Nanometer-Scale Four-Point Probe Resistance Measurements of Individual Nanowires by Four-Tip STM

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Abstract We present a review of our recent results about transport properties of nanowires measured by a four-tip scanning tunneling microscope (STM) installed with metal-coated carbon nanotube (CNT) tips. We first present our custom-made apparatus (with UNISOKU Co.) as well as CNT tips, and then some case studies with two different samples, Co-silicide nanowires self-assembled on Si(110) surface and Cu nanowires made by damascene processes used in LSI industry. It is shown that the four-tip STM with CNT tips is versatile and powerful for measuring the conductivity of individual nanostructures.

1 Introduction

Conductivity measurements in sub-micron or nanometer scale are of great interest in nanoscience and nanotechnology. For example, nanoelectronics such as semiconductor devices requires low and stable electrical resistance of interconnects to maintain device performance. Several kinds of methods to measure the conductivity at nanoscales have been developed including fixed electrodes made by microlithography techniques. A method which adopts tips of scanning tunneling
microscope (STM) as electrodes, however, has great advantages in positioning of the probes in arbitrary configurations as well as in high spatial resolution of measurements. But single-tip STM is not enough for versatile measurements of transport properties at various kinds of nanostructures: we need source, drain, and gate electrodes. For this reason, several groups [1–10] including companies [11] and our group [12–14] have developed four-tip STM. In which four independent STM tips are operated in an organic manner with aid of a SEM or optical one, and they are used as electrodes for microscopic two- or four-point probe (μ4PP) conductance measurements. In this article, we show our apparatuses including installation of carbon nanotube tips [15–17] and some results of resistance measurements of nanowires obtained in our group.

2 Four-Tip STM System

Figures 1a, b show schematic drawings of our new version of four-tip STM system [14], consisting of a main (STM) chamber, a sample preparation molecular beam epitaxy (MBE) chamber, and two load-lock chambers for sample and tip exchanges, all of which are UHV compatible. The STM tips can be installed into the main chamber from the tip load-lock chamber where a hot W filament is installed for out-gassing of the tips. The sample is introduced from the MBE chamber where cleaning of the sample, deposition of materials and reflection-high-energy electron diffraction (RHEED) observation can be done. The sample can be heated by direct current heating and cooled down to about 30 K by continuous-flow type cryostat in the MBE chamber. These capabilities are necessary for
preparing aimed surface superstructures, epitaxial thin films, nanodots, nanowires, and for making in situ measurements.

The STM stage is mounted on the thermal conducting Cu rod which is soaked in the coolant of the bath cryostat below. The STM stage including the sample and four sets of actuator units is wholly surrounded with two-fold radiation shields and movable shutters. The photo of Fig. 1c is the stage without the radiation shields, and Fig. 1d shows the whole system. The sample and tips can be cooled down to 7 K and can be kept for 23 h with liquid He as coolant. In the case of liquid N$_2$, the minimum temperature is 80 K and the preserved time is longer than three days.

The SEM column (APCO Mini-EOC) is mounted above the STM stage. The working distance of SEM is about 25 mm. The electron beam is irradiated from SEM column through a 1 mm diameter hole in the radiation shields. A multi-channel plate for the secondary electron detection for SEM imaging is placed on the inside wall the outer shield. The SEM image is obtained from the secondary electron signal or beam induced current signal electron-beam-induced current image (EBIC). The resolution of the SEM is about 20 nm for both signals.

A spring vibration isolator and an eddy-current damper are built between the thermal conductor and the STM stage to avoid vibration of STM stage. The spring isolator decoupled the STM stage from other components. However, during SEM observation, tip/sample exchanges, and cooling the stage, the STM stage is fixed to the thermal conductor (Cu rod) and therefore the isolator and damper are disabled. When we fix the STM stage, the Cu plate works as a thermal conductor and enlarges the contact area for good thermal connection. When we float the STM stage by the springs, this plate makes eddy-current damper. Since alternative arrangements of the small magnets make closed magnetic paths, the magnetization does not affect the SEM beam.

