A Raman Study of Potassium-Doped Double-wall Carbon Nanotubes

H. Rauf[1], T. Pichler[1], F. Simon[2], H. Kuzmany[2]

[1]*Leibniz Institute for Solid State and Materials Research Dresden, P.O. Box 270016, D-01171 Dresden, Germany*
[2]*Institut für Materialphysik, Universität Wien, Strudlhofgasse 4, A-1090 Wien, Austria*

Abstract. We report on studies of the n-type doping dependence of the Raman response of double-wall carbon nanotubes (DWCNT). The G-line is found to be shifting upon doping. The direction of the shift depends on if the exciting laser light is in resonance with mainly inner or outer tubes. The RBM response upon doping shows that a charge transfer from the dopant happens predominantly to the outer tubes at low doping. Charge transfer to the inner tubes occurs at higher doping levels. Charge transfer to the inner component is also shown to be starting earlier to the inner tube in DWCNT than to C_{60} in peapods.

INTRODUCTION

Double-wall carbon nanotubes (DWCNT) are a new member in the family of well-ordered carbon structures[1,2]. Due to their formation process from C_{60}-peapods as precursor in the clean interior of SWCNTs, the inner tubes are highly defect-free[3]. As it has been done extensively with other nanostructures [4,5], their electronic structure can be modified in a controlled way by doping with either electron donators or acceptors.

Resonant Raman spectroscopy is a powerful tool to monitor the electronic properties [3] and their changes due to the interaction between transitions in the electronic density of states and the vibrational modes. The intensity of the Raman response is increased dramatically if the excitation energy corresponds to a transition between van Hove singularities of the nanotube.

We present a study on the potassium intercalation (n-type doping) of these DWCNT investigated by Raman spectroscopy. We examine the effect of doping on the position of the G-line main component which is also influenced by the used excitation energy. Then, we investigate the differences in charge transfer to the outer and to the inner tube and compare the outcomes to known results on peapods.

EXPERIMENTAL

All Raman spectra were recorded at 25 K under high vacuum conditions with a Dilor triple monochromator, using different laser lines extending from 1.8 eV to 2.5 eV in 180° backscattering geometry. The response of the spectrometer was calibrated

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using gas discharge lamps with well known line positions. The nanotubes used as a base material for the production of the peapods have a mean diameter of 1.5 nm and were prepared by arc-discharge, purified and filtrated into mats of bucky-paper before being filled with C_{60} as described previously [6]. Subsequent annealing in order to form DWCNTs was performed at 1250 ^{o}C in dynamic vacuum.

The intercalation was performed *in situ* in a purpose built cryostat by exposing the tube material to potassium vapor in front of the spectrometer at a sample temperature of 500 K. After the exposure, an additional equilibration of at least 30 min was performed in order to increase the homogeneity of the sample. Additionally, samples of pristine nanotubes and peapods were intercalated and measured simultaneously for comparison and estimation of the intercalation degree.

RESULTS AND DISCUSSION

Figure 1a. shows the G-line of pristine and doped DWCNT for exciting laser wavelengths of 488 nm and 568 nm respectively. An excitation with a laser wavelength of 488 nm leads to a Raman resonance with the E_s^{33} transition of the outer tubes, while 568 nm laser light is in resonance with the E_s^{22} transition of the inner tubes [7]. Accordingly, we associate the G-line main components to the outer tubes for the former and to the inner tubes for the latter case. Common for both excitation energies is the loss of Raman intensity in the doped samples (upscaled by a factor of five in the figure). This corresponds to a filling of the conduction band at least up to the corresponding van-Hove singularity in the electronic density of states due to a charge transfer from the potassium and consequently a loss of the Raman resonance.

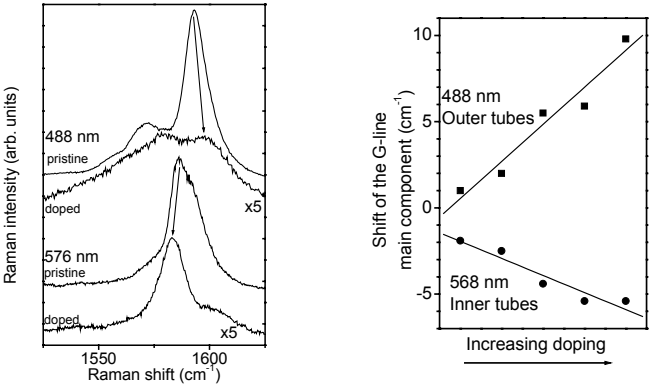

FIGURE 1. a) Raman spectra of pristine and doped DWCNT for laser wavelengths of 488 nm and 576 nm respectively. The shift is indicated by the arrows. b) Doping dependence of the G-line main component position for 488 nm and 576 nm laser wavelength and multiple intercalation steps.

