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The two peaks G′ band in carbon nanotubes

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In this work we discuss the nature of the extra peak that appears in the low frequency side the G′ band in the Raman spectra of single wall and double wall carbon nanotubes. This peak has been reported in many articles assigned as either the G′ band from small diameter nanotubes or the response for fulfilment of resonance conditions with incident and scattered light.

Here we show that this peak is present in the Raman spectra independently on the diameter distribution of the sample and disappears after heat treatment. We believe the lower frequency component of the two-peaks G′ band in carbon nanotubes is related to the presence of defects in the carbon nanotube structure.

1 Introduction The G′ band in the Raman spectra of sp^2 carbon materials is related to the iTO (in-plane transversal optical) branch in the phonon dispersion of these materials and it is observed around 2700 cm^{-1} [1, 2]. As a resonant process, the G′ band can be used to study the electronic and vibrational structure of these materials and the changes caused by defects or doping [3, 4]. A two-peaks G′ band structure has been observed by many groups, in SWNTs (single wall carbon nanotubes) [5, 6] and in DWNTs (double wall carbon nanotubes) [7, 8]. A. G. Souza Filho *et al.* [5] proposed that the two peaks appear because of the simultaneous resonance of the incident and scattered light with two different van Hove singularities in the SWNTs density of states. Cardenas and Gromov also proposed a model where the two peaks arise from the fact that the conditions of resonance with the incident and scattered light are being fulfilled [6]. Pfeiffer *el al.* [7] claimed that the peak of small frequencies is the G′ band of small diameter tubes inside DWNTs, implying that the G′ frequency should exhibit a stronger dependence on tube diameter (d_t) than the $1/d_t$ dependence proposed in Ref. [9]. Another work proposed the relation $\omega_{G'} \propto 1/d_t^2$ so that

the lower frequency peak fits the G′ position for the small diameter inner tubes of DWNTs [8]. Recent near-field Raman spectroscopy measurements, with a spatial resolution of 20nm, showed that the frequency of the G′ band downshifts at defect sites, i.e., at sites where the defect-induced D band is observed [4].

In this paper we show that the frequency of the G′ band follows the relation given by Ref. [9]:

$$\omega_{G'} = 2708.1 - \frac{35.4}{d_t}, \tag{1}$$

which is valid for the excitation laser energy $E_{laser} = 2.41$ eV in all diameter ranges. The second peak observed in frequency is indeed not related to the diameter distribution of the samples, but it is actually at lower defect-induced peak that disappears under heat treatment. Its diameter and E_{laser} dependencies are established here.

2 Experimental details The SWNTs used in this work were grown by arc discharge (AC-SWNTs) and chemical vapour deposition (CVD-SWNTs) methods. CVD-SWNTs

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were grown at 950 °C using a solution of ethanol with 1.25% in weight of ferrocene as a precursor, carried by a 1.2 l/min flux of argon during 30 min. The diameter range is from 0.8 nm to 1.9 nm. AC-SWNTs were grown at a 400 Torr He atmosphere and they have narrow diameter distribution range: from 1.2 nm to 1.5 nm. The diameter ranges were determined from the radial breathing mode (RBM) spectra and the relation $\omega_{RBM} = \frac{219}{d_t} + 15$ [10]. Resonance Raman spectroscopy measurements were performed with a Dilor XY triple-monochromator with an 80X objective and a Renishaw spectrometer with a 50X objective in a backscattering configuration. Both apparatus are equipped with CCD detectors. The excitation came from an ArKr laser with the following energies: 1.91, 2.18, 2.41 and 2.54 eV; and from a HeNe laser with 1.96 eV.

3 Results and discussion

3.1 Heat treatment analysis We have measured the AC-SWNT sample with 514.5 nm (2.41 eV) laser line using a laser power of 0.2 mW. The RBM and G′ features are shown in Fig. 1(a). The sample was then submitted to a 7 mW laser power during 10 s. The radial breathing mode (RBM) and G′ bands were measured again at 0.2mW and are shown in Fig. 1(b). The respective RBM spectra were superimposed to the G′ bands following the relation given by Eq. (1) and the RBM frequency relation with diameter $\omega_{RBM} = \frac{219}{d_t} + 15$ [10]. Figure 1(a) shows that the two-peaks feature is present in samples that have only large diameter tubes (1.2 nm $< d_t <$ 1.5 nm), the higher frequency G'_{hf} peak (*hf* for higher frequency) being consistent with Eq. (1). The lower frequency peak, which will be called G'_{lf} peak (*lf* for lower frequency), disappears after annealing the sample with high laser power, while no significant change in the diameter distribution is observed. The intensity of the D band (defect induced band, around 1300 cm^{-1}, not shown) decreases 33% after annealing showing that the number of defects decreased with heat treatment.

