Raman Spectra of Double-Wall Carbon Nanotubes under Extreme Uniaxial Stress

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ABSTRACT

We investigated the pressure dependence of the Raman frequencies and intensities of the D and G bands of double-wall carbon nanotubes under strong uniaxial conditions. Using moissanite anvils, we observed for the first time the evolution of the D band under extreme stress/pressure conditions. We find that the difference between D and G frequencies remains constant over the whole stress range. In addition, we observe that double-wall carbon nanotubes behave elastically up to the maximum uniaxial stress reached in our experiments, which is estimated to be about 12 GPa.

Resonant Raman spectroscopy (RRS) is widely used to characterize carbon nanotubes (CNTs) and other carbon-based materials. RRS combined with high-pressure devices have been also used to investigate the mechanical properties of CNTs, since application of pressure induces frequency shifts due to mechanical deformation. Most high-pressure studies are carried out in diamond anvil cell (DAC) devices, which, when appropriately gasketed with a pressurization medium, provide a hydrostatic environment to the sample, so most results are available under hydrostatic pressure conditions.[1–4] Recently, RRS has been also used to measure the uniaxial strain in CNTs by manipulation with the tip of an atomic force microscope (AFM),[5,6] allowing the probing of nanoscale uniaxial pressure effects. Comparison of these experiments points to a puzzling behavior of pressure/stress effects on the Raman spectra of CNTs. Thus, while positive frequency shifts are observed in hydrostatic DAC experiments, negative shifts are often observed in AFM experiments. The different behaviors found are a consequence of the different ways used to apply the pressure. In hydrostatic experiments both radial and axial compressions are induced on the sample. However, in the experiments of Cronin et al.,[5] radial compression and axial elongation were produced by the AFM tip. On the other hand, Yano et al.[6] claimed that in their experimental conditions, the stress was locally applied onto the CNTs from only the radial direction by the metallic tip. Furthermore, on the basis of Hertz's elastic contact theory, these authors concluded that the shearing stress along the axial direction was at least an order of magnitude smaller than that along the radial direction and estimated that the maximum stress exerted by the tip was close to 2 GPa.

In view of the above results, we have developed a novel procedure to study CNTs and other carbon-based materials under high uniaxial conditions in anvil devices. Using a moissanite anvil cell (MAC), we have investigated the dependences of the Raman frequencies and intensities of the D and G bands of double-wall carbon nanotubes (DWCNTs) subjected to strong uniaxial stress. We estimate that the maximum stress reached in our experiments is about 12 GPa, which extends by a factor of 6 the range achieved in AFM experiments. It must be emphasized that the use of moissanite anvils has allowed us to observe, for the first time, the evolution of the D band on a carbon-based material over a range of high pressures (or stresses). In fact, typical RRS experiments using diamond anvil cells are unsuited for studying pressure (or stress) effects on graphene, graphite,[7] or CNTs,[1–3,8] because the D band is masked by the strong first-order Raman signal from the diamond anvils, which appears around 1332 cm^{-1}. However, the recent introduction

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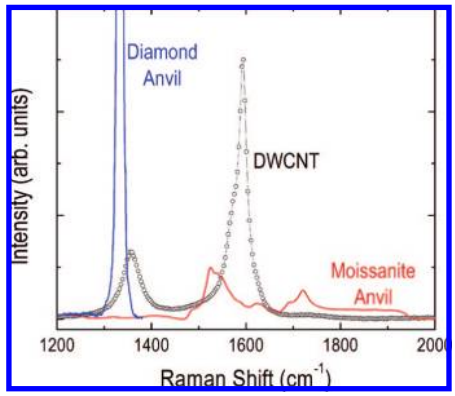

Figure 1. Raman spectra of DWCNTs measured at ambient conditions together with those measured in both diamond and moissanite anvils used in high-pressure experiments.

of synthetic moissanite anvils[9] allows for a wide range of studies under extreme pressure conditions. Figure 1 renders the overlap of the Raman spectra of diamond and moissanite anvils with that of one of our DWCNTs samples under ambient conditions. In the range of frequencies of interest, the Raman signatures of moissanite are due to second-order scattering, so their relative intensity is much lower than those exhibited by first-order features. This allows the study of the pressure behavior of both D and G bands with little background interference from the anvils. In any case, a separate Raman spectrum of the stressed anvils was measured to perform the corresponding background correction.

