

Raman study on single-walled carbon nanotubes with different laser excitation energies

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Abstract. The industrial use of carbon nanotubes is increasing day by day; therefore, it is very important to identify the nature of carbon nanotubes in a bundle. In this study, we have used the Raman spectroscopic analysis on vertically aligned single-walled carbon nanotubes (SWCNTs) grown by the chemical vapour deposition (CVD) technique. The grown sample is excited with two laser excitation wavelengths, 633 nm from He–Ne laser and 514.5 nm from Ar⁺ laser. Raman spectrum in the backscattering geometry provides the characteristic spectra of SWCNTs with its radial breathing mode (RBM), defect-induced disorder mode (D band), and high-energy modes (G and M bands). The Raman signal positions of the spectra in RBM, G and M bands confirm the grown sample to be of semiconducting type in nature.

Keywords. SWCNTs; wavelength dependent spectra; Raman spectroscopy.

1. Introduction

The chirality of a single-walled carbon nanotube determines whether the tube is metallic or semiconducting (Dresselhaus *et al* 1996). Both semiconducting as well as metallic carbon nanotubes (CNTs) find a number of potential applications (Trans *et al* 1998; Kong *et al* 2000; Javey *et al* 2003), however, their potential applications will go high on obtaining either purely metallic or semiconducting carbon nanotubes (Dai 2002). In recent years, efforts have been made to identify the nature of single-walled carbon nanotubes while surveying the electronic properties of carbon nanotubes (Wooning *et al* 2002; Islam and Shah 2006). For large-scale synthesis of carbon nanotubes, the most promising technique is chemical vapour deposition (CVD) of carbon molecular precursors, assisted by the catalytic activity of metal or transition metal particles (Laurent *et al* 1998). The CVD technique yields high percentage of semiconducting single-walled carbon nanotubes (S-SWCNT), which is much higher than those obtained using laser ablation (Wooning *et al* 2002). In this study, growth of vertically aligned single-walled carbon nanotubes is carried out using thermal catalytic CVD technique at ~750°C where CNT is grown on deposited iron catalyst particles using hydrocarbons as precursor.

Density function theory and first principle calculations are the tools which are used for the identification of the nature of single-walled carbon nanotubes (Laurent *et al* 1998; Zhou *et al* 2000; Wooning *et al* 2002; Islam and Shah 2006). Experimentally Raman spectroscopy 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. The analysis is carried out in low energy phonon spectra, normally called radial breathing mode (RBM), ~150–400 cm⁻¹ and the high energy modes (HEM) at ~1600 cm⁻¹. The study may help in characterization of preferential growth of semiconducting single-walled carbon nanotubes for their potential use in building arrays of field effect transistors and sensors.

2. Experimental

Raman scattering spectra are taken from the sample in backscattering geometry; the beam was focused to a circular spot of 1 μm diameter. The sample was irradiated with two wavelengths, 633 nm from He–Ne laser and 514.5 nm from Ar⁺-laser. The Raman spectra were recorded by employing a spectroscopic system consisting of a

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double monochromator (SPEX 1404), photomultiplier tube (9214B) as detector, an amplifier-discriminator assembly, notch-filter, and a photon counting arrangement. To enhance the signal, an objective lens, 100 \times , was used. SEM measurements were carried out by scanning electron microscope (LEO-1450 UP).

3. Results and discussion

3.1 Sample growth and its morphology

Aligned carbon nanotubes (CNTs) were prepared using CVD technique. Growth of carbon nanotubes was carried out using thermally heated chemical vapour deposition reactor having three independent process gas lines for sequential or simultaneous flow of gases. The flow of gases was controlled through mass flow controllers. The temperature profile of the reactor tube was measured using a K-type (Ni–Cr and Ni–Al) thermocouple to fix constant temperature zone inside the reactor. To start with, the substrate was precleaned to remove any greasy materials from the surface. Iron catalyst films of various thicknesses ranging from 10–20 nm were deposited onto a *n*-type Si (100) substrate of resistivity (ρ) \sim 4–6 Ω cm, using standard RF sputtering technique. The thickness of the film was measured using a surface profiler. The catalyst coated substrate was kept over quartz holder in the CVD reactor and heated at about 650°C for 20 min in H₂ flow of 100 sccm. After pretreatment of the substrate, C₂H₂ was introduced into the reactor and growth of carbon nanotubes was carried out with a 10 : 1 mixture of H₂ and C₂H₂ for about 8 min duration. The substrate surface was scanned by using SEM. Figure 1 shows the SEM micrograph where growth of vertically aligned SWNTs is observed.

