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Surface and Interface Analysis

Manipulation and four-probe analysis of nanowires in UHV by application of four tunneling microscope tips: a new method for the investigation of electrical transport through nanowires

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The electrical transport properties of nanosystems, including a few kinds of nanowires, have attracted much attention because of their potential application in nanoelectronics. However, the contact effect or impurities between the nanosystems and electrodes made it difficult to study the intrinsic $I-V$ properties in previous measurements. Here, we present a manipulation and four-terminal method electrical transport measurement of low-dimensional systems using a new instrument consisting of a specially designed tunneling microscope with four tips that can be positioned independently in three dimensions. The electrical conductivities of zinc oxide (ZnO), perylene, gallium sesquioxide (Ga_2O_3), and cuprum-7,7′,8,8′-tetracyanoquinodimethane (Cu-TCNQ) nanowires were obtained. Our results have shown that this technique is a powerful tool for studying the intrinsic transport properties of nanosystems. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: FOUR-STM-Tip Manipulation and Measurement System (4TMMS); four-terminal method; scanning tunneling microscope (STM); nanomanipulation; electrical transport; nanowire

INTRODUCTION

Manufacturing faster, smaller, and lower energy consumption nanocircuits is one of the goals in nanoscience and nanotechnology. Manipulating, constructing, and understanding the electrical behavior of nanosystems are the bases for applications in nanoelectronics. Therefore, in the last decades there has been extensive interest in studying the intrinsic electrical transport of low-dimensional systems.[1–7] The four-terminal method, or Kelvin method, including the four-point collinear probe method and the van der Pauw method, a classical method for measuring the electrical conductivity of macro objects, is now being developed[8] step-by-step for use on some micro-objects, for instance, to measure the anisotropy of thin films.[9] On the other hand, nanomanipulation is achievable after the invention of scanning tunneling microscopy (STM).

In this paper, we will present how to manipulate a few kinds of nanosystems and measure their electrical transport using an instrument named Four-STM-Tip Manipulation and Measurement System (4TMMS).

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INSTRUMENT

The Omicron Nanoprobe stage is the main part of the 4TMMS. It consists of a specially designed tunneling microscope with four tips, which can be positioned independently in three dimensions by the software and hardware developed for STM. In addition, an FEI scanning electron microscope (SEM), which can provide a resolution of better than 20 nm, is employed to search for the interesting nanostructures and navigate the STM tips to a certain region. The four tips and the SEM gun are in an ultrahigh vacuum (UHV) chamber, which shields them from the electrical influence outside. Besides these, 4TMMS includes a Keithley 4200 Semiconductor Characterization System (4200-SCS) for providing the source voltage or current and for measuring the voltage–current relation.

Keithley 4200-SCS, equipped with three independent source-measurement units (SMUs) as well as their preamplifiers (PAs), is used for electrical measurement. Three SMUs and a common ground unit (GNDU) provide four terminals for the Kelvin method. Therefore, Keithley 4200-SCS is suitable for the electrical measurement of nanostructures because of its high input impedance, accurate current/voltage source, and high resolution. The sample stage can move in the X–Y plane driven by piezo creeper, which makes it easy to find some monodisperse nanowires by SEM. With the two-terminal method, two tips touch the nanowire

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at different points. One tip is connected to the GNDU of the 4200-SCS, and the other to a SMU of the 4200-SCS through the PA. Sweep voltage or constant voltage is applied to the latter tip while the current is measured simultaneously. With the four-terminal method, four collinear tips touch the nanowire along the direction of the axis. One SMU (SMU1) and the GNDU are used to source the current between the outer two tips, and the other two SMUs (SMU2 and SMU3) are used to measure the voltage drop between the inner two tips.

EXPERIMENTAL

Manipulating nanowires

One of the most important functions of the 4TMMS is manipulating (include pulling, pushing, picking up, putting down, and constructing) nanostructures. Here the focus is on manipulating one-dimensional nanostructures, especially nanowires dispersed on substrates. In the investigation of nanosystems, the distance between tips should be in nanoscale. Therefore, the tips could not be made perpendicular to the substrate surface but are at an angle of about 45°. Figure 1 is the photo of the four probes, and the inset is a sketch of the tips and the substrate. Without further improvement, the slanting tips can only pull or push a nanowire roughly but cannot pick up a nanowire.

