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Eprints ID : 2538

To link to this article :
URL : http://dx.doi.org/10.1063/1.2199467

To cite this version : Bassil, Ayman and Puech, Pascal and Tubery, Lucien and Bacsa, Wolfgang and Flahaut, Emmanuel (2006) *Controlled laser heating of carbon nanotubes.* Applied Physics Letters, vol. 88 . pp. 173113-1-173113-3. ISSN 0003-6951

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Controlled laser heating of carbon nanotubes

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We investigate laser heating of double wall carbon nanotubes deposited on surfaces and immerged in liquids as a function of laser wavelength. Observing the Raman spectrum we find that laser heating of agglomerated double wall carbon nanotubes is six times larger at 488 nm than at 647 nm. The wavelength dependence of the Raman *G* band is linear in the visible spectral range. The frequency shift of the Raman *G* band obtained in methanol as a function of temperature is close to what is observed for graphite.   DOI: 10.1063/1.2199467

Carbon nanotubes (CNTs) have attracted much interest due to their unique diameter dependent properties and their large potential application range.[1–3] Single-walled carbon nanotubes (SWCNTs) are quasi-one-dimensional and made up of a rolled up graphene sheet which has semiconducting or metallic properties depending on the direction of tube axis with respect to the graphene lattice.[4,5] Double wall carbon nanotubes (DWCNTs) are the simplest form of multiwall carbon nanotubes (MWCNTs) with the specific property that the internal wall is well isolated from the environment which preserves its intrinsic properties. DWCNTs can be grown by the catalytic chemical vapor deposition[6] (CCVD) technique, by arc discharge, and by heating or irradiation of encapsulated fullerene molecules in SWCNTs.[7]

Raman spectroscopy is a noninvasive technique to characterize structural and electronic properties of CNTs. The Raman spectra of CNTs have three main characteristic bands:[8] the radial breathing mode (RBM) below 500 cm^{-1}, the *D* band (1350 cm^{-1}), and the *G* band (1590 cm^{-1}). The *G* band of agglomerated DWCNTs is composed of three components, one around 1550 cm^{-1} denoted as high energetic mode (HEM), and two at 1580 cm^{-1} which split with increasing hydrostatic pressure.[9,10]

The one-dimensional structure of CNTs leads to singularities in the electronic density of states (Van Hove singularities). This has the effect that the absorption of CNTs is particularly strong when the excitation wavelength corresponds to one of the transition energies between two corresponding singularities in the electronic states. Laser heating of CNT can be very efficient and has been suggested to be used for medical applications as a localized absorber.[11] Selective cell destruction is obtained through functionalized SWCNTs. SWCNTs have the advantage that lower laser power and shorter radiation times are needed compared to Au nanoshells. The electronic transitions of the internal tubes of DWCNTs are not or significantly less affected by functionalization. DWCNTs are as a result expected to reduce the needed laser power and radiation time to selectively destroy biological cells due to efficient thermalization at small scales. The heat dissipation created by the absorption depends on the tube environment, neighboring tubes, solvent, or substrate. We use DWCNTs with a large diameter distri-

bution in agglomerated form and study laser heating as a function of laser wavelength.

While some earlier studies reported high sensitivity of the Raman spectrum of SWCNTs on laser power[12] (5–50 mW/μm^2) other studies found no influence on the Raman spectrum at laser power (40 mW/μm^2).[13] We note that both samples contained catalytic particles. The discrepancy can be explained by the fact that the CNTs in the former case are not well connected to the substrate but they were connected through the catalytic metal particles in the latter case, which helps us to dissipate the absorbed energy. RBM band shape changes with increasing laser power have been observed for CNTs dispersed in suspensions and limits for laser induced changes of 0.3–3 mW/μm^2 have been reported.[14] When increasing the laser spot size laser heating is reduced while the Raman signal stays the same for uniformly distributed CNTs.[15] We explore laser heating of DWCNTs in methanol and determine the power needed to laser heat the tubes to the vaporization point of methanol for different laser wavelengths. The results are compared with what we find for highly oriented pyrolytic graphite (HOPG) in methanol.

The DWCNTs were prepared by the CCVD method.[6] High-resolution electron microscopy images showed the presence of individual and small bundles of DWCNTs with diameter ranging from 0.6 to 3 nm; the average diameters as determined by statistical averaging are 1.35 nm for the internal tubes and 2.05 nm for the external tubes. The tubes were single (15%), double (80%), or triple walled (5%). The Raman measurements were performed on an XY Dilor spectrometer using krypton and argon laser lines. A ×40 microscopic lens was used to focus the laser beam on the sample (spot size of about 2.5 μm). The output laser power is measured using a power meter (Coherent Inc.) after the microscope objective without including the effect of glass transmission and reflection.

