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Synthesis of Metal-Alloy-Coated Nanowires toward Functional Scanning Probe Microscope

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Using carbon nanotubes (CNTs) as templates, we have fabricated metal-alloy-coated nanowires by pulsed laser deposition. Superconducting and ferromagnetic materials were uniformly deposited around an isolated multiwalled CNT (MWNT), and reflected the shape of the MWNT. It was found that Nb_3Sn and CoFe layers were deposited at a rate of about 0.13 nm/min, which indicates that their film thicknesses can be accurately controlled with nanometer accuracy. We also fabricated a superconductor-coated W tip, and obtained an scanning tunneling microscopy (STM) image of the Au(111) reconstructed surface at 2 K. These results indicate that nanowires synthesized using CNT templates can be used as materials for the tips of a functional scanning probe microscopy (SPM) which provide the nanoscale proximity of superconducting or magnetic nanowires. [DOI: 10.1143/JJAP.45.3690]

KEYWORDS: carbon nanotubes, pulsed laser deposition, nanoprobe, superconducting materials, ferromagnetic materials, scanning probe microscopy

1. Introduction

In scanning probe microscopy (SPM), the resolution and accuracy of the resulting images are strongly dependent on tip geometry. Carbon nanotubes (CNTs)[1)] are used as materials for the tips of a SPM because of their unique properties. A CNT tip has advantages such as increased lateral resolution, faithful imaging of deep trenches, and increased longevity.[2)] Although a CNT tip for atomic force microscopy (AFM) is commercially available, a CNT tip used as a conductive probe for SPM has not yet been fully established because of high contact resistance and weak adhesion between the attached CNT and the supporting tip. To overcome these problems, we have recently developed a method for coating a CNT tip for scanning tunneling microscopy/spectroscopy (STM/STS) with a metal layer by pulsed laser deposition (PLD).[3,4)] The STM/STS observation using the metal-coated CNT tip demonstrated a stable atomic imaging and atom-resolved STS. From the results of the use of a metal-coated CNT tip, our method can be extended to the functionalization of SPM tips by coating with various functional materials such as insulators, metals, superconductors, and magnetic materials and so on.

Here, using CNTs as templates, we synthesized nanowires composed of superconducting and ferromagnetic metal alloys by PLD. It was found that the metal-alloy layers with a nanometer-scale thickness were uniformly deposited around the CNTs. The compositional ratio of the metal-alloy-coated nanowires was estimated to be almost the same as that of the target used in the PLD method. We demonstrated STM imaging at a low temperature using a superconductor-coated W tip. The synthesized superconducting and ferromagnetic nanowires are expected to be applicable for STM superconducting tips and magnetic force microscopy (MFM) tips with high spatial resolution.

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2. Experimental

A commercially available multiwalled carbon nanotube (MWNT) with an average diameter of 20 nm and a length of more than 3 μm, which was grown by the arc discharge method, was used as a template for the synthesis of metal-alloy-coated nanowires. PLD was utilized for coating MWNTs with metal-alloy materials. Conventional W tips were also coated with the metal-alloy materials by PLD. A pulsed Nd:YAG laser with a wavelength of 355 nm and a pulse duration of 5 ns was focused onto a target at a repetition rate of 10 Hz. The laser energy was fixed at 140 mJ. The isolated MWNTs were aligned on the edge of a Mo plate (ϕ3 mm) using an ac electrophoresis technique.[5)] The Mo plate with MWNTs or W tip was set at the tip of a specimen holder, and was placed 50 mm from the target. The angle between the axis of the holder and the normal direction of the target was 45°. The azimuth angle of the specimen was changed during PLD. The coating of CNTs with metal-alloy materials was carried out at room temperature using Nb_3Sn and CoFe (35 : 65 at. %) targets under a pressure of 1×10^{-4} Pa. Transmission electron microscopy (TEM) combined with energy dispersive X-ray spectroscopy (EDX) was utilized to characterize the morphology, internal structure and compositional ratio of the synthesized metal-alloy-coated nanowires and W tips coated with the metal-alloy materials. The Nb_3Sn-coated W tip was installed into an ultrahigh-vacuum (UHV) low-temperature (LT)-STM system and tip performance was tested. The temperature of the STM head was maintained at 2 K using a ^{3}He sorption refrigerator. We used a Au(111) thin film as a sample, which was prepared by the deposition of Au on a single-crystal mica substrate at 750 K.

