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Chiral angle dependence of resonance window widths in (2n+m) families of single-walled carbon nanotubes

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Raman spectra of isolated single-walled carbon nanotubes (SWNTs) were obtained for a wide range of laser excitation energies to study the resonance excitation window of the radial breathing mode feature for members of (2n+m) families. A chiral angle (θ) dependence of the resonance window width (Γ) was observed, which is much stronger than the diameter dependence. The implications of this work on nanotube metrology are discussed. © *2010 American Institute of Physics*.
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Single wall carbon nanotubes (SWNTs) are a promising material for nanoscale electronic devices. Experimental investigation of the electron-phonon scattering mechanism that governs electron transport and its relation to the nanotube's electronic structure is a high priority in route toward developing device applications.

Raman spectroscopy has found wide application in the field of carbon nanotube characterization[1] since it can provide noninvasive analysis. Resonant enhancement of the Raman signal occurs when the laser excitation energy E_{laser} coincides with an electronic transition and allows spectroscopic analysis even at the single nanotube level. The dependence of the Raman intensity of each feature in the Raman spectra on E_{laser} is called its resonance window or resonance profile and provides a powerful analysis tool for studying the electron relaxation in SWNTs (see Fig. 1). Furthermore, these resonance windows determine the signal from a mixture of nanotubes as generally obtained by SWNT synthesis.[6] Thus a comprehensive knowledge of the resonance window for each SWNT will enable a more reliable evaluation of the (n, m) distribution that is present in a synthesized SWNT sample using a limited set of E_{laser} values.[2]

The resonance window of each (n,m) SWNT, characterized by its resonance window width, is expected to depend sensitively on its electronic structure.[3,4] It will thus exhibit a dependence on both diameter (d_t) and chiral angle (θ). We here investigate resonance windows for different SWNTs experimentally within an (2n+m) family of metallic and semiconducting M-SWNTs and S-SWNTs. We chose to study SWNTs comprising complete (2n+m) families since they vary only weakly with d_t, while exhibiting a large variation in θ between zigzag (θ=0°) and armchair (θ=30°). Furthermore working with a whole (2n+m) family of SWNTs increases the accuracy of our measurements since a common trend for nanotubes of the same fundamental electronic structure can then be extracted. We here focus on the resonance window of the radial breathing mode (RBM) feature in the Raman spectrum because of its usefulness for nanotube metrology.

There has only been limited research on resonance windows of individual SWNTs.[2,4] Instead, most previous Raman resonance window studies have been attempted with SWNT ensembles (either aqueous solutions[5,6] or SWNT bundles[7]). Changes in the SWNT environment due to neighboring nanotubes or to surfactant wrapping introduce a broadening of the resonance window[6] and thus conceal effects caused by changes of the electronic structure and are only partly applicable to individual SWNTs on a SiO_2 substrate—a common device layout.

Individual SWNT samples were prepared using the electrostatic spray-assisted chemical vapor deposition method as described previously.[8] Such samples are expected to contain mostly individual SWNTs. In short, SWNTs were deposited

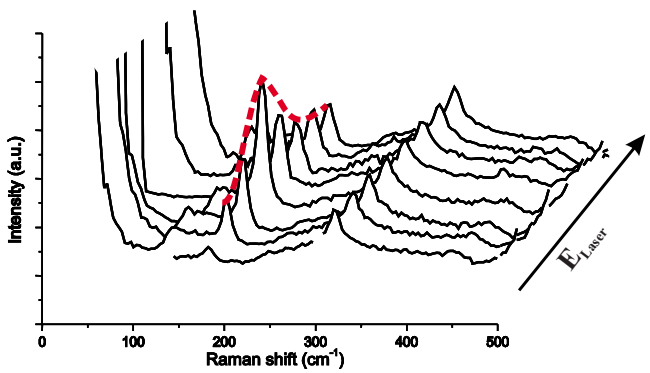

FIG. 1. (Color online) Plot of Raman spectra for various E_{laser} energies. The dashed line traces the resonance window of this (13,1) SWNT.

