Resonance Raman Scattering: Nondestructive and Noninvasive Technique for Structural and Electronic Characterization of Isolated Single-Wall Carbon Nanotubes

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Received on 10 May, 2002

We discuss how resonance micro-Raman spectroscopy can determine the electronic and structural properties of individual isolated single-wall carbon nanotubes (SWNTs) that can be further used for potential nanodevices or studied by different experimental techniques. We show that it is possible to mark the surface of the Si/SiO_2 substrate for localization of the isolated SWNTs by using a diamond tip. By timing the growth procedure, a low density of SWNTs on the substrate can be obtained so that the SWNT localization by atomic force microscopy (AFM) is trivial. We also characterize a SWNT by resonance Raman spectroscopy at the edge of a Si-SWNT-AFM tip. There results show that it is possible to make joint experiments on the same isolated SWNT.

Single wall carbon nanotubes (SWNTs) [1] have been intensively studied for their interesting one-dimensional (1D) physical properties, and for their high potential for technological applications.[2, 3] SWNTs have been considered as a candidate for post-Si nanotechnology, due to their interesting electronic properties, and for applications such as atomic force microscopy (AFM) tips, because of their special structural and mechanical properties.[3]

The remarkable electronic properties of SWNTs are uniquely defined by their diameter d_t and chiral angle θ, that are specified by the two integers (n, m) which describe the roll-up vector $C_h = n\mathbf{a_1} + m\mathbf{a_2}$ ($\mathbf{a_1}$ and $\mathbf{a_2}$ are the unit vectors of the graphene sheet).[2] Resonant Raman scattering can be used to assign (n, m) indices to isolated SWNTs based on the analysis of the radial breathing mode (RBM).[4] Furthermore, it has been shown that each of the several characteristic features observed in the Raman spectra from isolated SWNTs, namely the G-band, the D band and G' band, is highly sensitive to the detailed nanotube structure, changing their frequencies and relative intensities according to the (n, m) indices of the resonant SWNT. Conversely, these spectral features can also be used to provide structural and electronic characterization information about isolated SWNTs (see Refs. [5, 6, 7]). The goal of this paper is to show that resonance Raman scattering can be used to characterize nanotubes that will be further studied by different experimental techniques. This procedure can also be used to characterize SWNTs for potential use in nano-devices, or even SWNTs built *into* nano-devices. We here discuss the characterization of isolated SWNTs on Si/SiO_2 substrates that are generally used for transport measurements [8], and also the characterization of one SWNT nano-device, that is a Si-SWNT AFM tip.[3, 9]

Figure 1 shows Raman spectra taken from an isolated nanotube on a Si/SiO_2 substrate. The Si peak at $521\,cm^{-1}$ is known as a strong Raman feature and is clearly observed in the spectra of Fig. 1. In this spectrum we found a strong Raman signal coming from an isolated SWNT, where several SWNT Raman features, the RBM, D band, G band and other second-order features can be clearly observed. The insets to

Fig. 1(b) show that a detailed lineshape analysis can be performed on the disorder-induced D band and on the graphite-like G band. A doublet is observed for the D-band profile formed by peaks with full width at half maximum intensity (FWHM) of about $12\,\mathrm{cm}^{-1}$. The G-band exhibits the lineshape usually observed for semiconducting SWNT bundles, but with a much sharper FWHM of about $11\,\mathrm{cm}^{-1}$. The signal intensity of the SWNT is comparable to the strong Raman signal from silicon, although the number of carbon atom scatterers in the 1D SWNT is about 10^6 times smaller than the number of atoms on the illuminated 3D Si substrate. This extremely large Raman cross section of SWNTs under resonance conditions is due to the quantum confinement of the electronic states in this 1D material, resulting in an unusually high density of electronic states at the energies where the 1D van Hove singularities occur.[10]

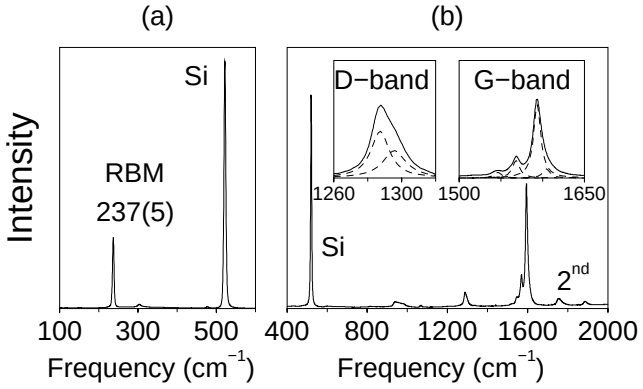

Figure 1. Resonant Raman spectra of a SWNT on a Si/SiO_2 substrate. (a) A strongly resonant RBM feature, and (b) a strongly resonant G-band feature. The Raman spectra were obtained with $E_{\mathrm{laser}} = 1.58\,\mathrm{eV}$.