3. Results and Discussion

Figure 1(a) shows the TEM image of a Nb_3Sn metal-alloy-coated nanowire synthesized using a CNT template for 30 min by PLD at room temperature. A Nb_3Sn layer was found to be uniformly deposited on the MWNT. Moreover,

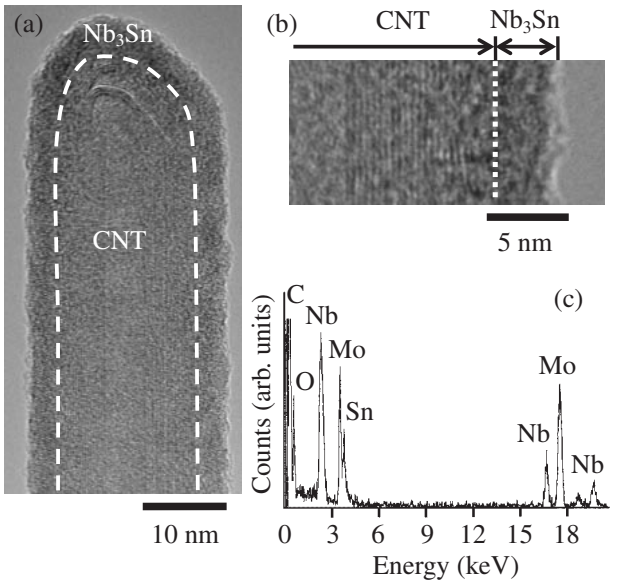

Fig. 1. (a) TEM image, (b) high-resolution TEM image and (c) EDX spectrum of Nb_3Sn nanowire synthesized by PLD using MWNT template.

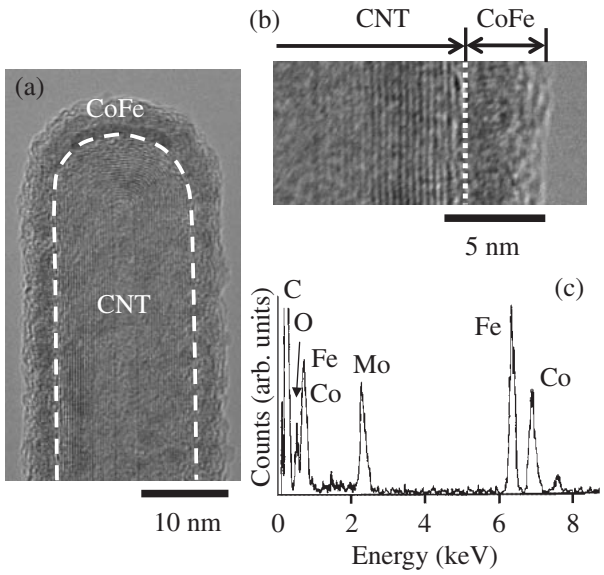

Fig. 2. (a) TEM image, (b) high-resolution TEM image and (c) EDX spectrum of CoFe nanowire synthesized by PLD using MWNT template.

the deposited layer was wrapped around the top and side of the MWNT, reflecting the shape of the inner MWNT. Figure 1(b) shows the magnified image of the interface between the Nb_3Sn layer and the MWNT. The inner MWNT shows good crystallinity because the lattice fringe of the graphite can be clearly observed. The thin-layer thickness and deposition rate of the Nb_3Sn layer were estimated to be approximately 4 nm and 0.13 nm/min, respectively. Figure 1(c) shows the EDX spectrum of the Nb_3Sn nanowire. Peaks originating from C, Nb, and Sn were predominantly observed. The Mo peak stems from the Mo plate of the specimen. The O peak indicates that the surface of the Nb_3Sn nanowire was oxidized due to the exposure of samples to air during their transfer to the *ex situ* EDX apparatus. From these peak intensities, the ratio of the composition of Nb to Sn was estimated to be 3.0 : 1.0. This result shows that the stoichiometry of the target is very well reproduced in one of the deposited layer.

Figure 2(a) shows the TEM image of a CoFe metal-alloy-coated nanowire. As shown in the case of the Nb_3Sn metal-alloy-coated nanowire, the CoFe layer was found to exhibit good wetting characteristic at the surface of the MWNT. The thickness of the CoFe layer was estimated to be approximately 4 nm from the magnified image of the interface between the CoFe layer and the MWNT in Fig. 2(b). The deposition rate is approximately 0.13 nm/min. Therefore, Nb_3Sn and CoFe layer thicknesses can be accurately controlled with nanometer accuracy. The lattice fringe of the CNT was clearly observed, indicating that the crystallinity of the inner MWNT was maintained. Figure 2(c) shows the EDX spectrum of the CoFe nanowire. In the spectrum, the peaks of C, Co, and Fe were predominantly observed. From the peak intensities, the compositional ratio of Co to Fe, was estimated to be 36 : 64. Thus, the thin layer was found to have a compositional ratio close to that of the target.

We also performed the deposition of Nb_3Sn on the W tip. Figures 3(a) and 3(b) show the SEM and TEM images of the

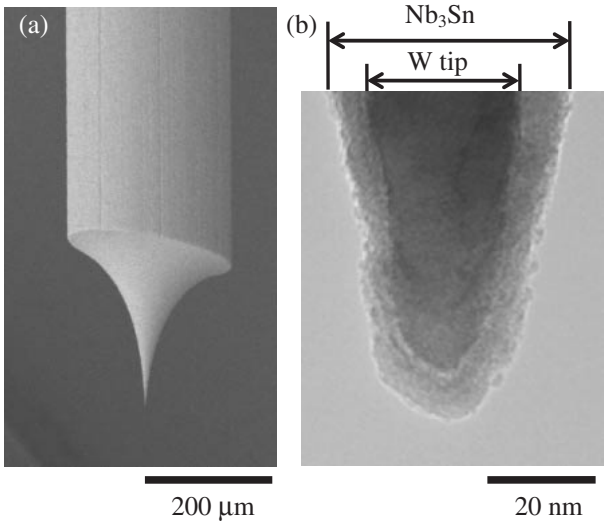

Fig. 3. (a) SEM image and (b) TEM image of Nb_3Sn-coated W tip.

