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Ultraviolet photon absorption in single- and double-wall carbon nanotubes and peapods: Heating-induced phonon line broadening, wall coupling, and transformation

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Ultraviolet photon absorption has been used to heat single- and double-wall carbon nanotubes and peapods in vacuum. By increasing the laser intensity up to 500 mW, a downshift and a broadening of the optical phonons are observed corresponding to a temperature of 1000 °C. The UV Raman measurements are free of blackbody radiation. We find that the linewidth changes for the G_+ and G_- bands differ considerably in single-wall carbon nanotubes. This gives evidence that the phonon decay process is different in axial and radial tube directions. We observe the same intrinsic linewidths of graphite (highly oriented pyrolytic graphite) for the G band in single- and double-wall carbon nanotubes. With increasing temperature, the interaction between the walls is modified for double-wall carbon nanotubes. Ultraviolet photon induced transformations of peapods are found to be different on silica and diamond substrates.

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I. INTRODUCTION

Carbon nanotubes (CNTs) can be seen in applications ranging from composites to single tube field effect devices. CNT applications depend to a large extent on processing techniques.[1,2] Strong optical 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 intensity 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 excitation implies that the excitation occurs above the fundamental band gap of CNTs and this 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 single-wall CNTs (SWNTs) in agglomerated form, double-wall CNTs (DWNTs), and peapods. First reports on Raman spectroscopy of SWNTs using deep ultraviolet excitation (4.8 eV, 257 nm)[4] show significant modification of the Raman spectra as compared with Raman spectra excited in the visible spectral range. Changes are observed in the G band shape and reduced D band intensity. Laser induced changes have been reported at relatively low power values (>0.125 W/cm^2 at 257 nm). No Raman D band is observed for glassy carbon when excited at 257 nm and for DWNTs excited at 325 nm.[5] Radial breathing modes are more difficult to observe due to the spectral cutoff performance of spectrometers in the ultraviolet spectral region.

Peapods, SWNTs filled with C_{60}, can be transformed into DWNTs by annealing in vacuum,[6] leading to structural transitions between 1280 and 1450 °C.[7] It has also been reported that annealing of peapods in the 800–1200 °C temperature range leads to the formation of DWNTs.[8] Using high intensity infrared laser excitation (140–400 mW), peapods can also transform into DWNTs after a short irradiation time (10 s).[7] Both methods can be combined to transform peapods into DWNTs. The conditions for transformation by irradiation with photons in the ultraviolet spectral region and combined with thermal heating have been reported.[9] When heating SWNTs up to 600 K, anharmonic effects in the G band linewidths have been observed.[10] Thermal treatment of SWNTs[11] and DWNTs[12] in air has 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 plays an important role in laser induced heating.[3,13]

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 of 1000 °C using laser power up to 500 mW.

II. EXPERIMENT

All spectra have been recorded using a Dilor UV spectrometer equipped with a charge coupled device detector. We have used ultraviolet laser excitation at 336 nm (3.7 eV). The laser power used is as indicated in the figure, and is reduced by a factor of 20 when passing through the plasma line filter and the UV microscope. The laser spot size after passing through the UV objective (×15) is estimated to be 5 μm. Typically, for 100 mW, the power density corresponds to 0.25 mW/μm^2. The samples were kept in vacuum (10^{-3} mbar). The tubes were deposited either in agglomerated form, on a polished silicon wafer, or on a synthetic diamond substrate. SWNT samples, produced by arc method,

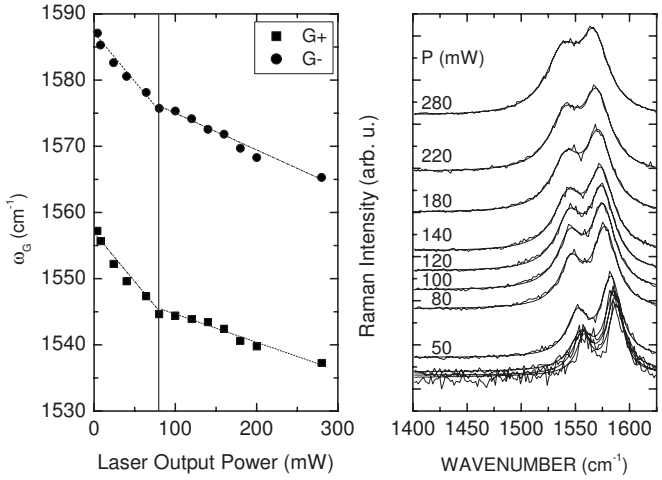

FIG. 1. Single-wall carbon nanotube with a mean diameter of 1.4 nm heated using UV 336 nm line. The frequencies of both G_+ and G_- modes are reported as a function of the used laser power after fitting the experimental spectra.

