RESONANCE RAMAN SCATTERING OF MULTI-WALLED CARBON NANOTUBES

H. KATAURA*, Y. ACHIBA**, X. ZHAO*** AND Y. ANDO***
* Department of Physics, Faculty of Science, Tokyo Metropolitan University, Tokyo 192-0397, JAPAN, kataura@phys.metro-u.ac.jp
** Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Tokyo 192-0397, JAPAN
*** Department of Physics, Meijo University, Nagoya 468-8502, JAPAN

ABSTRACT

Multi-walled carbon nanotubes synthesized by the carbon arc in hydrogen gas have very thin core channels. We have measured resonance Raman scattering of some samples synthesized in different conditions, and have observed radial breathing mode (RBM) peaks from 200 to 500 cm^{-1}. Resonance effect of each peak is similar to that of single-walled nanotube. However, the peak frequencies are about 5 % higher than those of single-walled nanotubes, which is probably due to the inter-layer interaction. Further, the highest RBM peak splits in three peaks. The result on the resonance effect and the zone-folding band calculation suggest that the thinnest core nanotube is (4,3) that have four candidates of second outer nanotubes. This suggests that the different outer nanotube gives different degree of the interlayer interaction.

INTRODUCTION

Usually, multi-walled carbon nanotube (MWNT) prepared by carbon arc is thought to be constructed with concentric tubes. For example, ^{13}C-NMR [1] and the magnetoresistance results[2,3] show Aharonov-Bohm effects that are led from the concentric tube structures. However, the thermal expansion measurement [4] and the doping effects [5] suggest that some kinds of MWNTs have scroll structures. If the radial breathing modes (RBMs), which is characteristics of single-walled carbon nanotube (SWNT) [6], were observed in MWNTs, it might be the experimental evidence of the concentric structure. In many cases, unfortunately, MWNTs have very large diameters compared with SWNTs even at the core, and no one succeeded to observe the RBMs, to date. However, Zhao and Ando have succeeded to synthesize MWNTs with very thin core by electric arc in hydrogen gas. [7] They confirmed that the core nanotubes has a diameter less than 1.0 nm by the transmission electron microscope (TEM) observation. Further, the sample indicates many Raman peaks in a low frequency region, which correspond to the RBMs in SWNTs. [8] If those peaks are RBMs, the resonance effect will be observed as well as the SWNTs.

In the case of SWNT, electronic states are expressed well by the zone-folding scheme. Indeed, for the SWNT, results of the optical absorption and the resonance Raman scattering can be explained by the optical transition between spikes in density of states originating from one dimensional van Hove singularities. If the similar resonance feature were observed for the low frequency mode in the case of MWNTs, it will be a sign of the true RBM. Furthermore, this resonance feature will become a standard for the individual SWNT because MWNT never constructs hexagonal bundle structure. Thus, it is very interesting to measure the resonance Raman scattering of MWNTs synthesized in hydrogen gas.
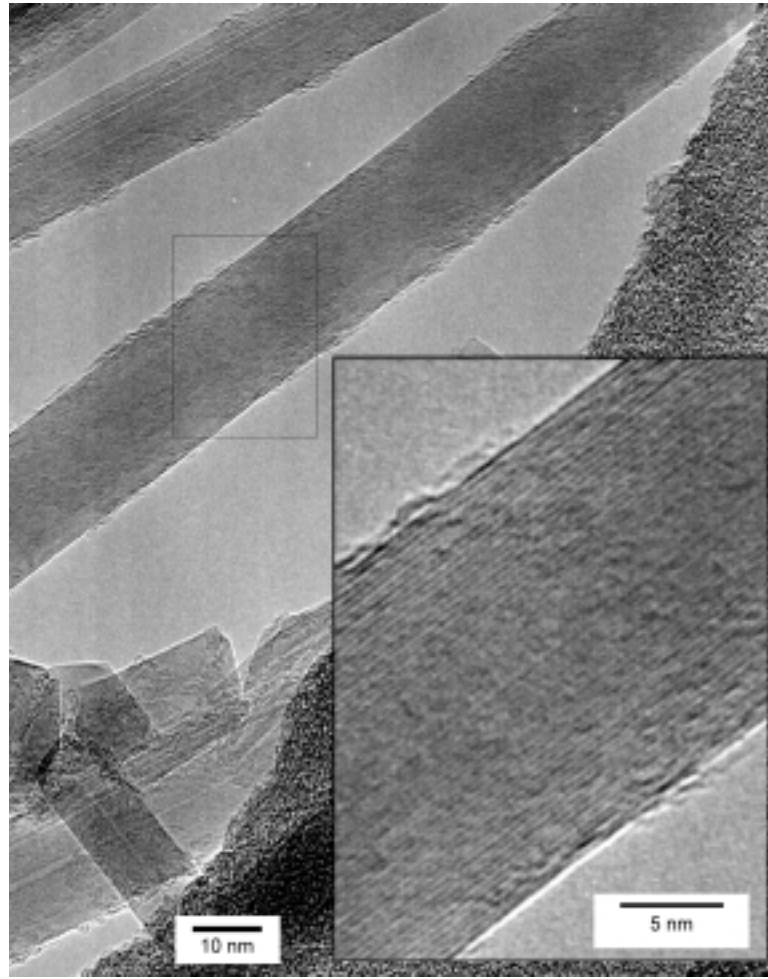
Fig. 1. TEM photograph of unpurified multi-walled carbon nanotubes fabricated by carbon arc in 120 Torr hydrogen gas. Inset shows a larger magnification image of the rectangle area. It can be seen that the core channel diameter is less than 0.7 nm.

