Observations of the *D*-band feature in the Raman spectra of carbon nanotubes

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We examine the behavior of the *D*-band feature in the Raman spectra of single-walled carbon nanotube (SWNT) bundles, observed between 1250 and 1450 cm^{-1}, as a function of the laser excitation energy. We used three SWNT samples with different diameters, and show that the *D*-band behavior of SWNTs differs from sp^2 carbons, depending on whether the SWNTs are metallic or semiconducting, and shows a frequency ω_D that is dependent on nanotube diameter.

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I. INTRODUCTION

One of the interesting features of the Raman spectra in sp^2 carbon materials is the linear laser excitation energy (E_{laser}) dependence of the frequency of the disorder-induced *D* band ω_D,[1] which is observed between 1250 and 1450 cm^{-1}. The *D* band is activated in the first-order scattering process of sp^2 carbons by the presence of in-plane substitutional hetero-atoms, vacancies, grain boundaries or other defects and by finite size effects, all of which lower the crystalline symmetry of the quasi-infinite lattice. The association of the *D* band with symmetry-breaking phenomena results in a *D*-band intensity that is proportional to the phonon density of states. This *D*-band behavior occurs in a similar way for all kinds of sp^2 carbon materials,[2,3] such as graphon carbon black,[4] hydrogenated amorphous carbon,[5] glassy carbon and crystalline graphite,[6-8] and multicomponent carbon films.[9] The *D* band also appears in well purified carbon nanotube samples, and recent work[10] shows an anomalous "step" behavior in the laser excitation dependence of the second-order *G'*-band frequency at $\sim 2\omega_D$. This latter result is interpreted[10] as a manifestation of the one-dimensional (1D) behavior of the phonon spectrum in carbon nanotubes. Polarized resonant Raman measurements on bundles of single wall carbon nanotubes (SWNTs),[11] and multiwall carbon nanotubes (MWNTs),[12] and on isolated SWNTs (Ref. 13) show that the *D* band exhibits a polarization dependence favoring maximum scattering intensity along the nanotube axis direction.

In this work we analyze the *D*-band spectra of three SWNT samples with different mean nanotube diameters and diameter distributions using different laser excitation energies E_{laser}. We show that the *D*-band feature for bulk SWNT samples does not behave as those of other sp^2 carbons, but rather exhibits properties that are unique to SWNTs, including a frequency dependence on mean nanotube diameter.

II. EXPERIMENTAL DETAILS

Three bulk samples of SWNTs with different mean diameters (d_t) and diameter distributions were used in this study. The first sample (S1) with $d_t = 1.35 \pm 0.20$ nm was produced through the pulsed laser vaporization method using a carbon target containing 1 to 2 atom% of Ni/Co catalyst in a furnace at 1200 °C. The second sample (S2) was produced by Carbolex Inc. using a 4:1 ratio of Ni:Y catalyst mixture to produce SWNTs with $d_t = 1.49 \pm 0.20$ nm. The third sample (S3) used a 2.6 at. % Ni, 0.7 at. % Fe, and 0.7 at. % Co catalyst mixture along with 0.75 at. % FeS, resulting in SWNTs with a broad distribution of diameters (mean diameter $d_0 = 1.85$ nm).[14]

The Raman experiments were performed under ambient conditions on bulk SWNT samples containing multiple bundles of SWNTs and using a back-scattering configuration. For laser excitation radiation, we used the 457.9 nm (2.71 eV), 488 nm (2.54 eV), and 514.5 nm (2.41 eV) lines from an Ar^+ laser; the 632.8 nm (1.96 eV) line from an air cooled He-Ne laser; the 568 nm (2.19 eV), 647.1 nm (1.92 eV), and 676.4 nm (1.83 eV) lines from a Kr^+ laser; the 782.0 nm (1.58 eV) line of a solid state Al-doped GaAs laser; and the 830 nm (1.49 eV) line of a Ti:sapphire laser.

