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Exploiting Metal Coating of Carbon Nanotubes for Scanning Tunneling Microscopy Probes

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By exploiting the metal coating of carbon nanotube (CNT) tips for a scanning tunneling microscope (STM), we demonstrated atomic imaging/spectroscopy and showed their potential for electrical nanoprobes. A CNT glued to a W tip was uniformly coated with a thin W layer 3–6 nm thick. Using this tip, stable atomic imaging and spectroscopy were carried out on clean Si(111)-7 × 7 and Si(100)-2 × 1 surfaces. The mechanical flexibility of the coated CNT was maintained by virtue of the thin-layer coating, enabling repeated direct contact to the sample surface. Two W-coated CNT tips were brought together within a distance of approximately 50 nm. These results indicate that the tips are useful for electronic transport measurements on a nanometer scale after installation into a multiprobe STM. [DOI: 10.1143/JJAP.44.5336]

KEYWORDS: carbon nanotube, metal coating, scanning tunneling microscopy/spectroscopy, Si(111)-7 × 7, Si(100)-2 × 1, multiprobe STM

1. Introduction

Multipurpose measurements combined with scanning probe microscopy imaging have been very important in the application of nanomaterials and nanostructures to devices as well as in studies of their fundamental properties. For example, the multiprobe scanning tunneling microscope (STM) has attracted much attention for measuring electrical properties of surface nanostructures.[1)] The surface-state conductivity of the topmost atomic layers, which is quite different from that in the bulk crystal, was directly measured for various surface phases using a multiprobe STM.[2,3)] However, the minimum spacing between the metal tips in the multiprobe STM is practically limited to being larger than several hundreds of nm. This arises because the radius of the end of electrochemically sharpened metal tips is usually larger than 100 nm, so that two tips begin to touch each other at probe spacing of ~200 nm. If the probe spacing can be reduced to be as short as an electron coherence length, measurements of quantum transport such as ballistic conduction and nonlocal conduction can be achieved, which may be among the most interesting properties in nanoscale transport. To realize such a multiprobe STM, conductive probes with smaller radii and high mechanical robustness are indispensable. It is likely that the metal-coated carbon nanotube (CNT) tip that we have recently developed[4)] is an appropriate approach to the nanoscale multiprobe STM in which probe spacing can be reduced to approximately 15 nm, the diameter of the CNTs.

In this paper, atom-resolved STM imaging and spectroscopy were demonstrated for silicon surfaces using a W-coated CNT tip. Towards its application to the multiprobe STM for electronic transport measurements, we evaluated the mechanical robustness and flexibility of the W-coated CNT tip from the curvature induced by bending the tips. By installing the tips in our multiprobe STM, we succeeded in making the two metal-coated CNT tips come together at a spacing of approximately 50 nm.

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2. Experimental

The fabrication procedure for the W-coated CNT tips was described in ref. 6. Briefly, after a CNT was glued to a W tip by irradiating the contact area with an electron beam[5)] in a field emission scanning electron microscope (FE-SEM), the tip ensemble was coated with a thin W layer 3 to 6 nm thick by using pulsed laser deposition (PLD).[4,6)] The deposition rate was approximately 0.1 nm/min. We used multiwalled CNTs (MWCNTs) made by arc discharge, which were 20 nm in diameter and over 3 μm in length. From transmission electron microscopy observations, the W layer was found to uniformly coat the MWCNT at both the end and side wall, preserving the shape of the inner MWCNT. The W-coated CNT tip was introduced into an ultrahigh vacuum (UHV) single-tip STM system (OMICRON). Si(111) and Si(100) wafers were used as specimens. The clean Si(111)-7 × 7 surface and Si(100)-2 × 1 surface were prepared by conventional thermal flashing in UHV. No pretreatments of the tip, such as thermal flashing or prolonged annealing, were carried out before imaging. Two W-coated CNT tips were also installed into a multiprobe UHV-STM combined with FE-SEM[1)] to demonstrate the multiprobe operation at a nanometer scale probe-spacing.

3. Results and Discussion

Figure 1(a) shows a typical SEM image of the W-coated CNT tip. The CNT tip was 150 nm in length and 32 nm in diameter, and the W layer was 6 nm thick. Figure 1(b) shows STM images of the empty state on the Si(111)-7 × 7 surface taken with the W-coated CNT tip at a sample bias voltage V_s of 1.55 V and a tunneling current I_t of 0.4 nA. The atomic images were stably obtained for a period of over one hour. Moreover, the same results were obtained using other W-coated CNT tips fabricated separately, indicating the high reproducibility of our method. Figure 1(c) is a STM image taken using a pristine CNT tip without W-layer coating. In this case, the STM image shows surface contamination by adsorbates from the CNT tip.[7)] Thus, W coating effects the passivation of the tip as well as electrical connections to the

