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Probing of Individual Semiconductor Nanowhiskers by TEM-STM

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Abstract: Along with rapidly developing nanotechnology, new types of analytical instruments and techniques are needed. Here we report an alternative procedure for electrical measurements on semiconductor nanowhiskers, allowing precise selection and visual control at close to atomic resolution. We use a combination of two powerful microscope techniques, scanning tunneling microscopy (STM) and simultaneous viewing in a transmission electron microscope (TEM). The STM is mounted in the sample holder for the TEM. We describe here a method for creating an ohmic contact between the STM tip and the nanowhisker. We examine three different types of STM tips and present a technique for cleaning the STM tip in situ. Measurements on 1-μm-tall and 40-nm-thick epitaxially grown InAs nanowhiskers show an ohmic contact and a resistance of down to 7 kΩ.

Key words: TEM-STM, transmission electron microscopy, STM tip preparation, nanowhiskers, nanowires

Introduction

Characterization of mechanical, physical, and chemical properties of nanometer-sized structures (0.1–100 nm) have become increasingly important because of downscaling of semiconductor devices. Nanowhiskers are highly anisotropic, crystalline structures first discovered for the Au/Si system (Wagner, 1970). Today a lot of work is based on III–V semiconductor materials such as GaAs, InAs, and InP. The electrical and optical properties of semiconductor nanowhiskers are essentially determined by their shape and size. Electrical measurements of nanostructures, such as nanowhiskers, are often made as a multistep process, including electron beam lithography, metal deposition, etching, and lift-off techniques. Each process step is a source of uncertainties and errors. Manipulators incorporated in electron microscopes have made it possible to do these measurements in a more controlled manner and at the same time observe the structures with high resolution.

Shortly after the first STM was built (Binnig et al., 1982), Spence presented an STM mounted in a TEM (Spence, 1988). This was used for comparing reflection electron microscopy (REM) images with STM images. Since then, a few other groups have pursued research with atomic force microscopes and STMs mounted inside electron microscopes (Kizuka et al., 1997; Kizuka, 1998; Erts et al., 2001).

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In this article, we present the use of TEM-STM as a method for electrical characterization of semiconductor nanowhiskers, *while observing them* at close to atomic resolution in a TEM.

Materials and Methods

Synthesis of Nanowhiskers

Our approach for nanowhisker production is the vapor-liquid-solid growth, which may be seen as a variety of liquid phase epitaxy. A supposedly molten and alloyed metal droplet on a semiconductor substrate surface catalyses the growth of nanowhiskers. By choosing very precise, size-selected gold particles, the diameter of the nanowhiskers can be controlled, whereas the length is essentially determined by the time of growth. The gold particles are produced in a furnace by heating gold to above its melting temperature. A carrier gas in the aerosol nanoparticle system cools down the particles and transports them through a charger and a differential mobility analyzer (DMA), where size selection takes place in two steps (Magnusson et al., 1999). The gold particles are then deposited onto the substrate. The nanowhisker growth takes place in a chemical beam epitaxy (CBE) system. In CBE, the growth sources are directed onto a heated substrate under ultrahigh-vacuum conditions. The different growth sources can be switched on and off to produce different types of III–V semiconductor materials. This can be made during the growth, and hetero-structures

can, hence, be formed within a single whisker (Duan et al., 2001; Björk et al., 2002*a*; Wu et al., 2002). This opens up the possibilities to make components such as diodes, light emitting diodes (LEDs), and resonant tunneling devices (Björk et al., 2002*b*) inside a single whisker. However, to develop the procedure, all structures that are measured here are pure InAs nanowhiskers.

STM-Tip and Sample Preparation

The size, shape, and aspect ratio of the STM tip is of great importance for acquiring good resolution and imaging of steep morphologies in STM, but for TEM-STM it is also important for accurate positioning. Several different types of STM tips are presented in the literature. Here we compare three different types of easily prepared tips: a mechanically cut gold wire, an electrochemically etched tungsten tip, and an electrochemically etched gold tip.