The shape of the tip is improved under UHV condition. The tungsten tips were made by alternating current (A.C.) etching in NaOH solution and were degassed in UHV environment by heating them up to about 1200 K to remove the oxide layer and some other impurities. After obtaining a normal tip, the process of forming a nanohook at the top of the tip was undertaken.[10] The shape of the tip was changed using a different technique, i.e. by crashing the tip against the substrate or another tip. Normally, the collision may give rise to a hook at the top of the tip. With SEM navigation and STM scanner positioning technique, the movement of the tip as well as the magnitude and direction of the collision force can be precisely controlled. Different collision forces give different hooks.

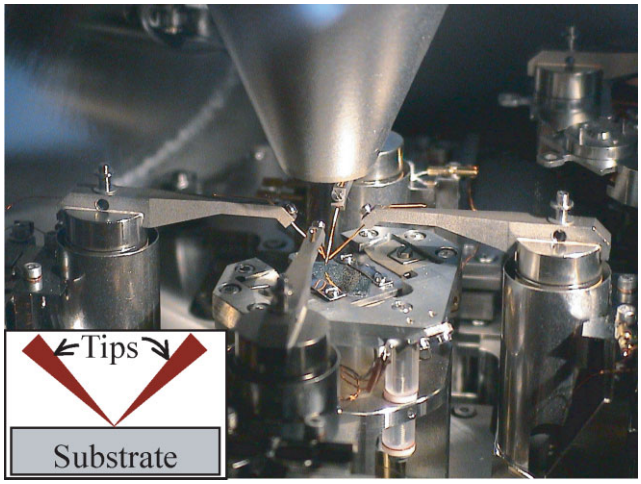

Figure 1. Four tips, substrate stage, and the head of a SEM gun are shown in the combined system. The inset is a sketch of the tips and the substrate, which reveals that the distance between two slanting tips can be very short.

Three types of hooks, called the A, B, or C-type, as shown in Fig. 2, were developed to manipulate nanowires. The A-type hook is used mainly in pulling or pushing nanowires along the surface of the substrate, as shown in Fig. 3. B and C-type hooks are needed to pick up nanowires. Figure 2 shows the process of picking up a nanowire. First, an A-type hook is used to push a nanowire toward a normal tip, which lifts the nanowire a little. Then another tip with a B-type hook is used to seize the nanowire and lift it some more. Finally,

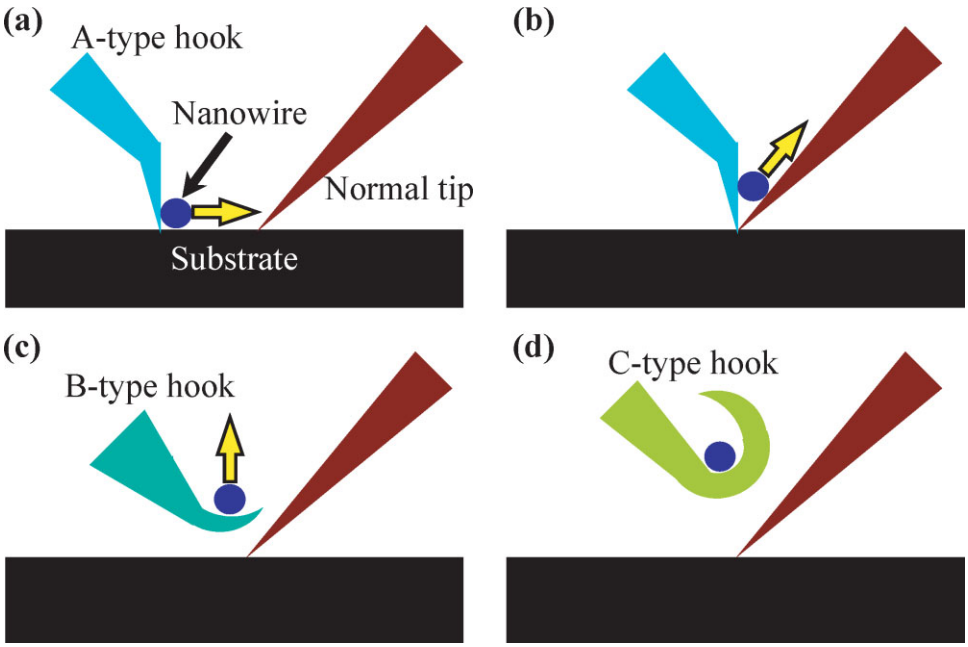

Figure 2. Sketch of a hooking process with tips. A-type hook pushes the nanowire toward a normal tip (a) and elevates it (b). B-type hook lifts the nanowire some more (c). C-type hook seizes the nanowire (d).