3.2 Raman spectroscopic analysis

The Raman spectra were taken in the backscattering geometry on the sample as grown without having any synthe-

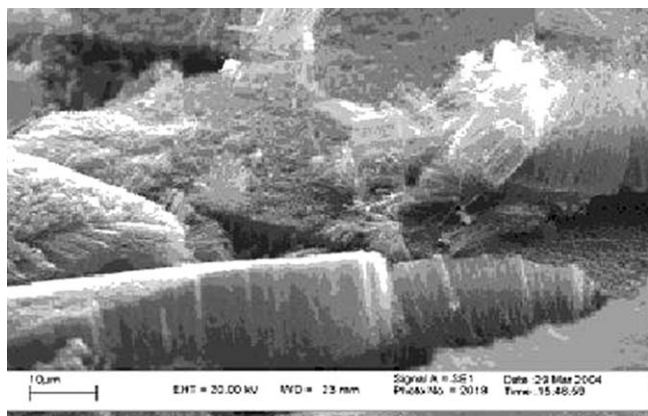


Figure 1. SEM image of single-walled carbon nanotubes (SWCNTs).

sis for purification as mentioned. Figure 2 shows the room temperature Raman spectra of SWNT material at a laser excitation energy of 1.96 eV ($\lambda = 633$ nm from He–Ne). The spectra is divided into four main zones: the low frequency region from 140–500 cm^{-1} , the intermediate zone from 500–1000 cm^{-1} , the high frequency zone from 1000–2000 cm^{-1} and second order scattering zone from 2000–3200 cm^{-1} (figure 2). The first three zones are the characteristics of SWCNTs and distinguish it from other carbon materials either in bulk or nanoform.

Two peculiarities make these spectra different from the spectrum of a planar graphite: (i) presence of RBM modes in the low frequency zone which is earmarked as a silence zone for graphite and other carbonaceous materials, and (ii) the splitting of G band at \sim 1600 cm^{-1} (Rao *et al* 1997). The phonon modes, < 400 cm^{-1} , are called acoustic modes. Among them the phonons of frequency in the range 150–220 cm^{-1} are called radial breathing modes (RBM) which are most sensitive (Rao *et al* 1997) and act as indicator about the quality of SWCNTs and its geometry.

3.2a Radial breathing modes (RBM): Radial breathing mode is conceptually the easiest mode to understand in carbon nanotubes. This mode has A_{1g} symmetry and all the carbon atoms move in phase in the radial direction creating breathing like vibration of the entire tube (Rao *et al* 1997). The RBM is associated with a periodicity imposed on a graphene sheet by wrapping it into a finite-size (small diameter) tube. It is widely applied to determine the diameter of nanotubes as it has particularly a simple relationship between its frequency and the diameter of the tube (Rao *et al* 1997; Jorio *et al* 2003). Also the mode shifts to higher wave numbers when SWCNTs are close packed into bundles, an effect associated with van der Waals forces, acting between nanotubes in a bundle (Rao *et al* 1997). The RBM (ω_{RBM}), the first order Raman modes with phonon wave vector, $q \approx 0$, appears at 162, 186, 216, 252 and 433 cm^{-1} . The diameters are calculated using the relationship between ω_{RBM} and the tube diameter for SWCNTs (Jorio *et al* 2003). The diameter range comes out to be 1.382–0.516 nm.

The nature of a tube in a bundle can be determined if a number of wavelengths are utilized (Rao *et al* 1997). Figure 3 depicts RBM spectra at room temperature using two laser wavelengths, 633 nm and 514.5 nm, on the same sample. It is known that SWCNTs can be truly metallic (*n, n*) armchair SWCNTs with $m-n = 3 \times \text{integer}$ and semiconducting (*m, n*) SWCNTs (S-SWCNTs) with $m-n \neq 3 \times \text{integer}$. To confirm that our sample is of semiconducting type, we carried out theoretical calculations at peak positions shown by both wavelengths. Figure 3 shows four peak positions at 180, 190, 216 and 252 cm^{-1} . Using the equation (Kurti *et al* 2002),

$$\omega_{\text{RBM}} = (A/d_t) + B,$$

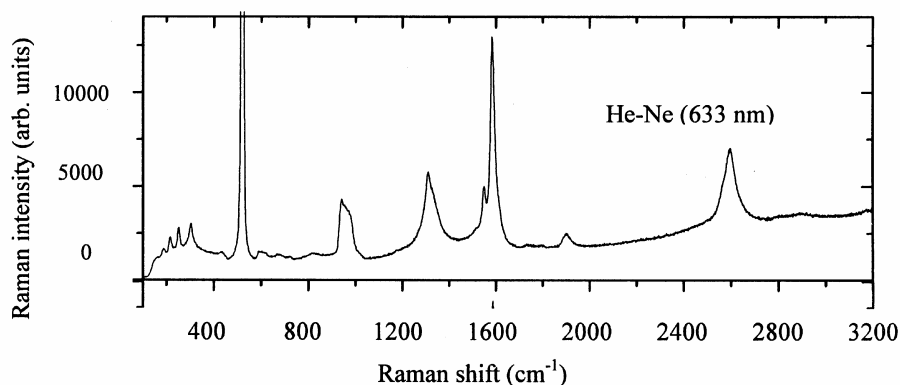


Figure 2. Room temperature Raman spectra of grown SWCNT material at a laser excitation energy, 1.96 eV ($\lambda = 633$ nm from He-Ne laser).

