Mechanical and Electrical properties of Multiwall Nanotube under Interlayer Sliding

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We have successfully measured the sliding force for an interlayer of individual multiwall carbon nanotubes using a combination of a well-controlled electrical breakdown process and a manipulation process using a scanning electron microscope. A sliding force of \( \sim 4 \) nN for an inner layer diameter of 5 nm is maintained constant during a sliding process. This result agrees well with the theoretical calculation. This agreement indicates that the layered structure exhibits ideal characteristics even after the electrical breakdown process. We have also proposed nanoscale variable resistors using the sliding mechanism of the interlayer of individual multiwall carbon nanotubes. The two-terminal resistance of the processed nanotube increases exponentially with the sliding distance under a low bias voltage and is proportional to the sliding distance under a high bias voltage. The variation of the resistance under the low bias voltage can be explained as a one dimensional localized system, with a characteristic localization length around 840 nm. On the contrary, the sliding nanotube acts as the diffusive conductor under a high bias voltage.

Keywords: Carbon nanotube; Electrical resistance; Localization; Variable resistor; Diffusive conduction

I. INTRODUCTION

Nanoelectromechanical systems (NEMS) have widely been studied on devices made with silicon technology. For the progress of the NEM devices, nanoscale displacement sensors, such as position sensors and strain gauges, are also crucial for the nanoscale system. Carbon nanotubes provide an interesting alternative because of their superior mechanical and electrical properties. Particularly, arc-produced multiwall nanotubes, which have a concentric shell structure of graphite sheet, show an extremely high strength and good electrical conduction because of a highly crystallized structure compared to the nanotubes produced by chemical vapor deposition. The nanotubes have been already applied to NEM devices such as nanotweezers, as nano-motors, and as switches in a random access memory device. In order to construct such NEM devices using the nanotubes, we have developed a nanoprocessing technique using a scanning electron microscope (SEM) manipulator, so-called nanofactory.

Recently, we have demonstrated the extraction of an inner shell of multiwall nanotubes using a combination of an electrical breakdown process of an individual nanotube and a manipulation process in the nanofactory. The extraction of the inner shell of the nanotube has also been demonstrated using a transmission electron microscope (TEM) and suggested a low friction force for interlayer slipping, but there was no quantitative experimental result for the sliding force. Similar experiments have also been reported by Yu, et al., but the estimated extraction force was on the order of \( \sim 10^{-10} \) Pa. The SEM has three independent movable stages as schematically shown in Fig.

II. SEM MANIPULATOR

All of the sliding measurement was carried out in a specially designed field-emission-type SEM with a base pressure less than \( 2 \times 10^{-5} \) Pa. The SEM has three independent movable stages as schematically shown in Fig.
In this system an inlet of several source gases was also installed to form thin films of insulator or metal by electron-beam induced deposition. For sliding force measurements, only two of the stages were used for the measurement: one for an individual nanotube attached to a Pt-coated Si cantilever with a spring constant of 2 N/m or 40 N/m and the other for a Pt-coated Si$_3$N$_4$ cantilever with a weak spring constant of 0.08 N/m, which acts as a force sensor. On the third stage we installed an optical fiber to measure the optical emission from an individual carbon nanotube. For the attachment of a nanotube on a Si tip, we have used the electron beam induced deposition of amorphous carbon film onto the nanotube. After the nanotube had been transferred onto the Si tip, the carbon film was deposited on it to make the attachment strong. The carbon source was hydrocarbons remaining in the SEM chamber or intentionally induced. It has been confirmed that the attachment force of the nanotube fixed by carbon films is at least 3 $\mu$N [2]. When the nanotube was brought into contact with the Si cantilever tip, the current passing through the nanotube was monitored at a bias voltage of $\sim$ 2 mV in order to check the electric contact between the nanotube and the SPM tip.

III. FORCE MEASUREMENTS

Multiwalled nanotubes used were synthesized by an arc discharge method. An arc was induced between carbon rods in a flow of helium at 500 Torr. The gas temperature in the arc was enhanced by cooling the gas surrounding the arc using a water coil, resulting in a narrow distribution of diameters and a high purity of nanotubes against nanoparticles [18]. Nanotubes thus prepared had multiple walls, 1 to 5 $\mu$m in length and 5 to 20 nm in diameter with an average diameter of 10 nm.