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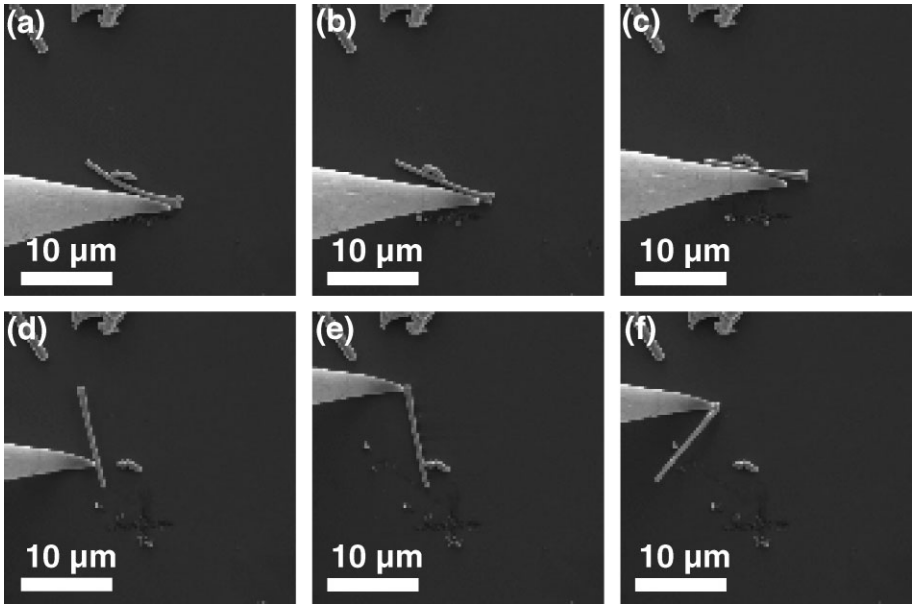

Figure 3. Shows a simple experiment pushing a ZnO nanowire moving along the surface of a SiO_2/Si substrate by a tip, demonstrating the nanowire manipulation capability of the system. From (a) to (c) pushing the nanowire to be horizontal; (c) to (d) pushing it to be vertical; (d) to (e) moving the nanowire toward the right; (e) to (f) changing the angle of the nanowire.

a C-type hook is employed to seize the nanowire firmly, in case it drops. In this way, a nanowire can be suspended by several tips or moved to any place; even the substrate can be moved or exchanged when the nanowire is being suspended.

This 'suspending' technique can be used in different ways. For example, it can be used to measure electronic transport through an individual nanowire without substrate influence that includes leak current, capacitance, and so forth. Furthermore, it can be used to construct a kind of junction, considering that a nanowire can be picked up and put down across another nanowire, as shown in Fig. 4. Besides, as shown in Fig. 5, 4TMMS also can be used to cut, melt, sublimate, and weld nanowires and even to make them stand up. When a heavy current flows through a nanowire, the thermal effect of the current may cause the nanowire to melt or sublimate; and two nanowires can be welded or connected using the thermal effect, which will be described later on.

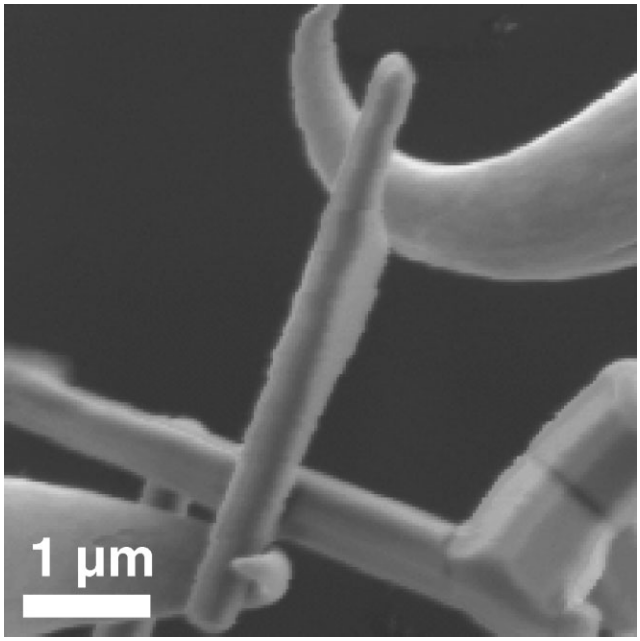

Figure 4. Two special tips with hooks picked up a ZnO nanowire and put it down across another to construct a junction.