III. RESULTS AND DISCUSSION

To study the dispersion of the *D* band in a bulk sample of SWNTs, it is important, first, to describe the resonant behavior of the SWNTs in our experiment. We use the resonantly enhanced broad tangential *G*-band features to determine the narrow resonance window for metallic carbon nanotubes and to distinguish between resonant metallic and semiconducting SWNTs, as has been previously discussed.[15-18] In brief, the Raman *G*-band features attributed to the metallic nanotubes in samples with narrow diameter distributions (as is the case for samples S1 and S2) are resonantly enhanced in a narrow laser energy window, when either the energy of the incident laser photon or the Raman scattered photon matches the E_{11}^M energy separation between the van Hove singularities in the valence and conduction bands of the metallic nanotubes. This resonant energy window for metallic nanotubes occurs between 1.7 eV and 2.3 eV for sample S1, and between 1.5 eV and 2.1 eV for sample S2, because the two samples have different diameter distributions and therefore have different energies for the first allowed electronic transition E_{11}^M between the van Hove singularities for the metallic nanotubes.[15-17] In Fig. 1(a) we show the Raman spectra for
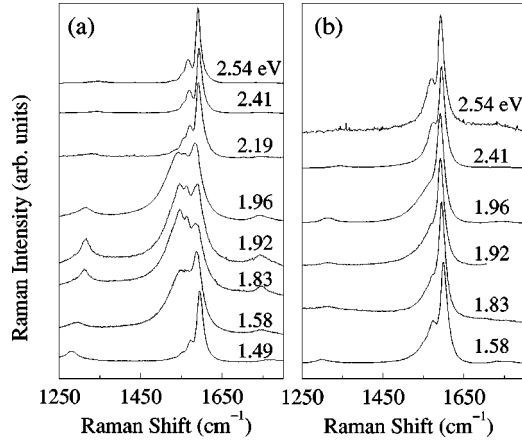
FIG. 1. Tangential G-band and D-band features in the Raman spectra for a sample of carbon nanotubes with a narrow diameter distribution (a) $d_t = 1.49 \pm 0.20$ nm (S2), as well as (b) a sample with a broad distribution of diameters peaked at $d_0 = 1.85$ nm (S3), using the indicated values of laser excitation energy (E_{laser}).

sample S2, where the tangential G-band feature is broader and the peak frequency is downshifted in the narrow laser excitation energy window 1.5 eV$<E_{laser}<2.1$ eV, relative to the tangential G-band feature obtained using energies outside this window.

Regarding the D band, the first interesting result we observe in the Raman spectra for SWNT bundles is the dependence of the D-band intensity on E_{laser}. Using the definition of the metallic resonant energy window discussed above, Fig. 1(a) shows that, for sample S2, a well defined D-band feature is observed within the metallic resonant window. The D-band feature increases in peak intensity relative to that of the tangential G band for E_{laser} in the metallic window. When $E_{laser}>2.1$ eV, the D band is very weak, broad, and poorly resolved. Figure 2 shows a plot for the D-band intensities of
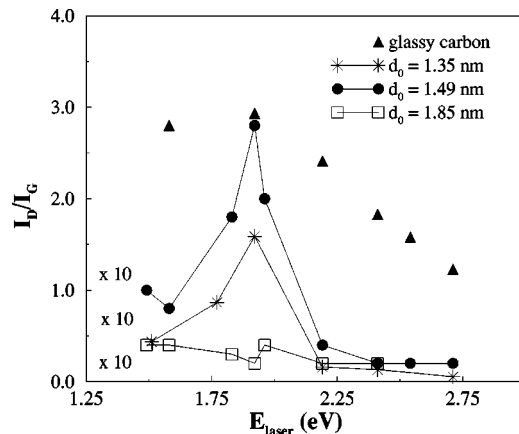

FIG. 2. Dependence of the I_D/I_G ratio of the peak intensity values on E_{laser} for three different samples of carbon nanotubes with $d_0 = 1.35$ nm($S1$), 1.49 nm (S2) and 1.85 nm (S3). Also shown is the ratio of the *integrated* intensity I_D/I_G for an sp^2 sample in the form of glassy carbon (taken from Ref. 8). The ratios I_D/I_G for the SWNT samples have been multiplied by a factor of 10, to facilitate easier comparison with the glassy carbon data.

samples S1 and S2 for various E_{laser} values. Here it is seen that, for samples S1 and S2, the D-band feature gains in peak intensity relative to that of the tangential G-band feature by a factor of 10 or more within the metallic window.[16] Throughout the present paper, I_D/I_G refers to the ratio of the intensity of the D- and G-band features at their most intense points, unless stated explicitly.

