Resonant Raman scattering of double wall carbon nanotubes prepared by chemical vapor deposition method

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Resonant Raman spectra of double wall carbon nanotubes (DWCNTs), with diameters from 0.4 to 3.0 nm, were investigated with several laser excitations. The peak position and line shape of Raman bands were shown to be strongly dependent on the laser energies. With different excitations, the diameter and chirality of the DWCNTs can be discussed in detail. We show that tubes (the inner or outer layers of DWCNTs) with all kinds of chiralities could be synthesized, and a DWCNT can have any combination of chiralities of the inner and outer tubes. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1619201]

I. INTRODUCTION

Resonant Raman spectroscopy has been shown to provide a convenient and powerful technique for characterizing both the vibrational and electronic structure of single wall carbon nanotubes (SWCNTs).[1–3] Each SWCNT has a unique set of interband energies (E_{ii}) denoting the energy differences between the *i*th van Hove singularities in the conduction and valence bands of their one-dimensional electronic density of states (DOS), and the interband energies have been found to depend on the diameter and chirality of SWCNTs.[4] The intensity of these Raman peaks is selectively enhanced when the photon energy of the incident or the scattered is in resonance with an allowed optical transition in an interband.

A DWCNT can be considered to be two coaxial SWCNTs coupled by the van der Waals interaction. Therefore, resonant Raman vibrations should also occur in the Raman scattering of DWCNTs.[5] However, studies of the resonant Raman scattering of DWCNTs have been scarce due to the difficulty of their selective production. Bandow *et al.* recently had a report on the resonant Raman scattering in DWCNTs,[6] which are obtained by heating C60 molecules encapsulated SWCNTs. In our previous research, we selectively produced double wall carbon nanotubes (DWCNTs) by a floating catalyst chemical vapor deposition (CVD) method.[7] In this article, we generated resonant Raman scattering by different laser lines on our as-grown DWCNTs. Their detailed structural information and electronic properties are analyzed according to the resonant Raman spectra.

II. EXPERIMENT

The detailed experimental procedures for the preparation of DWCNTs with our method were described elsewhere.[7] A two-stage furnace system fitted with a quartz tube was used. Ferrocene and sulfur powder (16:1, molar ratio) were mixed uniformly and ground with mortar. The catalyst mixture was first sublimed in the first furnace at ~70 °C, and then carried by the flowing argon (1600 sccm) and acetylene (C_2H_2, 1 sccm) mixture into the second furnace. The growth temperature of DWCNTs was 1100 °C. The grown DWCNTs in the second furnace were transported out of the reaction zone by the flowing gases and attached on the cooler part of the quartz tube inside wall. The products were easily peeled in large sheets. High resolution transmission electron microscopy (HRTEM) observations revealed that the dominant carbon nanotubes in the products are double walled. Figure 1 shows a scanning electron microscopy (SEM) picture of the as-grown DWCNT sample, the insert is HRTEM image of a DWCNT.

Raman scattering experiments were performed at ambient conditions with the following laser excitation lines: 457.9 nm (2.71 eV), 488 nm (2.54 eV), 514.5 nm (2.41 eV), 647.1 nm (1.92 eV), 676 nm (1.83 eV), and 752 nm (1.64 eV). The Raman spectra taken from different spots on the same sample by the same excitation were practically similar, and it indicates that our DWCNT samples studied are homogeneous.

III. RESULTS AND DISCUSSION

The Raman scattering spectra in the low frequency region taken with different laser excitations (1.64–2.71 eV) are shown in Fig. 2. It is indicated that the RBM frequencies of DWCNTs have a wider Raman frequency range from 100 to 400 cm^{-1} and display much richer peaks than that of SWCNTs.[1–3]

The van der Waals interaction between the outer and inner tubes may lead to some mixed vibrational modes.[8] However, we consider that this interaction may not significantly affect the basic vibration of the outer and inner tubes

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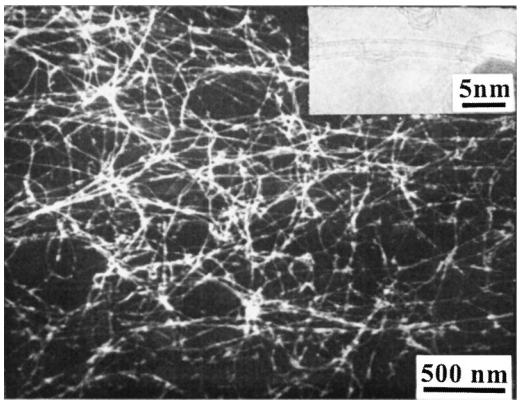