Figure 6 represents the use of the tips to make a nanowire stand up. First, a tip hooked one end of a nanowire (a); and then the tip was moved away from the substrate, which caused the nanowire to stand up, because one end was lifted by the tip while the other one was still on the substrate (b). Afterwards, the nanowire still stood firmly when the tip was withdrawn (c) and removed (d). Figure 6(e) shows the nanowire falling because of the collision with the tip, which further proves that the nanowire was standing up. It is easy to calculate that the angle is about 78° (f). There is an insulating layer (silicon dioxide) on the substrate and the electron beam from SEM may charge the nanowire. Therefore, the force that supports the nanowire standing up is believed to be an electrostatic force.

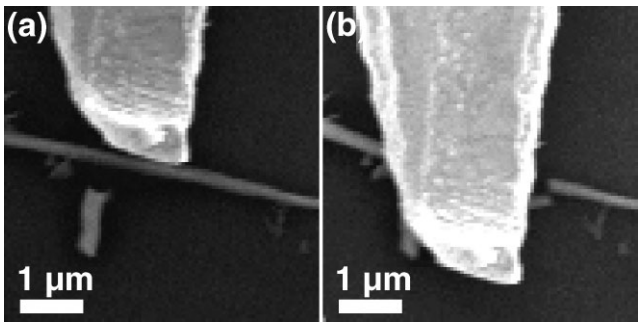

Figure 5. Two SEM images of a Cu-TCNQ nanowire that can be cut by a tip. Positioning of the tip close to the nanowire before cutting (a). The tip moving closer, breaking the nanowire (b).

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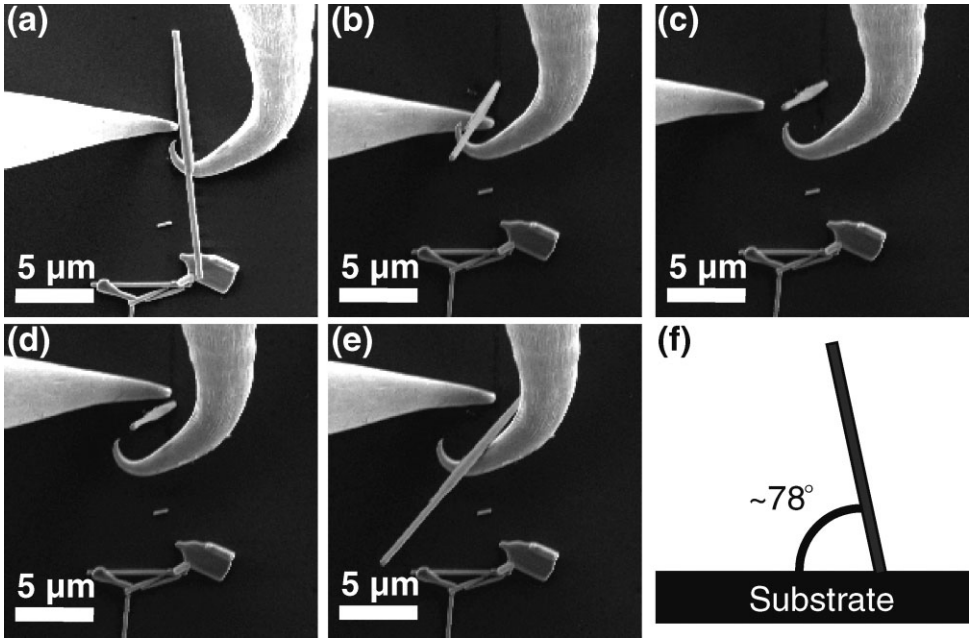

Figure 6. SEM images from (a) to (c) demonstrating how to make a ZnO nanowire stand up. From (c) and (d), it can be seen that the nanowire does not touch any tips. Image (e) shows the fallen nanowire. From the real length of the nanowire and the apparent length displayed in images (c) and (d), the angle is calculated to be about 78° (f).