Four sets of tip actuator units are mounted at the corner of the square STM stage, and a sample actuator unit is placed at the center. The actuator units consist of stacked piezo ceramics supported by sapphire plates. For fine positioning or scanning in nanometer or sub-nanometer range, tips and samples are driven by conventional piezoelectric effect of the ceramics by DC voltage. The maximum positioning range by this method is about 2 $\mu$m to each direction. For coarse positioning, the actuators are driven by stick–slip mechanism in 5 mm travel distance in XY directions and 2.5 mm in Z direction at accuracy of about 100 nm.

In addition to these three- or two-dimensional-motion actuators, the tip actuators also contain small piezo ceramics near the tips for fast STM feedback.

Figure 2 shows a series of SEM images of the four tips arranged in various configurations [12, 13, 18]. The tips are chemically etched W wires. The probe spacing can be changed from 1 mm to ca. 200 nm in Figs. 2a–c. They can be arranged on a line equidistantly (linear $\mu$4PP method) (c, d) in arbitrary directions, or in square arrangement (square-$\mu$4PP method) Figs. 2e–h. The square can be rotated with respect to the sample surface (rotational square-$\mu$4PP method) by re-positioning each tip under computer control. This is useful to measure anisotropic surface conductivity in which the conductivity is different depending on the crystal orientation.
3 Metal-Coated Carbon Nanotube Tips

An important issue for the four-tip STM is the probe spacing; the probe spacing should be in the order of 10 nm to measure various kinds of nanostructures. At the present the minimum probe spacing in the multi-tip STM is approximately 100 nm when W tips are used. This is due to the radius of tip apex of electrochemically etched W tips. This probe spacing is not small enough for observing ballistic transport and quantum interference effects because the coherence length of conduction carriers is shorter than 100 nm in many cases. For this reason, continuous efforts are made to shorten the probe spacing down to ca. 10 nm. To make the probe spacing shorter, carbon nanotube tips have been developed in which a carbon nanotube is glued at the end of W tip [19–22]. Since the radius of the (multi-walled) carbon nanotubes is usually ca. 10 nm and the aspect ratio is much higher than usual W tips, two carbon nanotube tips can be brought together into approximately 10 nm spacing. Another feature of the carbon nanotube tip is its mechanical flexibility which can reduce damage to delicate samples such as organic and biological molecules, and make the tips withstand numerous direct contacts to the samples. These properties are quite convenient for the transport measurements by multi-tip STM at nanometer scales. However, there have been problems in the carbon nanotube tips; high contact resistance between the supporting metal tip and the attached carbon nanotube strongly disturbs electron transport at the STM/STS measurements. Moreover, adsorbates contained in the carbon nanotube degrade the surface cleanliness of the specimen under STM operation.

A novel technique for overcoming these difficulties has been developed; the carbon nanotube together with the supporting metal tip is wholly coated with a thin metal layer [15]. Figures 3a,b show TEM images of a W-coated carbon nanotube tip glued on a W supporting tip. The W layer of ca. 3 nm thick was deposited by pulsed laser deposition (PLD) method. The W layer fully covers the tip even at the
end. Figure 3c shows flexibility and robustness of the W-coated carbon nanotube tip upon the direct contact to a sample surface. Figure 3d is a SEM image showing four CNT tips contacting a Co-silicide nanowire grown on a Si substrate [23]. We have also confirmed that the electrical resistance at the glued point between the carbon nanotube and supporting W tip is stably reduced by the metal coating; especially PtIr coating is the most efficient for this purpose [16]. Atomic-resolution STM imaging and STS spectra were acquired with the W-coated carbon nanotube tip at the first attempt [15]. With this metal-coated carbon nanotube tips, we have succeeded in bringing the two tips together into less than 30 nm [17, 23, 24]. Since the resolution of SEM is not enough for observing a smaller probe spacing, we believe that the minimum spacing can be reduced to ca. 20 nm, similar to the diameter of CNT itself.

