# THERMAL TRANSFER IN UV-IRRADIATED SWNTS AND PEAPODS AS REVEALED BY RAMAN SPECTROSCOPY

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## Abstract

We report here the results of UV irradiation experiments in vacuum on SWNTs and peapods, as followed by in-situ Raman spectroscopy and transmission electron microscopy. By increasing the laser power up to 300mW, photon absorption was found to generate local temperature increase up to 1000°C. UV micro-Raman was used to record spectra free of black body radiation. The changes in line width differ considerably for the SWNT-related G+ and G− bands respectively. This gives evidence that the phonon decay process in the nanotubes differs in axial with respect to radial directions. Meanwhile, a specific sensitivity to oxidation of the nanotubes from peapods was revealed, due to the fullerene-catalysed dissociation of molecular oxygen traces into active species. In addition, both silica and diamond substrates were used. The different thermal conductivity of the substrates has the effect of changing the laser power levels needed to induce structural transformations.

## Introduction

$C_{60}$ encapsulated in single-wall carbon nanotubes (SWNTs), thereby forming so-called peapods (Smith, 1998, 1999), have been shown able to coalesce into contained distorted capsules or SWNT upon electron irradiation and/or thermal treatment, thereby eventually forming DWNTs (Smith, 2000; Luzzi, 2000; Bandow, 2001; Sakurabayashi, 2003; Arrondo, 2005). Somewhat similar coalescence effects have been observed using Infra-Red and Ultra-Violet (UV) photon irradiation (Kramberger, 2005), as followed by Raman spectroscopy. However, related coalescence mechanisms are unclear. The work here presented aims to understand the effect of photon irradiation in the UV range (336 nm, 3.7 eV) in vacuum ($10^{-3}$ torr) on peapods as well as on pristine SWNTs (i.e., open but unfilled SWNTs) taken as reference. UV light was used to record spectra free of black body radiation. Both silica and diamond substrates were used. Revealing discrepancies with respect to previous observations on peapods interacting with electrons and/or infra-red photons (heat) was expected.

## UV-irradiation of pristine SWNTs

Figure 1 compares the evolution of the Raman spectra of pristine SWNTs with increasing power for both the diamond (left) and silica (right) substrates (both substrates mainly differ from the point of view of their thermal conductivity).
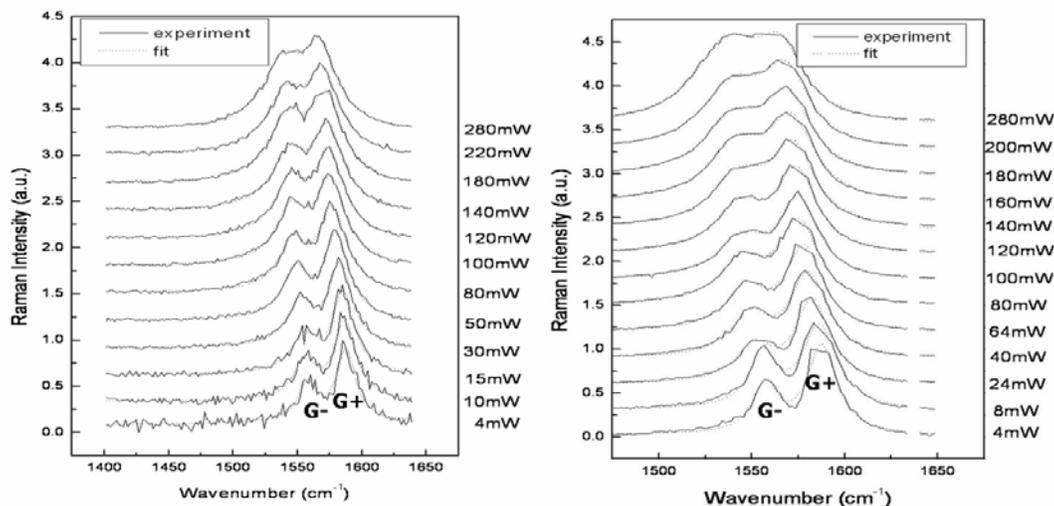