EXPERIMENT

We have prepared several MWNTs samples by carbon arc under different hydrogen pressure from 30 to 120 Torr. In the all conditions, we could get good MWNT samples. Relative yields were depending on the pressure and the current. Details about the synthesis method should be explained elsewhere. [7] Briefly, the highest yield of MWNTs was obtained at 60 Torr. The purity of the sample after the purification by infrared lamp is over 90%. The diameter distribution of core channel was measured by TEM. Figure 1 shows a typical TEM photograph of MWNTs. At sight, MWNT looks like a rod, but the high-resolution image indicates a very small hollow at the core. Most of MWNTs have core diameter around 1.0 nm, and sometimes we observed it less than 0.7nm.

Spectra Physics Ar^+ laser Stabilite 2016, dye laser 375B and Ti: Sapphire laser 3900S were used as light sources for Resonance Raman measurements. Jobin Yvon U1000 double monochromator, Hamamatsu Photonics R943-02 photomultiplier tube and photon counting system were used for the measurement. Raman shift was calibrated by the Raman peak of crystalline silicon. To avoid local heating effects on the Raman spectrum, laser beam was

focused linearly on the sample using a cylindrical lens. The laser power was set to 50 mW as an optimum value.

RESULTS

One-phonon Raman spectra of four kinds of samples are shown in Fig.2. All samples show typical Raman spectra of MWNTs. This is reasonable, because the structural differences between our samples and the other MWNTs are only a few layers at the center of MWNTs. On the other hand, we observed very strong new peak at 1850 cm^{-1}. The peak intensity strongly depends on the preparation condition. MWNTs at the lower hydrogen pressure show the larger peak intensity. There is no one-phonon density of states at 1850cm^{-1}, so that the unknown peak should be assigned as a two-phonon mode. Of course, in the reaction chamber, soot contains

Fig. 2. Raman spectra of four kinds of MWNTs samples fabricated in different hydrogen pressure.

many kinds of C-H compounds as impurities. One might think the peak is originating from the impurities. However, MWNTs were grown on the cathode, and were kept in very high temperature during the deposition. Thus, the most of C-H compounds were expected to be vaporized. Further, this peak show very sharp and strong resonance effect, just like a SWNT, from visible to infrared region. This suggests that the peak is concerning with the nanotube-like electronic states. The peak frequency 1850cm^{-1} is just the sum of the D-band frequency 1350 cm^{-1} and the observed highest RBM frequency 490 cm^{-1}. Tentative assignment of this peak is the combination of the RBM and the D-band.

