Nanoengineering of carbon nanotubes for nanotools

Yoshikazu Nakayama\textsuperscript{1,2} and Seiji Akita\textsuperscript{1}

\textsuperscript{1} Department of Physics and Electronics, Osaka Prefecture University, Sakai, Osaka 599-8531, Japan

\textsuperscript{2} Handai Frontier Research Centre, Osaka University, Suita, Osaka 565-0871, Japan

E-mail: y-nakayama@mte.biglobe.ne.jp

New Journal of Physics 5 (2003) 128.1–128.23 (http://www.njp.org/)
Received 30 June 2003
Published 3 October 2003

Abstract. We have developed a well controlled method for manipulating carbon nanotubes. The first crucial process involved is to prepare a nanotube array, named a nanotube cartridge. We have discovered a method of positioning nanotubes at the knife-edge. The nanotubes used were multiwalled and prepared by an arc discharge with a relatively high gas temperature. The second important process is to transfer a nanotube from the nanotube cartridge onto a substrate in a scanning electron microscope (SEM). Using this method, we have developed nanotube tips and nanotube tweezers that operate in a scanning probe microscope (SPM). The nanotube probes have been applied for the observation of biological samples and industrial samples to clarify their advantages. The nanotube tweezers have demonstrated their motion in an SEM and have operated to carry nanomaterials in a SPM.

We have also developed the electron ablation of a nanotube to adjust its length and the sharpening of a multiwall nanotube to have its inner layer with or without an end cap at the tip. For the sharpening process, the free end of a nanotube protruding from the cartridge was attached to a metal-coated Si tip and a voltage was applied to the nanotube. When a high voltage was used in the saturation current regime, the current decreased stepwise in the temporal variation, indicating the sequential destruction of individual nanotube layers. The nanotube was finally cut at the middle of the nanotube bridge, and its tip was sharpened to have an inner layer with an opened end. Moving up the cartridge before cutting enables us to extract the inner layer with an end cap.

It is evidenced that the maximum current in each layer during the stepwise decrease depends on its circumference, and the force for extracting the inner layer with \( \sim 5 \text{ nm diameter} \) is \( \sim 4 \text{ nN} \).
1. Introduction

It is well known that carbon nanotubes [1] have unique structure and properties which are quite suitable for probes in a scanning probe microscope (SPM). Conventional SPM probes are made of Si or Si$_3$N$_4$ and have shapes of a pyramid or cone with a tip radius of curvature of 10 nm or often much larger. On the other hand, nanotube probes have the following advantages.

(1) Small tip radii of curvature (the minimum value is \( \sim 0.35 \) nm) significantly improve their lateral resolution.

(2) High aspect ratios of 10–10$^3$ provide the ability to probe abrupt height transitions with high fidelity.

(3) Tips of nanotubes can be cut and chemically functionalized to be used as probes for chemical force microscopes [2].

(4) Nanotubes whose tips have a small particle of magnetic metal are used as a probe for a magnetic force microscope [3]. These probes have also operated with a high resolution due to the high aspect ratios.

(5) Nanotubes are mechanically flexible and can be elastically buckled without damage [4]– [7]. Thus nanotube probes are robust and will not be broken off by an accidental crash on a sample surface, whereas conventional probes are easily chipped. The elastic buckling of nanotubes also limits the maximum force that can be applied to a sample, which can prevent damage to delicate organic and biological samples.

(6) Both ends of nanotubes are generally capped when they are prepared by an arc discharge method. These caps are so chemically and physically stable that nanotube probes will have a long life (small wearing degree) and can be used for nanoprocesses such as deposition and etching using an SPM.
In order to fabricate nanotube probes, the attachment techniques of a nanotube onto a conventional Si tip under the observations of an optical microscope [4] and a scanning electron microscope (SEM) [6, 7] have been adopted. The growth of a nanotube from a Si tip has also been examined as a mass-production process [8]. However, only the manipulation process with SEM has a potential precisely to control the position, angle and length of a nanotube on a Si tip. Recently, using this process, we have developed nanotube tweezers formed on a Si tip and in addition an SPM-based nanomanipulator installed with the tweezers that enables nanosized substances to be carried. One expects that this system will provide a manipulation technique on a nanometre scale that is crucial for the progress of nanoscale science and technology. Nanotube tweezers formed on a glass rod were previously demonstrated [9], but they cannot operate in SPMs.

Arc-discharge produced multiwall nanotubes have a straight shape with extremely high strength due to their highly crystallized structure and are suitable for such nanotube devices as compared with single-wall nanotubes. However, in terms of a high resolution imaging single-wall nanotubes are superior to multiwall nanotubes, although multiwall nanotubes sometimes have small tip radii of curvature comparable to those of single-wall nanotubes. In order to overcome this disadvantage of multiwall nanotubes we have developed several processes based on the nanoengineering of nanotubes: a shortening process of nanotubes using electron ablation [10] and sharpening processes to prepare a thin tip with and without a cap using electrical breakdown [11, 12]. A multiwall nanotube probe with a tip consisting of the innermost layer provides the high resolution of the single-wall nanotube probe and has the high stiffness of the multiwall nanotube probe. The sharpened tip with an opened end can be chemically modified for chemical force microscopy.

