Heating of single and double wall carbon nanotubes with UV photons

P. Puech, A. Bassil, E. Flahaut*, R. Bacsa, M. Monthioux, W. S. Bacsa

nMat group/ CEMES CNRS, 29 rue Jeanne Marvig, 31055 Toulouse, France, bacsa@cemes.fr
*LCMIE, CIRIMAT, UMR CNRS 5085, Université Paul Sabatier, 31062 Toulouse, France

ABSTRACT

By using photons with energies significantly above the fundamental band gap of the electronic states, one can use the energy released in the inelastic decay process to efficiently heat carbon nanotubes. We show that double wall carbon nanotubes nanotubes can be heated upto 1000C using UV irradiation (338nm) by measuring the phonon line broadening as a function of irradiation intensity. The thermal expansion in double wall carbon nanotubes is found to lead to structural constrains between the two tube walls as evidenced by the spectral shifts of the optical phonon band of the internal end external tube. Differences are also found in the coupling of the optical phonon to acoustic phonons. UV photon absorption has the advantage that tubes of a given orientation can be selectively heated on specified positions on the substrate making it a powerful tool for processing of carbon nanotubes on surfaces.

Keywords: Carbon nanotubes, UV irradiation, Raman spectroscopy

1 INTRODUCTION

Light absorption leads inevitably to electronic excitation and inelastic scattering, creating phonons and resulting in the increase of the lattice temperature. By using photons with energies significantly above the fundamental band gap of the electronic states, one can use the energy released in the inelastic decay process to efficiently heat carbon nanotubes. Carbon nanotube applications depend on processing techniques. [1, 2] Ultraviolet absorption is of interest to be able to heat CNTs efficiently through irradiation and induce tube interaction or tube transformation. Using ultraviolet micro Raman spectroscopy we can follow the phonon bands of CNTs as a function of laser irradiation and observe phonon line broadening and softening in CNTs due to heating. Comparing with phonon softening observed in graphite, we can estimate the temperature of the irradiated CNTs. Ultraviolet photon absorption has the effect that the excitation decay channels increase the phonon population which leads to efficient tube heating. Anisotropic photon absorption properties give the possibility to heat tubes oriented in a particular direction. Increasing the photon energy leads to considerably more effective heating of the tubes [3]. We study here the effect of ultraviolet irradiation on the phonon bands of SWNTs in agglomerated form, double wall CNTs (DWNTs). First reports on Raman spectroscopy of SWNTs using deep ultraviolet excitation (4.8eV, 257nm) [4] show significant modification of the Raman spectra excited in the visible spectral range with changes in the G band shape and reduced D band intensity and laser induced changes have been reported at relative low power values (> 0.125 W/cm2 at 257nm). No Raman D band are observed for glassy carbon when excited at 257nm and for double wall CNT (DWNT) excited at 325nm [5]. Radial breathing modes are more difficult to observe due to spectral cut off performance of spectrometers in the ultraviolet spectral region. When heating SWNTs up to 600K anharmonic effects in the G band line widths have been observed [9]. Thermal treatment of SWNTs [10] and DWNTs [11] in air have shown that oxidation of the CNTs can lead to a reduction of the D band intensity. The tube environment such as the substrate or liquid medium play an important role in laser induced heating [3, 12]. In this paper we use ultraviolet laser excitation to study the stability, phonon decay, interaction and transformation processes of single, double wall carbon nanotubes and peapods. We show that ultraviolet laser heating under vacuum can be used to obtain temperature upto 1300C using 500 mW of UV laser power (338nm).

2 EXPERIMENTAL

All spectra have been recorded using a Dilor UV spectrometer equipped with a CCD detector. We have used ultraviolet laser excitation (338nm, 3.66eV). The laser power used and as indicated in the figure, are reduced by a factor 20 when passing through the plasma line filter and the UV microscope. The laser spot size after the UV objective (×15) is estimated to be 5 μm. Typically, for 100 mW, the power density corresponds to 0.25mW/μm2. The samples were kept in vacuum (10^{-3} mbar using a molecular turbo pump). The tubes were either deposited in agglomerated form on a polished silicon wafer or on a synthetic diamond substrate. SWNT samples, produced by arc method have been purchased from NANOCARBLAB (diameter range: 1.2-1.4 nm). DWNTs were prepared by CCVD [13]. The DWNTs sample contains CNT's with radius ranging from 0.3-1.5 nm with 15% SWNTs, 80% DWNTs and 5% TWNTs (triple wall CNTs).

