their unusual physical, electronic and mechanical properties. Since from the discovery of single wall carbon nanotubes (SWNTs) by Iijima and Ichihashi [1], much efforts have been devoted to improve the methods of nanotube production, and significant progress has been made to narrow the diameter distribution of nanotubes produced by different catalysts and growth processes [2]. The symmetry and electronic properties of carbon nanotubes depend upon how they can be generated by wrapping a graphite sheet along different directions as

given by the indices (n, m) known as chirality, where n and m are integers. Each pair of the indices defines a unique way to roll up the graphene sheet to form the nanotube, and each unique (n, m) nanotube has a distinct electron and phonon structure. The determination of the (n, m) pair(s) of a single SWNT (batch of SWNTs) comprises a nearly complete morphology characterization. The (n, m) characterization of carefully prepared SWNT samples has been accomplished by a number of authors in the past [3]. However, there is no method yet for selecting a specific chirality in the nanotube production process, since the nanotube structural energy depends weakly on chirality [4], and consequently actual nanotube samples appear to exhibit a homogeneous chirality distribution. Thus the development of techniques to assign a chirality (n, m) to a given SWNT is very important for the development of both future technological applications and specific studies.

The combined investigation of Raman scattering and optical absorption spectroscopy in a batch of SWNTs was presented by Namkung *et al* [5] and the authors have made the calculations for one peak position but the actual error range in diameter has been considered to be 15%. In their report [5] no calculation has been made to determine the number of atoms in a unit cell of SWNT, and the chiral angle, which has a pronounced effect on optical properties of SWNTs in a bundle. Kataura *et al* [6] proposed that within a zone-folding scheme, one third of SWNTs are metallic which have wider energy gaps between spikes than semiconducting ones with almost same diameters. In this study we report that it is possible to have less than one third of the SWNTs in a bundle as metallic by determining the (n, m) values of SWNTs. The contribution of metallic SWNTs in our sample is only 21% at peak position 162 cm^{-1} , 25% at peak position 186 cm^{-1} which is small when compared to the previously published results and 33% at peak position 216 cm^{-1} which is in agreement with the previous results. However the calculations at the other peak position 252 cm^{-1} in RBM has not been carried out in this study because the formula used here for the determination of frequency is not valid for tube diameter d_t less than 1 nm ($d_t < 1\text{ nm}$). Further, we believe that no study has been carried out so far in determining the nature of SWNTs in a bundle. The present study will help to use the carbon nanotubes in future nanoelectronics (computing, data storage, and manufacturing).

2. Experimental details

Iron catalyst films of various thicknesses ranging from 10 to 100 nm were deposited onto a silicon (Si) substrate of resistivity $\rho \sim 4\text{--}6\ \Omega\text{-cm}$, using standard RF sputtering technique. The catalyst deposited substrate was patterned using optical lithography followed by lift-off to retain iron islands of 20 nm diameter onto the Si substrate. After cleaning the patterned substrate, the growth of carbon nanotubes was carried out using NH_3 and C_2H_2 mixture at a substrate temperature of 800°C . The growth of 12-min duration results in carbon nanotubes of about 10 micron height.

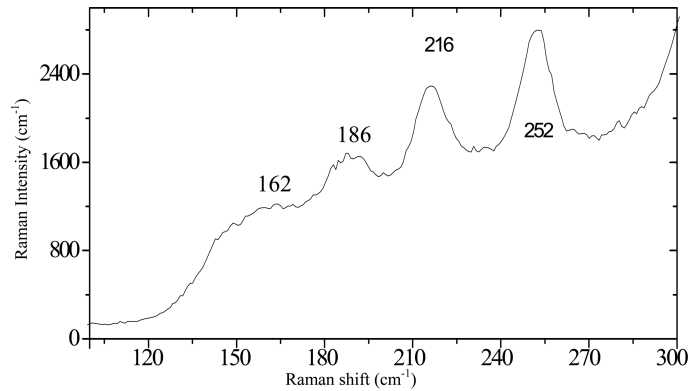


Figure 1. RBM Raman intensity vs. RBM frequency for a SWNT bundle excited with $E_{\text{laser}} = 1.96$ eV.