The first type of STM tip produced was a 0.25-mm-thick gold wire cut with a pair of cutting pliers. Observation in TEM showed a thick and blunt tip with multiple edges. The second type of tip is produced by electrochemical etching of tungsten wires with a diameter of 0.25 or 0.38 mm in 1 M KOH (Ekvall et al., 1999). The resulting tips are all very sharp with an edge diameter down to 5 nm. Figure 1a shows a SEM image of such a tip with a TEM image inserted showing the very edge of the tip. An insulating oxide layer usually covers the edge of the tungsten STM tip that has to be removed to obtain good contact for electrical measurements. This is performed by making contact with the bulk material of the sample while applying a high bias (4–6 V). This will cause the oxide layer to spallate and expose the metallic tungsten tip.

The third type of tip is formed by electrochemical etching of a 0.25-mm gold wire in hydrochloric acid (Libioulle et al., 1995; Knapp, 1998). The wire is cut into pieces 10 mm in length. A resistant painting, in this case pink nail polish, protects 0.5 mm of one end against etching. This end of the wire is dipped 1 mm into concentrated hydrochloric acid. The counter electrode is a 0.5-mm-thick platinum loop surrounding the gold wire in a 20-mm circle. The etching is realized by applying an AC potential of 5.0 V at 6 kHz with a DC offset of +2.5 V to the gold wire. The process is stopped as soon as the end protected by the painting falls of by lifting the tip out of the etching solution. By removing the tip from the solution, and not just breaking the current, postetching caused by the natural potential is prevented (Guise et al., 2002). The tip is then quickly rinsed in water and ethanol. Figure 1b shows a SEM image of a gold tip treated according to this procedure. A TEM image of the outermost edge is shown as an insert.

The TEM-STM sample holder is a side entry holder designed so that a sample can be mounted together with a piezo-controlled STM tip. The system that we used is a Nanofactory TEM-STM sample holder used in a JEOL JEM 2000FX transmission electron microscope. Figure 2 is a

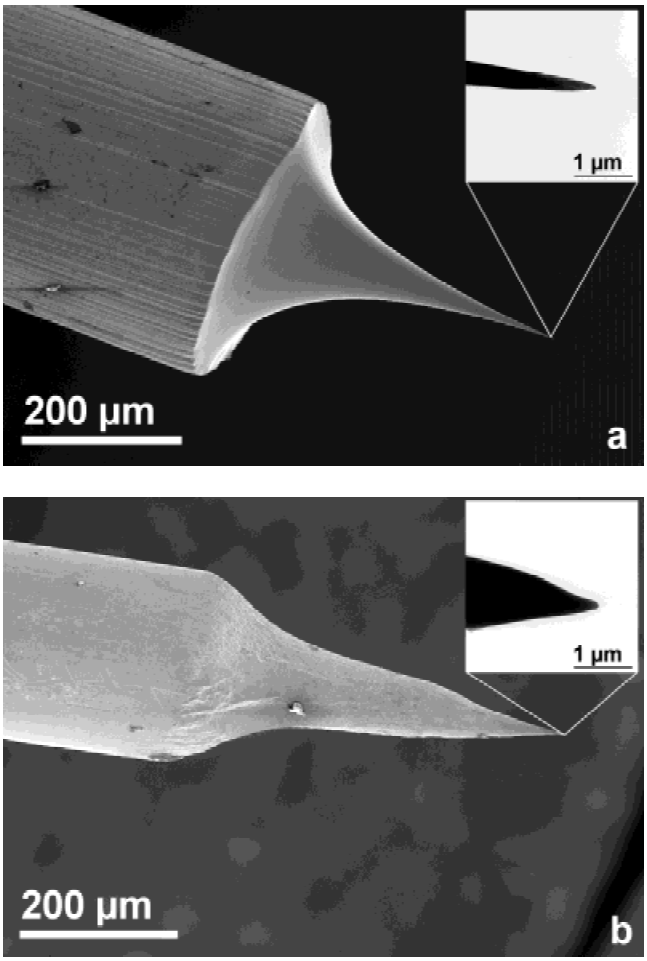


Figure 1. **a**: A SEM image of an electrochemically etched tungsten tip; a magnification of the outermost edge of the tip is shown as an inserted TEM image. **b**: A SEM image of an electrochemically etched gold wire; the edge of the tip is showed as an inserted TEM image.

photo of the TEM-STM sample holder with a nanowhisker sample mounted together with a STM tip. The nanowhisker samples are well suited for viewing in the TEM, because the whiskers are thin enough to be penetrated by the electron beam. The thin columnar structures are only 40 nm thick but more than a micrometer tall. The InAs nanowhiskers are grown on GaAs (111)B wafers with a thickness of 1 mm. The growth process also introduces a bulk growth resulting in a thin layer of InAs covering the GaAs substrate. A small piece of the wafer is cut to a size of about 2×2 mm and conductively glued to a small piece of gold wire with silver paint (see Fig. 3a). The silver paint covers the sides of the GaAs piece and connects the InAs layer with the gold wire. The gold wire is then mounted in the TEM-STM holder and wired up via a preamplifier to the control box.