The sliding force measurement was carried out in the nanofactory. The procedures for measuring the sliding force are as follows. First, an individual nanotube is bridged to two cantilevers with good electrical contacts of the two terminal resistance less than 100 k$\Omega$. When a certain voltage is applied to the nanotube, the electrical breakdown is started, where the current decreases stepwisely, indicating the sequential destruction of individual nanotube shells [11]. This gives us information on the number of destructed shells. It is noted that a continuous stepwise decrease in current cuts the nanotube and sharpens its tip [8]. After some number of steps, the Si cantilever with a larger spring constant gradually moves away to slide the inner shell of the nanotube and then the soft cantilever is deflected by the sliding force. The deflection is converted to the interlayer sliding force using the spring constant of the soft cantilever. Finally, the nanotube is completely separated and the soft cantilever moves backward to the original position. During the force measurement, both of the electrodes were connected to a ground plane in order to eliminate the electrostatic attraction. These motions were recorded on a videotape. Resultant nanotubes were also observed by TEM with an accelerating voltage of 200 kV.

Figure 2 shows a series of SEM images during the force measurement. The central part of the nanotube becomes thinner after the electrical breakdown process as shown in Fig. 2(a). While the hard tip moves downward, the soft cantilever is slightly deflected. The central part of the nanotube corresponding to the inner shell is elongated as
FIG. 2: A series of SEM images for the sliding force measurement: (a) just after the electrical breakdown process, (b) during the force measurement and (c) after the force measurement.

shown in Fig. 2(b). Finally, the nanotube is separated into two parts as shown in Fig. 2(c). The extracted part of the nanotube is ∼700 nm in length. Figure 3 shows a pair of TEM images of the resultant nanotubes, where Fig. 3(a) shows the outer shell and Fig. 3(b) shows the inner shell and the base of the nanotube. It is noted in Fig. 3(b) that the extracted portion was entangled during a transferring process in air between the nanofactory and the TEM chamber because of the flexibility of the

extracted portion. As shown in Fig. 3(a), the outer shell after the extraction of the inner shell is opened and is estimated to be ∼5 nm in diameter. In addition, it is also observed that the shell structure near the edge remains intact after the extraction.

Figure 4 shows the result of the force measurement, where ∆L is defined as the sliding distance of the nanotube. At ∆L < 700 nm, the sliding force is maintained constant at ∼4 nN in spite of varying the overlapping length between the inner and the outer shell of the nanotube. At ∆L > 800 nm, the force decreases rapidly, which corresponds to the separation of the nanotube.

FIG. 4: Sliding distance dependence of the sliding force for the interlayer of the nanotube shown in Figs. 2 and 3.

The sliding force that originated from the van der Waals force is given by $F_{vdw} = -dU(x)/dx$, where $U(x)$ is the van der Waals energy for overlapping length, x. Under an assumption that the interlayer is treated as two parallel planes with overlapping areas $S(x) = 2\pi r x$, the van der Waals energy is given by $U(x) = -(A/d^2)\cdot S(x)/12\pi$ [19], where $A$ is the Hamaker constant for the interlayer of the nanotube, $r$ the radius of the inner or outer shell of the nanotube and $d$ the interlayer spacing. It is found that the sliding force is independent of x, because the contact area of the interlayer is linearly proportional to x. Using the parameters of $A = 6 \times 10^{-19}$ J [20], $d = 0.34$ nm, $r = 2.5$ nm, the van der Waals force is estimated to be ∼2 nN, which is comparable to the experimental value.

Furthermore, the accurate calculation for the sliding force based on the van der Waals interaction has been reported [14]. This report predicts that the force is independent of the overlapping length, but depends on the diameter of the extracted portion and layer number. Applying a core diameter of 5 nm, the sliding force is estimated to be 3 to 5 nN. This range agrees well with the value estimated from the force measurement. This quantitative agreement indicates that the sliding force estimated here mainly originates from the van der Waals attraction between the interlayer except for another effect such as

FIG. 3: A pair of TEM images for the nanotubes after the extraction: (a) the outer shell and (b) the extracted inner shell of the nanotube.
FIG. 5: Illustration of a double-walled nanotube in which the both ends of the inner shell are capped and one end of the outer shell is capped. The inner shell and the outer shell are (5,5) and (10,10) nanotubes, respectively.

FIG. 6: Sliding distance dependence of the sliding force estimated from the molecular mechanics calculation for the double-walled nanotube: (a) for the entire force range and (b) for the expanded view of the plateau in (a).

the edge effect of the inner or outer shell of the nanotube.

In order to investigate the interlayer slipping of the nanotube, we have also performed molecular mechanics calculations for a double-walled nanotube, where an empirical potential field of MM3 [21] is used for stabilizing the structure. Figure 5 shows an illustration of the double-walled nanotube used in the calculations, in which both ends of the inner shell are capped and one end of the outer shell is capped. The inner shell and the outer shell are a (5,5) nanotube with a diameter of 0.64 nm and a (10,10) nanotube with a diameter of 1.3 nm, respectively. The lengths of the nanotubes are ∼4.5 nm. At first, the entire structure was stabilized without a tensile load, resulting in the complete extraction of the inner shell of the nanotube from the outer shell. After that, the total energy was calculated for each step with different sliding distances. The sliding force was estimated from the slope of the dependence of the total energy on the sliding distance.

