Raman and Transport Studies in Multi-Walled Carbon Nanotubes

K Maejima\textsuperscript{1}, O Suzuki\textsuperscript{1}, T Uchida\textsuperscript{2}, N Aoki\textsuperscript{1}, M Tachibana\textsuperscript{2}, K Ishibashi\textsuperscript{3} and Y Ochiai\textsuperscript{1}

\textsuperscript{1} Department of Electronics and Mechanical Engineering, Chiba University, 1-33 Yayoi, Inage-ku, Chiba 263-8522, Japan
\textsuperscript{2} Graduate School of Integrated Science, Yokohama City University, 22-2 Seto, Kanazawa-ku, Yokohama 236-0027, Japan
\textsuperscript{3} Advanced Device Laboratory, The Institute of Physical and Chemical Research (RIKEN), 2-1 Hirosawa, Wako, Saitama 351-0198, Japan

E-mail: ochiai@faculty.chiba-u.jp, Phone; 81-43-290-3430, Fax; 81-43-290-3427

Abstract. We report the characterization of electrical properties for multi-walled carbon nanotubes (MWNTs) synthesized by the arc-discharge method, as to the difference of characteristics between two diameters of 10 nm and 100 nm. In a result of Raman spectrums, we have observed clear radial-breathing-mode peak at approximately 255 cm\textsuperscript{-1}, which corresponds in turn to an innermost diameter of ~2 nm in the MWNT, and shows a good agreement with the TEM image of diameter of the thin MWNT. The results of two- and four-terminal measurements of the thin MWNTs show a power-law behavior as expected for the Tomonaga-Luttinger liquid model. The power-law exponent, $\alpha \sim 0.4$, seems consistent with the one-dimensional nature of the transport in these structures. We have also investigated the thick MWNTs.

1. Introduction

There has been great interest, in recent years, in new applications of carbon nanotubes as near-future nanoelectronic devices. The fundamental details of the physical properties in carbon nanotube have been widely investigated. Because of a high conductivity, multi-walled carbon nanotubes (MWNTs) would be more useful in electrical wiring and transistors in nanoscale circuits than single-walled carbon nanotubes (SWNTs) if we could control the electrical properties. In order to realize a nanoscale circuit consisting of MWNTs, multi-terminal devices must be developed. Raman spectroscopy and transport properties have been shown to be a powerful tool for studying and characterizing carbon nanotubes [1,2,8]. The Raman spectra (RS) of carbon nanotubes include some main features: a radial breathing mode (RBM), G-band and D-band lines. The RBM can give an easy and quick determination of the tube diameter of SWNTs. However, the RBM of MWNTs originates from the very thin innermost diameter of ~2 nm in MWNTs. The diameter of SWNT is determined by the relationship of $d = \frac{248}{\omega}$, where $d$ is the isolated SWNT diameter in nanometers and $\omega$ is the RBM frequency in wavenumbers. In the case of MWNTs, the RBM frequency is shifted up due to the quality of CNT samples. In addition, there are several transport studies for carbon nanotubes with
analyzing their power-law behaviors as expected for the one-dimensional nature of transport because of a fundamental attention for a recent discovery of their electron–electron interaction [1–4]. Electron transport in almost metallic conductors is usually described by one-particle Fermi-liquid theory. However, in one-dimensional systems, weak Coulomb interactions induce strong perturbations and the Fermi-liquid theory is broken. Therefore, a particular feature known as a Tomonaga-Luttinger liquid (TLL) behavior appears [5,6]. MWNTs have multi-channel conduction pathways so that their conduction mechanism might be slightly complex. It seems to be difficult to apply to such a TLL model into MWNTs. In this study, we report on result of RS, and two-terminal (2-t) and four-terminal (4-t) measurements to analyze TLL model in MWNTs. Moreover, we use transmission electron microscope (TEM) and scanning electron microscope (SEM) to investigate structure of the MWNTs.

