

Structural transitions in double-walled carbon nanotubes at high pressure

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Abstract. We report on our study of electrical resistance of double-walled carbon nanotubes (DWCNTs) at pressure up to 30 GPa. High pressure has been generated in the diamond anvil cell with conductive synthetic diamonds. We detect a decrease in DWCNTs resistance with increasing pressure and correlate the results with the corresponding structural transformations. Analysis of the DWNTs Raman spectra confirms the irreversible structural changes.

1. Introduction

Since its opening and until now, carbon nanotubes are still the object of numerous experimental and theoretical studies, and due to its unique mechanical, thermal and electrical properties are regarded as highly interesting for the future of materials technology.

Carbon nanotubes are rolled up sheets of graphene where the chiral vectors (n, m) describe their configuration based on the depending on chirality (or nanotubes diameter). Single walled carbon nanotubes at pressures undergo a structural phase transitions corresponding to distortion of the nanotube cross-section from circular to oval and flattened. Pressure P_c at which the collapse of SWNTs takes place is inversely proportional to the cube of the diameter of the nanotube [1, 2].

In DWCNTs outer tube protects the inner tube against chemical and mechanical influences, while the inner tube is a mechanical support for the outer. Thus, DWNTs are more sustainable to mechanical stress, than SWNTs, or SWNTs filled with fullerenes [3, 4]. Double-walled carbon nanotubes at high pressures show a higher structural stability than single-walled carbon nanotubes and demonstrate a series of structural transitions, similar to those observed in single-walled nanotubes.

It was considered for a long time that the deformation of the DWCNTs takes place continuously without any transitions. However, the results of recent studies [5, 6] reveal the two-stage distortion of cross section of double-walled nanotubes, which is associated with the sequential destruction of the first external and then internal tube. Methods molecular dynamics simulation were found the structural transitions for carbon nanotubes under high pressure, but the nature of those transitions still remains controversial [6, 7].

In the present work, we have investigated the resistance of double-walled carbon nanotubes at high pressures with the aim of studying the mechanism of destruction of the double-walled carbon nanotubes. Structural changes of DWCNTs properties under pressure should be accompanied



by the changes of the electronic properties, and thus, resistance measurements on DWCNTs under high pressure can be a complementary tool in detection such transitions.

Raman spectroscopy is a powerful tool in characterizing carbon nanotubes. Appearance of the radial breathing mode (RBM) in the low frequency range ($100\text{--}400\text{ cm}^{-1}$) is an evidence of intact nanotubes while the D-band ($\sim 1350\text{ cm}^{-1}$) over G-band ($\sim 1590\text{ cm}^{-1}$) intensity ratio ID/IG is a measurement of the amount of structural defects on the side walls of the tubes [8].

2. Experiment

Source sample of DWCNT was obtained by the method of chemical vapor deposition. The diameter of tubes was evaluated using a transmission electron microscope and is in the range of $4 \pm 1\text{ nm}$.

High pressure was generated in a diamond anvil cell (DAC) with electrically conductive anvils of the “rounded cone-plane” type made of synthetic diamonds [9]. Electrical resistance of DAC does not depend on pressure and is about 15 Ohm. The bundled DWCNTs powder material was placed on the plane anvil at ambient conditions, then, the cell was closed and load applied. In our experiment we use a rounded cone (top anvil) with a radius of about 1 cm. The diameter of the contact spot is about $200\text{ }\mu\text{m}$ and the sample thickness under pressure is close to $10\text{ }\mu\text{m}$. The pressure is estimated through calibration of the system where applied load is related to known resistance anomalies at phase transitions in different materials [9]. The error of the estimation depends on the mechanical properties of the compressed material and does not exceed 10% at pressure up to 30 GPa.

Resistance of powdered DWCNTs was measured using a multifunction device Agilent 34970A. For the characterization of DWCNTs sample before and after exposure to high pressure, we used the laser-induced Raman spectroscopy. There were investigated different resonance modes of the carbon nanotubes: radial breathing mode (RBM), D- and G-bands. The equipment consists of an Alpha 300 AR+ Raman setup, with an excitation a He-Ne (632 nm) laser. Spectra were collected in back scattering geometry with a spectral resolution of 2.3^{-1} . A 100x objective with a numeric aperture of 0.75 was used for focusing and laser power was 37 mW.

3. Results and Discussion

The resistance measurements of the DWCNTs at high pressure in the DAC (figure 1) reveal that sample resistance decreases with pressure. The resistance drops sharply at pressure about 2 GPa, and then, with a further increasing in pressure the decrease of resistance is observed. At pressures about 21 GPa and 24 GPa the features on the curve $R(p)$ take place, and the rate of resistance changing with a pressure is different in the intervals 21–24 GPa and 24–30 GPa.

A sharp drop of resistance at pressure about 2 GPa, may be associated with the transition of the cross section of a nanotube from a cylindrical to an elliptical shape. Subsequent change in the slope of $R(p)$ curve at the interval 2–21 GPa, can be connected with the remaining of elliptical cross-section shape in this pressure area. The drop in resistance at pressure about 21 GPa is probably due to transition from an elliptical cross-sectional shape to flattened. The feature of $R(p)$ curve at 24 GPa could be associated with destruction of the outer nanotube in DWCNTs structure.

Raman spectra of DWCNTs (figure 2) contain three groups of lines: RBM, D, and G. RBM is low frequency mode, it is associated with the radial vibrations of carbon atoms in the wall of the nanotubes.