Figure 3 shows the low frequency Raman spectra of the purified MWNTs measured using various lasers. Peaks between 150 and 200 cm^{-1} are due to the air. Peaks above 200cm^{-1} show very sharp resonance, which strongly suggests that these structures are originating from the RBM of nanotubes. Indeed, resonance feature of the peaks between 200 and 350 cm^{-1} is quite similar to that of SWNTs synthesized by laser ablation using RhPd catalyst. [9,10] Further, we found that peaks are located 4 or 5 % higher frequencies than the case of SWNTs. For example, the RBM peak at 280 cm^{-1} shows maximum intensity at 2.41 eV. This is the same behavior as the peak at 268 cm^{-1} in SWNTs. In the same way, the peaks at 239, 270 and 304 cm^{-1} correspond to the peaks at 227, 260 and 285 cm^{-1} in SWNTs, respectively. These up-shifts are probably due to the interlayer interactions. Recently, some reports about bundle effects on the RBM frequency of SWNTs were published. [11] In the theoretical calculation, RBM frequency of SWNT in the infinite bundle becomes 10% higher than the isolated SWNT. Unfortunately, there is no report about the interlayer interactions on the vibrational properties of the MWNTs. However, the similar effects should be expected in the case of MWNT.

For a region over 350 cm^{-1}, large bands at 388 and 490 cm^{-1} are observed with sharp resonance around 2.4 and 1.7 eV, respectively. The highest RBM peak observed in SWNTs is at 328 cm^{-1}. Thus, we don't have any references in this frequency region. If these are RBMs, however, candidates are strongly restricted. From the simple relationship between diameter and RBM frequency, [6] the candidates for the peak at 490 cm^{-1} are (5,1), (6,0), (4,3) and (5,2) having RBM frequencies at 509.6, 472.8, 466.4 and 454.3 cm^{-1}, respectively. If we take into
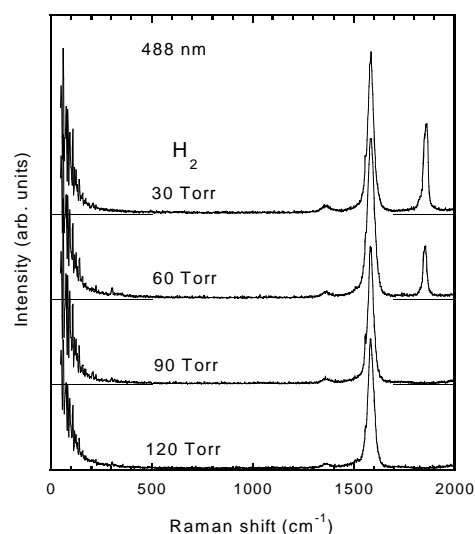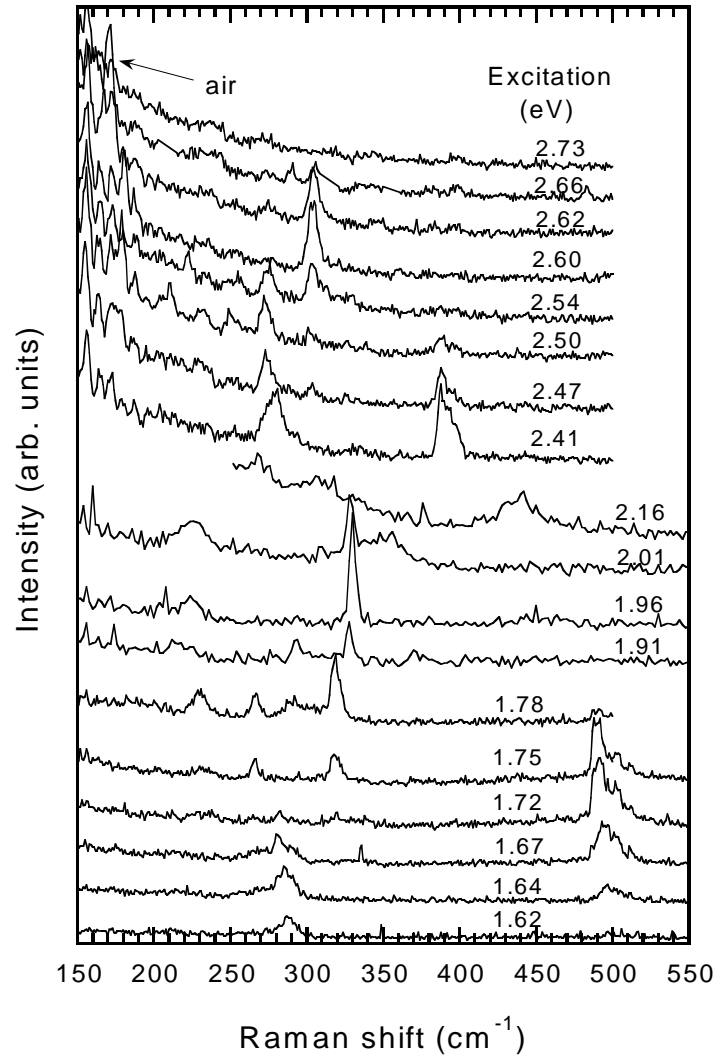
Fig. 3. Low frequency Raman spectra of purified MWNTs. Excitations are indicated in the figure. The complicated peak structures below 200 cm^{-1} are due to the air.