where ω_{RBM} is RBM frequency, d_t the tube diameter and A and B are constants, and for bundle $A = 234 \text{ cm}^{-1}$, $B = 10 \text{ cm}^{-1}$, the corresponding tube diameters are 1.376, 1.3, 1.135 and 0.966 nm, respectively. Within 5% error range in tube diameters in RBM, as presented earlier by Namkung *et al* (2004), with no preference in chirality, we find that the sample contains high percentage of semi-conducting single-walled carbon nanotubes and this confirms that our sample is of semiconducting type in nature.

3.2b Intermediate zone (500–1000 cm^{-1}): This region has few peaks at 520, 590, 668, 726, 824 and 948 cm^{-1} (figure 2). The peak at 520 cm^{-1} is due to Si substrate; and the other peaks can be identified as overtones and combinations of lower frequency modes (Journet *et al* 1997). In the range 750–800 cm^{-1} , Rao *et al* (1997) identified these peaks with phonon modes scattered from tubes of different diameters with different chiral index. So far very few workers have reported the appearance of intermediate modes in case of SWNTs (Journet *et al* 1997; Rao *et al* 1997; Wei *et al* 2003).

3.2c High energy modes (HEM) (1000–2000 cm^{-1}): This region contains mainly two prominent modes: the defect-induced disordered mode (D-band) at 1312 cm^{-1} , and tangential modes (G-band) with splitting of three modes at 1516, 1552 and 1584 cm^{-1} . Besides, two other modes (M-band) appear at 1732 and 1903 cm^{-1} (figure 2). The higher energy modes are not strongly dependent on nanotube diameter but they are very sensitive to the local movements of the atoms (Saito *et al* 1998). We have given here explanation of the characteristics of each band.

D-band (1332 cm^{-1}): The D-mode at 1350 cm^{-1} has been known in graphite for over a few decades and this is induced by disorder and not a Γ -point phonon (Tuinstra and Koenig 1970). In carbon nanotubes, this D-mode is observed at somewhat smaller frequency than in graphite

and shifts at a rate between 38 and 65 cm^{-1}/eV with laser excitation energy (Kastner *et al* 1994; Thomson 2000; Kurti *et al* 2002; Maultzsch *et al* 2002).

In figure 2, the D-mode is observed at 1332 cm^{-1} , usually lower than D-mode frequency from graphite and its intensity is quite large as compared to G-band. The bandwidth is $\sim 40 \text{ cm}^{-1}$. These two characteristics (frequency and linewidth) ensure that the sample is nanotube and not graphite (Rao *et al* 1997). The observation of large D-band peaks compared with the G peak intensity in SWCNTs bundles indicate the presence of amorphous carbon (Rao *et al* 1997; Ferrari and Robinson 2000). The origin of D-mode is explained in depth in literature (Thomsen and Reich 2000; Maultzsch *et al* 2001; Saito *et al* 2003) in terms of double resonance process and it enhances the intensity of the second order bands such as those labeled as M^- and M^+ that appear in the range 1700–1800 cm^{-1} and those close to 2700 or 3200 cm^{-1} (Brar *et al* 2002) or even higher energies (Tan *et al* 1998; Cansado *et al* 2002). The explanation of the shift as a function of laser excitation energy may be due to the selective enhancement of different tubes in resonant Raman scattering (Kastner 1994; Alvarez *et al* 2000).

G-band (1516–1585 cm^{-1}): In graphite and carbon nanotubes, the G-band Raman vibrational modes (E_{2g} derived modes) are present due to the in-plane vibrational movement of carbon atoms. The observation of characteristic multi-peak features around 1580 cm^{-1} provides a signature of carbon nanotubes. Unlike graphite (tangential mode at 1582 cm^{-1}), the tangential G-mode in SWCNTs gives rise to a multi-peak feature, also named the G-band. The two most intense G peaks are labeled G^+ for atomic displacement along the tube axis, and G^- for modes with atomic displacement along the circumferential direction and the lowering of the G^- mode is due to the curvature of the nanotube, which softens the tangential vibration in the circumferential direction (Rao *et al* 1997). Jorio *et al*