Figure 1. (a) SEM image of the sample-A. TEM image of the sample-A is also put in the inset of the figure. (b) SEM image of the sample-B. TEM image of the sample-B is also put in the inset of the figure.

2. Experiments
The MWNTs were synthesized by an arc-discharge method, which was used to obtain batches of MWNTs with average diameters of 10 nm and 100 nm that are determined by TEM shown in Figs. 1(a) and 1(b), respectively. These two kinds of MWNTs were provided by different manufacturers. We named the thin MWNTs for sample-A and the thick ones for sample-B. The outermost and innermost diameters, number of layers, and shapes of MWNTs are confirmed by TEM and SEM image. For RS, a drop of raw MWNT powder was placed on substrate. Raman measurements were performed at room temperature using a laser of 532 nm for excitation. For the transport measurement, the MWNTs purified only by a centrifugal separator without thermal oxidation in order to avoid damaging. The MWNT was dissolved in a solvent using ultrasonics, and dispersed on Si/SiO₂ substrates. Low-temperature resistances for individual MWNTs were measured using 2-t and 4-t resistance measurement. For sample-A, electrical contacts between the MWNT and the lead wires were made by electron beam (EB) -lithography and lift-off process with depositing Ti and Au to 15 and 35 nm, respectively. For sample-B, photolithography method and lift-off process with depositing Ti and Au to 100 and 200 nm, respectively. In order to improve the electrical contact performance between a MWNT and metals, rapid thermal annealing (RTA) was performed at 600 °C for 30 s in Ar and H₂ atmosphere. After RTA, the contact resistance was clearly lowered by a few orders of magnitude. A carbide formation between the Ti pad and the MWNT may contribute to the electrical contact during the RTA process and make a good ohmic contact. The low temperature transport measurement was performed using a conventional cryostat and a dc voltage source.

3. Results and discussions
A typical TEM image of a sample-A is shown in the inset of Fig. 1(a). The outer diameter of these nanotubes is approximately 10 ~ 15 nm and the inner diameter is several nm. The number of layers is about 10 ~ 20. The shape of sample-A was almost straight as shown in the SEM image in Fig. 1(a). The layers of sample-A are well parallel to each other as shown in the TEM image. On the other hand, the outer diameter of sample-B is approximately 100 nm and the number of layers is about hundred or
more. Many separations and junctions of the layers are observed in the TEM image of the inset of Fig. 1(b). Some kinks are also observed in the SEM image as shown in Fig. 1(b). The RS of sample-A (dotted line) and sample-B (solid line) are shown in Fig. 2(a). The G-band and D-band are observed at around 1600 cm⁻¹ and 1330 cm⁻¹ in both samples, respectively. The ratio of the intensity of G-band and D-band ($I_G/I_D$), which gives a quality of CNT, is 26 and 12 in sample-A and sample-B, respectively. Therefore, the quality of sample-A seems to be better than that of sample-B. This result is correspondent to TEM and SEM observation. Low frequency RS are shown in Fig. 2(b). The RBM peaks at about $\omega = 255$ cm⁻¹ are observed in sample-A. We put this value into the, $d = 248/\omega$, we estimate the innermost diameter ~1 nm in sample-A, which has a good agreement with the TEM image. On the other hand, because of imperfection of the inner walls, RBM of sample-B can not be observed as shown in Fig. 2(b). The peak at 480 cm⁻¹ is believed to be related to impurities such as C₆₀.

![Figure 2](image2.png)

Figure 2. (a) G-band and D-band of Raman spectra are shown with dotted line for sample-A and solid line for sample-B, respectively. (b) Low frequency Raman Spectra of sample-A (dotted line) and of sample-B (solid line). RBM peaks of MWNT were observed at 255 cm⁻¹ in sample-A.