account the 5% up-shift due to the interlayer interactions, the candidates are narrowed down to (6,0), (4,3) and (5,2). Their diameters are 0.470, 0.477 and 0.489 nm that are consistent with the TEM observations. It is very interesting that (6,0) nanotube has the same structure of D_{6h} C$_{36}$. [12] However, we have to consider the electronic states of the nanotube to see the resonance effect. By the zone-folding band calculation [13], assuming the transfer integral $\gamma = 2.75$ eV, it is found that (6,0) and (5,2) are metallic nanotubes and have the first energy gaps at 4.0 eV. Since the resonance energy of the peak is 1.7 eV, we assigned the peak at 490 cm^{-1} to (4,3) which is the semiconductor having the first gap at 1.6 eV. In the same way, the candidates for the Raman band at 388 cm^{-1} are (7,1) and (5,4). The nanotube (7,1) is metallic and has the first gap at 3.4 eV, while (5,4) is the semiconductor and has the first and second energy gaps at 1.28 and 2.52 eV, respectively. Thus, this peak should be assigned to (5,4) because of the resonance at 2.4 eV.

Now we consider the interlayer interactions. The band at 490 cm^{-1} is splitting into three peaks indicating the same resonance feature. These peaks cannot be explained by different

nanotubes, since there are no other candidates. The nanotube (5,1) is only the candidate having the nearest diameter and the nearest energy gap. However, the calculated energy gap of (5,1) is 1.7 eV, which is 0.1 eV wider than (4,3). If one of the peaks is originating from (5,1), the resonance feature should be different from the other peaks. Further, the RBM frequency of (5,1) becomes 534 cm^{-1}, taking into account the 5 % up-shift. Thus, it is proper to think that these three peaks are originating from the same nanotube. The possible reason of the splitting is the interlayer interaction. When the first layer is (4,3), (10,7) is the best selection as the second layer since the interlayer distance is 0.342 nm which is a typical value for MWNTs. [14] The other nearest candidates of the second layers are (13,3), (9,8) and (11,6) having inter-layer distances 0.339, 0.339 and 0.347 nm, respectively. The interlayer distance (13,3) and (9,8) have about 1% smaller than the typical inter-layer distance and (11,6) is 1.5% larger. A magnitude of the interlayer interaction should depend on the interlayer distance, and consequently, the RBM frequency of the first layer may depend on the chiral index of the second layer. Indeed, the observed frequency separation between split peaks is about 2%, which is consistent with the difference in interlayer distances. The splitting into three RBM peaks probably indicates that there are at least three kinds of second layers. In other words, the splitting means that the second layer nanotube has closed tube structure as well as the core nanotube. This strongly suggests that the MWNT fabricated by the electric arc in hydrogen gas has a concentric structure.