Figure 6 shows the sliding distance dependence of the sliding force estimated from the molecular mechanics calculations. The sliding force for a distance less than 0.8 nm shows a peak corresponding to the cap-cap interaction between the inner and the outer shell. In a distance region between 1∼3.5 nm, the distance dependence of the sliding force has a plateau of 1 nN. The force gradually decreases with increasing the distance and becomes zero corresponding to the complete extraction of the inner shell. It is noted that a small ripple of ∼5 pN on the sliding force with the period of the honeycomb structure of the nanotube has been observed on the plateau. Furthermore, we have also performed the calculation for the nanotube with (5, 5) and (10, 9) shells in order to investigate the effect of chirality on the sliding process. This system also shows a plateau with a sliding force of 0.7 nN and a ripple with an amplitude of ∼5 pN on the plateau.

IV. ELECTRICAL CONDUCTION DURING SLIDING

Pt-coated Si probes for an atomic force microscope were used as electrodes of the nanotube. All measurements were also performed in the nanofactory. The procedure for measuring the two-terminal resistance during the sliding process is shown in Fig. 7. First, an individual nanotube is bridged to electrodes, which are Pt-coated Si probes for SPM and Pt-coated knife edge. After a number of outer layers are removed by the electrical breakdown process, one of the electrodes gradually moves away to slide the interlayer of the nanotube and then the sliding distance dependence of the current is measured.

Figure 8(a) shows the current-voltage (I−V) characteristics. From a slope at V < 0.1 V, the two-terminal resistance of the nanotube, R, is estimated to be ∼17 kΩ. The electrical breakdown was started at V = 3.53 V and I ∼ 250 µA and the current then decreases stepwisely in a temporal variation as shown in Fig. 8(b). After the current decreased to ∼100 µA corresponding to R = 30 kΩ, the applied voltage was reduced to 0.2 V in order to
FIG. 7: Schematic illustrations for electric resistance measurement of the nanotube for the interlayer sliding.

prevent the further destruction of the nanotube. As a result, the current is reduced to 1.3 µA and the resistance becomes 150 kΩ. Corresponding $R - V$ property is also shown in Fig. 8(c). Figure 8(d) shows the sliding distance, $x$, dependences of $I$ and $R$. The resistance increases exponentially with $x$ with an initial slope of 121 Ω/nm. Finally, $R$ reaches 350 kΩ at $x = 800$ nm corresponding to the distance just before the full extraction of the inner shell. In this manner, the interlayer sliding of the processed multiwall nanotubes acts as the nanoscale displacement sensors with the resistance variation of ~0.1% per 1 nm. In order to realize the position sensor using this mechanism, the extracted nanotube must be retracted. In this experiment, the nanotube could be retracted with a range of ~100 nm. Further sliding causes an irreversible deformation of the nanotube, because of the flexibility of the thinned nanotube and the contamination deposition during the experiment.

Figure 9(a) shows the $I - V$ characteristic for another nanotube. From a slope at $V < 0.1$ V, $R$ is estimated to be ~34 kΩ. In this case, however, the resistance measurement during the slide was started at $I = 66$ µA with $V = 2.49$ V. This value is much higher than that shown in Fig. 8. As shown in Fig. 9(b), the resistance is proportional to $x$ with a slope of 46 Ω/nm at $x < 400$ nm and slightly deviates from the straight line at $x > 400$ nm. This behavior is quite different from the low current condition shown in Fig. 8(b).

It has been theoretically predicted that the transmission probability of the electrons for an interlayer of the double wall nanotube is varied from 0 to 1 at zero temperature depending on their chirality and the electron energy, even when their overlap is a few angstrom [22]. On the other hand, in our experiment, there are 5~10 layers with a wide variety of chiralities between the outermost layer and the inner layer for the sliding. In addition, the experiments are performed at room temperature under high electric field for the interlayer. Consequently, the chirality dependence is expected to be blurred and the transmission probability must be less than unity during the sliding process. This is consistent with the two terminal resistance of 150 kΩ at low bias region after the electrical breakdown process becomes higher than that before the process as shown in Figs. 8(a) and 8(c). This indicates that these layers act as a barrier for the electron transport through the nanotube. This barrier effect is consistent of the result obtained in previous section. The graphene layers couple with the ideal van der Waals interaction, so that very weak interaction can be expected for interlayer electrons under no electric field. In presence of the electric field between the layers, the electrons start to the hopping transition. In this case, we might expect that the transmission probability is proportional to the overlapping length of the slide. However, in the case of the low bias condition shown in Fig. 8, the current is not inversely proportional to $x$, but the resistance increases exponentially with $x$. This dependence may come from the electric field concentrations to the cutting edge of the removed carbon layers, so the electrons mainly hop at the edge because of the higher electric filed.