FIG. 1. SEM image of as-grown DWCNTs. The inset is HRTEM image of a DWCNT, the scale bar is 2 nm.

compared with that of their SWCNT counterparts.[1] This assumption was also verified by the recent diameter-selective resonant Raman scattering investigation on DWCNTs prepared by heating C_{60} encapsulated SWCNTs.[6] Therefore, the Raman spectra of DWCNTs could be interpreted similarly to those of SWCNTs.[3,9–14] The diameter dependence of the RBM frequency of DWCNTs can be fitted by the following equation[13]

$$\omega_{\mathrm{RBM}} = 238/d^{0.93}, \tag{1}$$

where $\omega_{\mathrm{RBM}}\,(\mathrm{cm}^{-1})$ is the RBM frequency, and $d\,(\mathrm{nm})$ is tube diameter. Here, we simply assume that the influence of the van der Waals interactions in the DWCNT bundles (the interactions in the bundles and the outer–inner tube interactions) is the same as that in SWCNT bundles.[12–14]

Considering the thinnest inner diameter of 0.40 nm and the interlayer spacing of 0.34 nm between the outer tube and the inner tube, and according to Eq. (1), it is clear from Fig. 2 that the higher ($>200\ \mathrm{cm}^{-1}$) RBM bands must be associated with the inner tubes, and the lower RBM bands can be originated from both the outer tubes and the larger inner tubes.

In Fig. 2, the peak positions and intensity of RBM bands taken with different laser excitation are different, and this