**Figure 1.** Raman spectra of empty SWNTs deposited on either a diamond (left) or silicon (right) substrate

Both shifting and broadening of the G+ and G- bands are observed for both substrates. The G+ band corresponds to all kind of SWNTs (metallic and semi-conductor), whereas the G- band corresponds to the semi-conductor SWNTs only. Both shifting and broadening phenomena reveal a temperature increase due to the enhancement of anharmonic effects which goes with the decay of one optical phonon into two acoustic phonons with half the initial energy (and opposed linear momentum). Both events can be plotted versus the laser power as Figure 2.
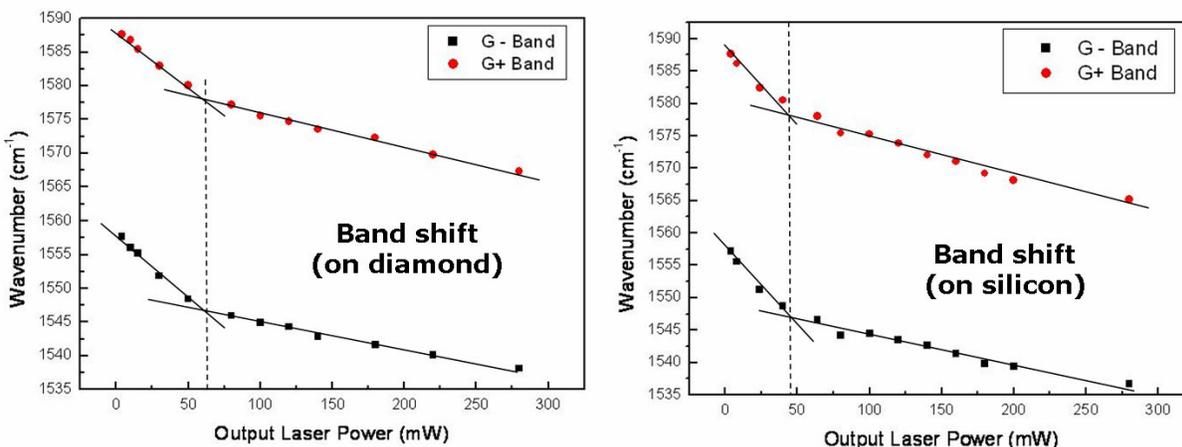


**Figure 2.** Plot of the G+ (top) and G- (bottom) band shift observed in Figure 1 (empty SWNTs) versus the output laser power when using a diamond (left) or a silicon (right) substrate.

From the downshift value of ~22 cm$^{-1}$ at 280 mW, a ~1000 K temperature increase can be estimated (Puech, submitted). On the other hand, the slope change of the G bands downshift reveals a structural change of SWNTs, possibly related to a mild oxidation effect by residual oxygen. The slope change occurs at lower power laser (< 50 mW) when a silicon substrate is used instead of diamond (~60 mW). Hence, diamond partly dissipates heat better than silicon, due to its higher thermal conductivity, so a higher laser power is needed to reach the temperature of structure change.

Band broadening of both G+ and G- bands may also be plotted versus the increasing band shift (Figure 3).
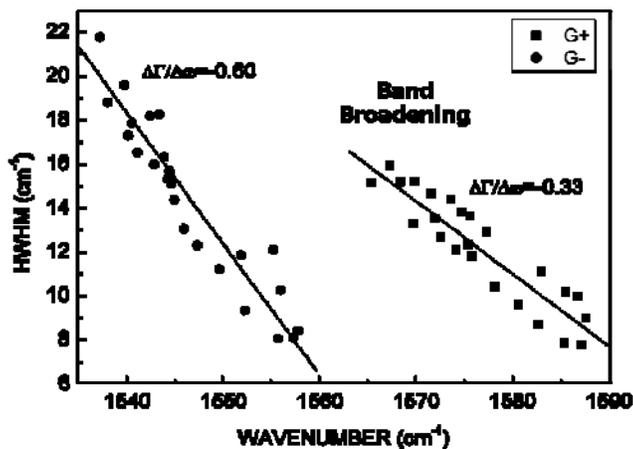


**Figure 3.** Plot of the G- (left) and G+ (right) band broadening versus the band shift observed in Figure 1 (empty SWNTs) output laser power when using a diamond substrate.

The temperature increase calculated from the broadening of the G+ band indicates ~880 K, which is considered to be consistent with that calculated from both G- and G+ band shift above (~1000 K). On the other hand, the broadening for the G- band is twice that of the G+ band, providing a calculated temperature increase of ~1470 K, which is out of range. Such a discrepancy indicates that the G- band broadening is not merely and only related to the temperature increase, but possibly indicates a difference in the phonon decay process between radial and axial directions.