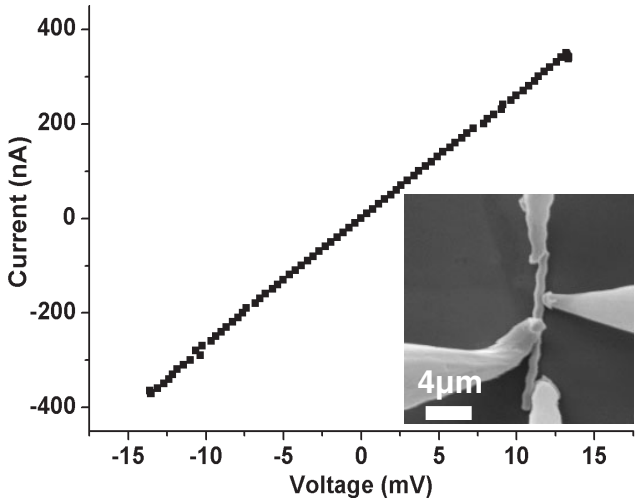

Figure 7. *I–V* curve obtained by the four-terminal method measurement showing a high conductivity and a good linearity. The inset is the SEM image of the ZnO nanowire and the four tips during the four-terminal method measurement. The outer two tips provide source current and the inner two tips get the voltage drop.

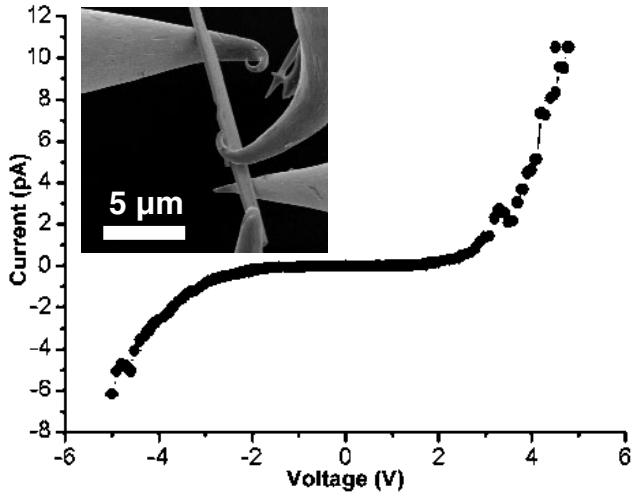

Figure 8. *I–V* curve by four-terminal method measurement exhibits nonlinear behavior and a low conductivity. The inset is the SEM image of the ZnO nanowire and the four tips during the measurement.

Measuring the electrical transport of nanowires

We have measured the electrical transport of a few kinds of nanowires with 4TMMS. The nanowires were dispersed on the silicon wafer (the substrate) covered with a 500-nm thick silicon dioxide layer as insulator. For the nanowires probably covered with organic molecules as surfactant from the earlier stages of synthesis, the sample was heated in UHV environment to remove the surfactant in order to avoid its effect on the electrical measurement.

RESULTS AND DISCUSSION

The conductivities of two kinds of zinc oxide (ZnO) nanowires have been measured. Either kind of ZnO nanowires is less than 1 μm in diameter and more than 10 μm in length. One kind of ZnO nanowires, deeply *n*-doped and therefore expected to have a high conductivity, have been studied using the four-terminal method. Figure 7 confirms the assumption of high conductivity. Figure 8 shows the other kind of ZnO nanowires suspended by four tips using the technique mentioned earlier. The *I–V* curve, also obtained using the four-terminal method, clearly demonstrates that the conductivity of this kind of nanowires is

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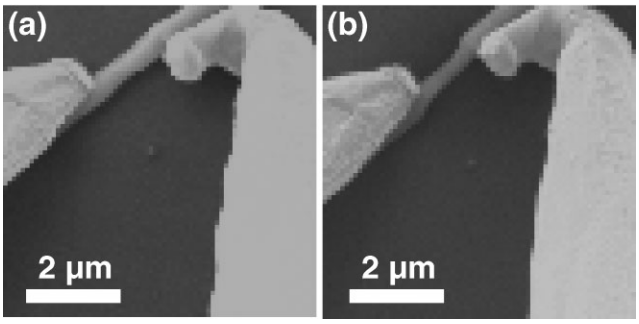

Figure 9. SEM images of a ZnO nanowire before (a) and after (b) a heavy current flowed through it, showing that the current can result in cleaning of the measurement system and even sublimation and thinning of the measured samples.

lower than that of the former. We can also melt or sublimate the nanowires by using the thermal effect of the current if the conductivity is suitable for the heating effect. Figure 9 shows two SEM images of a ZnO nanowire before and after a heavy current flowed through it. Obviously, some ZnO nanowires were sublimated and the nanowire became thinner than before.