These processes have also been performed in an SEM manipulator. Recently, we have succeeded in the measurement of optical emission from the nanotube during the sharpening process, which provides information on the carrier transport at the excess current state. We have also measured the sliding force when the inner layer of the nanotube is extracted after the electrical breakdown of some outer layers, where the extraction of the inner layer is the process used for preparing the sharpened tip with a cap.

In this section, we report the precise processes of the growth and manipulation of nanotubes, which enables us to fabricate not only nanotube probes but also nanotube tweezers. We then demonstrate SPM images taken by the resulting nanotube probes and the operation of nanotube tweezers. We also report the nanotube engineering for adjusting the length and sharpening the tip of multiwall nanotubes. In the last part, we discuss the carrier transport in the excess current state and the sliding force of the inner layer for the multiwall nanotubes.

2. Preparation of the nanotube cartridge

Nanotubes were prepared by a dc arc discharge method and had multiple walls. An arc was induced between carbon rods in a flow of helium at 200 Torr. The gas temperature in the arc was raised by cooling the gas surrounding the arc using a water cooling system, which was confirmed by optical emission spectroscopy [13]. At a higher arc temperature, the resultant nanotubes are thinner, the distribution of the diameter is narrower and the purity of nanotubes in the carbon products is higher. Nanotubes we used for probes and tweezers were 5–20 nm with an average of 10 nm in diameter and 1–5 µm long. The resultant carbon products are not yet free from carbon particles. Thus the separation of nanotubes from such large particles in the carbon products was carried out by ultrasonic dispersion in isopropyl alcohol followed by centrifugation.

New Journal of Physics 5 (2003) 128.1–128.23 (http://www.njp.org/)
Figure 1. (a) A schematic diagram of an experimental set-up used for preparing a nanotube cartridge by using ac electrophoresis and (b) a typical SEM image of the nanotube cartridge.

The nanotube cartridges were prepared using an ac electrophoresis method [14]. Figure 1 shows the experimental set-up for the ac electrophoresis and an SEM image of the nanotube cartridge [6, 7]. Two knife-edges were placed on a glass plate and separated with a 500 µm gap. The gap was filled with nanotube-dispersed isopropyl alcohol, and an ac electric field of 5 MHz and 1.8 kV cm\(^{-1}\) was applied to the two knife-edges. Although this nanotube suspension still contained nanoparticles, most nanoparticles did not move much and stayed between the two knife-edges, whereas nanotubes moved onto the knife-edges and in addition aligned almost parallel to the electric field. The nanotubes on the knife-edges remained fixed there by the van der Waals force after evaporation of the solvent.

This alignment and migration toward the region with higher electric field (electrodes) are caused by the Coulombic force acting on an induced electrical dipole in the nanotubes. This attraction depends strongly on the length of the dipole (the dipole moment), which is the reason why particles are hard to move but nanotubes move easily. The higher the frequency the more effective the electrophoresis phenomena become.

3. Fabrication of nanotube probes and nanotube tweezers

3.1. Manipulation of nanotube in an SEM

We have developed an SEM system equipped with two stages that could be independently manipulated from the outside [6, 7]. The nanotube cartridge and a conventional Si tip were set on the respective stages to transfer one of the nanotubes in the cartridge onto a conventional Si tip. This process is on the basis of the fact that most nanotubes are conductive. When an insulator tip of Si\(_3\)N\(_4\) was used instead of a Si tip, it was coated with a metal film such as Au or Os.

*New Journal of Physics* 5 (2003) 128.1–128.23 ([http://www.njp.org/](http://www.njp.org/))
Figure 2. Schematic diagram of an SEM equipped with three stages that can be independently manipulated from the outside and a gas source inlet for electron-beam induced deposition of thin films. Stages A and B are for a nanotube cartridge and a conventional Si tip, respectively. Stage C, on which nanotube tweezers prepared on a glass rod were installed, is used for the precise manipulation of nanotubes.

We have developed a more controllable SEM manipulator named the nanofactory as shown in figure 2. This has three stages. Two of them were used in the same way as those in the former SEM manipulator. On the third stage we installed a pair of nanotube tweezers prepared on a glass rod to manipulate nanotubes precisely. 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 the attachment of a nanotube on a Si tip, we have developed the following three processes. One is to use an electrostatic attraction as the driving force for transferring a nanotube [6, 7]. The Si tip and the nanotube were manipulated to adjust their gap to less than 1 µm, and a dc electric voltage of a few tens of volts was applied between the nanotube and the Si tip. The second one is to use a welding process to attach the nanotube onto the Si tip [15, 16]. The Si tip was manipulated to be in contact with a target nanotube and the dc current less than 1 mA was introduced into the contact for a fraction of a second to weld together. The target nanotube was finally pulled away from the cartridge. The corresponding current density is estimated to be $10^8$–$10^9$ A cm$^{-2}$ using the average diameter of 10 nm. The third one is to use a process of carbon deposition instead of the welding [15, 16], which has usually been used in the nanofactory. The carbon source was hydrocarbons remaining in the SEM chamber or intentionally induced. After the nanotube had been transferred onto the Si tip, the carbon film was deposited on it to make the attachment strong. It has been confirmed that the attachment force of the nanotube fixed by carbon films is at least 3 µN [7].

