Raman Spectroscopy Of Boron Nitride Nanotubes And Boron Nitride – Carbon Composites.

F. Hasi[1], F. Simon[1], H. Kuzmany[1], R. Arenal de la Concha[2] and A. Loiseau[2].

[1]*Institut für Materialphysik, Universität Wien, Strudlhofgasse 4, A-1090, Wien, Austria*
[2]*LEM, Onera-Cnrs, 29 Avenue de la Division Leclerc, BP 72, 92322 Châtillon, France*

Abstract. Boron nitride nanotubes (BN-NT) are topological analoges to single wall carbon nanotubes (SWCNT). We analysed and refined the filling process for SWCNTs and applied it to the BN-NTs. BN-NTs were first annealed in air to open the ends and to remove BN particles. A filling procedure with C_{60} fullerene via vapour phase was applied. Subsequently high temperature treatment was performed to transform the fullerenes. Some spectral features in the Raman spectra of the reaction products in the low frequency range may be assigned to small diameter carbon nanotubes inside the BN-NTs.

INTRODUCTION

The inside of carbon nanotubes [1] has been attracting the interest of chemists and physicists ever since the discovery of the fullerenes [2]. Smith et al. discovered the filling of single wall carbon nanotubes with C_{60} [3]. At temperatures of the order of 1400 K the fullerenes can be fused to a second tube, inside the master tube [4]. These inner tubes exhibit a strong Raman spectrum for the RBM [5]. BN-NTs are other tubular nanostructures which attract attention based on the theoretically predicted mechanical stability and electronic insulating behavior independent of chirality and number of tube walls [6]. Although BN-NTs and C-NTs are structurally very similar their electrical properties are different due to the polar lattice of boron nitride. The shielded inside of BN-NTs naturally presents the possibility to fill them with C_{60} which may enable the formation of boron nitride - carbon nanostructures.

EXPERIMENT

The BN-NTs were laboratory prepared by laser ablation of a hexagonal boron nitride (h-BN) target with a continuous CO_2 laser under a nitrogen flow at a pressure 1 bar [7]. From TEM analysis it was estimated that the yield of BN-NTs could be of the order of 25% of the ablated material and that about 80% of the nanotubes are single walled with diameter distribution centered at 1.4 nm (FWHM=0.6) [8]. SWCNTs were purchased from Med Chem Labs with purity of 50%. At first, in several experiments the dynamics of tube opening was investigated for carbon nanotubes. The SWCNTs

CP786, *Electronic Properties of Novel Nanostructures,* edited by H. Kuzmany, J. Fink, M. Mehring, and S. Roth

could be filled with C_{60} fullerenes as purchased by tempering them at 600 ^{0}C in a sealed and evacuated quartz ampoule for two hours together with excess amounts of C_{60}. This filling procedure was used throughout in the work presented here. The peapods were transformed to double wall carbon nanotubes by tempering in high vacuum at 1250 ^{0}C for two hours. This procedure of inner shell tube growth from the peapods was used throughout in this work. The transformed material was then checked by Raman spectroscopy in the range of the RBM for double wall carbon nanotubes. Closing of the tubes was performed at various temperatures between 800 ^{0}C and 1200 ^{0}C in an evacuated quartz tube at 10^{-6} Pa. Opening of the tubes was performed by exposure to air at various temperatures between 350 ^{o}C and 500 ^{0}C. BN-NTs were heat treated in air at 800 °C to open the tips and to remove boron particles. Filling and transformation was performed as for CNTs. Raman experiments were carried out with a Dilor xy triple spectrometer in the normal resolution mode. For the excitation various laser lines were used in the blue, red and yellow spectral range.

RESULTS FOR SWCNT FILLING

Figure 1a and 1b depicts some examples for the efficiency of C-NT filling after closing and reopening for various annealing conditions.