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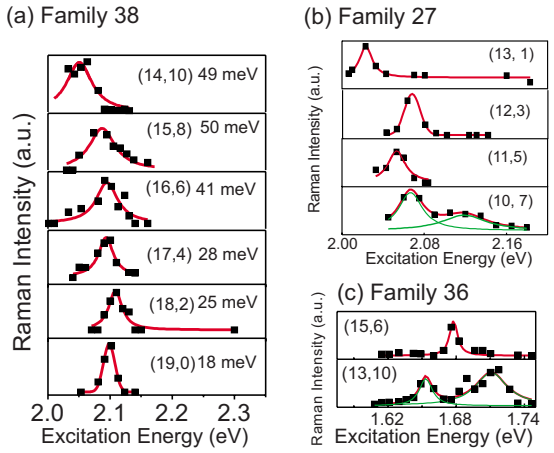

FIG. 2. (Color online) (a) Data (squares) and fitting (line) for Resonance windows for S-SWNT family 38 and for M-SWNT families 27 (b) and 36 (c), respectively. The thinner lines in (b) and (c) correspond to the upper and lower contributions of E_{11}^{M} and transitions to the resonance window of metallic nanotubes (Ref. 3).

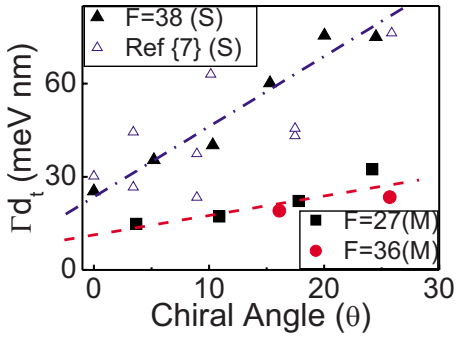

FIG. 3. (Color online) Plot of Γd_t vs θ with a linear fit to resonance window data acquired from individual M-SWNTs and S-SWNTs of this work. Data for Γd_t vs θ for the S-SWNTs from Ref. 7 is shown for comparison. (The Γ of Ref. 7 were obtained by fitting the original data with one Lorentzian peak.)

from the gas phase onto a Si substrate coated with a 100 nm SiO_2 thermal oxide after the SWNTs were grown at 1000 °C using a floating ferrocene catalyst.[8] From the good agreement between the d_t distribution obtained using AFM and Raman measurements,[8] we confirmed that our synthesis method produced mostly well isolated individual, nonbundled SWNTs. The low density [1 SWNT/(5 μm^2)] of the deposited nanotubes allows measurements of the Raman resonance window of individual SWNTs to be made without the interference from the presence of other SWNTs.[1]

Various laser excitation lines spanning two quasicontinuous ranges from 570 nm (2.17 eV) to 610 nm (2.03 eV) and from 720 nm (1.72 eV) to 810 nm (1.53 eV) (Dye and Ti-Sapphire Lasers, respectively) were used in this study. The experimental data for each laser excitation energy were taken by using 60×80 μm^2 Raman mappings with 0.5 μm resolution. Each map point contains a complete Raman spectrum. This allows us to account for errors in sample positioning during the experiment and to acquire resonance window data in parallel under identical laser conditions for several SWNTs in the same map area. A trade-off between acquisition speed and spectral resolution had to be made and laser excitation wavelengths were varied in 3 nm steps in data acquisition. In the investigated E_{laser} ranges, the resonance windows of the E_{11}^{M} and E_{33}^{S} electronic transitions[1] are probed in our SWNT sample.

Figure 2(a) shows the RBM resonance window for six SWNTs in the family (2n+m)=38 for many different E_{laser} values. In this figure the Raman intensity is normalized to the intensity of the Si 303 cm^{-1} peak in each spectrum.

The plot for each SWNT exhibits a resonance window which is characterized by its peak intensity I_{max}, its transition energy $E(I_{max})$ and its resonance window width. The shape of the resonance window is determined by contributions from two peaks associated with resonances between the electronic structure and the incident or scattered photons. Since the energy separation between those contributions (the RBM phonon energy $\hbar\omega_{RBM}$) is comparable with their peak widths (γ), it is difficult to distinguish these two contributions to the resonance profile from each other. Experimental results furthermore suggest that there might be varying intensities of the two peaks in the resonance window.[9] This multitude of unknown parameters and the limited experimental data points make a de-convolution into two peaks of varying width and intensities not viable. We therefore here report the total full width at half maximum (FWHM) of one Lorentzian peak (capital Γ) and note that it not only depends on the variation of γ and $\hbar\omega_{RBM}$ but is also affected by the variation of the relative intensities of the incident and scattered photon resonance peaks.

