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Four-Point Probe Resistance Measurements Using PtIr-Coated Carbon Nanotube Tips

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ABSTRACT

We performed four-terminal conductivity measurements on a $CoSi_2$ nanowire (NW) at room temperature by using PtIr-coated carbon nanotube (CNT) tips in a four-tip scanning tunneling microscope. The physical stability and high aspect ratio of the CNT tips made it possible to reduce the probe spacing down to ca. 30 nm. The probe-spacing dependence of resistance showed diffusive transport even at 30 nm and no current leakage to the Si substrate.

One of the main issues in nanotechnology research is developing useful methods for characterizing electrical properties of nanoscale objects and devices. Many attempts have been made by, e.g., patterning electrodes on the objects, directly growing them on the prepatterned electrodes, or using tips of scanning probe microscopes (SPM) as electrodes. A multiprobe SPM has a considerable potential, as it does not need any extra electrodes on the specimen and enables arbitrary arrangements of probe electrodes. Several groups have reported conductivity measurements on nano-objects by multiprobe scanning tunneling microscope (STM).[1−8] However, their measurements were often limited by contact problem: an electrical contact between metal tips and samples caused damages to both of the samples and probes, which prevented making the probe distance nanometer scale with good reproducibility. For realizing nanometer-scale measurements, carbon nanotube (CNT) tips[9] can be useful because of their high stability, mechanical flexibility, small radius, and high aspect ratio. We have reported that a few nm thick of platinum-iridium (PtIr) or W coating on the CNT probe stabilized the resistance of the probe glued on a W supporting tip down to as low as several kΩ.[10,11] This is important for using the tips in multiprobe STM for conductivity measurements.

In the present research, we have performed four-probe conductivity measurements on a $CoSi_2$ nanowire (NW) by using the four PtIr-coated CNT tips with the minimum probe spacing down to ca. 30 nm. There are two reports so far about 10 nm scale resistance measurements done by two-probe STM.[1,2] However, two serious problems remain in the two-probe method. First, precise control of contact condition is required in the two-probe method because the contact resistance between the probe and sample is inevitably included in the measured resistance. Second, the resistance of the sample must be (much) larger than the contact resistance, otherwise the measured resistance is dominated by the unwanted contact resistance between the probe and sample, not by the sample under investigation. Owing to the use of the four-probe method, we solved these problems as described below. The notable feature of the CNT tips we found was that direct electrical contacts caused no damage electrically and mechanically on the sample as well as on the tips even after repeated contacts. This enabled reduction of the minimum probe spacing down to 10 nm scale routinely. On the other hand, even using the PtIr-coated CNT tips, the contact resistance between the tip and sample could not be less than ca. 50 kΩ because of its very small contact area. This means that, by using the two-point probe method, one cannot measure the resistance of sample less than 50 kΩ. Owing to the four-point probe method, however, we could measure the resistance as small as 2 Ω, which was much smaller than the contact resistance. Combination of

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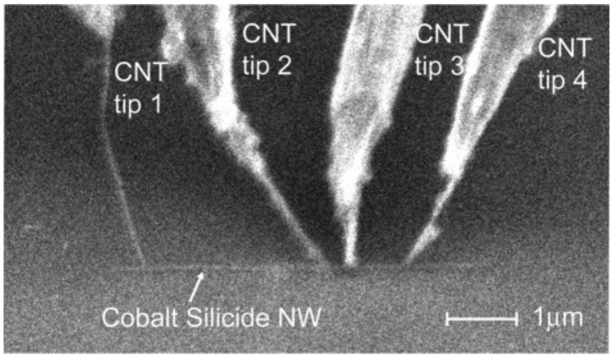

Figure 1. SEM image of a $CoSi_2$ NW being contacted with four PtIr-coated CNT tips (side view).

the CNT tips and a four-tip STM is very powerful for studies in nanoscience and nanotechnology.

PtIr-coated CNT tips were prepared by the following procedure. First, multiwalled CNTs (MWCNTs) were sonicated in dichloroethane and attached at the apex of an electrochemically etched W wire by AC dielectrophoresis method.[12] The MWCNTs, which had an average diameter of 20 nm, were purchased from Materials and Electrochemical Research Corporation. Second, the junction between the CNT and W supporting tip was reinforced by electron-beam-induced deposition of hydrocarbon around the junction using methyl isobutyl ketone (MIBK) under scanning electron microscope (SEM),[13] followed by heating at 500 °C in high vacuum. Finally, the CNT−W tip was wholly coated with 5 nm thick PtIr film using pulsed laser deposition technique,[14] which stabilized the resistance of the CNT−W junction down to less than 10 kΩ.[11] Without the metal coating, the resistance at the CNT−W junction scattered from 100 kΩ to several MΩ from tip to tip, which was too high for the probes in conductivity measurements. The details of the tip fabrication and its electrical and mechanical characterizations are discussed elsewhere.[11,15]