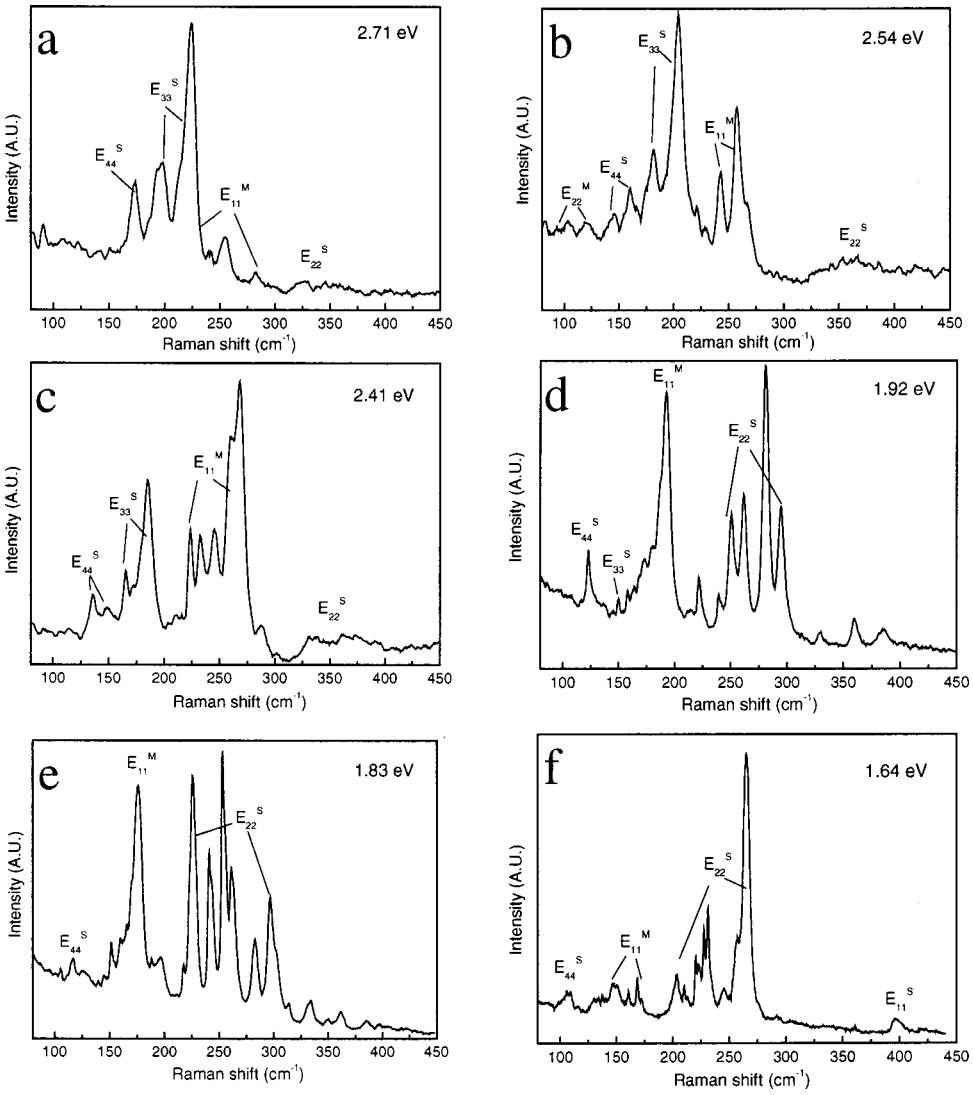

FIG. 2. RBM spectra of DWCNTs taken with several excitations: (a) 2.71 eV, (b) 2.54 eV, (c) 2.41 eV, (d), 1.92 eV, (e) 1.83 eV, and (f) 1.64 eV. $E_{ii}^{S/M}$ denotes the *i*th interband energy between the *i*th van Hove singularities of DOS of SWCNTs, and *S* and *M* denote semiconducting and metallic, respectively.

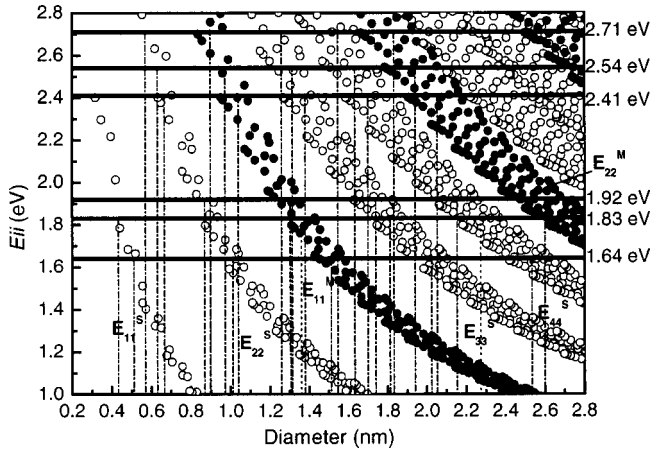

FIG. 3. Diameter and chirality dependence of the interband energy E_{ii} between the *i*th van Hove singularities (see Ref. 4). The solid circles are for metallic tubes, and the open circles are for semiconducting tubes.

TABLE I. Diameters and chiralities of some inner layers of DWCNTs, which is determined by the resonant Raman spectra.

Laser energy (eV)	Frequency of RBM (cm^{-1})	Diameter (nm)	Chirality
	223.5	1.07	metallic
	233.1	1.02	metallic
2.41	245.0	0.97	metallic
	259.8	0.91	metallic
	268.6	0.88	metallic
	250.7	0.95	semiconducting
1.92	261.8	0.90	semiconducting
	281.2	0.84	semiconducting
	295.0	0.79	semiconducting

difference should be associated with the resonant Raman scattering behavior. Kataura *et al.* recently calculated the interband energies of various SWCNTs with different diameters and helicities (as shown in Fig. 3).[4] Horizontal lines in the Fig. 3 denote the laser photon energies that are taken on the same DWCNT sample in our experiment. It is easy to know that the crosses of these lines with the interband energy bands mean the resonant Raman scattering windows for the relative carbon nanotubes. These vertical dash–dot lines correspond to the center of these resonant windows. Our HRTEM results indicated that the diameter distribution (including the outer and the inner tube) of our DWCNTs spans from the smallest 0.4 to 3.0 nm,[7] and the interband energies corresponding to these diameters span a wide range from infrared to ultraviolet energies. As indicated in Fig. 3, DWCNTs with different chirality in the various diameter ranges can be resonantly excited at a fixed laser line, and that is the reason that we can get wide RBM Raman bands from our DWCNT samples.

Different resonant widows with which various group of RBM bands match are labeled (in Fig. 2) as E_{44}^S, E_{33}^S, E_{22}^S, E_{11}^S, E_{11}^m, and E_{22}^m, where *S* and *M* denote semiconducting and metallic tube, respectively. Tube diameters from the Raman RBM bands were determined by the Eq. (1).