# UV-irradiation of Peapods

The evolution of the Raman spectra for peapods with increasing laser power is given in Figure 4 for both the diamond and the silicon substrates.
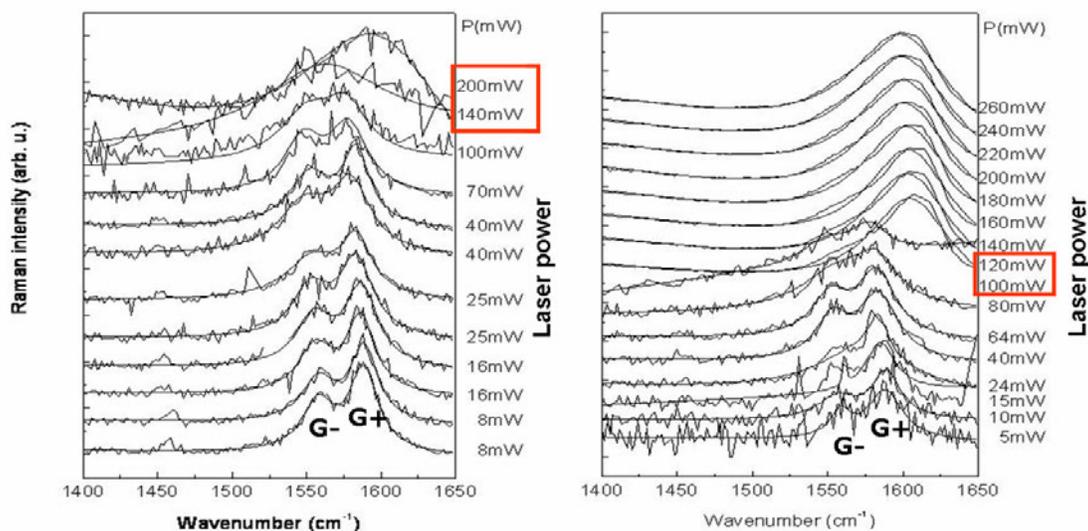


**Figure 4.** Raman spectra of peapods deposited on either a diamond (left) or silicon (right) substrate.

The broadening AND downshifting events of the G bands in peapods are hindered by a major structural change occurring at ~770 K (as calculated from the G+ band downshifting). Again, the temperature of major structural change is reached for a lower power laser (100-120 mW) when using a silicon substrate, as compared to a diamond substrate (140-200 mW), due to the higher thermal conductivity of the latter (see red squares in Figure 4, and Figure 5 below).
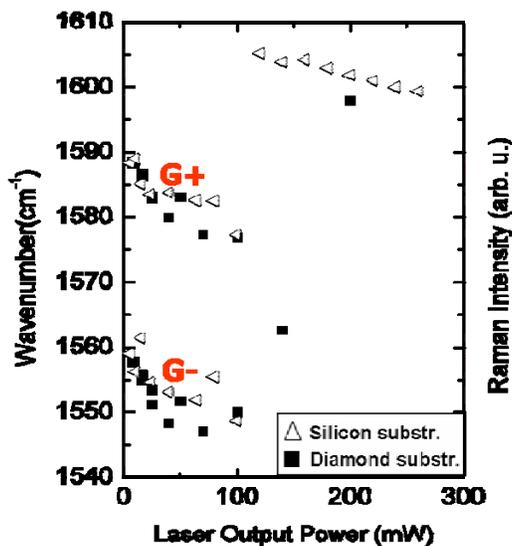


**Figure 5.** Plot of the G+ (top) and G- (bottom) band shift observed in Figure 4 (peapods) versus the output laser power when using a diamond substrate.

It is worth noting that the major structural change also goes with the disappearance of the contained $C_{60}$ fullerenes, as demonstrated by the vanishing of the tangential pinch mode at 1455 cm$^{-1}$ (Puech, submitted). The disappearance of the contained $C_{60}$ fullerenes is not due to the laser energy, for being to low (3.7 eV, versus 4.55 eV for the dissociation energy of $C_{60}$), nor to the fullerene coalescence (because the DWNT signatures which should result were not observed). It is therefore believed that a severe oxidation event of the peapods has occurred, due to the formation of highly reactive singlet oxygen species generated from $0_2$ traces by the photo-catalytic action of the irradiated fullerenes (Yamakoshi, 2003). The dramatic

effect of residual oxygen, yet with a partial pressure lower than $10^{-3}$ torr, can be explained by the fact that the active species (singlet oxygen) are generated right in the heart of the SWNTs due to the encapsulated (but accessible via the entry ports, which are still open) location of the fullerenes. This way every oxygen atom present in the medium may be used to oxidize the nanotube material.

## Conclusions

Irradiating SWNTs with UV induces energy absorption resulting in both a decay process of optical phonons and a temperature increase. The latter is revealed by the downshifting and broadening of the G bands, which can be used to calculate the local related temperature value in the spatial range of the Raman probe (i.e., the micrometer range). Temperatures as high as 1150-1300 K (and photo-emission) may be reached in SWNTs upon absorption of UV light (at 336 nm) for a laser power < 300 mW. On the other hand, carrying-out UV irradiation on peapods in presence of $O_2$ (even at low partial pressure) is fatal to the material for promoting severe oxidation processes catalyzed by the contained fullerenes.

It is therefore demonstrated that using UV-light while monitoring the shift and/or the broadening of the G+ band provides a tool for micro- and nano-engineering, able to anneal SWNT-based materials with micrometer range spatial resolution while insuring high heating dynamics, adjustable temperature, and reasonably accurate in-situ temperature reading. Possibly to phenomena related to phonon decay, following the temperature change via recording the G- band broadening is not reliable. Nano-engineering on fullerene-containing device components (e.g., peapod-to-DWNT transformation) could be achieved this way, provided oxygen–free atmosphere is used (with partial pressure better than $10^{-3}$ Torr).

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