The PtIr-coated CNT tips were installed in a homemade four-tip STM having four independently driven STM heads under SEM.[16] All electrical measurements were done in ultrahigh vacuum (UHV) at room temperature. $CoSi_2$ NWs were self-assembly formed in situ by sublimation of high-purity cobalt on a Si(110) clean surface held at 750 °C in UHV.[17] The $CoSi_2$ is known to be a high conductive metallic crystal, and its resistivity is 31 ± 9 $\mu\Omega$ cm for the NW[18] and $\sim$15 $\mu\Omega$ cm for the films[19] at 300 K.

Four CNT tips were made contact onto a single $CoSi_2$ NW under SEM observation (Figure 1). STM pre-amplifiers with variable gains of 10^8 and 10^6 A/V were used. To detect the contacts during tip approaching, the gain was set to 10^8 A/V. The tips were made to approach beyond the point of tunneling until the contact resistances became less than 1 MΩ. At the current−voltage ($I-V$) measurement, the STM feedback loops were cut. Even if the tip physically contacted to the NW, the contact resistance between the tip and sample was higher than 50 kΩ. It was difficult to reduce this resistance because of the small contact area. This is much larger than the resistance of the metallic NW, which should be less than 1 kΩ with probe spacing smaller than 1 μm.[18] Therefore, by two-terminal $I-V$ measurements, the resistance did not depend on the probe spacing due to the large contact resistance at the probe contacts. When the tip contacted on the bare Si substrate, a Schottky barrier was formed at the tip−substrate contact. The contact resistance in this case was always higher than several MΩ. We could then confirm that the tips contacted on the NW only by detecting lower two-terminal resistance.

Four-terminal $I-V$ measurements were done by sweeping the bias voltage between tips 1 and 4 with recording of the current flow I and the voltage drop V between tips 2 and 3 (Figure 2). Voltage probes absorbed current less than 0.1 pA in these $I-V$ measurements, which is negligibly small compared with the measurement current. The gain of the pre-amplifiers was set to 10^6 A/V to detect the current up to 2 μA. SEM observation was stopped at $I-V$ measurements to avoid possible influence on the resistance caused by high-energy electrons (10 kV). Figure 2 shows a series of SEM images around the voltage probes (tips 2 and 3) touching on a NW and corresponding four-terminal $I-V$ curves. We reduced the probe spacing between the voltage probes during taking the $I-V$ characteristics. The positions of the two current probes (tips 1 and 4) and one of the voltage probes (tip 2) were fixed in the measurements, and only tip 3 was made to shift. All $I-V$ curves were linear. The four-terminal resistance $R_{4t} = dV/dI$ around $I = 0$ decreased with shortening of the probe spacing. They were several Ω much smaller than the contact resistance. A voltage amplifier was introduced between the STM pre-amplifiers to detect small voltage drops resulting from the small resistance. Voltage and current resolutions were 0.1 μV and 0.1 nA, respectively, at 10^6 A/V gain. Finally, tip 3 bent as shown in Figure 2e, and R_{4t} became 0 Ω because of direct contact between the voltage probes. The CNT tips always bend when they touch each other under SEM observation. The minimum probe spacing on the NW before this shortening was 30 ± 20 nm, as shown in Figure 2d.

We plotted values of the four-terminal resistance R_{4t} as a function of the spacing between the contact points of the voltage probes on the NW (Figure 3). The linear proportional relation in the range from 30 to 600 nm means diffusive transport, and the fit line gives one-dimensional resistivity $\rho_{1D} = 57 \pm 3$ Ω/μm. By extrapolating the data points, there seems to be no residual resistance at zero probe spacing, which is owed to the four-point probe configuration. The gradient decreased to 19 ± 4 Ω/μm above 600 nm. This is due to an increase of the NW width from 100 ± 20 to 160 ± 20 nm, as shown in the SEM image (Figure 3).

We checked the reproducibility. First, the probe spacing was reduced from 1000 to 30 nm, as shown by red circles in Figure 2, and then it was increased up to 850 nm (blue circles). All data are on the same fit lines with reproduction of the gradient change around 600 nm. This indicates that the physical contacts of the CNT tips do not cause any significant damage to the NW. The SEM image of the NW after these measurements also shows no trace created by the contacts (Figure 3).