3.2. Fabrication of nanotube probe

These processes enabled us to select a nanotube in the cartridge and attach it to the specific position of the Si tip with an adequate protruding length. Figure 3 shows SEM images of
Figure 3. SEM images of nanotube probes with (a) a single nanotube (200 nm in protruding length) and (b) bundled nanotubes at the base and a single one at the very tip (650 nm in total protruding length). The diameters of the nanotubes are about 10 nm.

typical nanotube probes with different protruding lengths. The nanotubes were fixed at the most appropriate position on the Si tips. The tip in figure 3(a) has a single nanotube with an 11 nm diameter and the protruding length of 200 nm. On the other hand, the tip in figure 3(b) consists of bundled nanotubes to be thick at the base and a single nanotube of 10 nm in diameter at the very tip. The lengths of the base and tip are 600 and 50 nm, respectively.

The thick base is required for long nanotube probes to prevent the decrease in the resolution due to its thermal vibration. The amplitude at the tip is calculated to be larger than 0.5 nm when the nanotube probes are 10 nm in diameter and their length is longer than 500 nm. This causes, at least, 10% degradation of the resolution expected from the nanotube tip radius. Furthermore, the Euler buckling force of these long thin nanotube probes is less than 30 nN, which is comparable to the maximum compression force in a tapping mode AFM. Thus the unexpected deformation and vibration of the nanotube probes may occur during each tap.

3.3. Fabrication of nanotube tweezers

Repeating and combining the manipulation processes described above made it possible to attach two parallel nanotubes onto the Si tip, which is a pair of nanotube tweezers [17]. The relative position of the two nanotubes was adjusted using the third stage in the nanofactory. For the nanotube tweezers, two electric wires connecting to the respective nanotubes were prepared on the Si tip. A Ti/Pt film was coated on the tip and connected to three Al lines that were patterned on the cantilever by a conventional lithographic technique as shown in figure 4(a). The Ti/Pt film was separated into two by a focused ion beam of Ga and these two were independently connected to one or two Al lines as shown in figure 4(b). The dc voltage was applied between the separated Ti/Pt films through the Al lines to operate the tweezers.

After attaching two nanotubes onto the Si tip, the whole of the nanotube arms was coated with quite thin carbon films (a few nanometres to several nanometres) to be insulating outside, where the insulating nature of the carbon films was used. This film coating will prevent an enormous current flow when the two nanotube arms close, i.e. attach to each other or pick up

3 The Si tips with electric wires used for the nanotube tweezers were fabricated by Seiko Instruments Inc.
Figure 4. SEM images of a Si cantilever used as a base for nanotube tweezers. (a) Ti/Pt film was coated on the tip and connected to three Al lines patterned on the cantilever. (b) The Ti/Pt film was separated into two by a focused ion beam and these two were connected to one and two Al lines, respectively.

4. Properties of nanotube probes and nanotube tweezers

4.1. Stiffness of nanotube probes

One can expect that an atomic-force microscope (AFM) installed with a nanotube probe images with high fidelity an abrupt height change because of its high aspect ratio. However, if the nanotube probe interacts with the wall in terms of the van der Waals force and/or electrostatics to bend, the resulting image would be unstable. The electrostatics is especially serious because of the long-distance interaction. Thus we need information on the stiffness of nanotube probes in order to understand such behaviour. We measured the stiffness of nanotube probes using the SEM manipulator [18]. A single nanotube attached to a hard cantilever (spring constant of 40 N m$^{-2}$) was pushed laterally and perpendicularly using a soft cantilever (spring constant of 0.02 N m$^{-2}$). These results gave us the buckling force and the spring constant, respectively. From these measured values we estimated that the Young’s moduli of carbon nanotubes used ranged from 0.5 to 2 TPa. We also found out that the single-nanotube probe with the length of 500 nm does not have enough stiffness for the tapping mode imaging of the electrical insulator sample with an abrupt height change but the bundle one as shown in figure 3(b) works well, as is discussed later [18, 19].

4.2. Imaging using nanotube probes

We conducted tapping mode AFM imaging of several biological samples such as plasmid deoxyribonucleic acid (DNA) [6, 7, 20, 21], human erythrocytes [22], human proliferating cell nuclear antigen (PCNA) [23], and human replication factor C (RFC) [23, 24] to ensure the high potential of nanotube probes in this field because of their small tip radii as well as high aspect ratio. Figure 6 shows tapping mode AFM images of the human RFC complex taken using a conventional Si probe and a nanotube probe. The purified human RFC was incubated with 1 mM ATP, mounted on a freshly cleaved mica surface. After washing and drying, the sample
Figure 5. SEM images of nanotube tweezers at different applied voltages: (a) 0 V, (b) 2 V, (c) 4 V and (d) >4.5 V.

Figure 6. Tapping mode AFM images of the human RFC complex taken using (a) a conventional Si probe and (b) a nanotube probe.

was subjected to AFM observations. The carbon nanotube probe clearly visualized the molecular structure of the RFC, the heteromeric organization of five subunits aligned in an arc. The largest subunit was always positioned second from one end. The diameters of the largest subunit and smaller subunits were $31.2 \pm 1.3$ and $18.9 \pm 0.9$ nm, respectively. From this observation, we have proposed a molecular structure of RFC, in which one small subunit was on one side of the largest 145 kDa subunit, and the other three on the other side.