3. Results and discussion

One of the most widespread techniques for the analysis of CNTs is Raman spectroscopy. It is a non-destructive, non-dissipative measurement, which is made at ambient conditions. In particular, resonance Raman spectroscopy can select those nanotubes in the nanotube sample, which are resonant with excitation laser energy. Thus we can observe the properties of a nanotube by resonance Raman spectroscopy even for a bundle of nanotubes. However, a specific nanotube with a specific diameter or chirality cannot be produced or selected at will. Therefore, a single resonant peak in a bundle represents a number of nanotubes of different chiralities and diameters. This means that the diameter of a SWNT is a multi-valued function of (n, m) . In addition, one has to allow a reasonable degree of errors in the experiments. Therefore, one normally selects a list of possible (n, m) pairs by examining the Raman radial breathing mode (RBM) peak positions. The RBM ($100\text{--}300\text{ cm}^{-1}$) has been the object of many experimental and theoretical studies because of its high excitation cross-section and resonant behavior. Therefore, a reliable characterization of the atomic structure of SWNTs produced under various conditions is mainly based on the interpretation of low frequency ($100\text{--}300\text{ cm}^{-1}$) Raman spectra. Previous reports [7] conclude that the RBM frequency was inversely proportional to nanotube diameter for nanotubes with large diameters (≥ 0.7 nm). However, when the nanotube diameter is decreased the induced curvature effect will break this reciprocal relation. For SWNTs with large tube diameter (d_t) a unique (n, m) assignment with Raman spectroscopy could not be made because by increasing d_t (decreasing ω) the number of resonant SWNTs within the resonant window increases, making a unique (n, m) assignment difficult [3].

In this study the SWNT sample was excited by using He-Ne laser of wavelength 633 nm (1.96 eV) and the spectra were recorded in the backscattering geometry on the sample. A low power laser excitation was used to avoid SWNT modification. The spectra were recorded by employing micro Raman spectroscopic system. To enhance the signal the objective lense $\times 100$ was used. The spectrum of RBM is shown in figure 1. Let us consider the peaks at 162, 186, 216, 252 cm^{-1} , which

Table 1. List of (n, m) pairs corresponding to the diameters within 5% of 1.539 nm computed from the RBM peak at 162 cm^{-1} .

(n, m)	d_t (nm)	ω (cm^{-1})	E_{11} (eV)	Nature of the tube	No. of carbon atoms in unit cell	Chiral angle θ (deg)
(14, 7)	1.471	169.07	0.567	Semiconducting	196	19.10
(13, 8)	1.479	168.29	0.564	Semiconducting	1348	22.17
(17, 3)	1.484	167.68	0.562	Semiconducting	1396	7.9
(16, 5)	1.488	167.25	0.561	Semiconducting	1444	13.17
(19, 0)	1.509	165.06	0.553	Semiconducting	76	0
(11, 11)	1.513	164.65	1.656	Metallic	44	30
(18, 2)	1.516	164.35	0.550	Semiconducting	728	5.20
(13, 9)	1.522	163.74	0.548	Semiconducting	1468	24
(14, 8)	1.532	162.74	1.635	Metallic	230	21.05
(17, 4)	1.534	162.54	0.544	Semiconducting	1492	10.33
(15, 7)	1.547	161.26	0.539	Semiconducting	1516	18.14
(18, 3)	1.563	159.71	1.603	Metallic	516	7.58
(16, 6)	1.565	159.52	0.533	Semiconducting	776	15.29
(12, 11)	1.583	157.82	0.527	Semiconducting	1588	28.56
(13, 10)	1.587	157.44	1.578	Metallic	532	25.69
(20, 0)	1.589	157.26	0.525	Semiconducting	80	0
(14, 9)	1.594	156.80	0.523	Semiconducting	1612	22.84
(15, 8)	1.606	155.70	0.520	Semiconducting	1636	20.03
(18, 4)	1.612	155.16	0.518	Semiconducting	824	9.59

represent the major peaks in the tube diameter distribution of SWNTs. Using the relation

$$\omega_{\text{RBM}} = \frac{A}{d_t} + B, \quad (1)$$

where A and B are determined experimentally ($A = 234 \text{ cm}^{-1}$ and $B = 10 \text{ cm}^{-1}$ for SWNT bundle) [8], corresponding tube diameters d_t are to be 1.539, 1.329, 1.135, 0.966 nm. However, for $d_t < 1$ nm the simple relation (1) is not expected to hold due to nanotube lattice distortions leading to a chirality dependence of ω_{RBM} [9]. Moreover, for large tubes ($d_t > 2$ nm) the intensity of RBM feature is weak and is hardly observable. A list of (n, m) pairs for each RBM peak is constructed by allowing an error range and using the expression for tube diameter $d_t = (\sqrt{3}/\pi)a\sqrt{n^2 + m^2 + nm}$ [5]. The list of (n, m) pairs corresponding to the diameters within 5% of 1.539 nm, 5% of 1.329 nm and 5% of 1.135 nm calculated from the RBM peak positions at 162 cm^{-1} , 186 cm^{-1} and 216 cm^{-1} are respectively shown in tables 1–3. Using the above equation for ω the frequency corresponding to the tube represented by (n, m) pair is shown in the third column of each table. The fourth column of each table provides the first interband transition energy E_{11} calculated by using the equation $E_{ii} = (2ia_{\text{C-C}}\gamma_0)/d_t$, for metallic tubes $i = 3, 6 \dots$ and for semiconducting tubes $i = 1, 2, 4, 5, 7 \dots$ where $a_{\text{C-C}}$ is the carbon-carbon bond length (0.144 nm) and γ_0 is the nearest-neighbor electronic overlap integral, which

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Table 2. List of (n, m) pairs corresponding to the diameters within 5% of 1.329 nm computed from the RBM peak at 186 cm^{-1} .