Nb_3Sn-coated W tip, respectively. The thin Nb_3Sn layer was found to cover the W tip uniformly. The thickness of the Nb_3Sn layer was estimated to be approximately 5 nm. These results indicate that our method can also be adopted for the functionalization of conventional SPM tips.

To demonstrate SPM imaging using the tip fabricated by our method, we performed LT-STM measurement using a W tip coated with a 100-nm-thick Nb_3Sn layer. Figure 4 shows the STM image ($64 \times 50\,nm^2$) of a Au thin film deposited on a mica substrate using Nb_3Sn-coated W tip. During the STM observation, the tip and sample temperatures were maintained at 2 K. The STM image clearly shows the Au(111) herringbone reconstructed structure. The detailed results of the SPM imaging using our fabricated superconducting tip will be reported in our forthcoming paper.[6)]

It is also noteworthy to compare our superconducting and ferromagnetic tips with those reported previously. Concerning superconducting tips, Naaman *et al.* reported Pt–Ir tips

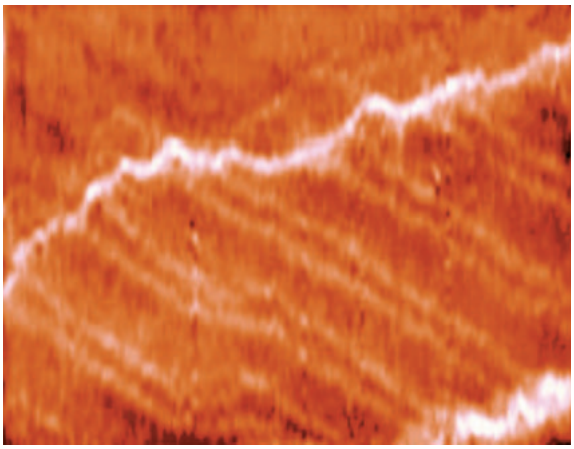

Fig. 4. Low-temperature STM image of Au(111) thin film deposited on mica taken using Nb_3Sn-coated W tip ($V_s = 48\,mV$, $I_t = 1.25\,nA$, $64 \times 50\,nm^2$).

coated with a Ag/Pb multilayer using the thermal evaporation method.[7] The thickness and deposition rate of the superconducting Pb layer were 500 nm and about 300 nm/min, respectively. Because the Pt–Ir tips were mechanically cut, their coated tip radii were roughly estimated to be in the micrometer scale. However, in the case of our superconducting tips, the thickness and deposition rate of Nb_3Sn were 4 nm and about 0.13 nm/min, respectively, and the coated tip radius was approximately 10 nm. Therefore, our superconducting tip has the advantage of having an accurate tip radius, which is strongly dependent on the spatial resolution of SPM. Concerning magnetic tips, Deng *et al.* reported CNT tips coated with a Ti/Co/Ti multilayer using the electron beam evaporation method.[8] The thickness and deposition rate of the ferromagnetic Co layer were 7 nm and about 12 nm/min, respectively. The coated tip radius was approximately 14 nm. Kuramochi *et al.* reported CNT tips coated with CoFe using the sputtering method.[9] The thickness and deposition rate of the ferromagnetic CoFe layer were 13 nm and about 0.7 nm/min, respectively. The coated tip radius was approximately 38 nm. The composition of the CoFe layer was unknown. However, in our ferromagnetic tips, the thickness and deposition rate of CoFe were accurately controlled at the subnanometer scale (thickness: approximately 4 nm, deposition rate: 0.13 nm/min), resulting in the tip radius of approximately 10 nm. Moreover, the composition of CoFe was precisely controlled similarly to the composition of the PLD target. Therefore, our ferromagnetic tips have the advantages of having an accurate tip radius and a precisely controlled composition. The relatively small tip radius and the precisely controlled composition originate from the features of PLD, which enables the control of deposition rate and composition.[10] Thus, the coating of nanowires by PLD for SPM tips is superior with regard to the precise control of thickness and the composition of the deposited layers. Moreover, the functionalization of SPM tips by PLD facilitates not only the applications of SPM tips to superconducting and magnetic probes but also the development of novel nanodevices.

4. Conclusions

We have performed the depositions of Nb_3Sn- and CoFe-alloy layers on MWNTs by PLD toward a functional SPM. By controlling the thicknesses of the deposited layers with nanometer accuracy, metal-alloy-coated nanowires were successfully fabricated reflecting the shape of the MWNT. The synthesized nanowires were found to have the same compositional ratios as those of the PLD target. The functionalization of SPM tips by PLD was also adopted for conventional W tips. The Nb_3Sn layer was uniformly deposited on the W tip. The LT-STM measurement using the Nb_3Sn-coated W tip indicated the potential of the coated tip.

Acknowledgements

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