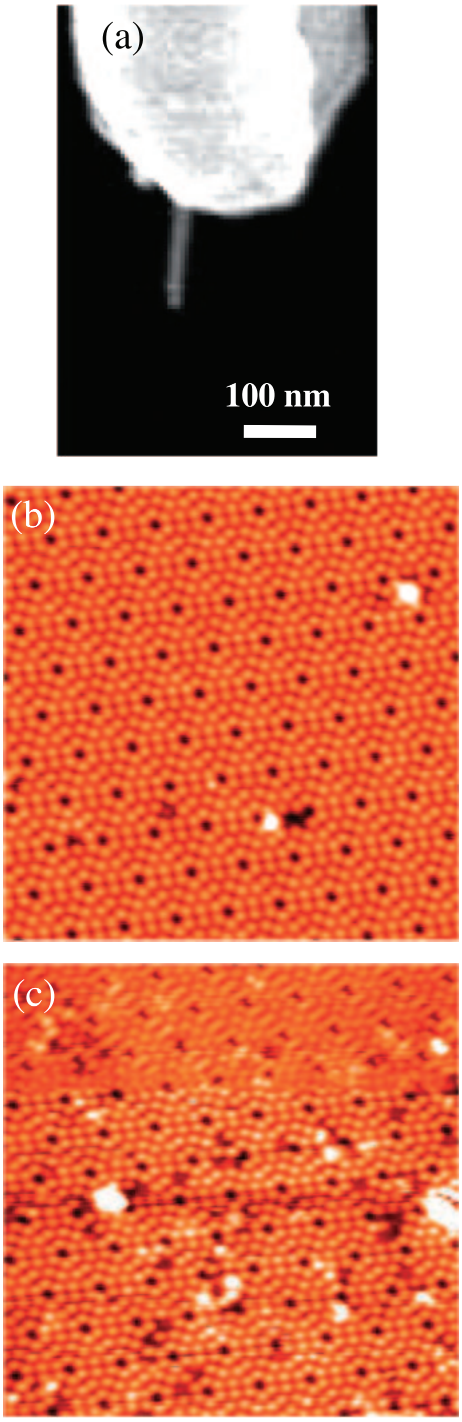

Fig. 1. (a) SEM image of a W-coated CNT tip. (b) and (c) STM images of a Si(111)-7 × 7 surface taken by the W-coated CNT tip, and by the pristine CNT tip, respectively. ($V_s = 1.55$ V, $I_t = 0.4$ nA, 30 nm × 30 nm).

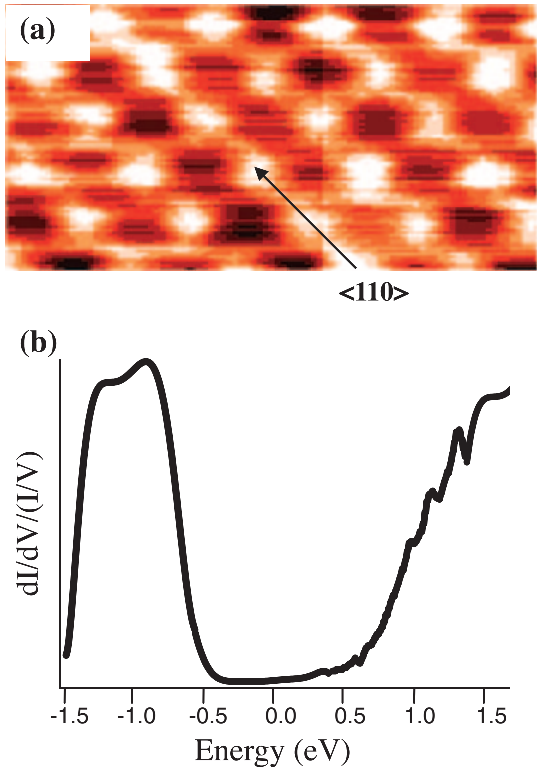

Fig. 2. (a) Room-temperature STM image of a Si(100)-2 × 1 surface using a W-coated CNT tip ($V_s = 1.20$ V, $I_t = 0.3$ nA, 6.6 nm × 3.3 nm), and (b) STS spectrum obtained at the dimer rows of the Si(100)-2 × 1 surface.

W tip.

Figure 2(a) shows an empty-state STM image of the Si(100)-2 × 1 surface. Each protrusion corresponding to a dangling bond of an individual atom in the dimer structure is separately observed. Figure 2(b) shows the STS spectrum obtained at the dimer rows of the Si(100)-2 × 1 surface. An intense peak at −0.9 eV and the weak plateau at +0.4 eV are observed. These peaks correspond to the occupied π and the unoccupied π^* bands of surface states which originate from the dangling bond of the clean 2 × 1 surface. A shoulder at +1.5 eV is due to a surface backbond state. This spectrum conforms qualitatively with previous reports.[8,9] One might argue that, from the reported scanning tunneling spectroscopy (STS) spectra on CNTs,[10,11] the electronic densities of states of the CNT in the protruding area of the tip strongly modulate intrinsic STS spectra of the surface. However, in this STS measurement, the electronic structure of the CNT at the tip does not influence the spectral features in STS, since the tip used in this study can be regarded as a W nanowire tip by virtue of the metal coating, in which W atoms contribute interatomic electron tunneling. Thus, these results indicate the high versatility of the W-coated CNT tip in probing surface electronic states by STM/STS.