(n, m)	d_t (nm)	ω (cm^{-1})	E_{11} (eV)	Nature of the tube	No. of carbon atoms in unit cell	Chiral angle θ (deg)
(16, 0)	1.271	194.10	0.657	Semiconducting	64	0
(15, 2)	1.279	192.95	0.645	Semiconducting	1036	6.17
(10, 9)	1.308	188.89	0.630	Semiconducting	1084	28.25
(11, 8)	1.312	188.35	1.989	Metallic	364	24.79
(12, 7)	1.322	187.0	0.624	Semiconducting	1108	21.36
(14, 4)	1.300	190.0	0.634	Semiconducting	552	12.21
(15, 3)	1.327	186.33	1.888	Metallic	372	8.9
(13, 6)	1.336	185.14	0.617	Semiconducting	1132	17.99
(17, 0)	1.350	183.33	0.611	Semiconducting	68	0
(14, 5)	1.355	182.69	1.849	Metallic	388	14.70
(16, 2)	1.357	182.43	0.608	Semiconducting	584	5.817
(10, 10)	1.376	180.05	1.820	Metallic	40	30
(11, 9)	1.379	179.68	0.598	Semiconducting	1160	26.69
(12, 8)	1.385	178.95	0.595	Semiconducting	76	23.41
(17, 1)	1.392	178.10	0.592	Semiconducting	1228	2.83
(17, 3)	1.396	177.62	0.591	Semiconducting	1396	7.99

Table 3. List of (n, m) pairs corresponding to the diameters within 5% of 1.135 nm computed from the RBM peak at 216 cm^{-1} .

(n, m)	d_t (nm)	ω (cm^{-1})	E_{11} (eV)	Nature of the tube	No. of carbon atoms in unit cell	Chiral angle θ (deg)
(14, 1)	1.078	227.0	0.765	Semiconducting	844	3.41
(8, 8)	1.101	222.53	2.275	Metallic	32	30
(14, 0)	1.112	220.43	0.742	Semiconducting	56	0
(13, 2)	1.12	218.92	0.736	Semiconducting	796	7.05
(11, 5)	1.126	217.81	2.225	Metallic	268	17.78
(12, 4)	1.146	214.18	0.720	Semiconducting	208	13.89
(13, 3)	1.170	210.00	0.705	Semiconducting	868	10.15
(10, 7)	1.176	208.97	2.130	Metallic	292	24.18
(11, 6)	1.186	207.30	0.695	Semiconducting	892	20.36

is 2.9 eV [10]. Metallic and semiconducting tubes are differentiated by $n - m \neq 3q$ for semiconducting and $n - m = 3q$ for metallic [5]. Accordingly the nature of the tube is given in the fifth column of each table. The chiral angle for each chirality is calculated using the relation $\theta = \tan^{-1}(\sqrt{3}m/(2n + m))$ [11], and is shown in the sixth column of each table. Seventh column provides the number of carbon atoms per unit cell of a tube defined by (n, m) , using the relation $2N = 4(n^2 + m^2 + nm)/d_r$ [12], where d_r is the greatest common divisor of $(2n + m)$ and $(n + 2m)$. Nanotubes

with small N such as the achiral nanotubes and chiral nanotubes with large d_r may show a clear resonance effect when the frequency of the laser light is tuned on. On the other hand, chiral nanotubes with large N may not show the resonance effect. Since N depends strongly on the chirality, the resonant Raman intensity depends on chirality. Our results reveal that only 21 and 25% of SWNTs are metallic at peak positions 162 cm^{-1} and 186 cm^{-1} respectively and rest of the tubes are semiconducting in the bundle. Therefore, the contribution of metallic tubes in the sample is small when compared to the semiconducting ones at these positions in the RBM mode. However, the contribution of metallic nanotubes at peak position 216 cm^{-1} is 33%, which is in agreement with the previously proposed results [6].

4. Conclusion

In this paper an investigation of the nature of single-walled nanotubes (SWNTs) in a bundle is described by developing an easy and simple method for constructing a list of (n, m) pairs. The calculated results reveal that the contribution of metallic SWNTs is small when compared to semiconducting ones at peak positions 162 cm^{-1} and 186 cm^{-1} . However, at peak position 216 cm^{-1} the present results are in agreement with the previous proposed results. The study presents a simple method for predicting the nature of the SWNT sample. However, to identify the true (n, m) pairs in a single wall nanotube (SWNT) bundle, more progress is necessary to understand the effects of intertube interaction on the experiments and other potential factors.

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