3 RESULTS

Figure 1 shows the Raman G band of SWNTs excited at 336nm (3.7eV) and increasing laser intensity upto 280mW. The excitation energy falls in the transition energy of E_{22}

electronic transition for several metallic tubes and the transition energy of E_{55} for several semiconducting tubes. For SWNTs the G band is split into a G- and G+ band. Figure 1 shows the spectral position of the G- and G+ band after fitting the spectra with two Lorentzian line profiles. The G- and G+ bands soften linearly with increasing laser power with the same rate up to 80 mW. Above 80mW the down shift is reduced when further increasing the laser power. The change of the temperature coefficient coincides with changes of the increased optical reflectivity of the sample. Oxidation by residual oxygen is a possible explanation for the change of the temperature coefficient. Using the exact G- spectral position at low laser intensity we can estimate the mean diameter to 1.63 in the case of metallic tubes and 1.27 nm (m-SWNTs) in the case of semiconducting tubes (s-SWNTs) when comparing with previous experimental studies of the G- spectral position as a function of diameter [14]. The signal corresponding to G- is attributed to semi-conducting tubes.

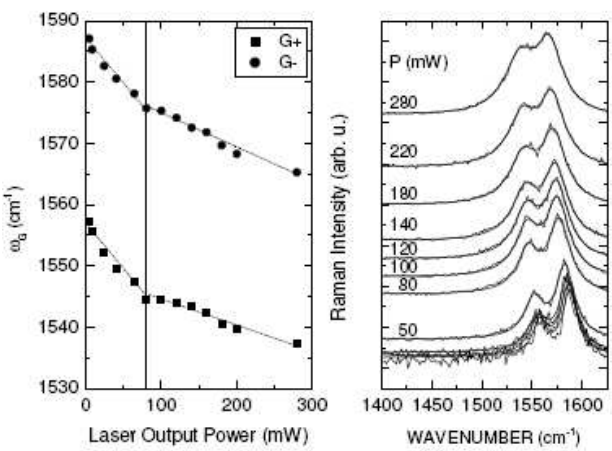

Fig. 1 Single wall carbon nanotube with a diameter of 1.4 nm heated using UV 336 nm line. The frequency of both G+ and G- modes are reported as a function of the used laser power after fitting the experimental spectra.

The deduced G- position corresponds to tubes with a too large diameter for m-SWNTs. Furthermore m-SWNTs have asymmetric G band line shapes with a shoulder. Using the G band shift with temperature for graphite and SWNTs (-0.022cm^{-1}/K) [15] we can estimate the absorption induced temperature. With 280mW of laser intensity the G+ band is shifted by 22 1/cm which corresponds to a change in temperature of 1000C.

We note that larger thermal coefficient for the G band have been reported (0.04cm^{-1}/K) [16] which results in a smaller change in temperature (500C). Recent studies on laser heating, however, suggest that the frequency shift with temperature of CNTs is the same as for graphite [3].

Fig. 2 shows changes of the G- and G+ band width as a function of band position. The half width at half maximum Γ (HWHM), has been extracted from fits using Lorentzian line shapes. The figure shows a clear difference of the line broadening for the two G bands with increasing temperature. The line broadening is by a factor of two larger for the G- band as compared to the G+ band, consistent what has been observed with heating SWNTs in the visible spectral range [9]. With increasing temperature anharmonic effects are more important and the spectral lines broaden and shift to lower energy. The optical phonon decays into two acoustic phonons of half the energy and opposite linear momentum. The HWHM of a phonon which decays into 2 acoustic phonons is given by [17]:

$$\Gamma(\omega_0, T) = \Gamma_0\left[1 + 2n\left(\frac{\omega_0}{2}, T\right)\right] + \Gamma_d$$

Between 300 to 1500K, the HWHM variation of phonon bands can be approximated by a linear function, considering the decay into 2 acoustic phonons: Γ(=1600 cm^{-1}) = $\Gamma_0 \times 0.00146$ T.

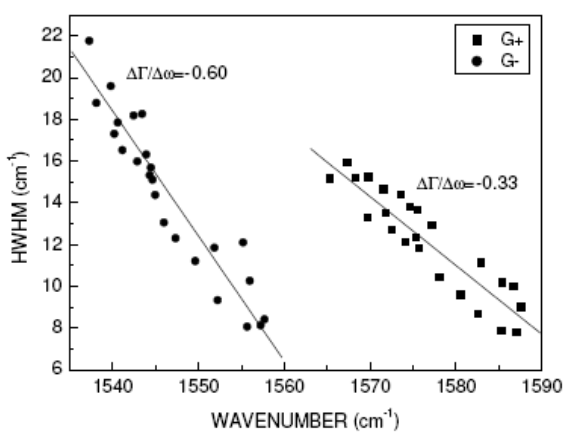

Fig. 2 Half Width at Half Maximum of G+ and G- bands as a function of band position from Fig 1.