4 Measuring Co-Silicide Nanowires

CoSi$_2$ nanowires are known to grow self-assembly by depositing high-purity cobalt on a Si(110) clean surface held at 750–850°C in UHV, as shown in Figs. 4a–c [25]. The nanowires become longer and thinner with lowering the substrate temperature during the Co deposition. The wires are single-crystalline, half of which is embedded in the Si substrate as observed by a cross-sectional TEM image of Fig. 4d [25]. The CoSi$_2$ is known to be highly conductive metallic
and its resistivity is $31 \pm 9 \, \mu\Omega \, \text{cm}$ for the nanowire [26] and $\sim 15 \, \mu\Omega \, \text{cm}$ for the films [27] at 300 K.

As shown in Fig. 3d, the four CNT tips were made contact onto one of the nanowires under SEM observation. The tips were made approach beyond the point of tunneling until the contact resistances became less than 1 M$\Omega$, corresponding to direct contact. At the current–voltage (I–V) measurement, the STM feedback loops were cut. Even if the tip physically contacted the NW, the contact resistance between the tip and sample was higher than 50 k$\Omega$. It was difficult to reduce this resistance because of the nanometer-sized contact area. This is much larger than the resistance of the nanowire itself, which is less than 1 k$\Omega$ with probe spacing smaller than 1 $\mu$m [26]. 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: four-point measurements are indispensable at nanometer scale.

Four-terminal I–V measurements were done by sweeping the bias voltage between tip 1 and tip 4 with recording the current I and the voltage drop V between tip 2 and tip 3, with changing the spacing between tip 2 and tip 3 as shown in Figs. 4e–h. The SEM beam was stopped at the I–V measurements to avoid possible influence on
the resistance caused by high-energy electron beam (10 kV). Figures 4e–h show a series of SEM images around the voltage probes (tip 2 and tip 3) touching on the nanowire, and corresponding four-terminal I–V curves are shown in (e’–h’). We reduced the probe spacing between the voltage probes during taking the I–V characteristics. The positions of the two current probes (tip 1 and tip 4) and one of the voltage probes (tip 2) were fixed in the measurements, and only tip 3 was shifted. All I–V curves were linear. The four-terminal resistance $R_{4t} = \frac{dV}{dI}$ around $I = 0$ decreased with shortening the probe spacing. They are several X, much smaller than the contact resistance. A voltage amplifier was introduced at the STM pre-amplifiers to detect small voltage drops resulted from the small resistance. Finally tip 3 bent as shown in Fig. 4i, and $R_{4t}$ became 0 Ω because of direct contact between the voltage probes. The minimum probe spacing achieved here was 30 ± 20 nm as shown in Fig. 4h. This was limited by the diameter of the CNT tip apex we used, 30 nm (20 nm diameter of CNT + 5 nm thick PtIr layer). The error bar in the probe spacing is determined by the radii of the apexes in tip 2 and tip 3.

We plot the measured four-terminal resistance $R_{4t}$ as a function of the spacing between the contact points of the voltage probes on the nanowire in Fig. 5. The linear proportional relation in the range 30–600 nm means diffusive transport, and the fit line gives one-dimensional resistivity $\rho_{1D} = 57 \pm 3 \ \Omega/\mu\text{m}$. By extrapolating the data points, there seems to be no residual resistance at zero probe
spacing, which is owing to the four-point probe configuration. The gradient decreased to $19 \pm 4 \Omega/\mu\text{m}$ above 600 nm probe spacing. This is due to an increase of the nanowire width from $100 \pm 20$ to $160 \pm 20$ nm as shown in the SEM image in Fig. 5. By checking the reproducibility we found that the physical contacts of the CNT tips did not cause any significant damage to the nanowire.