It is of interest to find out if the nanowire can be broken by the 4TMMS under heavy and long-time current flow. The $I-V$ curves of a nanowire measured by the two-terminal method are shown in Fig. 10(a). The $I-V$ curves are repeatable and similar to the results of four-terminal method shown in Fig. 8. The similarity suggests that the contacts between tips and the nanowire contribute little to the $I-V$ nonlinearity and the resistance. After measurement, a heavy and long-time current was sourced to the nanowire, which caused a break in the nanowire, as shown in Fig. 10(b). Then the $I-V$ curve was measured again although there was no nanowire anymore. Figure 10(c) shows the repeatable result, which indicates the presence of something with a better conductivity. A possible source of this conductive material is the molten or sublimated ZnO that was crystallized and formed a thin film on the substrate.

A negative differential resistance (NDR) characteristic, which is found often in other semiconductor compounds,[11] was found in the $I-V$ measurements of ZnO nanowire, as shown in Fig. 11. Four $I-V$ curves have been measured, and the time between two neighboring measurements is a few minutes. It can be seen that the peak maintains its shape but with a shift toward right while the height of the peak reduces. This slight change in conductivity is probably due to the thermal effect of the current on the sample. The thermal effect might cause cleaning of components or change the surface structure.

The electrical transport of perylene nanowires and gallium sesquioxide (Ga_2O_3) nanowires were also measured, besides those of ZnO nanowires. Figure 12 shows $I-V$ curves of a perylene nanowire and the corresponding SEM images. The nanowire is suspended between two tips as shown in Fig. 12(b), and the measurements made, which display a nonlinear property (as shown in Fig. 12(a)). When the third tip presses the nanowire (as shown in Fig. 12(d)),

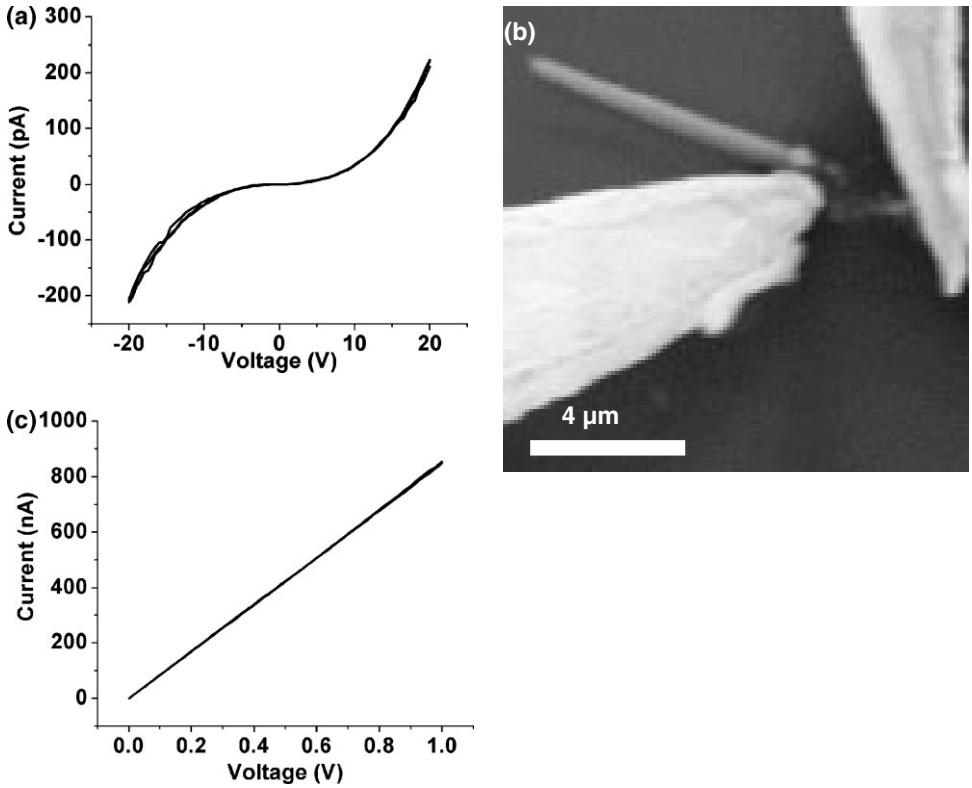

Figure 10. $I-V$ curves (a) before the ZnO nanowire was melted show a low conductivity and nonlinearity; but $I-V$ curves (c) after the nanowire was melted reveal a high conductivity and linearity. Each measurement was repeated three times and the results were repeatable. The difference between them suggests that there are some changes during the melting. The SEM image (b) shows the melted nanowire.