This result is different from the D-band intensity behavior for conventional disordered sp^2 carbons, where the ratio I_D/I_G increases monotonically as E_{laser} decreases, and then below 2 eV it saturates (see Fig. 2). Since E_{laser} is approaching the band gap of the finite crystallite size carbon clusters in the material, the intensity of the D band increases relative to that of the G band as the system approaches a preresonance condition. These clusters are not present in carbon nanotubes, and thus the ratio I_D/I_G is expected to behave differently as a function of E_{laser}.

Figure 2 also presents data for the ratio I_D/I_G for sample S3, which exhibits only a *modest* change in lineshape when the laser excitation energy is varied [see Fig. 1(b)]. I_D/I_G for sample S3 shows a completely different behavior than for samples S1 and S2, and the I_D/I_G ratio remains essentially constant as E_{laser} is varied (see Fig. 2). Since sample S3 contains a broad distribution of large diameter SWNTs, S3 does not have a well defined resonance window for metallic nanotubes.[19]

Figure 2 shows that for SWNT bundles there is a strong correlation between large values for I_D/I_G and the appearance of the broad, down-shifted tangential G-band features attributed to metallic SWNTs. The E_{laser} dependence of I_D/I_G is very different for SWNTs in comparison to sp^2 carbons, but the difference seems largely due to the contribution of the metallic nanotubes.

We now analyze the dependence of the D-band frequency ω_D on E_{laser}. It has already been reported [10] for a sample with $d_t = 1.37 \pm 0.18$ nm that the second-order G' band exhibits an anomalous dispersive behavior, where the frequency is not linearly dependent on the laser excitation, but it rather exhibits an oscillation around the linear dispersion curve.[10] The Raman spectra in the region of the D band (~ 1300 cm^{-1}) are shown in Fig. 3 for sample S2 for various values of E_{laser}. The measurement of the D-band frequency is very delicate in the case of SWNTs, with the peak frequency changing from spot to spot on the sample. In general, the peak shifts to higher ω_D values with increasing E_{laser}, and $\partial \omega_D / \partial E_{laser} \sim 60$ cm^{-1}/eV is obtained. However, the data show an oscillatory behavior around the linear dispersion curve, similar to previously reported work.[10]

Figure 4 is a plot of ω_D vs E_{laser} for three different samples. For S1 ($d_t = 1.35 \pm 0.2$ nm), the fixed position of the D band within the metallic window occurs at ~ 1308 cm^{-1}, while for sample S3 containing larger diameter nanotubes ($d_0 = 1.85$ nm), the D-band peak remains at ~ 1315 cm^{-1} within the metallic window. We report here that the approximately E_{laser}-independent ω_D behavior in the metallic window[10] has been reproduced in three samples having different diameter distributions of SWNTs. Furthermore, the results of Fig. 4 suggest that the ω_D values over
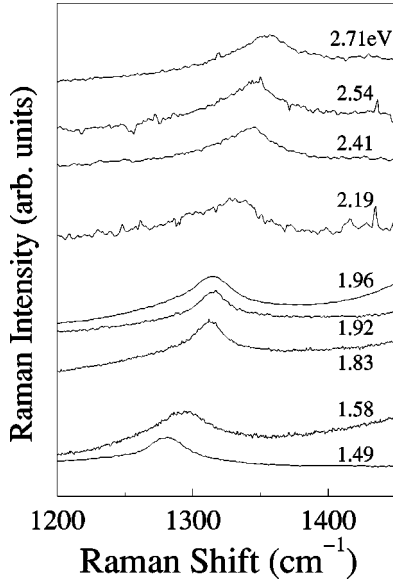
FIG. 3. Raman spectra in the range 1200–1450 cm^{-1} for SWNT sample S2 ($d_0 = 1.49$ nm) showing the anomalous (for the 1.83, 1.92, and 1.96 eV traces) frequency dispersion of the D-band peak with increasing E_{laser}.