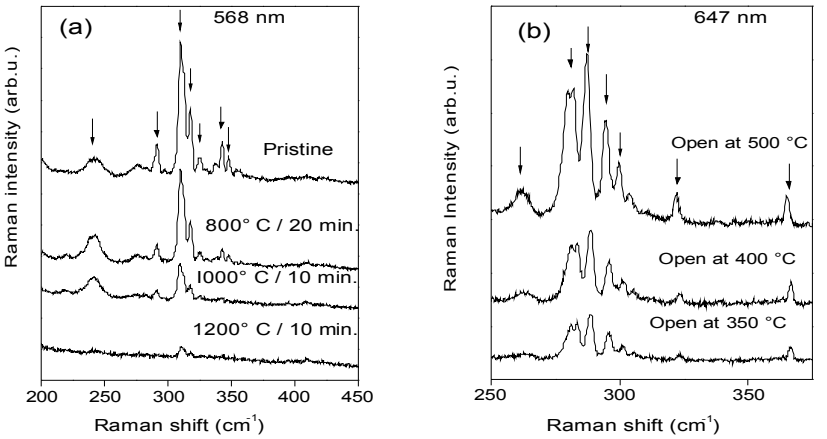

FIGURE 1. a) Raman response of the inner tube RBM of the untreated and standardized filled and transformed tube material (top) and after various annealing treatments as indicated before the filling and transformation processes; b) Raman response of the RBM of inner shell CNTs for standard filling and transformation procedures after the pristine tubes had been closed and reopened at temperatures indicated.

The top spectrum in Fig.1a represents the pristine tubes after standard filling and standard transformation. The three spectra below depict the response of the inner tube RBM for samples which were annealed under the conditions indicated in the figure before filling and transformation. As can be seen 800 °C annealing has almost no effect on the filling for the large diameter tubes but efficiently reduces filling of the smaller tubes with RBM frequencies larger than 300 cm^{-1}. After 20 minutes annealing,

the signal at 340 cm^{-1} has reduced to 35% of the signal of the pristine sample. After 10 minutes annealing at 1200 °C, only a very small response from the inner shell tubes is left. Figure 1b depicts Raman spectra of the RBM recorded for 647 nm excitation for tubes which were closed at 1000 °C for two hours and then reopened by exposure to air at temperatures indicated. As a result, the opening process becomes less and less efficient with decreasing temperature. However, the reduction in efficiency is hardly depending on the tube diameter. For opening at 500 ^{0}C, 95% of the closed tubes could be reopened. The dependence of tube closing and opening on annealing temperature and time was studied in more detail and will be published elsewhere.

RESULTS FOR BN-NTS

The Raman experiments carried out on BN-NTs turned out to be more difficult due to the inhomogeneity of the sample and a strong luminescence. We investigated the samples with a 488 nm excitation wavelength laser at room temperature. Results are presented in Fig. 2. As can be seen from the spectra, (a), (b), (c), the sample appears to be very heterogeneous. Many of the Raman modes observed in the (a) spectra are not present in (b) and (c) spectra. In the high frequency range peaks at 1054, 1306 cm^{-1}, and 1368 cm^{-1} show the presence of cubic BN (c-BN) and hexagonal BN (h-BN) in the material. For comparison, Raman spectra of c-BN and h-BN are depicted in 2d and 2e. In the low frequency range, peaks at 129, 207, 498 and 881 cm^{-1} can be observed which are believed to originate from boron acids produced during the laser ablation process of the h-BN target. The absence of resonant Raman modes for BN-NTs in the spectra proves the theoretically predicted larger band gap than in C-NTs.

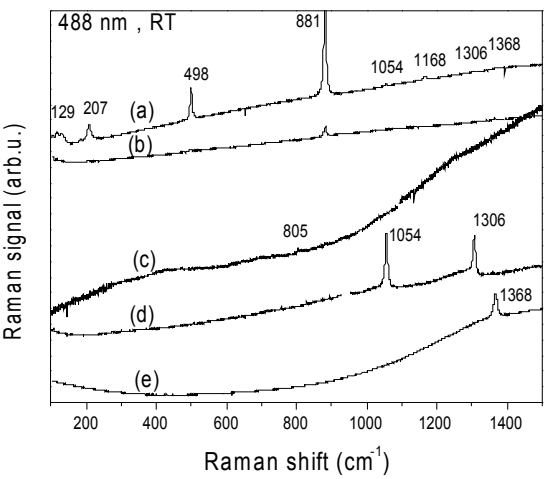

Figure 2. Raman spectra of BN- NT sample from three different spots (a), (b), (c). Raman spectra of cubic boron nitride and hexagonal boron nitride (d), (e) respectively.