Figure 1 shows typical spectra of DWCNT in the *G* band region. The *G* band of DWCNTs has contributions from the internal and the external wall. From the splitting of the *G* band with applied pressure due to the pressure gradient in multiwall tubes, we can extrapolate a *G* band of the internal and external walls at 1582 and at 1592 cm^{-1} at normal pressure.[9,10] In Fig. 1(a) we have fitted three Lorentzians and a linear background with six free parameters (we have fixed

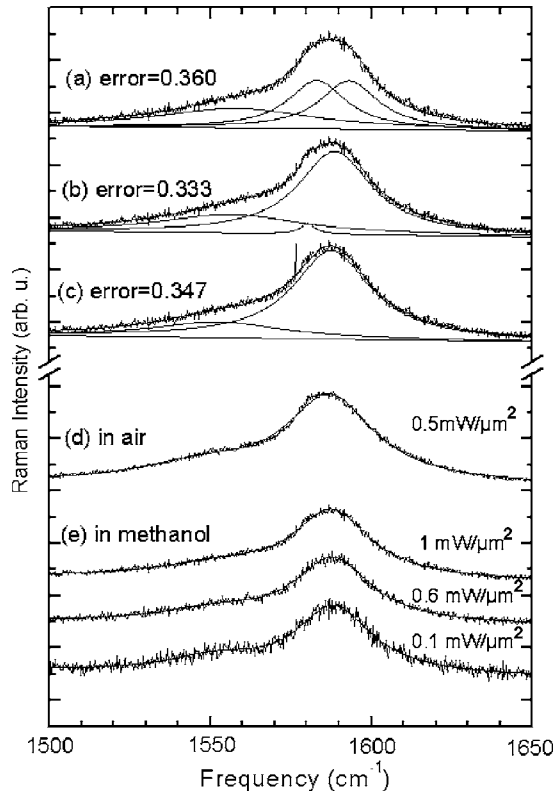[a]Electronic mail: ayman.bassil@lpst.ups-tlse.fr

FIG. 1. G band of DWCNTs at different power levels. Fit with (a) three Lorentzians and six free parameters, (b) three Lorentzians, and (c) two Lorentzians. (d) and (e) Spectra with fit using two free Lorentzians in air and in methanol at different power levels.

FIG. 2. G-band frequency of DWCNT in methanol as a function of temperature.

the splitting between the two peaks at 1582 and 1592 cm^{-1}, their line width, the relative intensity, and the frequency of the peak at 1550 cm^{-1}). Figure 1(b) shows the results when fitting with 11 fitting parameters and not keeping any parameter fixed. The lowest fitting error gives for the band at 1580 cm^{-1} a very narrow linewidth (2.8 cm^{-1}). Figure 1(c) shows the result by fitting the spectra to two bands located at 1550 and 1585 cm^{-1} and eight fitting parameters. Although the fitting in Fig. 1(b) has the lowest fitting error, the obtained parameters are not physically acceptable and the sensitivity of the result on the initial parameters is too high. The two other fitting procedures are more stable. We use in the following the fitting with two bands [Fig. 1(c)]. We notice that the power induced changes of the G band for tubes on surfaces are not the same on different locations due to the nonuniform thermal contact of the tubes with the substrate. Figure 1(d) shows the spectrum from DWCNTs on a silica surface. When increasing the laser power from 0.6 to 2 mW/μm^2 the G band shifts by 15 cm^{-1}. By immersing the agglomerated DWCNTs in methanol, the heat exchange is larger and more uniform. Using 647 nm laser excitation, the G band shifts in methanol from 1588.2 cm^{-1} at 0.1 mW/μm^2 to 1587.9 cm^{-1} at 0.6 mW/μm^2 and 1587.6 cm^{-1} at 1 mW/μm^2.

We determined the rate at which the G band shifts with temperature for agglomerated DWCNTs by changing the temperature between the melting point of methanol (−97.7 °C) and room temperature. Figure 2 shows the G band shift with temperature (−0.022 cm^{-1}/K). This G band shift is in agreement with literature values for SWCNTs (−0.019 to −0.029) (Refs. 16–18) and for DWCNTs.[19] Oss-