The semiconducting tubes with the second interband energy (E_{22}^S) should be resonantly excited by the laser with energy of 2.41–2.71 eV because these laser line have crosses with E_{22}^S band in Fig. 3. However, we did not observe strong RBM band in these frequency ranges where E_{22}^S is labeled in Figs. 2(a)–2(c). It means that the excitations with the photon energies of 2.41–2.71 eV are unsuitable for the resonant Raman scattering of the tubes with diameter of 0.6–0.7 nm. This may be due to the fact that the number of tubes that fit in these resonant windows is very few. On the other hand, these excitation energies in the range of 1.64–1.92 eV match well with E_{22}^S of the semiconducting tubes in the diameter range of 0.8–1.1 nm, and their RBM bands were resonantly enhanced.

A contrary phenomenon occurs for these tubes with E_{33}^S. As shown in Figs. 2(a)–2(c) the semiconducting tubes with the third interband energy were resonantly excited by the laser lines of 2.41–2.71. However, we did not observe obvious enhanced bands that couple with E_{33}^S in the spectra of Figs. 2(d)–2(f), which were excited by the excitations of 1.64–1.92 eV, though these laser lines all have crosses with E_{33}^S band.

As shown in Figs. 1(d) and 1(e), there are many obvious RBM peaks in the frequency range of 300–400 cm^{-1} that is excited with the excitation of 1.83–1.92 eV. These RBM peaks are relative to the carbon nanotube with diameters of 0.6–0.8 nm. Apparently, these peaks are not resonantly enhanced, because carbon nanotubes in this diameter range do not fit in any resonant windows associated with the excitation of 1.83–1.92 eV. That means DWCNTs with the inner tube of 0.6–0.8 nm exist in our samples, and this is agreement with our HRTEM observation.[7]

In Table I, we calculated the diameters of the inner tubes in the range of 0.7–1.1 nm, which are corresponding to the RBM frequency range of 220–300 cm^{-1} according to Eq. (1). We just considered two excitations of 2.41 and 1.92 eV. RBM peaks above frequency of 200 cm^{-1} displayed more symmetric and separate feature, and most of these peaks could be separately fitted by a single Lorentzian line. This means that each RBM peak in this frequency range should correspond to one kind of inner tube. With 2.41 eV excitation, the metallic inner tubes were resonantly excited, and with 1.92 eV excitation, different chiralities of the semiconducting inner tubes were determined in this diameter range. Even though it is possible to determine (n,m) assignment for each SWCNT by the resonant Raman scattering technique,[15] considering the uncertainty of the relationship between RBM frequency and diameter,[9–14] (n,m) assignment for each inner tube here seems no more important meaning. However, the smaller diameter interval between them indicates that those inner tubes should include all types of the chiralities, including zigzag $(n,0)$, armchair (n,n), and other (n,m) $(n \neq m)$. This suspicion does not agree with the previous report, which indicated that the growth of the chiral carbon nanotubes, as opposed to zigzag or armchair ones, is favored due to their lower symmetry.[16] It may mean that the structure of a DWCNT can be any chirality pairs of the inner and outer layers.[17] For more exact analysis, resonant Raman spectra of