We found that the sliding distance dependence of the resistance can be fitted as “localization” of the electrons on the nanotube described as $R = R_c + R_0\{\exp[2(x + L_0)/L_c]\}^{-1}$, where $R_c$ is the contact resistance, $R_0$ is a half of a quantum resistance of 6.45 kΩ, $L_0$ the initial length and $L_c$ the localization length [23]. From the fitting, $R_c$, $R_0$, $L_0$ and $L_c$ are estimated to be 140 kΩ, 6.35 kΩ, 255 nm and 840 nm, respectively. The estimated initial length and $R_0$ are close to the initial extracted length of 220 nm estimated from the SEM image and a half of a quantum resistance, respectively. These good agreements indicate that the extracted part of the nanotube acts as the localization system with the localization length of 840 nm.

Cumings, et al. also reported similar localization length of the multiwall nanotubes around 1 µm obtained from similar method and similar argument [17]. Furthermore, Hobara, et al. reported that the conductance of the
multiwall nanotube is proportional to the ratio between the cross section and the length and saturates at certain ratio which corresponds to the length less than 800 nm [24]. This result supports that the localization length of the multiwall nanotube is around 840 nm. However, the formula for the localization used here is applicable to the case in which the localization length is much smaller than the system length, i.e., the nanotube length. This is a subject for further study.

On the other hand, under the high current condition of 66 µA, the nanotube temperature during the sliding process is expected to be more than 1000 K [25], so that the electron transport in the nanotube must be diffusive rather than ballistic. The experimental data at \( x < 400 \) nm can be fitted well with \( R = R_c + \rho L_0 + x / 2\pi r \) as indicated by a solid line in Fig. 9(b), where the 2nd part of the equation corresponds to the diffusive transport, where \( \rho \) is the resistance per unit length of the nanotube, \( L_0 \) the initial length of the extracted part of the nanotube and \( L \) the sliding distance. We estimate \( R_c + \rho L_0 / 2\pi r \) to be 37.1 kΩ from the fitting.

Bourlon, et al. proposed a Zener tunneling model for the conduction mechanism of the multiwall nanotube under the high bias condition [26]. In this model, the transmission probability for the nanotube along the tube axis shows exponential dependence at the high bias condition and is independent of the length under the low bias condition. However, in our experiments, the resistance shows exponential dependence under the low bias condition and is proportional to the length at the high bias condition. This discrepancy may come from ignoring the bias voltage dependence of the interlayer transmission probability on the Zener tunneling model. Particularly, the interlayer transport of charge carrier in c-axis of the graphite shows much lower probability than in-plane (ab-plane) transport probability because of the weak coupling of the interlayer of the graphene sheet. Furthermore, in our experiments, the nanotube is suspended and free from the substrate, so that the temperature of the nanotube depends on the current passing through the nanotube and becomes high.
over 1000 K under the high bias condition [25]. Consequently, we can conclude that the interlayer hopping acts as the barrier and induces a strong nonlinear dependence of the resistance after the destruction shown in Fig. 8(c).

It is noted that the current during the sequential distractions of the nanotubes, which is given by \( R_c + \rho L_0 / 2\pi r \), is proportional to the radii of the extracted part of the nanotube, i.e., \( 2\pi r / \rho L_0 \). Therefore, the contact resistance \( R_c \) under the high current density is close to zero. This indicates that the transmission probability of the electrons for the interlayer at high temperature is close to unity. At the sliding distance larger than 400 nm, the data slightly deviate from the line. This is because the temperature on the extracted part of the nanotube decreases due to the decrease in the current, so that the transport mechanism of the electrons is changed.

V. CONCLUSIONS

We have investigated mechanical and electrical properties of the freestanding individual multiwall carbon nanotube during the interlayer sliding using the nanofactory. The sliding force for the interlayer with a diameter of 5 nm is maintained constant at 4 nN. This phenomenon agrees well with both of the theoretical prediction based on the van der Waals attraction and the molecular mechanics calculation using the empirical potential. The molecular mechanics calculations have also revealed a small ripple of ~5 pN on the sliding force with the period of the honeycomb structure of the nanotube. From the electrical conduction measurements, the resistance increases exponentially with increasing sliding distance under low current condition such as 1.3 µA. This can be explained as the weakly localized one dimensional system with the localization length of ~1 µm. On the other hand, under the high current condition of 66 µA, the resistance is proportional to the sliding distance. This indicates that the nanotube acts as the diffusive conductor at high bias voltage because of high temperature. Finally, the proposed process provides an ideal linear sliding interface of the interlayer of the nanotube and is useful for construction of a nanomechanical system using a multiwall nanotube.

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