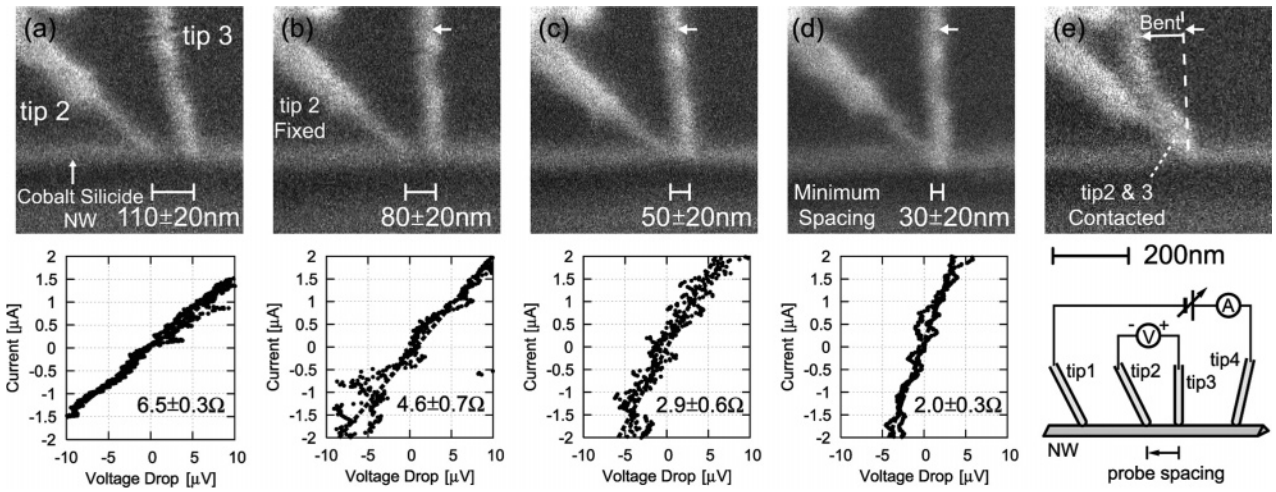

Figure 2. SEM images of the voltage probes (tips 2, 3) at different spacings, and corresponding $I-V$ characteristics. The current probes (tips 1, 4) are about 1 μm away from these voltage probes (see Figure 1). The bottom-right figure illustrates the four-terminal $I-V$ measurement. (a−d) The four-terminal resistance R_{4t} decreased with reducing the probe spacing. (e) The voltage probes contacted each other, and the CNT tip 3 was bent. (d) The minimum probe spacing before the contact is 30 ± 20 nm. The error bar in the probe spacing is determined by the radii of the apexes in tips 2 and 3.

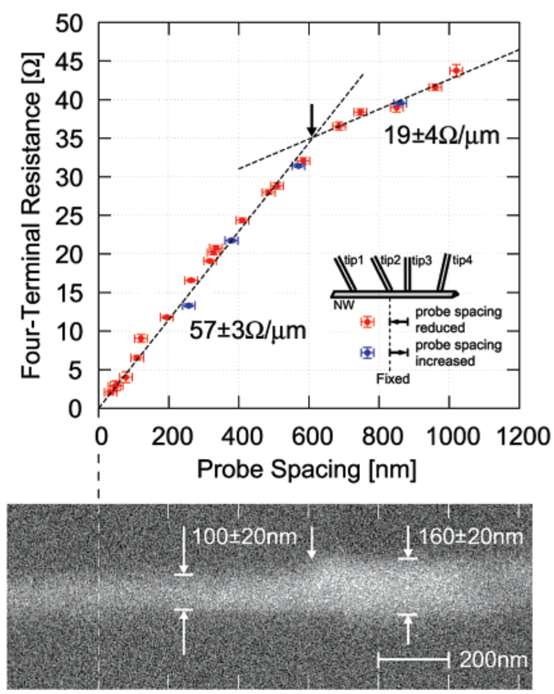

Figure 3. Plot of four-terminal resistance R_{4t} vs spacing between the voltage probes, and SEM image of the NW under measurement (top view). The black arrow around 600 nm in the graph and the white arrow in the SEM image indicate the position where the NW width changes, resulting in a change of the resistivity. No difference is found between before and after the physical contacts of CNT tip 3 on the NW (see red and blue circles in the graph).