The nanotube probes have also been applied for observing industrial samples. The AFM observation of deep grooves prepared on a Si wafer [25] and pits in a 4.7 GB digital versatile disc, a so-called DVD, made from polycarbonate and before the metal coating [15, 16], revealed that the nanotube probe can image a steep slope at an abrupt height change of more than 80° but a conventional Si cannot. This is because of the high aspect ratio of nanotube probes. It has
been pointed out that increasing the stiffness using bundle nanotubes at the base of probes is important to prevent the instability caused by the electrostatic force from the wall of such an abrupt height change [18, 19]. Because of its high aspect ratio, the nanotube probe has revealed the existence of local solvation of water [26].

Using the electric conduction of nanotubes we successfully applied nanotube probes to Kelvin force probe microscopy [27] and SPM lithography with a high resolution [28, 29]. We also applied a nanotube probe to a scanning tunnelling microscope (STM) [30]. Figure 7 shows a series of atomic images of the Si(111)-7×7 surface (20×20 nm²) taken every 10 min using a nanotube probe with the length of 800 nm attached to a tungsten tip. This indicates no degradation atomic-scale imaging for 80 min. Even if the nanotube probe touched the sample surface, the atomic nature in STM images did not degrade.

Metal-capped nanotubes have enabled us to observe magnetic information in a hard disk [3, 31]. The physical stability of nanotubes has demonstrated a high potential as a nanoindentation tips [32, 33], which will realize information storage with an order of 10¹² bytes. In this way, the nanotube probe (or tip) has been proved to be the ultimate for SPM imaging and SPM processing.

4.3. Operation of nanotube tweezers

The operation of the nanotube tweezers was examined in the SEM chamber [17]. Various voltages were applied between the two arms to get them to close due to an electrostatic attraction force. The motion of the nanotube arms was recorded on videotape. Figures 5(b)–(d) show the motion of the nanotube arms as a function of the applied voltage $V$. The left- and right-hand arms were grounded and positively biased, respectively, which is reflected in the poor image contrast of the right-hand arm. It is clearly seen that the arms bend and the separation between the tips becomes narrow on increasing the applied voltage. The separation becomes 500 nm at $V = 4$ V and zero at $V > 4.5$ V. It is noted that the motion in figures 5(a)–(d) could be repeated many times without any plastic deformation.

Figure 7. A series of STM images of the Si(111)-7×7 surface (20×20 nm²) taken using a nanotube probe every 10 min. The sample bias voltage and tunnelling current were +1.9 V and 0.5 nA, respectively.
Figure 8. Applied voltage dependence of the separation between the tips of the nanotweezers. Open circles denote the experimental results and dotted, solid and dash–dotted curves denote the numerical calculations for the different diameters of nanotubes: 10, 13.3 and 15 nm, respectively. In the calculations a length of the nanotube arms of 2.5 µm and Young’s modulus of 1 TPa are used.

It is also noted that the carbon films coated on the nanotube arms work well to prevent the current flow through the nanotube arms at $V > 4.5$ V. A pair of tweezers, where the nanotube arms do not bear the carbon films, can be used for measuring the electrical conduction of nanomaterials. However, the operation voltage is restricted so that a large current did not flow through the nanotube arms. When a voltage was applied beyond the threshold value for which the nanotube arms close completely, the nanotube arms suddenly deformed or sometimes disappeared.

The motion of nanotube arms shown in figure 5 was well explained by a numerical calculation based on a balance between the electrostatic attraction and the bending moment of the nanotube arms [17]. Figure 8 shows the applied voltage dependence of the separation between the tips of the nanotube arms, in which a typical value of 1 TPa of Young’s modulus was used and the diameter of the nanotube arms was changed as a fitting parameter. It is clear that the calculation with the diameter of 13.3 nm (solid curve) agrees well with the experimental data (open circles). This indicates that the assumption adopted in the calculation is reasonable. The nanotubes can be treated as an elastic material being uniform and continuous. The calculation shows that the sudden closing at $V > 4.5$ V in figure 5 is not caused by the buckling of the nanotubes but by losing the balance between the electrostatic attraction and the bending moment of the nanotube arms.

The numerical calculation also allows us to estimate the grasp force of the nanotube tweezers. The grasp force ranges from less than nN to a few tens of nN, depending on the size of nanomaterial to be grasped.

We have developed a specially designed SPM in which the nanotube tweezers operated to carry nanomaterials [34, 35]. The work flow was the following: (1) the observation of the sample surface with the closed tweezers, (2) the movement of the tweezers to a target nanomaterial, (3) the transfer of the nanomaterial (picking up, carrying and release) and (4) the confirmation of the result by imaging the sample surface.

*New Journal of Physics* 5 (2003) 128.1–128.23 (http://www.njp.org/)
When the attraction between the tweezers and the nanomaterial is higher than that between the nanomaterial and the substrate, the electrostatic force induced by a voltage applied to the tweezers against the substrate is necessary to release the nanomaterial after opening the tweezers.

Figure 9 shows the demonstration of the manipulation of a nanoparticle using the tweezers shown in figure 5. One silica particle with the diameter of ~200 nm on a Si substrate appearing in the AFM image of figure 9(a) was grasped and moved ~200 nm left. This is confirmed by the image shown in figure 9(b), which was taken after the transfer process.

Figures 10(a) and (b) also show AFM images before and after the manipulation of a nanotube with the diameter of 20 nm and the total length of 1 µm lying on a Si substrate. The lower part of the nanotube was grasped and moved ~500 nm left. However, the image after the process indicates that only the lower part of the nanotube moved so that the nanotube bent. Eight minutes later, the bent part of the nanotube moved slightly back as shown in figure 10(c), because of the strong restoration nature of the nanotube.