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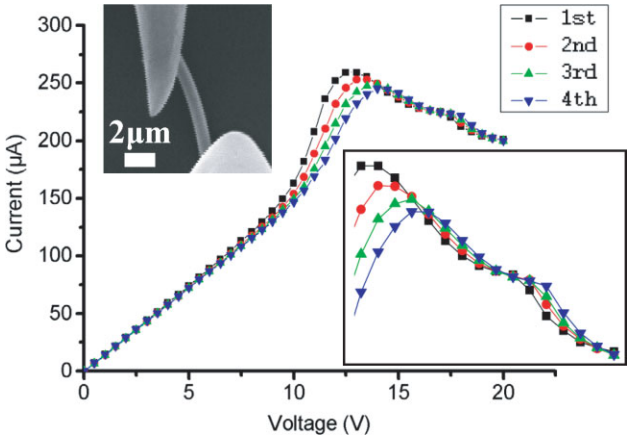

Figure 11. Unusual *I*–*V* curves show an NDR-like characteristic. The measurements were taken four times with a few minutes gap between two neighboring measurements. The upper left inset is a SEM image of the ZnO nanowire and the tips. The right lower inset is the enlarged figure of the peaks.

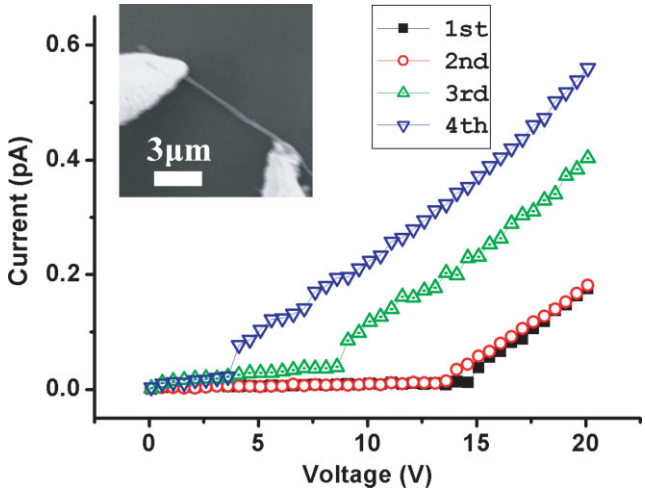

Figure 13. Transition points are displayed in the *I*–*V* curves of Ga_2O_3 nanowires clearly. The measurement was done four times and it was found that the transition point voltage became lower with subsequent measurements. The inset is an SEM image of nanowire and tips.

the nonlinearity vanishes (as shown in Fig. 12(c)), which is believed to be a result of better contact under pressure. Figure 13 shows a sharp transition point for each *I*–*V* curve of a Ga_2O_3 nanowire. When the applied voltage is lower than the transition point, the current is almost equal to zero. Nevertheless, if the voltage is higher than the transition point, the current will linearly increase (dI/dV is a constant). Moreover, with increasing measurement times, the transition voltage becomes lower. The reason for this is not clear yet. The same phenomena were observed in cuprum-7,7′,8,8′-tetracyanoquinodimethane (Cu-TCNQ) nanowires (see Fig. 14) too.

