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Electrical Characterization of Metal-Coated Carbon Nanotube Tips

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Electrical characteristics of bare and metal-coated carbon nanotube (CNT) tips were investigated with an independently driven four-tip scanning tunneling microscope (STM). The CNT was glued on a W tip apex and wholly coated *ex situ* by metal thin layers. The resistance between the CNT-tip end and the W supporting tip scattered very widely from *ca.* 50 kΩ to infinity for the bare tips, while coating the tip with a 6-nm-thick PtIr film stably reduced the resistance to less than approximately 10 kΩ. The W coating was also effective for stabilizing the resistance, although they showed slightly larger resistance (*ca.* 50 kΩ). The metal-coated tips kept their low resistance and flexibility even after 100 repeated contacts to an object for conductivity measurements. They are expected to be useful for nanometer-scale transport measurements with multiprobe STM as well as for conventional single-tip STM. [DOI: 10.1143/JJAP.44.L1563]

KEYWORDS: carbon nanotube (CNT), multiprobe scanning tunneling microscope (STM), pulsed laser deposition (PLD)

In addition to conventional single-tip scanning tunneling microscopy (STM),[1] multiprobe STM has recently attracted considerable interest because of its versatility for measuring electrical conductance through atomic- and nanometer-scale structures such as nanowires,[2] arrays of atomic chains,[3] and atomic steps.[4] In these measurements, electrochemically etched tungsten (W) tips were brought together within a distance from micrometers to several 100 nm; the minimum distance between the tips is limited by the radius of the W tip apex, which is larger than *ca.* 50 nm. Since such a probe spacing is not small enough compared with nanometer-scale objects/devices and the carrier mean free paths therein, a STM tip with a much smaller radius must be developed using, *e.g.*, carbon nanotubes (CNTs) because of their small radius.[5,6] We have demonstrated the minimum probe spacing of approximately 50 nm with two CNT tips in our multiprobe STM.[7] Furthermore, the CNT tips have many advantages over conventional W tips such as a high aspect ratio, physical and chemical stabilities and elastic flexibility,[8] which are very important as electrical probes directly contacting samples.

Recently, several investigators have developed such CNT tips by attaching a CNT on a supporting metal tip,[9–12] and reported STM imaging with the CNT tips. The fabricating methods are (1) bonding a CNT to a metal tip apex using an acrylic adhesive,[5] (2) growing a CNT directly on a metal tip apex by chemical vapor deposition,[11] (3) gluing a CNT on a metal tip apex by electron–beam-induced deposition of amorphous carbon,[13,14] and (4) connecting a CNT on a metal tip apex by AC dielectrophoresis.[15,16] However, the electrical resistance at the junction between the CNT and supporting metal tip scatters very widely from tip to tip. This may be because there exist insulating oxide/contamination layers between the CNT and metal tip in many cases. On the other hand, some of the present authors have recently succeeded in developing a method of coating the CNT tips uniformly with metal thin layers by pulsed laser deposition (PLD),[17] and demonstrated stable STM observations with the metal-coated CNT tips.[7,18] The ultrathin metal overlayer is expected to be a good conductive layer without disturbing the small curvature radius and flexibility of a CNT.[7,18]

In the present research, we have investigated electrical properties of both bare and metal (W or PtIr)-coated CNT tips with an independently driven four-tip STM. All the metal-coated and noncoated CNT tips studied here were prepared *ex situ* in different vacuum chambers by the method (3) mentioned above. Through the three-terminal measurement on a bare CNT tip, the resistance between the CNT tip end and the supporting W tip was found to scatter very widely from *ca.* 50 kΩ to infinity. However, by wholly coating the CNT tip with a thin PtIr layer, the resistance became stable and less than 10 kΩ. The W coating was also effective for stabilizing the resistance around 50 kΩ. It was also revealed that the metal-coated CNT tip survived even after 100 repeated contacts to an object for conductivity measurements. These results indicate that the PtIr-coated CNT tip is a promising probe for conductivity measurements of nanoscale materials and devices by multiprobe STM.

The multiwalled CNTs used here were commercial ones made by the arc discharge method (Materials and Electrochemical Research Co.), and typically 20 nm in diameter and over 3 μm in length. First, a CNT was glued on the end of an electrochemically etched W tip by electron–beam-induced deposition in a high-vacuum scanning electron microscopy (SEM)/STM system. Then in a separate chamber, the CNT–W tip was wholly coated with a metal thin film (5 nm W or 6 nm PtIr) by PLD.[17] These tips with or without metal coating were installed in a different chamber of the four-tip STM with SEM (Fig. 1).[19] It is noted here that the tips were thus fabricated *ex situ* and exposed to air, and no pretreatments were carried out before the electrical measurements. All measurements were done at $1\text{–}3 \times 10^{-8}$ Torr and room temperature.