5. Nanoengineering of nanotubes

In the nanoengineering of nanotubes, we have used the electric conductance of nanotubes. Thus the nanotube cartridge was prepared using a razor coated with Pt in order to improve the electric...
contact with nanotubes. Si tips were also coated with Pt. When a nanotube in the cartridge was brought into contact with the Pt coated Si tip, the current passing through the nanotube was monitored at a bias voltage of $\sim 2 \text{ mV}$ in order to confirm the electric contact between the nanotube and the Si tip.

The contact resistance was measured from the current–voltage ($I$–$V$) characteristics in the low bias voltage region of $V < 10 \text{ mV}$. It is noted that the current is as low as the order of nanoamperes just after making contact because of the high contact resistance. The current drastically increases by exposing the contacted region of the nanotube and the electrode to the electron beam for 3–60 s. This is because of deposition of amorphous carbon that makes the contact area increase.

5.1. Electron ablation of nanotubes

In order to adjust the nanotube length, we have proposed an electron ablation method, which utilizes electrons emitted from the counter nanotube by field emission [10]. To process the nanotube on the probe, the nanotube probe was manipulated in front of a nanotube on the cartridge, which was used as a field emission source, as schematically illustrated in figure 11, where a gap between the two nanotubes was maintained to be $0.5–2 \mu m$. The voltage applied between the nanotubes was varied from 0 to 200 V. This process was performed inside the nanofactory at a pressure less than $2 \times 10^{-4} \text{ Pa}$.

Figure 12(a) shows an SEM image of the as-prepared nanotube probe with the length of $4.8 \mu m$ positioned in front of the emitter nanotube with the length of $\sim 2 \mu m$. After several cycles, the nanotube was successfully shortened to $1.6 \mu m$ as shown in figure 12(b). Figure 12(c) shows an SEM image after one additional cycle. The nanotube length has become $1.3 \mu m$. Three more processes reduced the length to be $500 \text{ nm}$ as shown in figure 12(d). It should be noted that the nanotube used as the field emitter does not change its initial length. Figure 12(e) shows a transmission electron microscope (TEM) image of the end of the processed nanotube. The end is open and not sharpened. It has been evidenced that this process reduces the length of nanotubes by $\sim 100 \text{ nm}$ range per step.
Figure 12. A series of SEM images of the shortening process of the nanotube probe. (a) and (d) correspond to the initial and final states, respectively, and (c) is after one cycle of processing applied to (b). (e) TEM image of the processed tip.

Figure 13 shows the $I-V$ characteristics during the process with the gap of 1 $\mu$m as shown in figure 12(b). The emission current appears at $\sim 60$ V and increases monotonically with the voltage. At voltages higher than $\sim 95$ V, the current suddenly fluctuates and shows a spike of $\sim 1$ $\mu$A at 115 V, as indicated by the thick arrow in figure 13. When the voltage is decreased before the spike appears, the nanotube on the probe retains its original length. Therefore, the nanotube is shortened at the current spike.

There are some possibilities causing electron ablation of the nanotube. Excess electrons at the bonding states, the lattice vibration due to Joule heating and the field effect at the positive electrode can cause the instability of C–C bonds. However, the physical sputtering of carbon atoms and the bond breaking due to the excitation of core electrons do not take place because of an insufficient kinetic energy. It is difficult to imagine that the field evaporation of carbon atoms is a main reason, because the electric field of 2–3 V nm$^{-1}$ at the tip estimated from $V/2\beta r$ is less than one-third of the reported threshold, of the order of 10 V nm$^{-1}$ [36], where $V$ is the applied voltage and $\beta$ and $r$ are the shape factor of 3–5 and the radius of the tip, respectively. However, the threshold decreases steeply with increasing temperature [37]. The fact that the ablation occurs when the spike appears indicates that the spike is due to a microplasma initiated by the carbon ion clusters emitted from the nanotube tip. Thus the most probable mechanism is the combination of the electronically and thermally induced bond instability and the field effect.
5.2. Sharpening of nanotube tips

To sharpen nanotube tips we have proposed an excess current method that peels off the layers of multiwalled nanotubes one by one from the outermost layer [11]. A nanotube was bridged over the gap with 240 nm between two electrodes of the Pt coated knife-edge and the Pt coated Si tip as shown in figure 14(a). Figure 14(b) shows the $I$–$V$ characteristics for the nanotube. The current is proportional to the voltage in a low bias regime, which shows the resistance of $\sim 30\, k\Omega$. With increasing voltage, the current tends to increase superlinearly and saturates at $\sim 190\, \mu A$. The current then decreases stepwise in a temporal variation as shown in figure 14(c). The current finally became zero and the nanotube was cut. The discrete steps correspond to the sequential destruction of individual layers from the outer in the multiwall, which is the upper process illustrated in figure 15. The TEM image (a) shows the cut end of the Si-tip side. The cut end is sharpened to have the innermost layer at the tip. The damage of the layer seen in the figure was induced during the TEM observation. This is not essential.