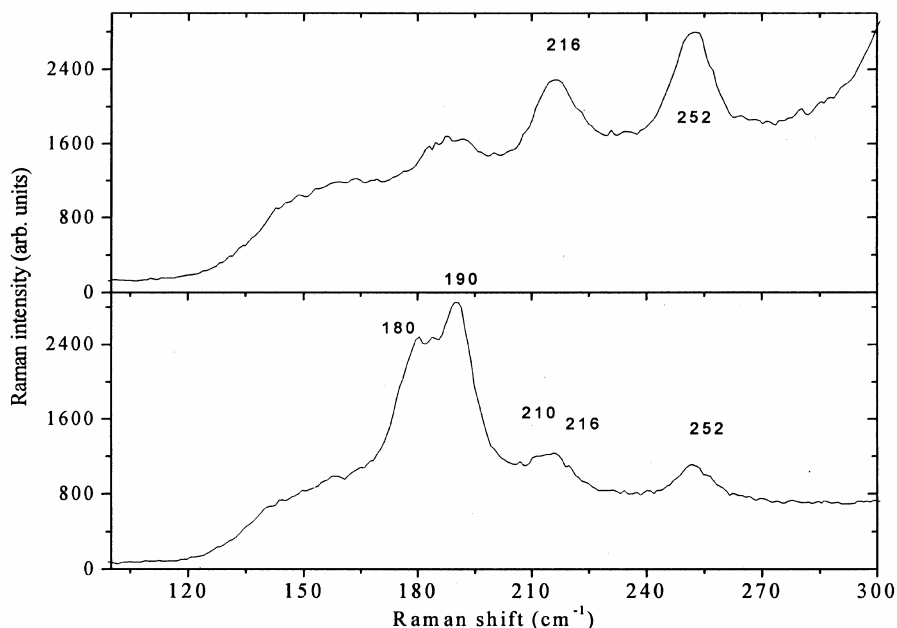


Figure 3. Wavelength dependent radial breathing mode (RBM) spectra of SWCNTs.

(2000) observed the G-band with a prominent mode around 1592 (G^+) along with two shoulders in the low energy side for SWNT samples.

Our spectra (figure 2) shows G band with peak position at 1584 (G^+) of maximum intensity and two shoulders at 1552 (G^-) and 1516 cm^{-1} . These features have previously been reported in the literature (Rao *et al* 1997; Jorio *et al* 2000; Thomsen *et al* 2000), where the spectral profile resembles our spectra but with a difference in the peak positions. Our spectra (figure 2) resemble the Raman spectra (Tan *et al* 1998; Thomsen *et al* 2000; Shirolshi *et al* 2003) and it is of semiconducting type. They typically arise at laser energies around the transition energies between the singularities in the electron density of states (EDOS) for semiconducting tubes (Rao *et al* 1997). The Bright–Weigner–Fano (BWF) line is observed in many graphite-like materials with metallic character as well as metallic SWCNTs. The BWF line at 1540 cm^{-1} which is the characteristic of metallic type, is absent in the spectra. This, in turn, reinforces our suggestion that the grown nanotubes are of semiconducting type and not metallic. In MWNT, there is a single peak at 1589 cm^{-1} corresponding again to the high-energy graphite like mode; the low energy RBM mode is generally not seen (Thomsen *et al* 2000). It also confirms that the grown tubes are not even multi-walled carbon nanotubes (MWCNTs).

M-band (1600–2000 cm^{-1}): The spectra (figure 2) shows appearance of two peaks at 1732 and 1900 cm^{-1} in the high frequency region. The band at 1732 cm^{-1} is termed as M-band (Brar *et al* 2002; Sanjuan *et al* 2004). In our case, the mode frequency of M band are in agreement with Brar *et al* (2002) though our laser excitation energy is

1.96 eV. The shift rate is $-3 \text{ cm}^{-1}/\text{eV}$ with increasing laser excitation energy (Brar *et al* 2002). Therefore, the shift of M-band with laser excitation energy is considered to be negligible in our case. The origin of the mode at 1732 cm^{-1} is explained as due to the combination of 1516 cm^{-1} of G-band mode and the radial breathing mode at 216 cm^{-1} . The origin of the mode at 1900 cm^{-1} is due to the overtone of the mode at 948.9 cm^{-1} in the intermediate range.

4. Conclusions

Vertically aligned single-walled carbon nanotubes (SWCNTs) are grown on Si-substrate using iron catalyst under thermally heated chemical vapour deposition technique (CVD). In order to determine the nature of the nanotubes in the grown bundle sample, the sample was excited by two-laser excitation wavelengths, 633 nm from He–Ne laser and 514.5 nm from Ar^+ . Raman spectroscopic analysis at peak positions in radial breathing mode (RBM) and high energy modes (HEMs) confirms that the excited sample has high percentage of semiconducting single-walled nanotubes. Moreover, the study provides an alternative method for the identification of nature of single-walled carbon nanotubes in a bundle for their potential use in consumer electronics.

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