We also examined the mechanical robustness and flexibility of the tips. The W-coated CNT tip and the pristine CNT tip were used for tests in which the tips were pressed against a Mo plate in the SEM. We used a 2-μm-long CNT coated with a 3-nm-thick W layer [Fig. 3(a)]. Upon contact with the plate, both tips bent gradually, as seen in Fig. 3(a). However, when the tips were retracted from the contact point, they returned to their initial shape. The curvature of the bending tip R was measured as a function of the distance d between the root of CNT and the Mo plate [see the inset of Fig. 3(b)]. Figure 3(b) shows the results for both the W-coated CNT tip and the pristine CNT tip. The W-coated CNT tip was apparently harder than the pristine CNT tip. Nevertheless, we found that the flexibility was maintained by virtue of the metal layer of nanometer-order thickness. By adjusting the thickness of the coated layer, the mechanical robustness of the tip can be controlled. These results indicate

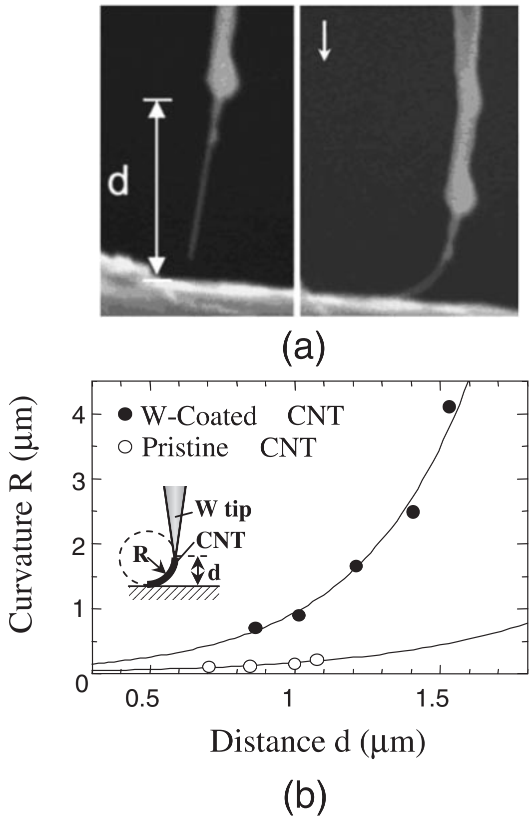

Fig. 3. (a) SEM images during the flexibility test of the W-coated CNT tips. (b) The distance between the root of CNT and the Mo plate d versus the curvature R of the CNT tips.

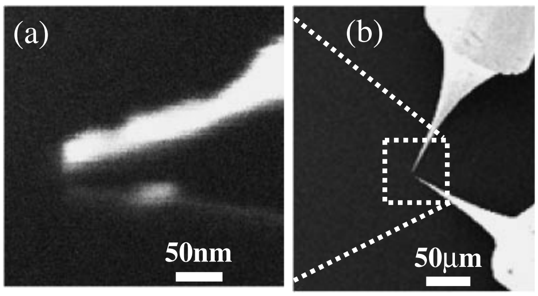

Fig. 4. SEM image of two W-coated CNT tips in the independently-driven multiprobe STM.

that the W-coated CNT tips have an advantage over metal tips when they are used for electron transport measurements in multitip STM, which requires repeated direct contact to the sample.

Next, we demonstrate the potential of the W-coated CNT tips for a multiprobe STM. The SEM image shown in Fig. 4 is the preliminary result from two W-coated CNT tips installed in our multiprobe STM.[1)] Each tip can be driven independently by a piezo-scanner. The CNTs glued to the W tips were approximately 1 μm long and 30 nm in diameter, with W coating layers 6 nm thick. The W-coated CNT tips could be brought together with an approximately 50 nm space between them. This minimum spacing could be further reduced by improving the SEM resolution.

Our results using the W-coated CNT tip showed stable atomic imaging and reproducible spectroscopy. In the use of pristine CNT tips, both the high contact resistance between a W tip and a CNT and the surface contamination from CNTs degrade the imaging and spectroscopy in STM. The W coating of a CNT tip improved the conductivity between the W tip and the CNT and passivated adsorbates in the CNT. It was demonstrated that the W-coated CNT tips are useful as probes for electron transport measurements on the nanometer scale. The probe spacing in the multiprobe STM measurements was reduced to approximately 50 nm, which has not been attained with conventional W tips. Moreover, the mechanical robustness and flexibility of the metal-coated CNT tips are a great advantage in making direct contact with sample surfaces. Once a conventional W tip contacts the sample surface, it is broken or the radius of its point increases. However, the W-coated CNT tips bend flexibly with repeated contact to the sample.

4. Conclusions

We characterized the capability of metal-coated CNT tips to function in multiprobe STMs. Using the W-coated CNT tip, atomic imaging and spectroscopy for the Si(111)-7 $\times$ 7 and the Si(100)-2 $\times$ 1 surfaces were stably achieved. The W-coated CNT tips exhibited mechanical robustness and flexibility similar to the pristine CNT tips. Furthermore, in a multiprobe STM operation, the probe spacing between the two tips was reducible to approximately 50 nm.

Acknowledgements

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