We have also measured CVD-SWNTs with low laser power and annealed the samples either by using the laser or by heating the sample in an inert atmosphere (0.5 l/min argon flow, during 30 min). Figure 2 shows the G′ bands of these samples before and after heat treatment at 400 °C and at 600 °C [4]. Like in Fig. 1, the RBM spectra are also superimposed to the G′ bands according to Eq. (1) and the ω_{RBM} *vs.* d_t relation of Ref. [10]. Before annealing, the intensity of the low frequency peak is comparable to the intensity of the G'_{hf} band. The G'_{hf} band was decomposed in two peaks at 2667 and 2686 cm^{-1} to follow the two largest intensities of the RBM spectra (see RBM superposition in Fig. 2). The G'_{lf} peak was also deconvoluted into two Lorentzians, for consistency. After annealing at 400 °C, the G'_{lf} peaks at 2644 and 2323 cm^{-1} decrease in intensity while no change is observed in the RBM, showing that these peaks are not related to the diameter distribution. The intensity of the D band (not shown) decreases 50% after annealing. At 600 °C, the more reactive small diameter

Figure 1 The RBM and G′ features of AC-SWNT samples before (a) and after (b) annealing with high laser power. $E_{laser} =$ 2.41 eV. The band at 2650 cm^{-1} disappears after annealing, while no significant change in the RBM distribution is observed. The corresponding RBM spectra was superimposed to the G′ according to Eq. (1) [9] and the ω_{RBM} *vs.* d_t relation from Ref. [10].

tubes are destroyed, and the RBM intensities of the small diameter tubes decrease. A change in the G'_{hf} band is observed in good agreement with the change in the diameter distribution.

Figure 2 The G′ features of CVD-SWNT samples before and after heat treatment at 400 °C and at 600 °C ($E_{laser} =$ 2.41 eV). The spectra were deconvoluted into four Lorentzians (dashed lines for G'_{hf} and dotted lines for G'_{lf}). The corresponding RBM spectra were superimposed to the G′ according to Eq. (1) [9] and the ω_{RBM} *vs.* d_t relation of reference [10].

Figures 1 and 2 show that the superposition of the RBM to the G′ spectra following the Eq. (1) and the ω_{RBM} *vs.* d_t relation of Ref. [10] matches the position of G'_{hf}, giving a good fitting to the measured data for both samples used in this work. In Figure 2, before annealing and after annealing at 400 °C, the main peak of the G'_{hf}, according to Eq. (1), comes from the smaller tubes. After annealing at 600 °C, the RBM intensities for smaller diameter

tubes decrease, and the main peak of the G'_{hf} shifts to the position of the larger tubes (2686 cm^{-1}). This behavior, together with the fact that the lower frequency peak G'_{lf} disappears with annealing at 400 °C with no change in the RBM, shows that the G'_{hf} band follows Eq. (1). Note that, even though the intensity of the RBM band of the small diameter tubes is smaller when compared to the larger diameter tubes in the non-annealed sample, these tubes contribute more to the intensity of the G' band. This happens because, for this excitation laser line, the smaller diameter tubes that are in resonance are metallic, and the intensity of the G' band increases with the metallicity of the nanotubes sample [11].

3.2 Excitation energy analysis To analyze the energy dispersion of the two-peaks G' band, Fig. 3(a) shows the G' band of the AC-SWNT sample measured with different laser excitation energies. The dashed Lorentzians are related to the pristine G'_{hf} and the dotted Lorentzians are the extra peaks G'_{lf} that disappear with annealing, as shown in Figs. 1 and 2. Figure 3(b) shows the frequency of the two G' peaks as a function of laser excitation energy for different samples, i.e. for the DWNTs of Ref. [7], the AC-SWNTs and CVD-SWNTs samples presented here. The higher and the lower frequency peaks for the different samples follow similar dispersions:

$$\omega_{G'_{hf}} = (99 \pm 3)E_{\text{laser}} + (2442 \pm 8) \qquad (2)$$

$$\omega_{G'_{lf}} = (70 \pm 6)E_{\text{laser}} + (2464 \pm 13) \qquad (3)$$

shown by the solid lines in Fig. 3(b), where E_{laser} is the excitation energy. This is an evidence that no matter the sample, the nature of the extra peak to the left is the same. As it disappears with annealing, it must be related to defect sites in the carbon nanotube structure.