FIG. 4. The dispersion of the D-band frequency ω_D with laser excitation energy (E_{laser}) for three SWNT samples, each having different mean diameters d_0 and different diameter distributions, and for an sp^2 carbon in the form of PPP-2400 (taken from Ref. 8). Also shown is one E_{laser} measurement (open square point) for multiwall nanotubes (MWNTs) (taken from Ref. 12).

the same E_{laser} range depend weakly on the nanotube diameter d_t, ω_D being slightly smaller for SWNTs with smaller d_t values. This result is reasonable, since ω_D for SWNTs should approach the ω_D value for sp^2 carbons as $d_t \rightarrow \infty$ at the same value of E_{laser}. The open square in Fig. 4 gives ω_D for a MWNT sample composed of large carbon nanotubes (~ 25 nm),[12] and the value is very close to that for the sp^2 carbon PPP-2400 at the same value of E_{laser} (see Fig. 4).

Regarding the different dispersive behavior in the case of metallic SWNTs, two explanations are possible: (i) The anomalous dispersive behavior is a reflection of the diameter dependent D-band frequency; (ii) The special behavior exhibited by the D band is related to the metallic nature of the resonant SWNTs. The diameter dependence of the D-band frequency [explanation (i)] can result in the oscillatory behavior observed in the frequency dispersion since, for a given E_{laser}, the resonant SWNTs have different diameters and the d_t dependence with E_{laser} oscillates when the E_{ii} transition is changed, as was observed for the radial breathing modes ω_{RBM} by Milnera *et al.*[20] This explanation implies that the anomalous oscillatory behavior would be observed also when, by changing E_{laser}, the resonance would change between, for example, E_{33}^S to E_{44}^S. This kind of oscillatory behavior was observed recently by Grueneis *et al.*[21] and might explain the smooth oscillation observed for sample S3 (see Fig. 4). However, we cannot ignore the possibility that the special behavior exhibited by the D band in metallic
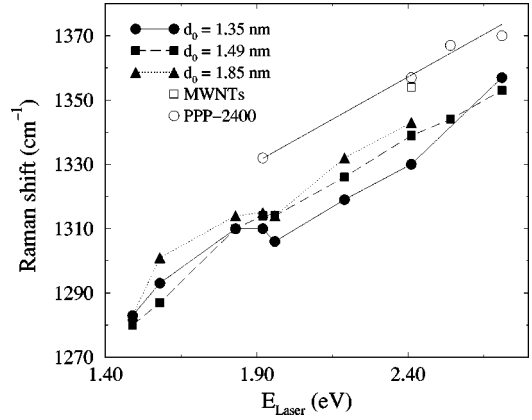
SWNTs may be connected with the electron-plasmon coupling arising from the nanotube curvature.[19]

IV. CONCLUSIONS

Raman spectra from three bulk samples of SWNTs with different diameter distributions are here reported. We show that the D-band for nanotubes exhibits different behavior than for other sp^2 carbon materials. The results suggest that ω_D is slightly smaller for SWNTs with smaller d_t values. The frequency ω_D exhibits an anomalous oscillatory dispersive behavior superimposed on the linear behavior observed in other sp^2 carbons. This anomalous dispersive behavior can be understood as a reflection of the diameter dependent D-band frequency, since for different E_{laser} values, resonant SWNTs with different diameters contribute to the D-band feature. However, we do not discard the possibility that the special behavior exhibited by the D band is related to the metallic vs semiconducting nature of the resonant SWNTs.

To gain further insights into the resonance Raman process associated with the D-band feature, Raman measurements on isolated semiconducting and metallic SWNTs are needed.[22]

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