From the values of measured R_{4t} and the one-dimensional resistivity ρ_{1D}, the probe spacing in Figure 2d is estimated to be 35 nm. This is around the minimum distance we achieved, which was limited by the diameter of the tip apex we used, 30 nm (20 nm diameter of CNT + 5 nm thick PtIr layer). By using conventional electrochemically etched W tips with the diameter of the apex typically 100 nm, the minimum probe spacing should be larger than 100 nm. Furthermore, the W tips are easily bent and their diameters become larger by repeated physical contacts to samples, resulting an enlargement of the probe spacing. The notable feature of the CNT tips is physical stability and flexibility. Direct electrical contacts do not change the shape of the CNT tip. In this experiment, the length of the CNT tip did not change at all.

We now discuss the transport properties for the NW. The probe-spacing dependence of resistance in $CoSi_2$ NW showed a linear one-dimensional Ohmic feature ($R_{4t} \propto L$). This behavior is due to a one-dimensional conduction path through the NW without leakage of current to the three-dimensional substrate or to the two-dimensional substrate surface. This is because a Schottky barrier between the NW and the Si substrate confines the current.[18] The mean free path of the electrons in $CoSi_2$ is around 6 nm at room temperature,[20] which is much smaller than the width and height of our NW as well as the probe spacing. Therefore, our result of diffusive conduction is reasonable. The three-dimensional resistivity of the NW can be calculated. The width of the NW is determined by the SEM image, and the height can be determined by the transmission electron microscope image.[17] In the probe spacing less than 600 nm, the width is 100 ± 20 nm and the height is evaluated to be 60 ± 10 nm. By multiplying the one-dimensional resistivity, we obtain the three-dimensional resistivity 22 ± 6 $\mu\Omega$ cm. In the same way, we obtain 19 ± 5 $\mu\Omega$ cm for the region larger than 600 nm. These values are comparable to the previous results (31 ± 9 $\mu\Omega$ cm) in which similar $CoSi_2$ NWs were measured with W tips in larger probe-spacing range.[18] Also, these values are comparable with that of molecular beam epitaxy-grown films of $CoSi_2$ on Si substrate, for which $\rho \sim 15$ $\mu\Omega$ cm.[19] One might expect an excess resistance due to inelastic scattering at the NW boundaries (buried interface and exposed surface). According to the temperature-dependent resistance measurements of the $CoSi_2$ film done by J. C. Hensel et al., boundary scattering is specular and resistivity increased only ~0.6 $\mu\Omega$ cm from bulk value even in a 12.5

nm thick film at 4.2 K.[19] Excess resistivity is expected to be negligibly small in the 100 nm width NW at room temperature.

In the ballistic transport regime, two-terminal and four-terminal resistances (R_{2t} and R_{4t}) do not depend on the probe spacing.[21] They depend only on the total transmission probability T_{23} of electron wavefunction between the voltage probes, tips 2 and 3 (which are also the current probes in the two-terminal measurement). A remarkable feature of the ballistic transport is that R_{4t} takes any value between $-R_{2t}$ and $+R_{2t}$, meaning that R_{4t} can be negative by quantum interference effects.[22] At liquid He temperature, the mean free path of conduction electrons in a $CoSi_2$ film with the thickness of 110 nm becomes ca. 100 nm.[19] Therefore, at low temperatures, we can possibly observe quantum interference effects in resistance at probe spacing we achieved here by using the PtIr-coated CNT tips.

In summary, we used PtIr-coated CNT tips in a four-tip STM to achieve reliable electrical measurements on a single $CoSi_2$ NW. The minimum probe spacing on the NW in the four-point probe resistance measurement was reduced to around 30 nm, which was due to the physical stability and sharpness of the CNT tips. No electrical changes were found in the NW before and after repeated contacts of CNT tips, which meant no significant damage on the sample by the contacts. The four-terminal method with our electrical circuits and tips made it possible to measure the sample resistance as small as 2 Ω, which was impossible by the two-terminal method because of the large contact resistance (typically higher than 50 kΩ) at the probe contacts. The electrical transport in the NW is one-dimensional without current leakage into the substrate.

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References

(1) Kubo, O.; Shingaya, Y.; Nakayama, M.; Aono, M.; Nakayama, T. *Appl. Phys. Lett.* **2006**, *88*, 254101.

(2) Watanabe, H.; Manabe, C.; Shigematsu, T.; Shimizu, M. *Appl. Phys. Lett.* **2001**, *78*, 2928.

(3) Matsuda, I.; Ueno, M.; Hirahara, T.; Hobara, H.; Morikawa, H.; Liu, C.; Hasegawa, S. *Phys. Rev. Lett.* **2004**, *93*, 236801.

