Coating Carbon Nanotubes with Compound Ultrathin Film: A Novel Route to Functional SPM tips

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We demonstrated the coating of carbon nanotubes (CNTs) with compound ultrathin films towards functional SPM tips. Conductive, ferromagnetic, and superconducting materials were uniformly coated around isolated multi-walled CNTs (MWNTs). As a conductive probe, the CNT glued on a W tip was wholly coated with a thin PtIr layer 6 nm thick. The current-voltage characteristics of the resultant PtIr-coated CNT tips indicated that the PtIr coating stably reduced the resistance between the CNT tip end and the W supporting tip. Our method will facilitate the development of family of novel functional scanning probe microscopies (SPMs) using CNT tips.

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I. INTRODUCTION

In scanning probe microscopy (SPM), the structural and physical properties of tip apex are important factors to achieve the high resolution imaging and related spectroscopies of nanomaterials and devices. Recently, various functional SPMs have been developed, such as multi-probe scanning tunneling microscopy (STM) [1], spin-polarized STM (SP-STM) [2], photon STM (P-STM) [3], electrochemical STM (EC-STM) [4], Kelvin force microscopy (KFM) [5], scanning capacitance microscopy (SCM) [6], magnetic force microscopy (MFM) [7], scanning near field optical microscopy (SNOM) [8], and so on. Since carbon nanotubes (CNTs) [9] have intriguing properties such as the high aspect ratio, small tip radius, chemical inertness, and mechanical robustness, they are suitable for use as the tips of SPM. CNT tips have two superiorities. First, due to the small tip radius, the distance between the tips in multi-probe mode can be reduced. Second, by exploiting coating method to CNT tip, the functionalized probes can be fabricated. However, to date, when a CNT tip is applied to STM, it is often difficult to achieve stable atomic imaging and spectroscopy. In response to this, we have recently developed the method for coating of a CNT tip with the metal layer using pulsed laser deposition (PLD), and demonstrated atom-resolved STM/scanning tunneling spectroscopy (STS) measurements with the W-coated CNT tip [10, 11]. Our method can be extended to the functionalization of SPM tips by coating with various functional materials such as magnetic material, superconductor, insulator, dielectric, and so on.

In this paper, we demonstrated the coating of CNTs with PtIr, CoFe, and Nb₃Sn ultrathin films using PLD towards functional SPM tips. All compound layers with nanometer-scale thickness were uniformly wrapped around the CNTs. We fabricated the CNT tip wholly coated with PtIr. From the electrical characterization of the PtIr-coated CNT tips, it was found that the contact resistance between the CNT and the supporting tip became stable and less than 10 kΩ. The CNT tips coated with compound ultrathin films can facilitate multipurpose SPM measurements.

II. EXPERIMENTAL

Figure 1 shows the fabrication process of a pristine CNT tip, in which a CNT was attached to a W tip in a field emission scanning electron microscope (FE-SEM) chamber equipped with STM. An electrochemically etched W

FIG. 1: SEM images of the fabrication process of a pristine CNT tip. (a) Approach of the W tip to the MWNT. (b) Deposition of the amorphous carbon by irradiating the contact area with an electron beam. (c) Retraction of the CNT tip from the CNT cartridge.
tip and multi-walled CNTs (MWNTs) aligned on a Mo plate by electrophoresis were set on the former and latter stages, respectively. We used MWNTs made by the arc discharge method, which were 20 nm in diameter and over 3 μm in length. The W tip was moved to contact the MWNT (Fig. 1(a)), and by irradiating the contact area with an electron beam, amorphous carbon was deposited (Fig. 1(b)). Then, the tip ensemble was retracted (Fig. 1(c)) [12]. Figure 2 shows the pulsed laser deposition (PLD) apparatus used in this work, which consists of a laser, a specimen holder with a heater, and multi-target holders. The base pressure of the PLD apparatus was $8 \times 10^{-7}$ Torr. A pulsed Nd:YAG laser was focused onto a target at a repetition rate of 10 Hz. The laser energy was fixed at 140 mJ. The CNT tip or MWNT cartridge on the Mo plate [13] was set at the tip of the specimen holder, and was placed 50 mm from the target. The angle between the axis of the specimen holder and the normal direction of the target was 45°. The azimuth angle $\phi$ of the specimen was changed during PLD. The coating of CNTs with compound materials was carried out at room temperature using PtIr (80:20 at.%), CoFe (65:35 at.%), and Nb3Sn targets. A transmission electron microscope (TEM) was utilized to characterize the morphology and internal structure of the synthesized the CNTs coated with compound materials. For measurements of current-voltage ($I-V$) characteristic, the CNT tips coated with PtIr were installed in the four-tip STM equipped with SEM. The tips thus fabricated ex situ were exposed to air, and no pre-treatments for the tips were done before the electrical measurements. The $I-V$ characteristic measurements were done in $1 \sim 3 \times 10^{-8}$ Torr at room temperature.