The most reasonable consideration for the destruction of the layers is that the excess current passing through the nanotube induced the heating due to the electron–lattice interaction and evaporation started from the outermost layer. Since the process was done in vacuum of $\sim 10^{-5}\, \text{Pa}$, an effect of oxygen cannot be ignored. However, it might only give an initiation and does not dominate a main process, because of the insufficient amount of oxygen. In figure 14(c) gradual decreases of the current are observed in addition to the clear step decreases. The clear step decrease indicates instantaneous evaporation of the outer layer and the gradual decrease indicates the progress of partial evaporation.

We have measured the protruding length of the nanotubes after cutting. One is the length for the Si tip side denoted by $L_t$ and the other is for the knife-edge side denoted by $L_k$. Figure 16 shows these values plotted as a function of the initial length $L_B$ which is the gap between the knife-edge and the Si tip. It is noted that the values of $L_t$ and $L_k$ almost fall on a straight line with a slope of $1/2$. When the nanotube has a lattice defect, the local heating might occur at this point by an excess current. We have confirmed that the deformed nanotube is cut at the
Figure 14. Electrical breakdown process. (a) SEM image of nanotube before the process, (b) \( I-V \) characteristics and (c) the temporal variation of the current.

Figure 15. Sharpening process to produce a tip with and without a cap. TEM images of (a) opened tip, (b) capped tip and (c) a typical multiwall nanotube. The arrow indicates the end cap of the innermost layer.

dehomed point by an excess current. From this point of view the result in figure 16 suggests that uniform heating takes place instead of localized heating. For the uniform heating the centre of the bridged nanotube is especially heated up because the heat can only flow along the nanotube toward the knife-edge and the Si tip in vacuum. Thus the centre becomes a cutting point and the length of the nanotube probes is adjustable by changing the bridge length.

The second approach for sharpening nanotube tips is the lower process illustrated in figure 15. After removing a certain number of layers, the knife-edge is moved to extract the inner layer of the nanotube [12]. It is noted that the inner layer of the multiwall nanotube often
Figure 16. Lengths of the cut nanotubes for the Si tip side $L_t$ and the cartridge side $L_k$ plotted against the bridged length $L_B$.

Figure 17. $I$–$V$ characteristics and the temporal variation. The inner tube was extracted at the thick arrow.

ends with a short length. The TEM image (c) in figure 15 is an example. The nanotube has a diameter of 12 nm and 14–15 layers. The thick white arrow points to the end of the innermost layer which has a cap. Figure 17 shows the $I$–$V$ characteristics for the extraction process. From a slope at $V < 0.1$ V, the two-terminal resistance is estimated to be $\sim 40$ k$\Omega$. With increasing applied voltage, the current increases superlinearly and saturates to be $\sim 150$ $\mu$A around 2.7 V. The temporal variation of the current after the saturation shows the stepwise decrease. These behaviours are similar to those in figure 14. Drawing of the nanotube was performed when the current became $\sim 100$ $\mu$A corresponding to the current after three steps as indicated by a thick arrow in figure 17.
Figure 15(b) shows a TEM image of the extracted nanotube. The extracted nanotube has a diameter as small as $\sim$3 nm and the length of $\sim$80 nm. Its very tip has a rounded structure, indicating a cap, which is different from the sharpened nanotube shown in figure 15(a). The diameter of the original nanotube was measured to be 7 nm from the TEM image near the base. The number of broken layers is estimated to be six from the reduced diameter and the interlayer distance of 0.34 nm. However, the counted number of steps is only three as described above. The discrepancy suggests that three layers were suddenly broken during the drawing process. This is possible because the excess current flowed under the tensile load. In this way, we have successfully fabricated the sharpened nanotube probe with a capped tip.

5.3. Excess current phenomena

We have investigated in detail the excess current phenomena which were used for the sharpening process of nanotube probes [38]. Figure 18(a) shows $I-V$ characteristics cyclically measured for a nanotube. Trace 1 is the curve measured just after the nanotube was attached on a Pt coated Si tip by carbon deposition. The curve in a low voltage region $V < 10$ mV shows the resistance of $\sim$30 k$\Omega$. At a high voltage of $\sim$2.5 V the current steeply increases, which is trace 2. The curves in traces 3 and 4 indicate that the resistance decreases to 15 k$\Omega$ which is comparable to the quantum resistance $G_0$. This change is caused by the decrease of the contact resistance mainly at the Pt coated Si tip. It can be considered that a few molecular layers of amorphous carbon covered the Pt coated Si tip during the manipulation of the nanotube to be attached and worked to increase the contact resistance. A large current of $\sim$200 $\mu$A heated the contact portion to induce the phase change of carbon from amorphous to crystalline, and hence the resistance became low.

In trace 4 the current increases superlinearly to have a resistance as low as 6.5 k$\Omega$ and then reaches saturation. The electron transport in metallic nanotubes is ballistic [39] so that the superlinear increase appearing in a high voltage regime is due to the space charge limit transport. The injection of the excess electrons in the nanotube induces the electron–phonon interaction to have current saturation and heating. With increasing temperature some portion in the outermost layer starts to evaporate and the current decreases stepwise. In trace 5 this process is repeated.
and several steps of the current decrease appear. This is clearly seen in figure 18(b) where the temporal variation of the current is plotted.