![Figure 3](image3.png)

Figure 3. The scaled differential conductance $(dI/dV)/T^n$ measured at different temperatures are plotted against $eV/k_B T$. (a) 2-t transport property of sample-A. Power–law exponent, $n = 0.44$, can be obtain with the slope at higher $eV/k_B T$ region. (b) 4-t transport property measurement of sample-A.
Power–law exponent, $\alpha = 0.34$, can be obtained with the slope at higher $eV/k_B T$ region. (c) 2-t transport property of sample-B. (d) 4-t transport property of sample-B. As for thick MWNT, all data points cannot be scaled in the same TLL plot.

We show the results of the scaled differential conductance of the MWNTs at a series of different temperatures. For biases much larger than $k_B T$, the conductance show power-law behavior as expected for the TLL model in both case of 2-t and 4-t measurements of sample-A as shown in Figs. 3(a) and 3(b), respectively. The power-law exponent estimated from these 2-t measurements shows $\alpha = 0.44$ which seems to be consistent with result of the one-dimensional nature observed in photoemission spectroscopy [12]. However, in the case of 4-t measurement, we obtained a smaller exponent, $\alpha = 0.34$. This may come from an effect of existence of the voltage contacts in MWNT and also affect transport properties. However, it cannot be concluded clearly yet. On the other hand, for sample-B, we cannot fall on a common power-law behavior as expected for the TLL model both 2-t and 4-t transport measurements as shown in Figs. 3(c) and 3(d). It is believed to relate to the thickness of diameter and low degree of quality.

4. Conclusion

In this study, we characterize two kinds of MWNTs using TEM, SEM, RS, and transport measurements. Clear differences are observed in the TEM and the SEM images. From RS results, the quality of sample-A is better than that of sample-B by the $I_C/I_D$ ratio. RBM peaks of innermost core of MWNT are observed only in sample-A, and the corresponding diameter 1 nm is consistent with the TEM results. From the transport measurements, both of the 2-t and the 4-t measurements show power-law behavior as expected for TLL model however the results of sample-B does not fit on TLL model. These differences would due to the quality of walls and diameter of the MWNTs.

Acknowledgements

This work was supported in part by a Grant-in-Aid for Scientific Research from the Japan Society for the Promotion of Science (16656007 & 16206001). The authors would like to thank Dr. T. Aoki for help in the TEM observations.

References
[1] Ogata M and Fukuyama H 1994 Phys. Rev. Lett. 73 468
[2] Ogata M and Fukuyama H 1995 Jpn. J. Appl. Phys. 34 3363
[3] Ishikawa S, Enomoto R, Aoki N, Umishita K, Ishibashi K, Aoyagi Y and Ochiai Y 2001 25th International Conference on the Physics of Semiconductors, Springer Proceedings in Physics 87 1661
[4] Graugnard E, De Pablo P.J, Walsh B, Ghosh A, Datta S and Reifenberger R 2001 Phys. Rev. B 64 125407
[5] Tomonaga S 1950 Prog. Theor. Phys. 5 544
[6] Luttinger J M and Math J 1963 Phys. 4 1154
[7] Zhao X, Ando Y, Qin L C, Kataura H, Maniwa Y and Saito R 2002 Chemical Phys. Lett. 361 169
[8] Zhao X, Ando Y, Qin L C, Kataura H, Maniwa Y and Saito R 2002 Physica B 323 265
[9] Shiraishi M and Ata M 2003 Solid State Comm. 127 215
[10] Bockrath M, Cobden D H, Lu J, Rinzler AG., Smalley R E, Balents L and McEuen P L 1999 Nature 397 598
[11] Enomoto R, Horiuchi K, Miyamoto K, Matsunaga Y, Aoki N and Ochiai Y 2002 Physica B 323 249
[12] Ishii H, Kataura H, Shiozawa H, Yoshioka H, Otsubo H, Takayama Y, Miyahara T, Suzuki S, Achiba Y and Nakatake M 1999 Nature 462 54