Defects contribute to a constant line broadening constant in temperature (Γ_d). The line width of the G+ band observed here is consistent with line width variations observed by Jorio et al [9] in the 300K to 600K temperature range. If we consider a decay into 2 phonons, we obtain for the G+ mode and the data shown in fig. 1 Γ/Γ_0 = 9/7 = 1.3 leading to T = 880K and for G-, we have Γ/Γ_0 = 15/7 = 2.1 leading to T = 1430K. The different line broadening for the two bands evidence that the phonon decay process is different in axial and radial directions. The coupling between acoustic and optical phonons is influenced by the curvature. We notice that the variation of the intensity of the G- band is larger as compared to the G+ band when increasing the

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temperature. The origin of the G+ and G- band in metallic SWNTs has been recently attributed to a resonance between phonons and electron-hole pairs at the Fermi level [17]. Here the reported line widths at room temperature are narrower and correspond to s-SWNTs. From the temperature induced shifts of the G+ mode shown in Fig. 2, we can deduce the temperature coefficient $d\omega/d\Gamma$ ($d\omega/d\Gamma = d\omega/d\Gamma \times \Gamma \times 0.00146$). We obtain $0.028 cm^{-1}/K$ which is close to reported literature values of $-0.022 cm^{-1}/K$ [15] for the G+ band.

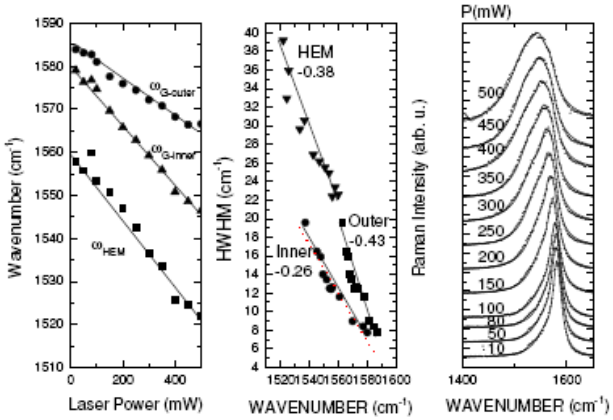

Fig. 3: G and HEM band position in function of laser power, HWHM in function of band position and Raman spectra of DWNTs recorded when excited with different laser power.

Fig. 3 shows the Raman spectra of DWCNT in function of laser power using the 336 nm laser excitation. The spectra have been fitted using a linear background, single Lorentzian for the HEM ($1560 cm^{-1}$) band and two Lorentzian line shapes with 4 adjustable parameters for the G band of DWNTs. The G band of DWNTs consist of two main contributions due to contributions of both internal and external tubes. This is evident when applying pressure; the G band splits for DWNTs [19, 20]. At zero pressure we use therefore two Lorentzian line shapes with equal intensity and line width which reduces the parameter space and improves the stability of the numerical fit. Taking the same line width for the two contributions is consistent with high pressure experiments and assumes that the phonon decay process is the same for internal and external tubes at room temperature. With increasing laser power the G band shifts linearly. The intrinsic HWHM of the G band is $7\text{-}8 cm^{-1}$ consistent with the line width of SWNTs. Interestingly the G band shift for the two walls is different with increasing temperature (Fig. 3). The linear expansion in radial direction is proportional to the tube diameter and implies that the distance between the two tube walls increases with temperature. The interaction between the tubes walls can then induce an effective pressure on the two tubes which in turn influences the deduced temperature coefficient. In Fig. 3, we show that the external tube with an average diameter of 2 nm has a temperature coefficient of -0.43 (variation of the broadening versus the frequency) which results for $d\omega/dT$ to $-0.023 cm^{-1}/K$. The internal tube with an average diameter of 1.4 nm has a slope of -0.22 which results for $d\omega/dT$ to $-0.045 cm^{-1}/K$. This indicates indirectly that the internal tubes are experiencing a negative pressure or lattice dilatation and shows that the wall interaction in DWNTs is significant as is also observed by their different G band position compared to SWNTs.

4 CONCLUSION

We have used UV irradiation to heat SWNTs, DWNTs and have observed Raman spectra free of black body radiation as a function of laser intensity. When the temperature increases with laser intensity, we observe a downshift and a broadening of the observed phonon bands. From the G band shift we estimate that UV irradiation can be used to heat CNTs up to 1000C. For SWNTs, we have observed the same decrease of the G+ and G- band but the broadening and the intensity variation of the G- band is larger than for the G+ band. This shows that the optical phonon decay process is different in axial and radial tube directions. We observe the same intrinsic line width (HWHM) of the G+ band in SWNTs, G bands for internal and external tubes in DWNTs and graphite ($7 cm^{-1}$). The splitting of the G band in DWCNT increases with increasing temperature which is attributed to changes in the distance and interaction between the tube walls.

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