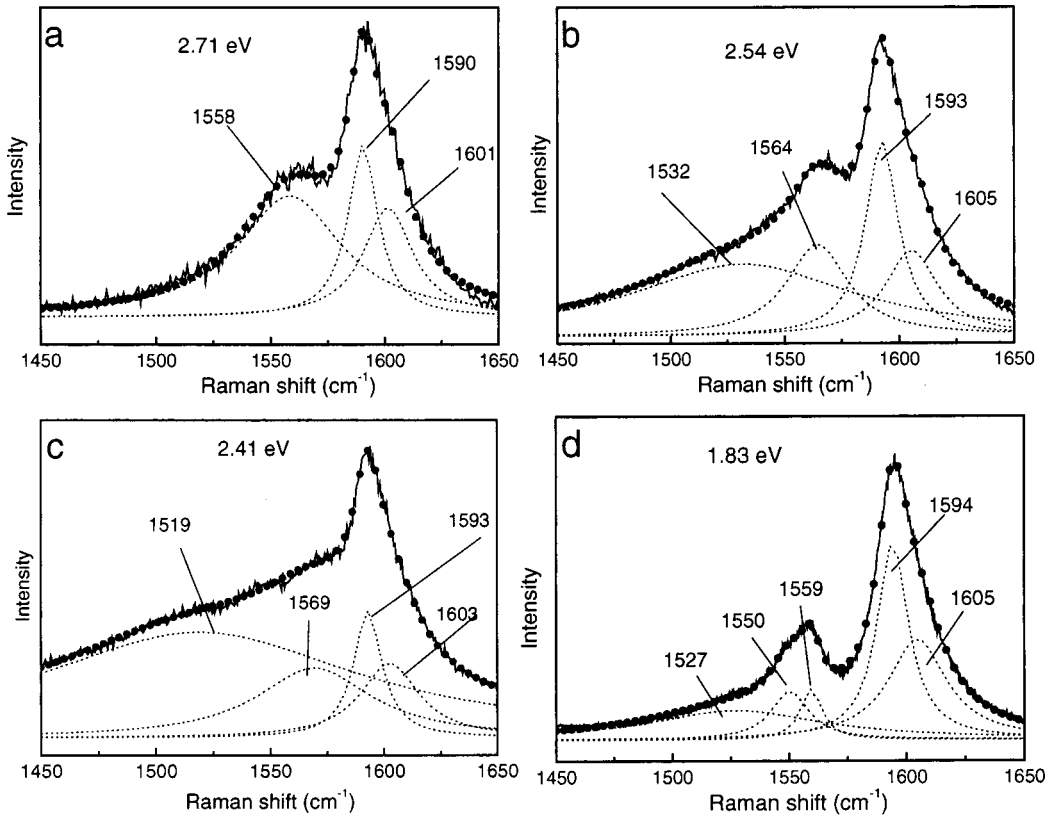

FIG. 4. GM bands of DWCNTs taken with several excitations: (a) 2.71 eV, (b) 2.54 eV, (c) 2.41 eV, and (d) 1.83 eV.

individual DWCNT with different excitations are needed, and this work is still carrying on.

Due to the resonant Raman scattering behavior, we can see that the peak position, the peak intensity, and the peak number are different for the different excitations. For comparison, we found that the red laser energies (1.83–1.92 eV) seemed more sensitive to our DWCNTs, and the Raman spectra taken with the red excitations displayed much higher intensity and much richer RBM peaks. However, if we want to reveal the detailed structural information of the sample, different excitations must be needed, as indicated in Table I.

Figure 4 shows the Raman spectra in the high frequency region 1450–1650 cm^{-1}. Four spectra are displayed, which were taken with the excitations of 2.71, 2.54, 2.41, and 1.83 eV, respectively. We first carried out Lorentzian fit of the GM spectra. The results are shown in Fig. 4 with the dashed lines. Raman-active modes between 1500 and 1600 cm^{-1} associated with the tangential displacement C–C bond stretching motions of carbon nanotubes (GM band).[18,19] Previous investigations showed that the frequencies and number of the peaks in the GM bands depend on the diameter and chirality of the nanotubes.[18–21]

As displayed in Fig. 4(a), the GM bands with 2.71 eV excitation show a feature of semiconducting carbon nanotubes,[20] and it indicates that the semiconducting carbon nanotubes were mainly resonantly excited under this excitation. With 2.54 eV excitation [as shown in Fig. 4(b)], the GM bands exhibit an asymmetric broadening to the low frequency, which indicates the resonant scattering of the metallic components.[4,21] the GM bands with 2.41 eV excitation display a more asymmetric metallic feature [Fig. 4(c)]. The metallic inner tubes coupling E_{11}^{M} resonant window were well excited under this laser energy, as also indicated in Fig. 2(c). For 1.83 eV excitation, the metallic tubes with ~1.4 nm diameter were resonantly excited. On the other hand, the semiconducting inner tubes with 0.8–1.1 nm diameters displayed the much stronger resonant excitation. Therefore, the GM bands with this excitation display more semiconducting features.

IV. CONCLUSION

In summary, DWCNTs prepared by the floating catalyst CVD method were characterized by Raman scattering with different laser excitations of 1.64–2.71 eV. According to the diameter and chirality dependence of the resonant Raman scattering behavior of SWCNTs, the resonant Raman spectra of our DWCNTs with diameters of 0.4–3.0 nm were discussed, and the intensity and line shape of the RBM and GM bands were shown to be strongly dependent on the energy of the inclined laser lines. Each excitation excited several groups of resonant RBM bands whose frequencies span from 100 to 400 cm^{-1}, and the corresponding electronic properties were also assigned. With different excitations, the diameters and chiralities of DWCNTs were discussed in detail. Our results suggest that DWCNTs with combination of all kinds of chiralities, including zigzag, armchair, and other (n,m) chiralities could be synthesized.

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