The excitation energy $E(I_{max})$ at the maximum RBM intensity I_{max} together with the ω_{RBM} for each SWNT gives a characteristic point on the Kataura plot of the resonant transition energy versus ω_{RBM}.[1] When compared with the theoretical Kataura plot calculated by Samsonidze *et al.*,[10] using the equation $\omega_{RBM}=217.8/d_t+15.7$ cm^{-1} (Ref. 11), excellent agreement is found. Thus the (n, m) chirality of the investigated SWNTs and their (2n+m) family can be assigned, and both the d_t and θ for each SWNT can be extracted.

All members of the S-SWNT family 38 have similar diameters but large changes in Γ are observed for their respective resonance profiles in Fig. 2(a). We will subsequently correlate these variations in Γ with changes in θ.

To analyze the intrinsic θ dependence of Γ in more detail, we have to account for the d_t dependence of Γ. We therefore also investigated SWNTs in the (2n+m) metallic family (27 along with two members of family 36) whose constituents span a wider range of diameters than the investigated S-SWNT family 38. The resulting data are shown in Figs. 2(b) and 2(c). Following theoretical modeling[10] and our own experimental observations we account for changes in Γ due to d_t by approximating these changes with a $1/d_t$ dependent term. We therefore plot in Fig. 3 the product Γd_t versus θ for the two investigated M-SWNT families, and find that the Γd_t data for both M-SWNT families with different values for d_t and Γ indeed collapses on to a single line with a clear θ dependence. The same is true for the S-SWNTs and in particular we see that our Γd_t data for family 38 is consistent with other experimental data obtained by Yin *et al.*[7] for S-SWNTs from families 22 and 29. The large scatter in their data might be related to bundling effects. When extrapolating Γd_t to $\theta=0°$ from the plot in Fig. 3, we find that the minimum profile width denoted by $\Gamma_0 d_t$ for E_{33}^{S} S-SWNTs (~20 meV nm) is larger than that for E_{11}^{M} M-SWNTs (~10 meV nm).

Theoretical modeling based on phonon-assisted electron relaxation like in Refs. 3 and 12 predicts that Γ is larger for S-SWNTs than for M-SWNTs of the investigated transitions but it does not predict the two main findings of our experiments. First, the value of $\Gamma_0 d_t$ is overestimated significantly by theory (i.e., Ref. 4 calculates a Γ for members of Family 38 that is twice as large as our observed value). Second, the clear dependence of Γ on θ, observed experimentally in Fig. 3, is not described by the theoretical modeling.

Our experimental findings open a new research area, and future experiments and theoretical modeling are required for explaining explain the experimental observations reported here. Future investigations have to determine if the observed dependence of Γ on the chiral angle is an intrinsic effect not captured by theory or caused by electronic interactions of the nanotube with adsorbates or with the substrate. Studies of the influence of nanotube properties (metallicity, S-SWNT type (type I or type II), optical transition energies E_{ii}, and nanotube diameter d_t) will help to better interpret the dependence of Γd_t on θ.

The observed changes of Γ with metallicity and chiral angle have implications on applications such as the metrological analysis of carbon nanotube samples. Since most evaluations of chirality and metallicity distributions of SWNTs are performed using a limited set of laser excitation energies, only a small set of nanotubes contributes to the Raman signal. For these nanotubes, the laser energy falls within their resonance window around their transition energies. Thus the experimental evidence of a larger Γ for S-SWNTs compared to M-SWNTs implies errors in the analysis of these M-SWNT to S-SWNT ratios since the S-SWNTs present in the sample will contribute more to the measured Raman intensity. Furthermore, the strong influence of θ on Γ could lead to an overestimation of near armchair over near zigzag nanotubes for each metallicity. The results reported here would thus require a revision of the current methodologies used for SWNT sampling for metrological applications to be made.

In conclusion, measurements of the resonance windows for two carbon nanotube families show that the resonance window width Γ has a clear chiral angle dependence. The findings reported in this work open a new research direction for further experimental and theoretical study of resonance windows in carbon nanotubes.

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