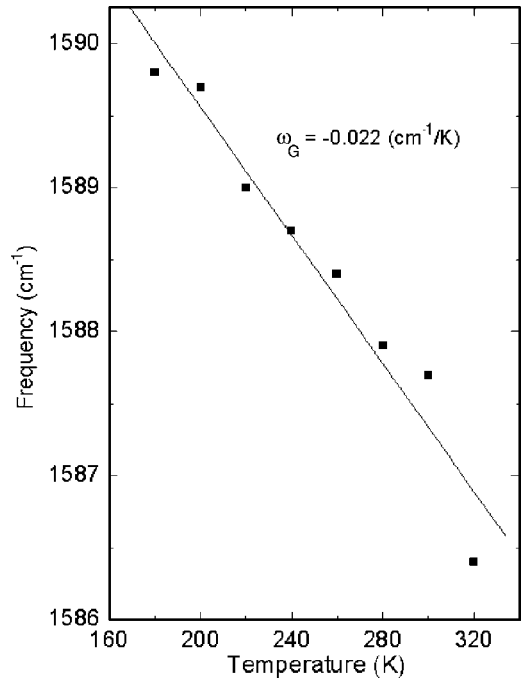wald *et al.* found this rate for DWCNTs when fitting two bands at −0.026 and −0.028 cm^{-1}/K.[15] Chiashi *et al.* found the same result for the G^+ peak of SWCNT at −0.028 cm^{-1}/K.[20] Our observed value for DWCNTs is slightly lower and is identical to what is found for graphite.[15,21] From the observed laser power induced shift of 0.6 cm^{-1} by increasing the laser power from 0.1 to 1 mW/μm^2 we can then deduce a temperature change of 20 °C. The average temperature of the illuminated part of the sample (40 °C) is lower than the evaporation temperature of methanol at normal pressure (65 °C). At larger power levels the methanol starts to vaporize around the agglomerate and this has the effect that the agglomerate drifts out of the focal point of the objective. We take the laser power at which the agglomerated tubes in methanol drift out of the focal point which is the observation limit, as a reference point. We find that this reference point is the same within an agglomerate size range of 5−20 μm. This implies that the heating remains local at the power levels used.

By changing the laser wavelength we notice that the power needed to reach this reference point is related to the wavelength. Table I lists the wavelength and the corresponding power needed to reach this reference point. For comparison we have also included the power level needed to cause a surface transformation on a reflecting HOPG. We notice that G band of HOPG (1582.3 cm^{-1}) does not shift with increas-

TABLE I. Laser power limit for DWCNTs immersed in methanol and laser power needed to transform HOPG for four different wavelengths.

Wavelength (nm)	Limit DWCNT (mW/μm^2)	Transformation HOPG (mW/μm^2)	Probe depth HOPG (nm)
647	0.9	>10	34
568	0.5	4	31
515	0.22	0.9	30
482	0.14	0.6	30

ing laser power, even when the beam transformed the surface. While the laser power can be increased up to 1 mW/μm^2 in the red spectral region without any irreversible transformation, it can only be increased up to 0.05 mW/μm^2 in the blue spectral region for DWCNTs on silica. We note that the values for CNTs on silica depend on the local thermal contact with the substrate.

While metallic and semiconducting tubes are expected to laser heat differently, no apparent differences are seen in the Raman spectra when a distribution of tubes with different diameters is observed. We attribute this to effective heat dissipation and averaging effects. We assume that the internal and external tubes are in thermal equilibrium since we excite with a continuous wave laser. Diameter selective absorption implies that the temperature might be different for internal and external tubes and a constant temperature gradient is formed. We do not see any temperature induced broadening within the temperature range accessible in our experiment with methanol. By taking the dielectric constant of graphite into account[22] we find that the penetration length changes only by 10% (Table I) when changing the wavelength from the red to the blue spectral range while the power needed to reach the critical point varies by a factor of 6. We find a similar large factor for the power needed to cause a surface transformation on a reflecting HOPG (Table I).

Laser heating occurs through the energy transfer from highly excited electrons to the lattice via electron-phonon scattering. A high concentration of excited electrons weakens in general the covalent bonds and this can induce structural transformations.[23] Chen et al. observed that the optical transmission in CNTs in ethanol at 532 and 1064 nm is reduced for smaller power levels than for carbon black in distilled water.[24] This has been attributed to stronger plasma excitations for carbon nanotubes. The optical absorption of CNT and graphite in the considered wavelength interval (640–480 nm) is similar and increases monotonously with decreasing wavelength.[25] Above 1 eV photoexcitation leads to the population of several higher excited states. The large diameter range leads finally to a uniform optical absorption as a function of wavelength despite of the one-dimensional density of state of the CNTs. The significantly larger laser heating with smaller wavelength can then be understood by the population of several higher lying excited states which multiplies the energy transfer to the lattice via electron phonon scattering.[26,27] Apart from the selective absorption and heating of DWCNTs the coupling to the surrounding tubes due to the tube anisotropy (antenna effect)[28] is expected to contribute in the absorption process.

We conclude that laser power induced changes in the Raman spectrum of DWCNTs are highly nonuniform for agglomerated DWCNTs on surfaces but not for agglomerated DWCNTs in methanol. When increasing the laser power for DWCNTs in methanol we use the laser power at which the DWCNTs drift out of the focal point as critical point. We find that the power needed to reach this critical point depends strongly on the used optical wavelength. The power induced G band shifts have been compared with temperature induced shifts and found to correspond closely to those observed in graphite. The wavelength dependent laser heating is attributed to the differences in the population of excited states.

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