(4) Lin, X.; He, X. B.; Yang, T. Z.; Guo, W.; Shi, D. X.; Gao, H.-J.; Ma, D. D. D.; Lee, S. T.; Liu, F.; Xie, X. C. *Appl. Phys. Lett.* **2006**, *89*, 043103.

(5) Guise, O.; Marbach, H.; Yates, J. T., Jr.; Jung, M.-C.; Levy, J.; Levy, J. *Rev. Sci. Instrum.* **2005**, *76*, 045107.

(6) Ishikawa, M.; Yoshimura, M.; Ueda, K. *Jpn. J. Appl. Phys.* **2005**, *44*, 1502.

(7) Takami, K.; Akai-Kasaya, M.; Saito, A.; Aono, M.; Kuwahara, Y. *Jpn. J. Appl. Phys.* **2005**, *44*, L120.

(8) Grube, H.; Harrison, B. C.; Jia, J.; Boland, J. J. *Rev. Sci. Instrum.* **2001**, *72*, 4388.

(9) Dai, H.; Hafner, J. H.; Rinzler, A. G.; Colbert, D. T.; Smalley, R. E. *Nature* **1996**, *384*, 147. Hafner, J. H.; Cheung, C. L.; Lieber, C. M. *Nature* **1999**, *398*, 761.

(10) Ikuno, T.; Katayama, M.; Kishida, M.; Kamada, K.; Murata, Y.; Yasuda, T.; Honda, S.; Lee, J.-G.; Mori, H.; Oura, K. *Jpn. J. Appl. Phys.* **2004**, *43*, L644.

(11) Yoshimoto, S.; Murata, Y.; Hobara, R.; Matsuda, I.; Kishida, M.; Konishi, H.; Ikuno, T.; Maeda, D.; Yasuda, T.; Honda, S.; Okado, H.; Oura, K.; Katayama, M.; Hasegawa, S. *Jpn. J. Appl. Phys.* **2005**, *44*, L1563.

(12) Ueda, K.; Yoshimura, M.; Nagamura, T. *Jpn. Kokkai Tokkyo Koho* **2004**, 3557589. Tang, J.; Gao, B.; Geng, H.; Velev, O. D.; Qin, L.-C.; Zhou O. *Adv. Mater.* **2003**, *15*, 1352.

(13) Koops, H. W. P.; Kretz, J.; Rudolph, M.; Weber, M.; Dahm, G.; Lee, K. L. *Jpn. J. Appl. Phys.* **1994**, *33*, 7099.

(14) Ikuno, T.; Katayama, M.; Kamada, K.; Honda, S.; Lee, J.-G.; Mori, H.; Oura, K. *Jpn. J. Appl. Phys.* **2003**, *42*, L1356. Ikuno, T.; Yasuda, T.; Honda, S.; Oura, K.; Katayama, M.; Lee, J.-G.; Mori, H. *J. Appl. Phys.* **2005**, *98*, 114305.

(15) Konishi, H.; Murata, Y.; Wongwiriyapan, W.; Kishida, M.; Tomita, K.; Motoyoshi, K.; Honda, S.; Yoshimoto, S.; Kubo, K.; Hobara, R.; Matsuda, I.; Hasegawa, S.; Yoshimura, M.; Lee, J.-G.; Mori, H.; Katayama, M. *Rev. Sci. Instrum.* **2007**, *78*, 013703.

(16) Hasegawa, S.; Shiraki, I.; Tanabe, F.; Hobara, R. *Curr. Appl. Phys.* **2002**, *2*, 465. Shiraki, I.; Tanabe, F.; Hobara, I.; Nagao, T.; Hasegawa, S. *Surf. Sci.* **2001**, *493*, 633.

(17) He, Z.; Smith, D. J.; Bennett, P. A. *Phys. Rev. Lett.* **2004**, *93*, 256102.

(18) Okino, H.; Matsuda, I.; Hobara, R.; Hosomura, Y.; Hasegawa, S.; Bennett, P. A. *Appl. Phys. Lett.* **2005**, *86*, 233108.

(19) Hensel, J. C.; Tung, R. T.; Poate, J. M.; Unterwald, F. C. *Phys. Rev. Lett.* **1985**, *54*, 1840.

(20) Allen, P. B.; Schulz, W. W. *Phys. Rev. B* **1993**, *47*, 14434.

(21) Datta, S. *Electronic Transport in Mesoscopic Systems*; Cambridge University Press: Cambridge, U.K., 1997; pp 74−78.

(22) Gao, B.; Chen, Y. F.; Fuhrer, M. S.; Glattli, D. C.; Bachtold, A. *Phys. Rev. Lett.* **2005**, *95*, 196802.

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