The DWCNTs used in our high-pressure RRS experiments were produced by catalytic chemical vapor deposition (CCVD) method by decomposition of a H_2-CH_4 mixture over an MgO-based catalyst.[10] The carbon content of the as-produced CCVD product was ~8 wt %, as determined by flash combustion elemental analysis. CNTs are then obtained by treating the required amount of CCVD product with a concentrated aqueous hydrochloric acid solution. After being washed with deionized water until neutrality, the CNTs are maintained in wet conditions in order to limit agglomeration. The carbon content of the CNTs sample was ~90 wt %, as obtained by elemental analysis. The CNTs obtained in those conditions contain ~80% DWCNTs, together with ~15% single-wall CNTs (SWCNTs) and ~5% triple-walled carbon nanotubes. The outer diameter of DWCNTs is typically ranging between 1 and 3 nm. Average diameters for DWCNTs are 2.1 ± 0.5 nm and 1.4 ± 0.5 nm for inner and outer tubes, respectively.

Our experimental setup is based on gem anvil cells coupled to a micro-Raman spectrometer.[11] An argon-ion laser (λ: 488 nm) was used for excitation. The typical diameter of the laser spots at the sample was about 15 μm. The scattered light is collected in near backscattering geometry using a 10× Mitutoyo long working distance objective coupled to a 10× Navitar zoom system and focused on to the slit of an ISA HR460 monochromator equipped with two holographic diffraction gratings of 600 and 2400 grooves/mm. A liquid-nitrogen-cooled CCD detector (ISA CCD3000) is used to record the spectra. Spatial filtering was performed through the optical path to optimize the signal from the DWCNTs

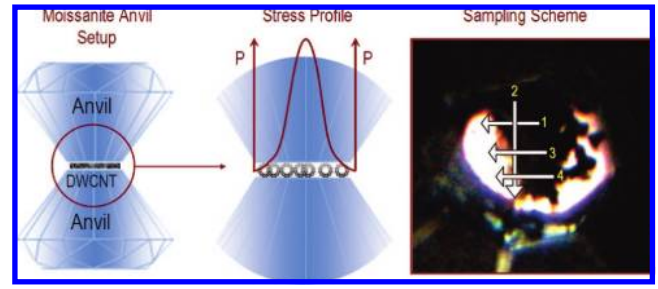

Figure 2. Scheme of the experimental setup, stress distribution inside the cell, and photograph of the sample under uniaxial conditions. The paths labeled in the photograph correspond to the four experimental runs described in the text.

sample. The spectra reported here were measured at ~4 cm^{-1} spectral resolution and always calibrated with a neon emission lamp.

In order to perform the uniaxial experiments, no gasket was included between the anvils and the sample, as is customary in typical hydrostatic experiments. It is well-known in high-pressure experiments using anvil devices that the anvils will surely break if they get into direct contact. Thus, in order to perform the uniaxial experiments in the MAC, it was necessary to customize the moissanite culet to prevent breakage of the anvils on the application of pressure. Moissanite stones with brilliant cut were obtained from Charles & Colvard Ltd. We first cut and polished to optical quality the culet of the anvils using a faceting machine. The tip of the anvils had an initial diameter of about 300 μm. The next step was to round off the culet edges with diamond paste. We therefore have a slightly curled surface on the tip of the anvils that will create an effective stress gradient when the two opposed anvils are compressed. As sketched in Figure 2, this allows us to perform several series of measurements as a function of stress without changing the load applied to the cell. In this way, we have performed four runs along the paths indicated in Figure 2.

A small quantity of DWCNTs bundles was spread on the tip of the lower anvil, and the cell was closed. Since we were interested in compressing the DWCNTs directly onto the anvils, no pressure marker (typically micrometer-sized ruby particles) or pressure media were added to the sample in order to avoid bridging between the anvils. This experimental procedure has the advantage that the Raman spectrum is free from contributions of foreign particles or the hydrostatic medium. This is quite an important advantage, since some authors have recently reported strong interference in the Raman spectra of CNTs from different pressure media under both normal[12] and high-pressure conditions.[13,14] However, this implies that the real stress acting on the sample needs to be estimated from the Raman shifts of the DWCNTs. For this purpose we have used the pressure slopes reported by Puech et al.[3] and the frequencies of the tangential bands measured in our experiments.

As the moissanite anvils approach each other, the DWCNTs bundles located in the vicinity of the tip of the anvils are compressed along the anvil cell axis (see Figure 2). As demonstrated by Bendiab et al.[15] from X-ray experiments,

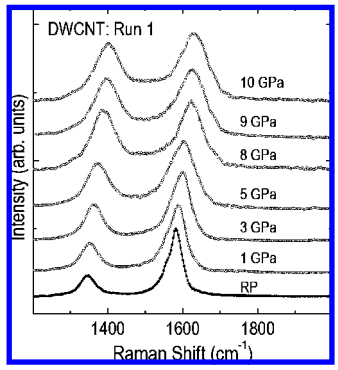

Figure 3. Raman spectra of DWCNTs at selected uniaxial stresses along the run 1 indicated in Figure 2. All the spectra have been corrected for the moissanite background. Spectra have been scaled and shifted for comparison. RP refers to room pressure conditions.