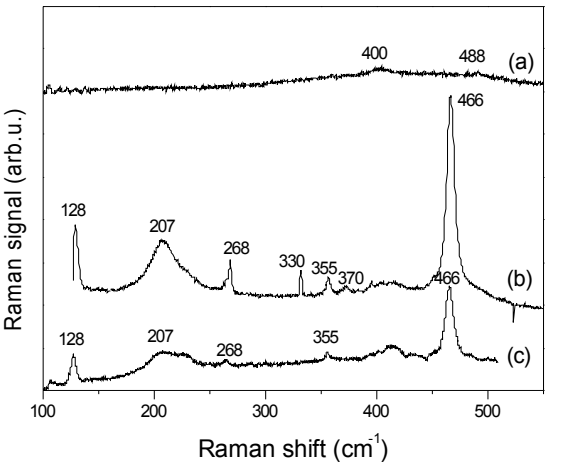

Figure 3. Raman response of the reaction product of BN-NTs with C_{60}. BN-NTs heated at 1250 °C for 2 h in dynamic vacuum, 568 nm, RT (a). Standardized transformation on BN-NTs, 568 nm, RT (b). Standardized transformation on BN-NTs, 647 nm, RT (c).

Similarly to the opening procedure for carbon nanotubes we applied oxidation in air at 800 °C to open the tips of the boron nitride nanotubes and to remove boron particles. Standardized reactions of the BN-NTs with C_{60} fullerene and transformation was performed as mentioned above. Figure 3 show the Raman response in the low frequency range of the reaction products of BN-NT material with C_{60} for 568 and 647 nm excitation wavelength. The Raman investigation of the reaction products shown in (b) and (c) for the radial breathing mode range for carbon nanotubes reveals new spectral features which are not present in the untreated BN-NT or in the BN-NT material heated at 1250 °C in dynamic vacuum without the presence of the fullerenes, spectrum (a). The structured peak at 268 cm^{-1} and the peaks at 330 and 355 cm^{-1} in the (b) and (c) for 568 and 647 nm excitation, respectively, may be assigned to reaction products of the carbon inside the BN-NTs. Also a sharp peak at 466 cm^{-1} is detected.

CONCLUSIONS

In conclusion, we have presented a Raman study of the reaction processes of fullerenes with SWCNTs and BN-NTs. A controlled closing and opening for SWCNTs was performed. The absence of the resonant Raman modes for BN-NTs in the spectra confirms the theoretically predicted larger band gap than in C-NTs. Critical temperatures for the opening process in BN-NTs must be determined. The investigation of the reaction product of BN-NTs with fullerenes revealed spectral features which may be assigned to phonon modes of inner shell carbon nanotubes inside boron nitride nanotubes.

ACKNOWLEDGMENTS

This work was supported by the Fonds zur Förderung der Wissenschaftlichen Forschung in Austria, project 14893 and by the EU project PATONN Marie Curie MEIF – CT- 2003 – 501099 grants.

REFERENCES

1. S. Iijima, Nature(London) 354, 56 (1991)
2. H. Kroto et al. Nature 318, 162, (1985)
3. B. W. Smith, M. Monthioux, D. E. Luzzi, Nature 396, 323 (1998)
4. S. Bandow, M. Takizaw, K. Hirahara, M. Yudasaka and S. Iijima. Chem. Phys. Lett. 337 48 (2001)
5. R. Pfeiffer, H. Kuzmany, C. Kramberger et al. Phys. Rev. Lett. 90, 225501 (2003)
6. A. Rubio et al, Phys. Rev. B 49, 5081 (1994)
7. R. S. Lee, J. Gavillet, A. Loiseau et al, Phys. Rew. B 64, 121405 (2001)
8. R. Arenal de la Concha et al., in Molecular Nanostructures edited by H. Kuzmany et al. AIP Conference Proceeings 685, 384-388 (2003)