Figure 2(a) shows a SEM image during a three-terminal measurement of the bare CNT tip (Tip A). By monitoring the current flow between Tip A and Tip B (conventional W tip) with 10 mV applied, Tip B was made to come in contact with the end of the CNT. We did not use STM feedback control to make direct contact to the CNT. When the current (I_{AB}) between Tip A and Tip B became larger than 1 nA, we

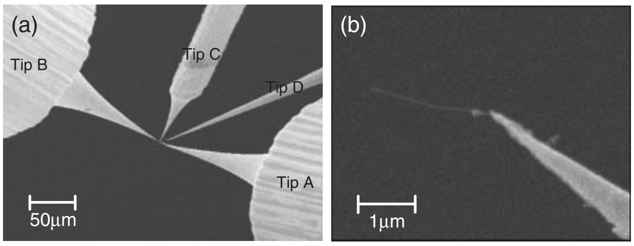

Fig. 1. (a) SEM image of tips in four-tip STM. One of the four-tips is the CNT tip (Tip A) and others are conventional W tips (Tips B, C, and D). (b) Closer look of CNT tip (Tip A).

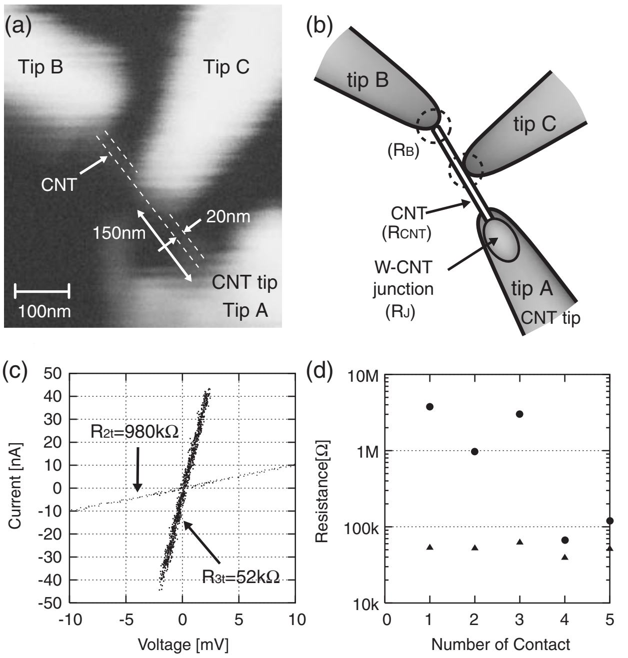

Fig. 2. (a) SEM image at three-terminal measurement of bare CNT tip. (b) Schematic drawing of tip arrangement. Tip A is a CNT tip, Tip B and Tip C are conventional W tips. (c) *I–V* curves at two- and three-terminal measurements. (d) Two-terminal resistance R_{2t} (●) and three-terminal resistance R_{3t} (▲) as functions of contact number.

measured the current–voltage (*I–V*) curve by measuring the voltage (V_{AB}) between Tip A and Tip B, giving the two-terminal resistance $R_{2t} = dI_{AB}/dV_{AB}$. Next, the third Tip C (conventional W tip) was made to come in contact with the CNT between Tip A and Tip B, and the voltage (V_{AC}) between Tip A and Tip C was measured with changing I_{AB}, giving the three-terminal resistance $R_{3t} = dI_{AB}/dV_{AC}$. In this case, no current flows through Tip C because of the large input resistance of the voltmeter, which ensures that the contact resistance between Tip C and CNT is not involved in the measured voltage drop. Since all the *I–V* curves were linear in the bias range of ± 10 mV for both two- and three-terminal measurements as shown in Fig. 2(c), we focus on the gradients to obtain the resistances.

R_{3t} is the sum of the resistance of CNT itself (R_{CNT}) and the resistance at the CNT–W junction of Tip A (R_J) [see Fig. 2(b)], while R_{2t} includes the contact resistance between the CNT and Tip B (R_B) as well. The resistance of conventional W tips is negligibly small compared with R_{CNT} and R_J.