Resonance Raman spectroscopy can be used to characterize isolated SWNTs in nano-devices. Fig. 2(a) shows an optical image (100×) obtained from a Si AFM tip containing a SWNT at the edge [upper left inset shows a transmission electron microscope (TEM) image of a Si-SWNT AFM tip, taken from Ref. [9]]. Fig. 2(b) shows Raman spectra obtained by focusing the laser at the edge of the AFM tip. From the RBM frequency ω_{RBM}, we can obtain the nanotube diameter ($d_t = 248/\omega_{\mathbf{RBM}}$).[4] The inter-band electronic transition energy E_{ii} involved in the resonant Raman scattering process of the measured SWNT can also be obtained, since the Raman intensity is proportional to the square of the joint density of states (JDOS).[10, 11] In this case, resonance with the SWNT was found using an Ar:Kr laser. Fig. 2(b) shows the Raman spectra with $E_{\mathrm{laser}} = 2.18$, 2.41 and 2.54 eV. The SWNT shows a resonance near $E_{\mathrm{laser}} = 2.41\,\mathrm{eV}$ and $\omega_{\mathrm{RBM}} = 196\,\mathrm{cm}^{-1}$ ($d_t = 248/196 = 1.27\,\mathrm{nm}$).[4] The SWNT at the AFM tip can be assigned as a semiconducting $(16, 0)$ tube, that has $d_t = 1.27\,\mathrm{nm}$ and $E_{33}^S = 2.40\,\mathrm{eV}$.

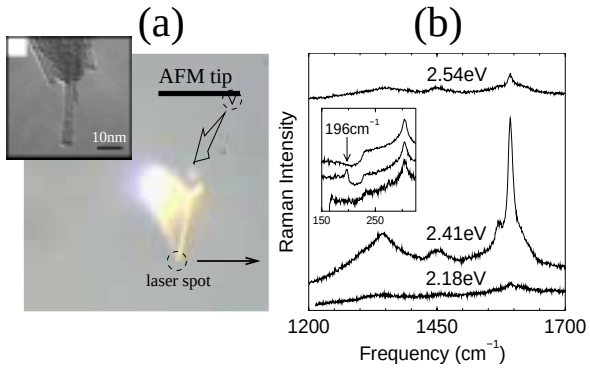

Figure 2. (a) The optical image of a Si-SWNT AFM tip. One isolated SWNT is attached to the edge of the Si tip by the procedure discussed in Ref. 9. Upper left inset shows a TEM image of another Si-SWNT AFM tip, taken from Ref. 9. (b) The SWNT G-band Raman spectra obtained with three laser lines focused at the edge of the Si tip shown in the optical image (a). The inset shows the corresponding RBM frequency region.

It is important to comment that the (n, m) assignment is based on the experimental determination of the tight binding overlap integral, $\gamma_0 = 2.90\,\mathrm{eV}$ and the atomic distance between carbons atoms $a_{\mathrm{C-C}} = 0.142\,\mathrm{nm}$. This γ_0 value is found to describe optical experiments with high accuracy, as, for example, optical absorption studies on SWNT bundles [12], the asymmetries in the Stokes vs. anti-Stokes Raman measurements on SWNTs [11, 13, 14, 15], the oscillatory behavior of the RBM spectral moments [16], the oscillation in the dispersive D-band frequencies for SWNT bundles [5], and unusual G-band [6] and G'-band [7] spectral features. Scanning tunneling spectroscopy (STS) experiments are better described with $\gamma_0 \sim 2.6\,\mathrm{eV}$ [3], and the origin of the different γ_0 values needs further research.

The electronic transition energy E_{ii} can be obtained with high accuracy ($\pm 3\,\mathrm{meV}$) by using a frequency tunable laser. In Ref. 10 a SWNT with $\omega_{\mathrm{RBM}} = 173.6\,\mathrm{cm}^{-1}$ ($d_t = 1.43\,\mathrm{nm}$) [4] and $E_{ii} = 1.655 \pm 0.003\,\mathrm{eV}$ was measured with a tunable Ti:Sapphire laser, uniquely identifying the resonant SWNT as the metallic $(18, 0)$ SWNT. The structure of the localized SWNT is determined and the measurement is non-destructive. This SWNT was sitting on a Si/SiO_2 substrate containing lithographic markers, and the same SWNT can be further imaged by AFM (see Ref. 10), or used for transport measurements.[3, 8]

The general problem of performing more than one experiment on the same SWNT is to localize the tube spatially. Fig. 3 shows an experimental procedure, similar to the one discussed in Ref. 10, but using a simpler method for spatially localizing the SWNTs. Fig. 3(a) shows an optical image (50×) of markers made on the

substrate with a diamond tip. AFM images can be taken on such a sample to describe the surface and to identify the presence of isolated SWNTs [see Fig. 3(b)]. The density of tubes can be controlled by timing the catalyst formation and SWNT growth procedure. The very low density of isolated SWNTs on the surface of this sample makes it trivial to identify the tube that is resonant with E_{laser}. Raman spectra were taken at the position shown in Fig. 3(b) to obtain the resonant Raman signal from the isolated SWNT close to the diamond marker. Fig. 3(c) shows the G-band Raman spectra from this SWNT, obtained with different laser lines from a DCM dye laser. With Raman spectroscopy and AFM, we analyzed three other nanotubes close to the diamond markers on the sample shown in Fig. 3. Therefore, the use of a low nanotube density sample with diamond markers makes it relatively easy to analyze the same SWNT with different techniques, i.e., AFM and Raman spectroscopy.