Additionally, a shift of the G-line main component, indicated by the arrows in Figure 1a, can be observed. This shift is depicted in Figure 1b for multiple

intermediate doping levels and both excitation energies. For excitation with 488 nm wavelength, the G-line, which we assign in this case to the outer tubes, shifts steadily to higher Raman frequencies with increasing doping. At the highest doping level, the shift adds up to 10 cm^{-1}. This upshift is in reasonable agreement with recent results [8] obtained with a similar excitation energy and p-type doping. Peapods also exhibit this upshift upon K-doping [5] while SWCNT are reported to show a downshift of the G-line main component with only a slight initial upshift at low doping [9]. In contrast to this, when excited with the 568 nm laser, the G-line main component, associated with mainly the inner tubes, exhibits a downshift, although with 5 cm^{-1} smaller than the upshift seen before.

In Figure 2, the radial breathing mode (RBM) is depicted for pristine as well as for low and medium doped DWCNT, this time with 676 nm (a) and 568 nm (b) excitation wavelength. In both cases, the RBM of the inner and outer tubes are clearly distinguishable, with the inner tubes exhibiting a more structured and outspread response and higher Raman shifts in the range from 250 to 350 cm^{-1}. Already at low doping, the outer tube signal decreases strongly for both wavelengths, meaning a loss of Raman resonance for the outer tubes. The resonance for the inner tube is only lost at further doping. This indicates that a charge transfer from the dopant, and as such a filling of the conduction band, happens first to the outer tubes while the inner tube is nearly not affected. This is similar to previous observations on peapods [5]. Only very thick inner tubes (d ≈ 1.0 nm) which are visible in the 568 nm spectrum at a shift of about 250 cm^{-1} (indicated by the arrows in Fig. 2b) are doped as soon as the outer tubes. Due to their larger diameter, the transitions between the van Hove singularities of these big inner tubes are narrower and thus filled up earlier.

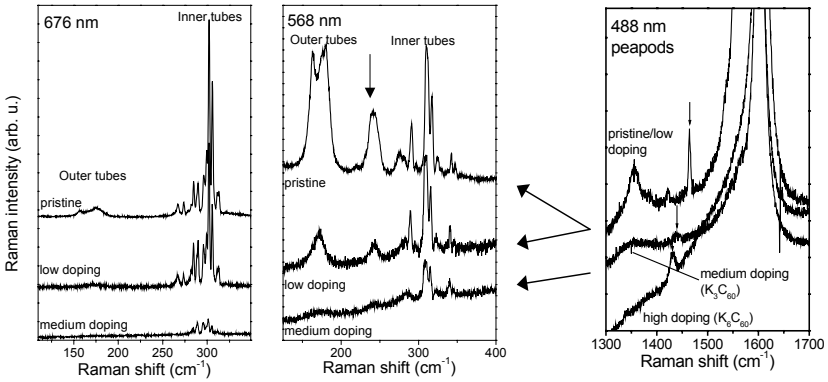

FIGURE 2. Raman response of the RBM of pristine, medium doped and low doped DWCNT excited with (a) 676 nm and (b) 568 nm wavelength laser light. c) Doping dependence of the simultaneously measured peapod sample in the pristine state and at medium and high doping. The arrows mark the position of the $A_g(2)$ mode. The arrows between the figures indicate similar doping levels.

In Figure 2c., the simultaneously intercalated peapod sample, measured with a 488 nm laser, is shown. Here, the charge transfer to the C_{60} can be derived from the shift of the $A_g(2)$ mode [10] indicated by the arrow in the figure. Due to the similar sample volume and exposure time to potassium vapor, this can also be used to give an estimate of the doping level achieved in the DWCNT sample. The upper peapod spectrum corresponds to the pristine state but also is not changed at low doping, where at least some of the inner tubes already start to dope. At a medium intercalation level, where the peapods are doped only up to K_3C_{60}, the inner tube signal of the DWCNT is already strongly supressed. This shows that in DWCNT charge transfer to the inner tube starts earlier than the charge transfer to C_{60} in peapods.

As a reason for this difference in charge transfer to the inner component in DWCNT and peapods, two scenarios can be imagined. The inner tube in DWCNT could have a higher electron affinity than the C_{60} in peapods. Alternatively, the charge transfer could start earlier in the DWCNT, because the distance of the inner tube to the outer tube is somewhere close to the van der Waals radius and therefore smaller than the mean distance between C_{60} and the nanotube in peapods. C_{60} peas only have a diameter of 7 Å, resulting in a pea to tube distance of about 4 Å which is slightly larger than the wall distance of 3.4 - 3.8 Å in DWCNT.

In summary, we found that upon n-type doping with potassium, the shift of the G-line main component depends on which tubes are mainly in resonance with the excitation. For the outer tubes, an upshift, similar to results in the literature, is found, while the G-line shifts down when the excitation is in resonance with mainly the inner tubes. The doping dependence of the RBM response proves that at the beginning of the doping process, charge is only transferred to the outer tubes. Charge transfer to the inner tube sets in later but still earlier than charge transfer to the C_{60}-filling in the peapod reference sample.

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