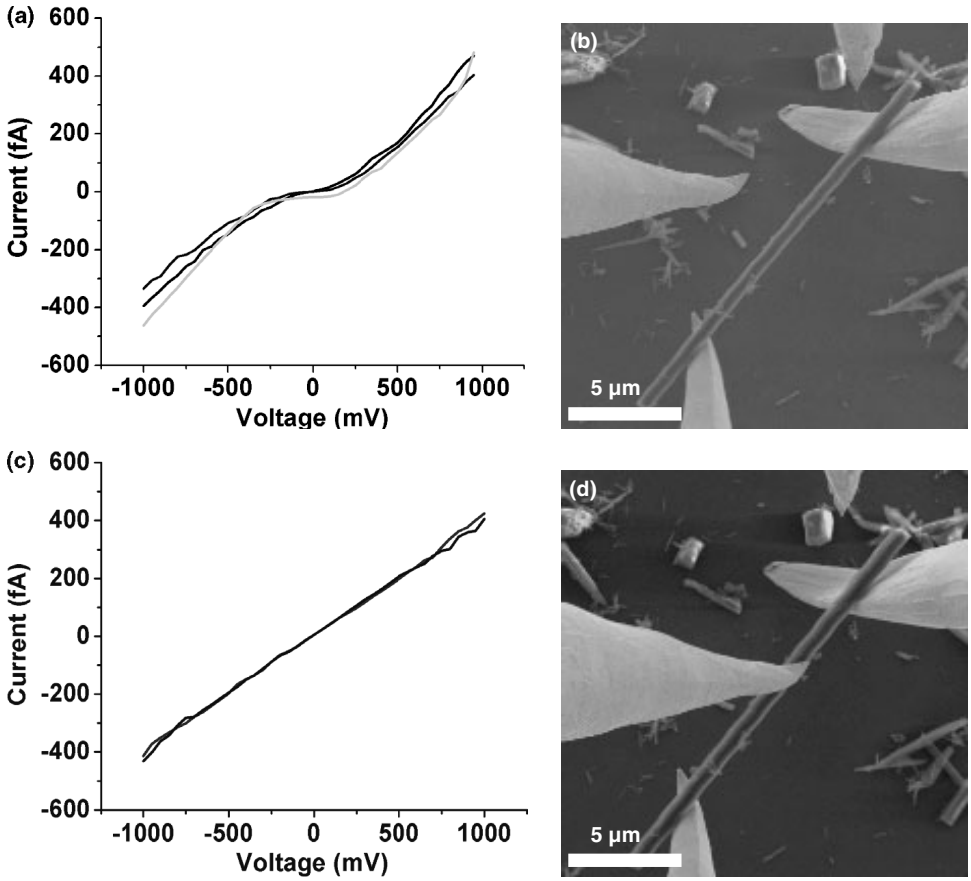

Figure 12. *I*–*V* curves of a perylene nanowire and the corresponding SEM images. The contacts between the tips and the nanowire contribute nonlinearity to the *I*–*V* curves (a), without the third tip (b). The nonlinearity vanishes (c) when the third tip is pressed on the sample, improving the contact (d).

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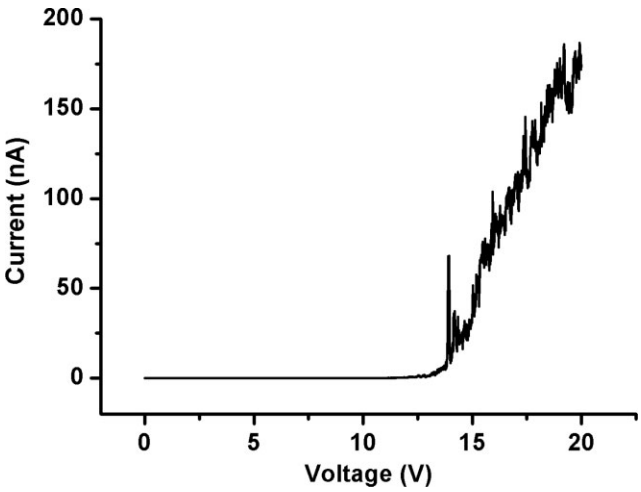

Figure 14. *I–V* curve of Cu-TCNQ nanowire reveals the transition point.

CONCLUSIONS AND PROSPECTIVE

It is shown by this study that the 4TMMS system enables the manipulation and processing of nanowires as well as the performance of *in situ* $I-V$ measurements on those wires. Since all the procedures are carried out in UHV and the four-terminal method can be applied for electrical transport measurements, possible influences from the environment that are present if these procedures are performed at ambient conditions, such as contamination, chemical reactions, and impurities, more importantly, contact effect during the $I-V$ measurement, can be excluded by applying this new method. The tip–nanowire contacts are quite reliable and so the results of repeated measurements agree satisfactorily for the time being. Preliminary results on the electrical transport properties of different kinds of nanowires were obtained. The 4TMMS system shows very powerful abilities for applications in nanoscience and nanotechnology, e.g. detailed $I-V$ measurements on nanowires and nanotubes under well-defined conditions, and also as a function of the temperature of conductors.

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