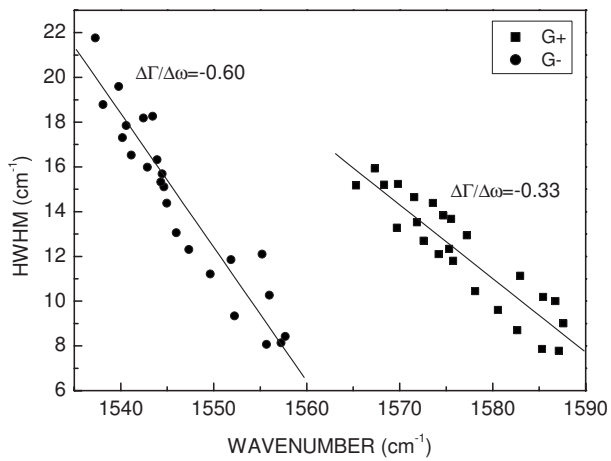

FIG. 2. Half-width at half maximum of the G_+ and G_- bands as a function of spectral band position from Fig. 1.

have been purchased from NANOCARBLAB (diameter range: 1.2–1.6 nm). DWNTs were prepared by the combustion chemical vapor deposition method.[14] High-resolution electron microscopy images show the presence of individual and small bundles of DWNTs with diameters ranging from 0.6 to 3 nm. The DWNT sample contains 15% SWNTs, 80% DWNTs, and 5% triple-wall CNTs. Peapods have been prepared using the SWNTs supplied by NANOCARBLAB and have been filled in our laboratory using sublimation of C_{60} along with SWNTs in a sealed ampoule at 500 °C.

III. DISCUSSION

Figure 1 shows the Raman G band of SWNTs excited at 336 nm (3.7 eV) and increasing laser intensity up to 280 mW. The excitation energy falls in the transition energy of E_{22}^{m} of several metallic tubes and the transition energy of E_{55}^{SC} of several semiconducting tubes. For SWNTs, the G band is split into the G_- and G_+ bands. G_+ corresponds to atomic displacements along the tube axis, while G_- corresponds to atomic displacement perpendicular to the tube axis. This attribution is consistent with *ab initio* calculations for semiconducting tubes.[15] Figure 1 shows the spectral position of the G_- and G_+ bands after fitting the spectra with two Lorentzian line profiles. The G_+ and G_- bands soften linearly with increasing laser power at the same rate up to a power level of 80 mW. Above 80 mW, the downshift is reduced when further increasing the laser power. The change of the temperature coefficient coincides with visible observed higher optical reflectivity of the sample. Oxidation of the tubes by residual oxygen and the formation of a more compact tube agglomeration is a possible explanation. Using the exact G_- spectral position at low laser intensity, we can estimate the mean diameter in the case of metallic tubes (1.63 nm) and semiconducting tubes (1.27 nm) when comparing with previous experimental studies of the G_- spectral position as a function of diameter.[16] The signal corresponding to G_- band is attributed to semiconducting tubes (s-SWNTs). We can estimate the temperature using the G band shift with temperature for graphite and SWNTs (-0.022 cm^{-1}/K).[17] With 280 mW of laser intensity, the G_+ band is shifted by 22 cm^{-1} which corresponds to a change in temperature of 1000 °C. We note that a larger thermal coefficient for the G band has been proposed (-0.04 cm^{-1}/K),[13] which results in a smaller change in temperature (500 °C), leading to some uncertainties. Recent studies on laser heating, however, suggest that the frequency shift with temperature of CNTs is the same as in graphite.[3]