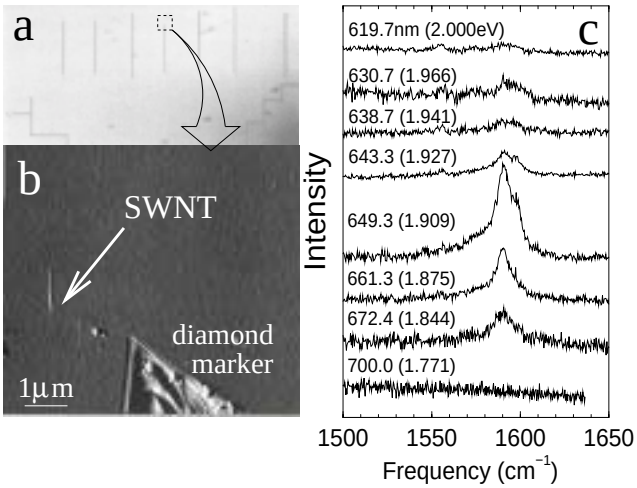

Figure 3. (a) An optical image of a Si/SiO_2 substrate with markers made by a diamond tip. (b) An AFM image of the edge of one marker, indicating the presence of one isolated SWNT. (c) G-band Raman spectra of the isolated SWNT shown in (b) for various laser excitation energies.

It is important to discuss the experimental limitation of the (n, m) assignment procedure, related to the energy ranges accessible by the experimental set up. Fig. 3(c) shows a resonant process at about $E_{\text{laser}} = 1.909\,\text{eV}$. The spectra in the RBM region do not show any Raman features, indicating that this resonance process occurs with scattered photons, and involves G-band phonons, so that a precise d_t determination cannot be performed using the ω_{RBM} characterization approach.[4] However, the inter-band electronic transition energy can still be evaluated approximately by $E_{ii} = E_{\text{laser}} - E_{\text{phonon}} = 1.91 - 0.20 = 1.71\,\text{eV}$. The RBM spectra should be observed using a laser at $E_{\text{laser}} = 1.71\,\text{eV}$, were such a laser line available.

The use of a tunable laser is important for the detailed characterization of one specific SWNT. However, one laser line can be used to select specific SWNTs. To build a SWNT device using only semiconducting SWNTs with a given E_{ii}, it is possible to select those tubes from a marked Si/SiO_2 substrate that are in resonance with a fixed laser line $E_{\text{laser}} \simeq E_{ii}$. Resonant metallic or semiconducting SWNTs can be differentiated according to their diameters (obtained from ω_{RBM}) [4] and from analysis of their characteristic spectral features.[5, 6, 7]

The advantage of Raman spectroscopy as a characterization tool is that the technique is non-destructive and relatively easy to perform. Raman setups are readily available and the experiment can be done under ambient temperature and pressure conditions. Due to the large density of states at the 1D van Hove singularities, Raman signal from one isolated SWNT is observed without using the surface enhanced Raman scattering (SERS) technique. Therefore, Raman spectroscopy is a very accurate and non-invasive spectroscopic technique for using light as a weakly interacting probe, and the resonant inter-band electronic transitions can be determined with high accuracy (about $\pm 3\,\text{meV}$).[10]

In summary, we show here how to characterize the structure of a SWNT that can be further used for other measurements. We show that it is possible to mark the surface of the Si/SiO_2 substrate for localization of the isolated SWNTs by using a diamond tip. By timing the growth procedure, a low density of SWNTs on the substrate can be obtained so that the SWNT localization by AFM is trivial. This procedure is easy and non-expensive, and might be adopted for research work. We also show that it is possible to characterize a SWNT by resonance Raman spectroscopy at the edge of an AFM tip. These results show that it is possible to make joint experiments on the same isolated SWNT. Future diameter characterization of one isolated SWNT at the edge of an AFM tip by using the Raman and TEM techniques would give us a definitive relation between ω_{RBM} and d_t, and the appropriate γ_0 value for the system.

The experimental work was performed at the micro-Raman laboratory, Department of Physics - Universidade Federal de Minas Gerais (UFMG), Brazil. We acknowledge the NSF/CNPq joint collaboration program that makes possible exchange trips between MIT and UFMG researchers (No. NSF INT 00-00408 and No. CNPq 910120/99-4). A. J. and A.G.S.F. acknowledge financial support from the Brazilian agency CNPq, under Profix (350039/2002-0) and DCR (301322/2001-5) contracts, respectively. The MIT authors acknowledge support under NSF Grants DMR 01-16042, INT 98-15744, and INT 00-00408. R.S. acknowledges a Grant-in-Aid (No. 13440091) from the Ministry of Education, Japan.

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