Tip B was made to come in contact with the end of the CNT several times, and R_{2t} and R_{3t} were recorded each time, of which results are shown in Fig. 2(d). R_{2t} scatters from 70 kΩ to 4 MΩ, which means R_B varies at each contact. On the other hand, R_{3t} is kept around 50 ± 10 kΩ, because it does not depend on the contact resistance R_B. This means R_{CNT} and R_J are stably constant and exhibits no structural change during the measurements. Note that the data in Fig. 2 is for a sample showing the minimum resistance we obtained from about 10 samples; other samples showed larger resistances, which were frequently too large to be measured.

The resistivity of the CNTs used here was already measured in another experiment, which was 1×10^{-3} Ω·cm with diffusive conduction at room temperature.[20] The CNT has a diameter of *ca.* 20 nm and a length of 150 nm between Tip A and Tip C, giving 5 kΩ for R_{CNT}. Then, since R_{3t} was ten times higher than R_{CNT}, *the three-terminal resistance is dominated by the resistance at the CNT–W junction* R_J. Even if we assume ballistic transport through the CNT,[21] the above conclusion does not change because the measured R_{3t} is larger than 12.9 kΩ (the maximum resistance at quantized conduction).

Now, since we are sure that the resistance of CNT tips mainly comes from the junction between the CNT and W supporting tip, the next step is to stabilize and reduce the resistance by metal coating.

It is worth mentioning that coatings of the suspended CNTs with some metals (Au, Fe, for example) result in isolated droplets on the CNT surface without continuous metal layers formed.[22] However, we confirmed PtIr and W coatings, which are the materials frequently used for STM tips, produced continuous films on a CNT by PLD, as seen in an image of transmission electron microscopy (TEM; Fig. 3).[7,18] The continuous films consist of coalescent fine islands (less than *ca.* 2 nm in diameter); which cover uniformly the very end and side wall of the CNT as well as the junction between the CNT and W tip. From the elemental analysis by energy-dispersive X-ray spectroscopy (EDX) in TEM, the atomic ratio of Pt to Ir was estimated to

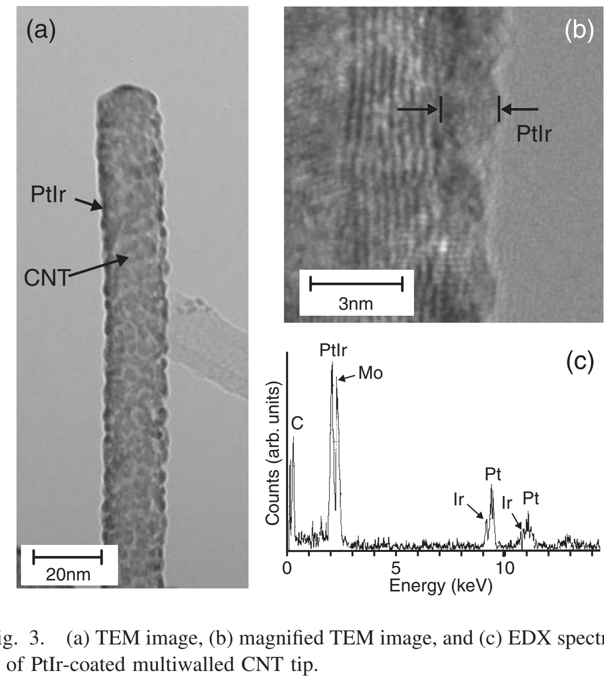

Fig. 3. (a) TEM image, (b) magnified TEM image, and (c) EDX spectrum of PtIr-coated multiwalled CNT tip.