We now discuss the transport property of the NW. Table 1 shows a list of the probe spacing $L$ dependence of the four-terminal resistance in various conduction mechanisms. The probe spacing dependence of resistance in CoSi$_2$ nanowire showed a linear one-dimensional Ohmic feature ($R_{4t} \propto L$). This behavior is due to a one-dimensional conduction path through the nanowire without leakage of current to the underlying three-dimensional substrate or to the two-dimensional substrate surface. This is because a Schottky barrier between the nanowire and the Si substrate confines the current [26]. The mean free path of the electrons in CoSi$_2$ is around 6 nm at room temperature [28], which is much smaller than the width and height of our nanowire as well as the probe spacing. Therefore, our result of diffusive conduction is reasonable. The three-dimensional resistivity of the nanowire can be calculated. The width of the nanowire is determined by SEM image, and the height can be determined by the transmission electron microscope image [25]. We obtain the three-dimensional resistivity $22 \pm 4 \ \mu\Omega \ cm$. In the same way, we obtain $19 \pm 4 \ \mu\Omega \ cm$ for the region larger than 600 nm. These values are comparable to the previous results ($31 \pm 9 \ \mu\Omega \ cm$) in which similar CoSi$_2$ NWs were measured with W tips in larger probe spacing range [26].

In the ballistic transport regime, two-terminal and four-terminal resistances ($R_{2t}$ and $R_{4t}$) do not depend on the probe spacing. They depend only on the total transmission probability $T_{23}$ of electron wavefunction between the voltage probes, tip 2 and tip 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 [21]. 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 [27]. 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. The probe spacing dependence of $R_{4t}$ in the present experiment also excludes observable effects of carrier localization.

<table>
<thead>
<tr>
<th>Conduction mechanism</th>
<th>1D Ohmic</th>
<th>2D Ohmic</th>
<th>3D Ohmic</th>
<th>1D strong localization</th>
<th>1D weak localization</th>
<th>Ballistic</th>
</tr>
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<tbody>
<tr>
<td>$L$-dependence of $R_{4t}$</td>
<td>$\propto L^1$</td>
<td>$\propto L^0$</td>
<td>$\propto L^{-1}$</td>
<td>$\propto \exp \left( \frac{L}{L_0} \right)$</td>
<td>$\propto \frac{L}{L_0-L}$</td>
<td>$\propto L^0$</td>
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$L_0$ is the localization length.
5 Measuring Cu Nanowires

Copper (Cu) wires are now widely used for interconnects in semiconductor devices. But, as the wire width reaches down to the sub-micrometer scale, which is comparable to the mean free path of conduction electrons in the wires, a significant increase in the resistivity has been observed. This is speculated as due to the increased surface and grain boundary scatterings. As the wire width scales down, electrons will undergo reflections more frequently at the surfaces/interfaces, so the collisions with the surfaces/interfaces will become a significant fraction of the total number of collisions. In addition, grain boundaries in polycrystalline wires may act like partially reflecting planes for electron waves, so they also contribute to the increase of resistivity. To investigate these effects directly, the conductivity measurements by the four-tip STM at nanometer scales is very useful [29].

Cu wires having the width between 70 nm and 1 \( \mu \)m were prepared using a Cu/Low-k damascene processes which are now very common in semiconductor industry. Figure 6 shows the cross-sectional SEM images of the damascene structure made in SiO\(_2\) layer. Tantalum (Ta) was used as a barrier metal (BM) in this experiment. Cu damascene lines were formed using conventional Cu process such as seed Cu, electrochemical plating (ECP) Cu for trench filling, and chemical–mechanical polishing. The Cu nanowires are not single-crystalline; they are consisted of small gains. By the electron back-scatter diffraction (EBSD) method, such grains are visualized along the Cu damascene lines [29]. The average grain size was measured to be about 100 nm at 70 nm wide Cu nanowires, which did not change so much with the width, because the grain size is thought to be determined by the height when the width is smaller than the height.