![FIG. 2: A schematic illustration of the pulsed laser deposition apparatus.](image)

![FIG. 3: A line profile of empty state STM image of the Si(100)-2 $\times$ 1 surface along the perpendicular direction to the dimer row. Inset is a schematic illustration of Si(100)-2 $\times$ 1 surface.](image)

![FIG. 4: (a) An SEM image of the PtIr-coated CNT tip. (b) $I-V$ curve by the two-terminal measurement of PtIr coated CNT tip.](image)

### III. RESULTS AND DISCUSSION

The STM observation using the W-coated CNT tip exhibited the stable atom-resolved imaging [10, 11]. Figure 3 shows a line profile of empty state STM image of the Si(100)-2 $\times$ 1 surface along the perpendicular direction to the dimer row. The peaks correspond to dangling bonds of individual atoms, indicating atom-resolved imaging by the metal-coated CNT tip. In the use of pristine CNT tips, stable imaging and spectroscopy are hardly obtained due to the high contact resistance between a W tip and a CNT. It is thought that the metal coating of a CNT tip improved the conductivity between the W tip and CNT. Also, it is likely that stable tunneling in STM measurement occurs between the metal layer at the tip apex and the surface.

Next, to fabricate a conductive probe, the CNT tip was coated with PtIr. Figure 4(a) shows an SEM image of the PtIr-coated CNT tip. The thickness of the PtIr layer was approximately 6 nm. The curvature of the W tip apex was about 300 nm, and the length and diameter of the attached CNT were about 3.5 μm and 50 nm, respectively. Figure 5 (a) shows a TEM image of the PtIr-coated CNT. The PtIr layer was found to exhibit good wetting characteristic at the surface of the MWNT. The lattice fringe of the CNT was clearly observed, indicating that the crystallinity of the inner MWNT was maintained. From the elemental analysis by energy dispersive X-ray spectroscopy (EDX) in TEM, the atom ratio of Pt...
FIG. 5: TEM images of CNTs coated with (a) PtIr, (b) CoFe, and (c) Nb$_3$Sn ultrathin films using PLD. The inset in these figures is the high-resolution TEM image of each coated CNT.

to Ir was estimated to be 74:26, which was similar to the composition of the target [14].

To investigate the conductivity of metal-coated CNT tips, we measured the $I-V$ curves of the PtIr-coated CNT tips by a two-terminal method using four-tip STM. The $I-V$ curves were measured when the PtIr-coated CNT tip was made contact with another W tip. Figure 4(b) shows a typical $I-V$ curve. The curve showed ohmic property in the bias range of ±10 mV. The two-terminal resistance was estimated to be approximately 13.0 kΩ. The two-terminal resistance contains the resistance of PtIr-coated CNT itself, the resistance of the junction between the CNT and the supporting tip, and the contact resistance between the PtIr-coated CNT tip and another W tip. The two-terminal resistance value scatters due to variation of the contact resistance between the PtIr-coated CNT tip and another W tip at each contact. The contact resistance at the CNT-tip junction of the PtIr-coated CNT tip should be smaller than minimum value of the measured two-terminal resistance. Thereby, we performed more than 100 times $I-V$ measurements, and derived the contact resistance at the CNT-tip junction of the PtIr-coated CNT tip. The contact resistance of the PtIr-coated CNT tip ranges from several kΩ to 10 kΩ, which is lower than that of W-coated CNT tip (~50 kΩ) [14]. Since the PtIr is hardly oxidized in air and the W is easily oxidized, it is thought that the W thin layer was oxidized due to the exposure of CNT tips in air during the transfer from the PLD apparatus to the four-tip STM. From these results, PtIr coating is expected to be useful for not only stable STM/STS measurements but also electron transport measurements on the nanometer scale.

Figures 5(b) and 5(c) show the TEM images of CNTs coated with CoFe and Nb$_3$Sn, respectively. These compound layers were found to be uniformly coated on the MWNT. Moreover, the deposited layer wrapped around the MWNT reflects the shape of the inner MWNT. The inner MWNT has good crystallinity because the lattice fringe of the graphite can be clearly observed. The thicknesses of CoFe and Nb$_3$Sn layers were estimated to be approximately 3 nm and 4 nm, respectively. In the EDX spectra from the CNTs coated with CoFe and Nb$_3$Sn, the ratio of the compositions of Co to Fe and Nb to Sn were estimated to be 36:64 and 3.0:1.0, respectively [15].

As for the ferromagnetic tips, Kuramochi, et al. [16] reported that a CNT tip was coated with CoFe using sputtering method and was applied to MFM. However, the composition and morphology of the CoFe layer was not well-controlled. In this study, the thickness of CoFe on CNT was controlled in nanometer accuracy, maintaining the good thickness uniformity. Moreover, the composition of CoFe was precisely controlled to be the same composition of the PLD target. Therefore, our CNT tip coated with the CoFe layer has advantages in controlling the tip radius and composition. The coating of CNTs with ferromagnetic materials is expected to be applicable for not only MFM probes but also SP-STM tips with high spatial resolution.

On the other hand, as a superconducting tip, Naaman, et al. [17] reported that PtIr tip was coated with Ag/Pb multilayer using thermal evaporation method. The thickness of the superconducting Pb layer was 500 nm. The tip radius was roughly estimated to be 1~2 µm. In contrast to this, we controlled the thickness of Nb$_3$Sn on CNT to be 4 nm, resulting in the tip radius of approximately 10 nm. The coating of CNTs with superconductor is expected to be applicable to study of the proximity effect of superconductor on nanometer scale.

IV. CONCLUSIONS

We demonstrated the synthesis of the CNTs coated with PtIr, CoFe and Nb$_3$Sn ultrathin films towards functional SPM tips. The coating of the CNTs with compound
layers was uniformly covered around MWNT, reflecting the shape of the inner MWNT. It was found that the PtIr-coated CNT tips stably have low resistance enough for conductive probes to investigate transport properties of nanomaterials and devices. The CNT tips coated with compound ultrathin films can facilitate multipurpose SPM measurements.

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