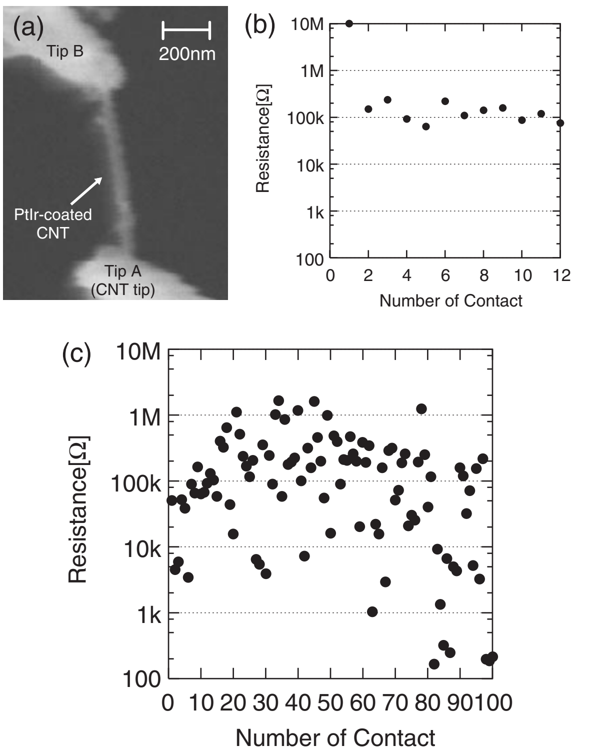

Fig. 4. (a) SEM image at two-terminal measurement of PtIr-coated CNT tip. Two-terminal resistances of W-coated tip (b) and PtIr-coated tip (c) as functions of contact number.

be 74 : 26, which was similar to the composition of the target (80 : 20). The Mo peak in the EDX spectrum originated from a Mo mesh supporting the tip.

We measured the *I–V* characteristics of the metal-coated CNT tips by the two-terminal method as in Fig. 2. Figure 4(a) shows a SEM image during the measurement of a PtIr-coated CNT tip. Tip B was made to come in contact with the end of the PtIr-coated CNT tip many times (10–100 times). At each contact, we measured linear *I–V* characteristics in the bias range of ± 10 mV. Figures 4(b) and 4(c) are the results for W-coated and PtIr-coated CNT tips, respectively. The resistance value scatters from contact to contact due to the contact resistance R_B between Tip B and the CNT end. The minimum resistance was 64 kΩ for the W-coated tip, while it is 0.17 kΩ for the PtIr-coated tip. Note that these data are typical data, meaning that the data scattering in resistance from tip to tip was much smaller than in the case of bare CNT tips. Since R_J should be smaller than the measured two-terminal resistance R_{2t}, the R_J of the PtIr-coated CNT tip is much smaller than that of the bare CNT tip (*ca.* 50 kΩ). On one hand, the W-coated CNT tip showed a similar value of resistance as the bare CNT tip, although the resistance became much more stable.

We compared these resistances with the bulk resistivity of W and PtIr (80 : 20 weight %), 5.5×10^{-6} and 32×10^{-6} Ω·cm,[23] respectively. Because the CNT has a diameter of *ca.* 20 nm and a metal film has a thickness of 5 nm (W) or 6 nm (PtIr), the resistance of metal layers is calculated to be 140 Ω (W) or 650 Ω (PtIr) per 1 μm length along the metal-coated CNT. Applying these values to our samples in Figs. 4(b) and 4(c), we estimated 60 Ω for the W-coated CNT (*ca.* 400 nm long) and 130 Ω for the PtIr-coated CNT (*ca.* 200 nm long). The latter value is similar to the minimum resistance for the PtIr-coated CNT tip in Fig. 4(c), meaning that the resistance of the tip is reduced by the PtIr layer down to a value smaller than the resistance of the CNT itself. The W-coated CNT tip has a thousand times higher resistance than the value estimated from the W resistivity. However, the resistance shown in Fig. 4(b) is much smaller than the tunneling resistance under normal STM imaging conditions, which enables the stable STM imaging with the W-coated CNT tip.[7,18)]

We performed the same measurements with several different W- or PtIr-coated CNT tips. The minimum two-terminal resistance of PtIr-coated tips was typically less than 10 kΩ as in the case shown in Fig. 4(c). All PtIr-coated CNT tips had two-terminal resistances lower than 50 kΩ. On the other hand, the W-coated CNT tips had resistances similar to or higher than that of the noncoated one, ranging from 60 to several 100 kΩ.

Why does the W-coated CNT tip show such high resistances? There are two possible explanations for this. One is the high contact resistance R_B between Tip B and the end of the W-coated CNT tip, and another is the oxidization of the W thin layer due to the exposure of CNT tips to air during the transfer from the PLD apparatus to the four-tip STM chamber. Since we changed the contact conditions between the CNT tip and Tip B more than ten times at each tip, the former one does not seem to account for the high resistance. Since PtIr is hardly oxidized in air and W is easily oxidized, the latter explanation is more plausible.

The PtIr-coated CNT tip measured in Fig. 4(c) kept its conductance and flexibility after 100 repeated contacts for the *I–V* measurements, meaning that the CNT–W junction as well as the PtIr layer at the tip apex are very robust.

In summary, we can conclude that PtIr-coated CNT tips stably have resistances low enough for electrical probes to investigate transport properties of nanometer-scale materials and devices.

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