We have measured the optical emission intensity from the nanotube in addition to the current. These data are also plotted in figure 18(b). The optical intensity increases stepwise from 1100 to 1160 s, which corresponds to the voltage increase from 2.6 to 2.8 V with the step of 10 mV. Similar correspondence appears when increasing the voltage for 1200–1220 s, 1280–1300 s and 1370–1390 s. However, it is noted that the current does not change for those terms, i.e. being independent of the voltage. The optical intensity is stable when the voltage does not change, but decreases steeply as the current does when the outer layer is broken. These results indicate that the increase in the voltage is applied only to the heated portion and some mechanism works to limit the current but increase the optical intensity. The most probable mechanism is that the increase in the voltage is not used for accelerating the velocity of electrons but for amplifying the lattice vibration. This suggests that when an electron is accelerated to a certain velocity, it transfers to a lower energy state by emitting a phonon, and therefore the increase in voltage decreases the mean free path of an electron to increase the number of phonons emitted per electron.

If this model works, the optical emission is due to the blackbody radiation and the circumference of the corresponding outermost layer determines the current at each step. We have confirmed the first one, which will be reported elsewhere. In order to clarify the second one, the current in figure 18(b) is plotted as a function of the number of the broken layer in figure 19. The calculation was performed using \( I = 2\pi r J_0 \) with \( J_0 = 7.14 \text{ mA nm}^{-1} \), where the radius \( r \) of the original nanotube is assumed to be 8.5 nm. Other experimental data including the data in figures 14 and 17 are also plotted in figure 19. The radius of the nanotube in figure 17 is known to be 3.5 nm as described above and this is consistent with the plot in figure 19. It is obvious that several experimental data are in agreement with the calculation, which strongly suggests that our model is correct.

5.4. Sliding force of inner layer

In order to estimate the sliding force needed to extract the inner layer of a multiwall nanotube, we have performed the force measurement in the nanofactory. The procedure to measure the sliding force is schematically illustrated in figure 20. First, the nanotube is bridged between two cantilevers as shown in figure 20(a), where one of the cantilevers has a spring constant of 2 N m\(^{-1}\) which is relatively hard and the other has a spring constant of 0.08 N m\(^{-1}\) which is much softer. After several steps of the electrical breakdown process, the hard cantilever is gradually moved to extract the nanotube. Thus the soft cantilever is deflected as shown in figure 20(b). The deflection is converted to the force for sliding the inner layer using the spring constant of the cantilever. Finally, the nanotube is completely apart and the soft cantilever moves backward to the original position as shown in figure 20(c).

Figure 21 shows the series of SEM images during the force measurement. The central part of the nanotube becomes thin after the electrical breakdown process as shown in figure 21(a). When the hard tip moves downward, the soft cantilever deflects slightly. The central part of the nanotube corresponding to the inner layer elongates as shown in figure 21(b). Finally, the nanotube is apart as shown in figure 21(c). The extracted part of the nanotube is \( \sim 700 \text{ nm} \) in length.
Figure 19. Current during the stepwise decrease plotted as a function of the number of steps. #2 and #4 are the data shown in figures 14 and 17. The estimated radius is also given.

Figure 20. Procedure to measure the sliding force for the extraction of the inner tube.

The result of the force measurement is also shown in figure 21, where \( \Delta L \) is defined as the change of the nanotube length. It is noted that both of the electrodes were set to \( V = 0 \) V in order to eliminate the electrostatic attraction. At \( \Delta L < 700 \) nm, the force for extraction keeps constant at \( \sim 4 \) nN, although the overlapping length between the inner and the outer layers is changed. At \( \Delta L > 800 \) nm, the force decreases rapidly, which corresponds to the separation of the nanotubes. It is noted that the extracted part of the nanotube is \( \sim 5 \) nm in diameter as estimated from TEM observation.

Under the first orders of approximation, the sliding force originating 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 area \( S(x) = 2\pi r x \), the van der Waals energy is given by \( U(x) = -(A/d^2)S(x)/12 \) [40], where \( A \) is the Hamaker constant for the interlayer 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, \( d = 0.34 \) nm and \( r = 2.5 \) nm, the van der Waals force is estimated to be \( \sim 2 \) nN, which is comparable to the experimental value.

New Journal of Physics 5 (2003) 128.1–128.23 (http://www.njp.org/)
Furthermore, the accurate calculation for the sliding force based on the van der Waals interaction has been reported [41]. This report predicts that the force is independent of the overlapping length, but depends on the diameter of the extracted portion and their layer numbers. Applying the core diameter of 5 nm, the sliding force is estimated to be 3–5 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 edge effect of the inner or outer layer of the nanotube.

In order to investigate in detail the interlayer slipping of the nanotube, we have also performed molecular mechanics calculations for a double-wall nanotube, where an empirical potential field of MM3 [42] is used for stabilizing the structure. Figure 22(a) shows an illustration of the double-walled nanotube used in the calculation. Both ends of the inner layer are capped and one end of the outer layer is capped. The inner layer and outer layer 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 length of the nanotube is \( \sim 4.5 \) nm. At first, the whole of the structure was stabilized without tensile load, resulting in the inner layer of the nanotube being fully retracted in the outer layer. After that, the total energy was calculated for each step with different sliding distances. The sliding force is estimated from the slope of the dependence of the total energy on the sliding distance.