The peaks in range of frequencies $100\text{--}400\text{ cm}^{-1}$ characterize the presence of nanotubes in the sample. In the case of double-walled nanotubes at low frequencies, there are two peaks: right, more intense, is responsible for the inner tube, and the left peak—for the external tube. The spectrum of DWCNTs sample at pressure 30 GPa consists only one peak near 220 cm^{-1} , corresponding to vibrations of inner tube. The absence of the peak corresponding to vibrations of

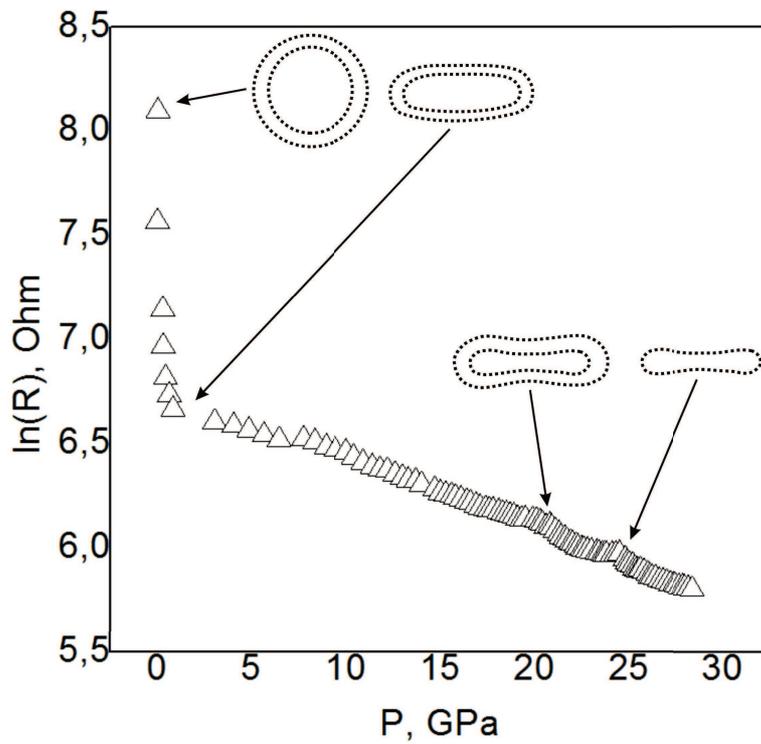


Figure 1. Pressure dependence of the electrical resistance of DWCNTs.

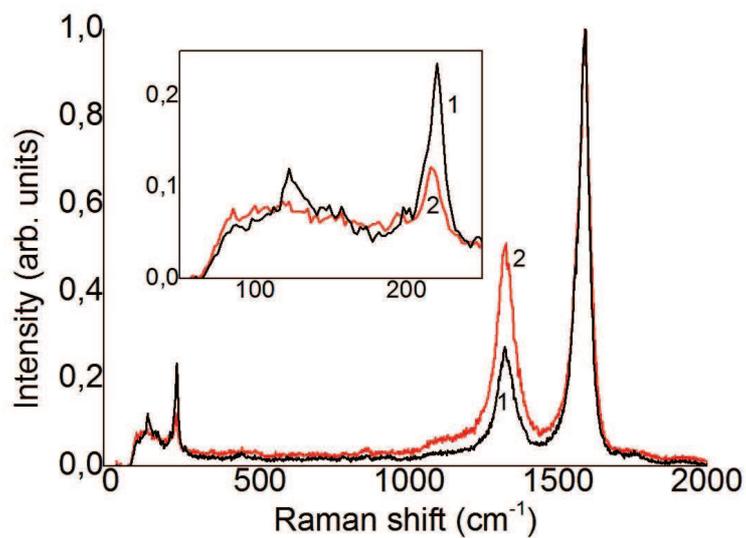


Figure 2. Raman spectra of the source DWCNTs at ambient pressure (line 1) and sample after exposure to pressure 30 GPa (line 2). Insert indicates RBM-mode.

outer nanotubes (122 cm^{-1}), may be attributable to their destruction. G-band has the greatest intensity, and is located in the region $1500\text{--}1600\text{ cm}^{-1}$; vibrational modes of this group are associated with longitudinal and transverse vibrations of the atoms in the graphene plane (in the wall of the nanotubes). D-band lies in the frequency range $1250\text{--}1450\text{ cm}^{-1}$ and is present on all of the Raman spectra of carbon materials. The intensity of the D-peak characterizes the structure defects, that is, the degree of disturbance of the symmetry of a perfect graphene layer with sp^2 carbon atoms.

The intensity ratio D/G peak characterizes the correlation between the amount of disordered and ordered atoms in the structure of the nanotubes. For source sample and sample after exposure the high pressure, there were obtained the following values of the ratio D/G: 0.27 and 0.5 respectively. Almost a twofold increase of the D-peak reveals the significant increase in the number of defects in the sample after pressure treatment. This ratio is also used to determine the purity of samples of carbon nanotubes obtained by synthesis [8].

4. Conclusion

We observed a strong dependence of the resistance of double-walled carbon nanotubes from their structural state, which varies with pressure, similarly as it was in the case of single-walled nanotubes [2]. Features found on the baric dependences of resistance of about 2 and 21 GPa correspond to structural transitions associated with changes in the cross-section of the nanotube. The drop in resistance of about 24 GPa, probably due to the destruction of the outer nanotube. The absence of the RBM peak corresponding to the external vibrations of nanotubes, may also be evidence of their destruction.

Acknowledgments

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