Besides the E_{laser} dependence of $\omega_{G'_{lf}}$, Fig. 3(b) indicates that the frequency of the G'_{lf} peak depends slightly on SWNT diameter, like $\omega_{G'_{hf}}$, since $\omega_{G'_{lf}}$ is higher for the AC-SWNT sample (open stars in Fig. 3(b)). The AC-SWNT sample only contains large diameter tubes when compared with DWNTs [7] and CVD-SWNTs. Figure 4(a) shows the position of the G' peaks minus the energy dependency of Eq. (2) for different samples reported in the literature and for the samples studied here. The closed symbols stand for the G'_{hf} peak and the opened symbols stand for the G'_{lf} peak. We only used open symbols when the authors report the observation of two peaks. The two peaks have very distinct linear dependencies with the inverse of the diameter, the G'_{hf} peak following the solid line, which gives:

$$\omega_{G'_{hf}} - (99E_{\text{laser}} + 2442) = 23 - \frac{35.4}{d_t} \qquad (4)$$

Figure 3 (a) The G' Raman spectra of AC-SWNT samples for different excitation energies. (b) Dependence of the two peaks position on laser energy for the AC-SWNT, CVD-SWNT and for the DWNT sample of reference [7] (see legend). The dotted lines are guides to the eyes like in Ref. [7] and the solid lines are the dispersion relations given by Eqs. (2) and (3), obtained by fitting the AC-SWNT, CVD-SWNT and the DWNT data.

and corresponds to Eq. (1). In order to get the correct $1/d_t$ behavior of the G'_{lf} peak, Fig. 4(b) shows $\omega_{G'_{lf}}$ after subtracting the E_{laser} dependence as given by Eq. (3), and the solid line gives the linear relation:

$$\omega_{G'_{lf}} - (70E_{\text{laser}} + 2464) = 60 - \frac{53.2}{d_t} \qquad (5)$$

The G'_{lf} peak has then a stronger dependence with diameter than the G' band.

4 Conclusions The extra peak appearing at the lower frequency side of the pristine G' band disappears with annealing and it is related to a renormalization of the energies of the phonons and the electrons of the nanotubes at localized defect sites of the carbon lattice [4]. We have studied the two-peaks G' band of SWNTs with different diameter

Figure 4 (a) The G'_{hf} (filled symbols) and G'_{lf} (open symbols) frequencies dependence on $1/d_t$ for different samples reported in the literature (see legend) after subtracting the E_{laser} dependence given by Eq. (2). In the legend, isolated stands for isolated tubes in a substrate, dispersed stands for tubes dispersed in a solution. AC-SWNTs and CVD-SWNTs are the tubes measured here and discussed in Section 2. The solid line is given by Eq. (4), that is equivalent to Eq. (1) by a constant. (b) The $1/d_t$ dependence of the G'_{lf} peak position after correcting the E_{laser} dependence of Eq. (3). The solid line is given by Eq.(5).

distributions and we found that the dependence of the G′ peaks on E_{laser} and $1/d_t$ can be obtained by Eqs. (2)–(5), that rearranged give:

$$\omega_{G'_{hf}} = 99E_{laser} + 2465 - \frac{35.4}{d_t} \qquad (6)$$

$$\omega_{G'_{lf}} = 70E_{laser} + 2524 - \frac{53.2}{d_t}. \qquad (7)$$

It should be pointed out that, even though the G'_{lf} is related to the existence of defects, it is not due to a symmetry break in the carbon nanotube network. The rearrangement of the structure of the electrons and phonons at the defect site changes the phonon wavevector that fulfils the double resonance process [4]. The observation of a two-peaks G′ band is due to the information coming from defect sites (G'_{lf}) and non-defective tube segments (G'_{hf}).

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