Figure 2 shows changes of the G_- and G_+ band widths 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. We find that the line broadening is by a factor of 2 larger for the G_- band as compared to the G_+ band, consistent with what has been observed with heating SWNTs in the visible spectral range.[10] 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. Ecsedy and Klemens[18] estimate that four-phonon processes are more than 2 orders of magnitude less important than the three-phonon processes. Consequently, we neglect four-phonon processes in the following. The HWHM of an optical phonon which decays into two acoustic phonons is given by[19]

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

where n is the Bose-Einstein factor: $n(\omega,T)=\frac{1}{\exp\left(\frac{\hbar\omega}{k_BT}\right)-1}$. Between 300 and 1500 K, the HWHM variation of the phonon bands can be approximated by a linear function, considering the decay into two acoustic phonons: $\Delta\Gamma(\omega=1600\ \text{cm}^{-1})=\Gamma_0\times 0.001\,46\Delta T$. Defects contribute to an additional line broadening constant in temperature, which is not taken into

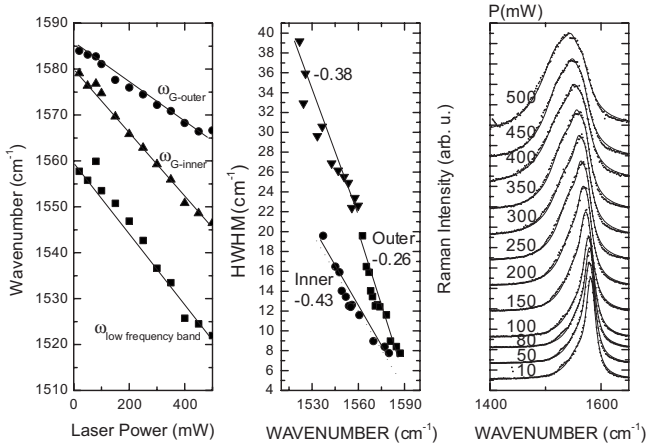

FIG. 3. G and low frequency band (1560 cm^{-1} at room temperature) positions as a function of laser power, HWHM as a function of spectral band position, and Raman spectra of DWNTs recorded as a function of laser power.

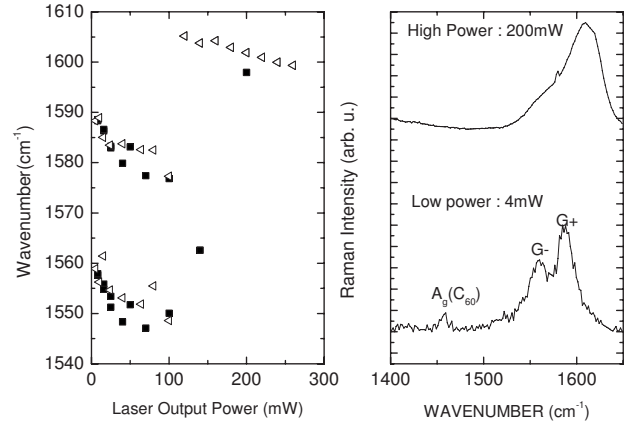

FIG. 4. Position of the G_+ and G_- bands of peapods on silicon (triangle) and diamond (square) substrates as a function of laser power and two Raman spectra of peapods at low and high laser power.

account here. The linewidth of the G_+ band observed here is consistent with linewidth variations observed by Jorio *et al.*[10] in the 300–600 K temperature range. If we consider a decay into two acoustic phonons, we obtain for the G_+ mode and the data shown in Fig. 2 $\Gamma_G/\Gamma_0=9/7=1.3$, leading to $\Delta T=880$ K, and for G_-, we have $\Gamma_G/\Gamma_0=15/7=2.1$, leading to $\Delta T=1430$ K. 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 clearly influenced by curvature. We notice that the variation of the intensity of the G_- band is larger as compared to that of the G_+ band when increasing the temperature. The origin of the G_+ and G_- bands in metallic SWNTs has been recently attributed to a resonance between phonons and electron-hole pairs at the Fermi level.[20] Here, the reported linewidths at room temperature are narrower and attributed to s-SWNTs. From the temperature induced shifts of the G_+ mode shown in Fig. 2, we can deduce the temperature coefficient $d\omega/dT$ ($d\omega/dT=d\omega/d\Gamma\times\Gamma\times 0.001\,46$). We obtain -0.028 cm^{-1}/K, which is close to the reported literature values of -0.022 cm^{-1}/K (Ref. 17) for the G_+ band.