The four-tip STM was used to measure the resistance of individual wires as shown in Fig. 7. By using Pt-coated CNT tips, the probe spacing can be reduced down to the order of several ten nm routinely [23]. When the Pt-coated CNT tips were used, the contact resistance between the tip and sample could not be smaller than 50 k\( \Omega \) because of its very small contact area. This means that it is impossible to measure conductive materials whose resistance is less than 50 k\( \Omega \) by the two-point probe method. Only with the four-point probe method, resistances much smaller than the contact resistance (as small as 0.1\( \Omega \) in the present case) can be measured. Therefore, the combination of the CNT tips and the four-tip STM is very powerful for studies in nanoscale measurements.
Four-terminal I–V measurements were performed by sweeping the bias voltage between the outer pair of tips and recording the current I and the voltage drop V between the inner pair of tips (Fig. 7c). The probe spacing between the voltage probes was reduced while measuring the I–V characteristics. The two current probes (tip 1 and tip 4) and one of the voltage probes (tip 2) were fixed during the measurements, and only tip 3 was moved between tip 2 and tip 4 (Fig. 7c).

The measured values of four-terminal resistance as a function of the probe spacing between the contact points of the voltage probes on the Cu wires are shown in Figs. 8 and 9. For all of them, the probe spacing dependence of resistance basically showed a linear one-dimensional feature, meaning a diffusive transport. By multiplying the gradient of the fitted straight lines and the cross section of Cu wires (which was estimated from SEM image in Fig. 6), the three-dimensional resistivity was calculated as 4.6, 3.7, and 3.4 Ω cm, for the 70, 50 nm, and 1 μm wide Cu wires, respectively. The resistivity of Cu increased as the line width decreased as shown in Fig. 9b. This result is understood by the Fuchs–Sondheimer theory for the surface-scattering effect and the Mayadas–Shatzkes model for the grain boundary effect [29]. No change in the measured resistance.

![Figure 7](image-url)
Fig. 8  a The measured resistances of the 70 nm wide Cu wire are shown as a function of probe spacing. b The enlargement of the area under 600 nm of probe spacing [29].

Fig. 9  a The measured resistances of Cu wires are shown as a function of probe spacing for the 500 nm and 1 μm wide wires. b Plot of the resistivity versus Cu line width [29]. The resistivity coming from the grain boundary scattering is assumed to be constant because the grain size is roughly independent of the line width in our samples.

was found in each measurement before and after repeated contacts of CNT tips. It means no significant damage on the sample by the probe contacts.

In this experiment, the probe spacing was reduced to the scale which is comparable with the grain size. Therefore, it can be expected that there will be some change in the resistance when the probe spacing becomes so short that electrons do not undergo grain boundary scattering. This has been indeed observed. Figure 8b shows the enlarged view of the data shown in Fig. 8a for the probe spacing smaller than 600 nm. There is a slight jump in resistance when the probe spacing is shorter than 200 nm. This directly corresponds to the grain boundary scattering where additional resistance occurs at the grain boundary due to the reflection of electron wave there.
6 Concluding Remarks

Electrical measurements using metal-coated CNT tips in the four-tip STM have been demonstrated for the CoSi$_2$ nanowires and Cu damascene wires. Since the apex of CNT tips is around 10 nm and the aspect ratio is so large, it is able to measure the resistance at nanoscale surface areas. The minimum probe spacing in the four-point probe resistance measurement was reduced to a few 10 nm, which is similar or less than the grain size of polycrystalline wires and even the carrier mean free path. The resistance along the wires present here increased linearly with the measured length, meaning classical diffusive transport. But very recently, we have found quasi-ballistic transport in semiconducting FeSi$_2$ nanowires at room temperature where the carrier mean free path is much longer than that of the metallic wires. The details will be reported elsewhere. In the case of Cu damascene wires, the resistivity increased as the wire width decreased. This is due to the surface/interface scattering of carrier. We have evaluated the surface/interface scattering quantitatively to obtain the specularity factor in Fuchs-Sondheimer theory. At the very narrow probe spacing which was comparable to the grain size, the resistance jump due to a single grain boundary was clearly observed. As demonstrated by the measurements presented here, the four-tip STM with CNT tips is a very useful tool for transport physics at nanoscale as well as industrial purposes.

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References