Figure 22(b) shows the sliding distance dependence of the sliding force estimated from the molecular mechanics calculations. The sliding force for distance less than 0.8 nm shows a peak corresponding to the cap–cap interaction between the inner and the outer layer. In the region of the distance between 1 and 3.5 nm, the distance dependence of the sliding force has a plateau of 1 nN. The force gradually decreases and becomes zero when the inner layer is completely extracted. The small ripple of \( \sim 5 \) pN on the sliding force with the period of the honeycomb structure of the nanotube has been observed on the plateau as shown in figure 21(c). Furthermore, we have also performed the calculation for the nanotube with two layers of (5, 5) and (10, 9) in

---

New Journal of Physics 5 (2003) 128.1–128.23 (http://www.njp.org/)
order to investigate the influence of chirality on the sliding process. This system also shows the plateau with the sliding force of 0.7 nN and the ripple with the amplitude of $\sim 5$ pN and the pitch of 2.4 Å.

The estimation of the force for the nanotube used in the experiment from the calculation described above using the scaling rule gives $\sim 4$ nN that agrees well with the experimental result. This agreement indicates that our process provides the ideal sliding interface even after the electrical breakdown process.

6. Conclusion

The well controlled processes of the growth and manipulation of nanotubes have been developed to fabricate nanotube probes and nanotube tweezers. The growth process developed provides multiwalled nanotubes with an average diameter of $\sim 10$ nm and a high purity. The manipulation process developed enables us to fabricate nanotube probes with the most adequate structures for their purpose and in addition nanotube tweezers on the Si tip.

The application of nanotube probes to AFM observation of biological samples and industrial samples has revealed their advantages such as high resolution and traces of deep crevices with high fidelity. Other applications of the nanotube probes in SPM are also described.
The operation of the nanotube tweezers has been demonstrated. The separation between the tips of the nanotube arms decreases with increasing applied voltage and becomes zero beyond a certain voltage. The numerical calculation based on the balance between the electrostatic attraction and the bending moment of the nanotube arms well explained the experimental result of the electromechanical response and also gave the estimation of the grasp force of the nanotube tweezers. The resulting nanotube tweezers were installed in an SPM to manipulate nanomaterials such as SiO₂ particles and carbon nanotubes. This system will be used in organic and inorganic ultrafine particle research (mass measurements, electrical conductance measurements and elucidation of inter-particle effects), basic experiments in connection with molecular electronics and the assembly of compound devices as well as measurements of their characteristics, and research on gene functions by probing their correlations with proteins.

Furthermore, we have developed the nanoengineering of multiwall nanotubes to adjust the length and to sharpen the tip. The collision of electrons with the nanotube tip is effective for its ablation to adjust the length. The possible mechanism of the ablation is the electronically and thermally induced bond instability under a relatively high electric field at the positive electrode.

For the sharpening process, the excess current as large as in the saturation induces the electric breakdown, i.e. evaporation of the outermost layer, and then the current decreases stepwise. This process repeats to induce the sequential destruction of individual nanotube layers. Then finally the nanotube is cut and has a sharpened tip without an end cap. The nanotube which is extracted before cutting has a sharpened tip with an end cap. Even in the saturation region of current, the optical emission intensity increases with increasing applied voltage. From this result, we have concluded that the increase in the voltage is applied only to the heated portion and does not increase the velocity of electrons but amplifies the lattice vibration. The maximum value at each layer during the stepwise decrease is determined by its circumference.

The measurement of the sliding force for the inner layer with 5 nm in diameter showed that the force is \(\sim 4\) nN independent of the overlapping length, which is consistent with the result from the accurate calculation taking account of the van der Waals forces between the layers.

References

[1] Iijima S 1991 Nature 354 147
[2] Wong S S, Joseleievich E, Woolley A T, Cheung C L and Lieber C M 1998 Nature 394 52
[3] Arie T, Nishijima H, Akita S and Nakayama Y 2000 J. Vac. Sci. Technol. B 18 104
[4] Dai H, Hafner J H, Rinzler A G, Colbert D T and Smalley R E 1996 Nature 384 147
[5] Wong S S, Harper J D, Lansbury P T and Lieber C M 1998 J. Am. Chem. Soc. 120 603
[6] Nishijima H, Kamo S, Akita S, Nakayama Y, Hohmura K I, Yoshimura S H and Takeyasu K 1999 Appl. Phys. Lett. 74 4061
[7] Akita S, Nishijima H, Nakayama Y, Tokumasu F and Takeyasu K 1999 J. Phys. D: Appl. Phys. 32 1044
[8] Hafner J H, Cheung C L and Lieber C M 1999 J. Am. Chem. Soc. 121 9750
[9] Kim P and Lieber C M 1999 Science 286 2148
[10] Akita S and Nakayama Y 2002 Japan. J. Appl. Phys. 41 4887
[11] Negishi H, Akita S and Nakayama Y 2002 Int. Conf. on Science and Application of Nanotubes http://dielc.kaist.ac.kr/nt02/abstracts/P136.shtml
[12] Akita S and Nakayama Y 2003 Japan. J. Appl. Phys. 42 4830
[13] Akita S, Kamo S and Nakayama Y 2002 Japan. J. Appl. Phys. 41 L487
[14] Yamamoto K, Akita S and Nakayama Y 1998 J. Phys. D: Appl. Phys. 31 34
[15] Nishijima H, Akita S and Nakayama Y 1999 Japan. J. Appl. Phys. 38 7247

New Journal of Physics 5 (2003) 128.1–128.23 (http://www.njp.org/)