For the thinnest nanotube (4,3), the RBM frequency of the second layer is 191 cm^{-1}. This should be the highest RBM frequency of the second layer nanotube. Since the low frequency region is affected by the signals from the air, we measured Raman spectra keeping the sample in argon gas. However, we could not observe any peak below 200 cm^{-1}. This result suggests that only the core nanotube has the considerable Raman intensity. The core layer has only the outer nanotube as a neighbor while the other nanotubes, except for the outermost layer, have both the inner and the outer nanotubes. The interlayer interaction probably broadens the one-dimensional band structure, in like manner to the bundle effect in SWNTs. [15] The band broadening decreases joint density of states at the energy gap. Then, the resonance Raman intensity of the second layer may become very weak. On the other hand, the RBM frequency of the outermost layer is too low to measure because of its large diameter. Thus, we can observe the RBMs only of the core nanotubes.

CONCLUSION

Resonance Raman spectra of MWNTs were measured and RBM peaks originating from very thin core nanotubes were observed. The assigned thinnest nanotube (4,3) has very close diameter to (6,0) or D_{6h} C$_{36}$. [12] The splitting of RBM peaks indicates that both the first and the second thinnest layers have closed tube structures. This result strongly suggests that the MWNTs fabricated by carbon arc in hydrogen gas have the concentric structures. On the other hand, the fact of the existence of the thin nanotubes is very important to think about the growth mechanisms, because these thin nanotubes cannot be closed by the hemispherical cap satisfying the isolated pentagon rule (IPR). When we think about the nucleation of core nanotubes, we have to consider the possibility of the non-IPR carbon cage structures. Now, we have much interested in the cap structures of these thin nanotubes. Further, the new strong Raman band at 1850 cm^{-1} is very interesting, since the frequency is basically in the silent region of the one-phonon density of states in the two-dimensional carbon network structure. It makes us imagine new carbon network structures.

ACKNOWLEDGMENTS

REFERENCES

1. Y. Maniwa, M. Hayashi, Y. Kumazawa, H. Tou, H. Kataura, H. Ago, Y. Ono, T. Yamabe, and K. Tanaka, AIP Conference Proceedings **442**, 87 (1998)
2. A. Fujiwara, K. Tomiyama, H. Suematsu, M. Yumura and K. Uchida, Phys. Rev. B **60**, 13492 (1999)
3. A. Bachtold, C. Strunk, J. P. Salvetat, J. M. Bonard, L. Forro, T. Nussbaumer and C. Schönenberger, Nature **397**, 673 (1999).
4. S. Bandow, Jpn J. Appl. Phys. **36**, L1403 (1997).
5. V. Z. Mordkovich, Molecular Crystals and Liquid Crystals, in press.
6. R. Saito, T. Takeya, T. Kimura, G. Dresselhaus and M.S. Dresselhaus, Phys. Rev. B **57**, 4145 (1998).
7. X. Zhao, M. Ohkohchi, M. Wangm S. Iijima, T. Ichihashi and Y. Ando, Carbon **35**, 775 (1997).
8. X. Zhao and Y. Ando, Jpn. J. Appl. Phys. **37**, 4846 (1998).
9. H. Kataurta *et al*., Jpn. J. Appl. Phys. **37**, L616 (1998).
10. H. Kataura *et al*. Synthetic Metals **103**, 2555 (1999)
11. L. Henrard, E. Hernández, P. Bernier and A. Rubio, Phys. Rev. B **60** R8521 (1999).
12. C. Piskoti, J. Yarger and A. Zettl, Nature **393**, 771 (1998).
13. R. Saito, M. Fujita, G. Dresselhaus and M. S. Dresselhaus, Appl. Phys. Lett. **60**, 2204 (1992)
14. Y. Saito, T. Yoshikawa, S. Bandow, M. Tomita and T. Hayashi, Phys. Rev. B **48**, 1907 (1993).
15. Y. K. Kwon, S. Saito and D. Tománek, Phys. Rev. B 58, R13314 (1998).