Figure 3 shows the Raman spectra of DWNT as a function of laser power using the 336 nm laser excitation. The spectra have been fitted using a linear background, a single Lorentzian for the band located at 1560 cm^{-1}, and two Lorentzian line shapes with four adjustable parameters for the G band of DWNTs. The G band of DWNTs consists 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.[21,22] At zero pressure, we therefore use two Lorentzian line shapes with equal intensity and linewidth. This reduces the parameter space and leads to a stable numerical fit. Taking the same linewidth 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 bands of DWNTs shift linearly. The intrinsic HWHM of the G band is 7–8 cm^{-1} for the inner and outer tubes, consistent with the linewidth 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 tube walls can then induce an effective pressure on the two tubes which influences the deduced temperature coefficient. In Fig. 3, we show that the external tube with an average diameter of 2 nm has a broadening coefficient of $d\Gamma/d\omega=-0.43$, which results to a temperature coefficient of $d\omega/dT=-0.023$ cm^{-1}/K. The internal tube with an average diameter of 1.4 nm (Ref. 14) has a broadening coefficient of $d\Gamma/d\omega=-0.26$, which results to a temperature coefficient of $d\omega/dT=-0.045$ cm^{-1}/K. This indicates indirectly that the internal tubes are experiencing a negative pressure or lattice dilatation due to the increase of the tube separation. It also shows that the wall interaction in DWNTs is significant as evidenced by their different G band spectral position as compared to SWNTs. The temperature is estimated to reaches 1000 °C at the largest laser power (500 mW) used.

In the following, we examine the effect of ultraviolet laser excitation on the transformation of peapods. C_{60} has strong ultraviolet absorption bands[23] which can be used to induce transformations in peapods.[9] The energy corresponding to the used UV wavelength (<3.7 eV) is smaller than the dissociation energy of C_{60} (4.55 eV) and any transformation implies two photon excitation.[24] Figure 4(a) shows the position of the G band as a function of applied laser power and two spectra recorded at high and low laser power. The spectra recorded at low laser power show the tangential pinch mode of C_{60} at 1455 cm^{-1}.[25] The shift of 5 cm^{-1} compared to C_{60} in bulk form can be attributed to the interaction of C_{60} with the SWNT wall. Depending on the substrate, we observe a transformation at about 100–150 mW. From the G_+ band shift, we can estimate a temperature of the SWNT of 500 °C. When placing the peapods on a diamond substrate, the transformation takes place at higher laser power values, which we can be attributed to the different thermal conductivity of the substrate. The transformation has the effect that the G_+ and G_- bands disappear and instead a broader band at

higher band energy is observed. It has been reported that peapods are transformed into DWNTs when annealed to 1200 °C,[7,8] assisted by UV lamp,[9] and using IR-laser irradiation (at 1064 nm), the transformation occurs quasi-instantly.[7] The G band of the peapod at high laser power as observed here has a shoulder at the lower energy side and is different to the corresponding band observed for DWNTs. This indicates that the laser heating using UV did not result in a transformation of peapods into DWNTs. The G band of peapods at high laser power is similar to what is observed for the G band of glassy carbon. Continuous irradiation appears to have the effect to heat the sample too strongly and leads to disintegration of the fullerene cage.

IV. CONCLUSION

We have used UV irradiation to heat SWNTs, DWNTs, and peapods in vacuum and have observed Raman spectra free of blackbody radiation as a function of laser intensity. By increasing the laser intensity, we observe a downshift and a broadening of the optical phonon bands due to optical absorption and heating of the tubes. From the G band shift, we estimate that UV irradiation can be used to heat CNTs up to 1000 °C. For SWNTs, we have observed the same decrease of the G_+ and G_- bands but the broadening and the intensity variation of the G_- band are larger than those for the G_+ band. This shows that the optical phonon decay process is different in axial and radial tube direction. We observe the same intrinsic linewidth (HWHM) of the G_+ band in SWNTs and the G band for internal and external tubes in DWNTs and graphite (7 cm^{-1}). The splitting of the G band in DWNTs increases with increasing temperature, which is attributed to changes in the wall spacing and interaction between the tube walls. The observed transformation of peapods near 500 °C is attributed to the disintegration of C_{60}.

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