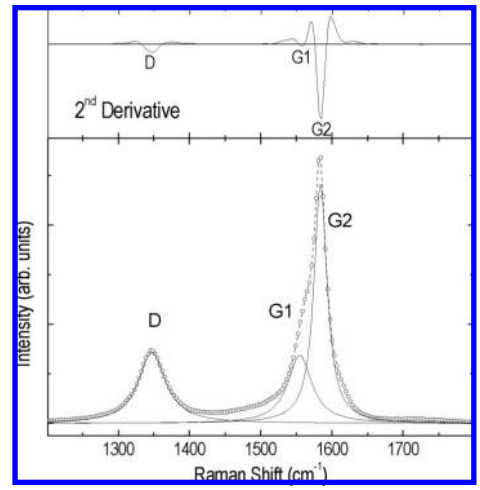

Figure 4. Band analysis for D and G modes of DWCNTs. The Raman spectrum shown in the figure was measured at 4 cm^{-1} resolution at room conditions.

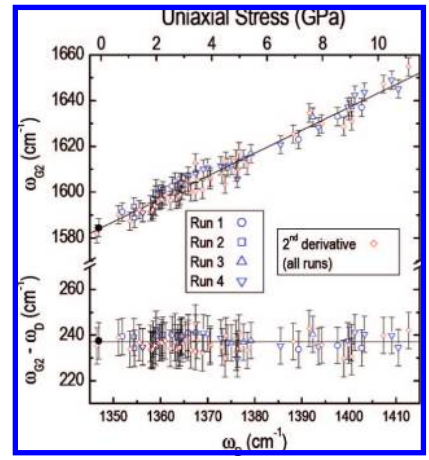

Figure 5. Raman frequencies of the D and G2 bands of DWCNTs. Different symbols stand for the runs indicated in the inset, corresponding to those indicated in Figure 2. Filled circles correspond to the initial measurement at room conditions. Diamonds represent the overall results obtained from the analysis of the second derivative of the Raman spectra. ω_D (cm^{-1}) = ω_G (cm^{-1}) + 237.

application of uniaxial pressures of the order of 1 GPa leads to an isotropic orientation of CNTs bundles within a plane perpendicular to the compression axis. Very recently, Kumar and Cronin[16] confirmed that the main effect of moderate strains is to debundle the CTNs, so only a small fraction of the applied strain is transferred to individual nanotubes within the bundle at low loads. These observations are confirmed in our measurements, as the Raman spectrum remains essentially unchanged in the corresponding pressure range (see Figure 3). This indicates that the compression of the DWCNTs is only effective above ~1 GPa in the initial run, being the compression applied along the radial direction of the CNTs. We do believe that this experimental procedure is the most suitable to provide truly uniaxial conditions on the CNTs, in contrast to AFM experiments, so our results can be directly compared with theoretical calculations.[17]

All the spectra have been analyzed as follows. We first split each Raman spectrum into three Lorentzian functions leaving all the parameters, frequencies, bandwidths, and areas, as adjustable. On a second step, we obtained the second derivative of all the spectra in order to locate the center of the three main bands, namely, D, G1, and G2. We follow the notation introduced by Puech et al.[3] for the tangential bands. An example of the spectral analysis of DWCNTs at room pressure is presented in Figure 4. We subsequently split each spectrum into three Lorentzian functions centered at the frequencies obtained from the analysis of the second derivative of the spectrum; such numerical procedure improves the reliability in the analysis of the relative intensities described below.

An example of the Raman spectra measured along the paths indicated in Figure 2 is shown in Figure 3 at selected pressures. A steady increase of the relative intensity of the D band is clearly observed. It appears that the (D/G) intensity ratio starts to collapse above 5−6 GPa. The overall results for the D and G2 frequencies are analyzed in Figure 5. Both band profile and second derivative analyses yielded comparable results, and both indicate that uniaxial compression has a negligible effect on the frequency difference between D and G2 bands over the whole pressure range. The difference between D and G2 frequencies remains constant in about 237 ± 4 cm^{-1}. This is quite an interesting result, since it indicates that both frequencies belong to the same phonon branch, a conclusion that might have important impact in solving the assignment of the D band.[18,19]

Finally, changes in both Raman shifts and relative intensities were confirmed to be reversible when the load was released from the DWCNTs samples. Furthermore, the original (D/G) intensity ratio was also almost restored. Interestingly, the Raman spectra of the uncompressed DWCNTs resemble the intensity ratio and frequencies of those measured around 1 GPa, which confirms that the CNTs remain unbundled once the uniaxial load has been released. In addition, this demonstrates that the deformation of DWCNTs was elastic up to uniaxial stresses exceeding 10 GPa and confirms[20] that plastic deformation is not achieved even at these extreme conditions. This information is essential for understanding both the fundamental physics of DWCNTs and also their potential technological applications.

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