Procedures for Approach by the STM Tip

The TEM-STM allows us to freely maneuver the STM tip in all three directions. The lateral positioning (defined as x

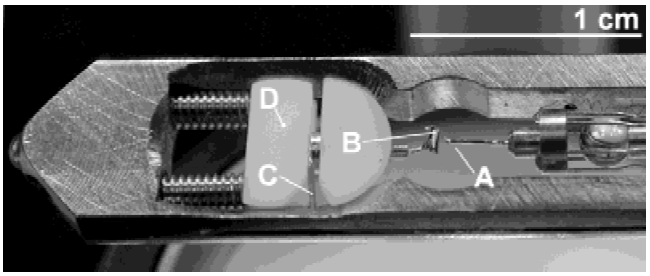
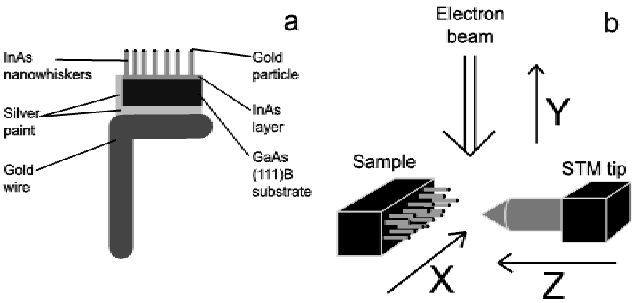


Figure 2. The specimen area of the TEM-STM sample holder. A STM tip is mounted together with a nanowhisker sample. The STM tip (A) is mounted in the tip holder hat to the right. The sample (B) is connected to the control unit via a wire (C), which is isolated from the rest of the holder (D).



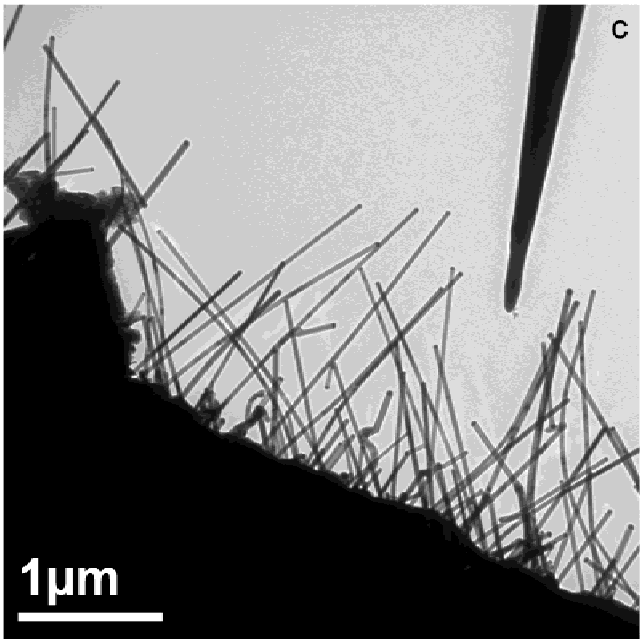


Figure 3. **a**: A schematic drawing of a nanowhisker sample glued to a gold wire. **b**: The defined directions in the TEM-STM system; the lateral direction (x), the (opposite) direction of the electron beam (y), and the tip approach direction (z). **c**: A TEM image of a tungsten STM tip maneuvered in a forest of nanowhiskers.

direction) and positioning in the approach direction (defined as the z direction) are both visible in the TEM and easy to control, whereas positioning along the direction of the electron beam (defined as the y direction) is not trivial (see Fig. 3b). The TEM image in Figure 3c shows an overview of a tungsten STM tip maneuvered in a "forest" of nanowhiskers. One way of getting accurate height control is to oscillate the tilt around the specimen holder axis on the side entry holder. In practice, this is rather difficult, as the sample rarely is at the exact tilting axis. A better way is to monitor the objective lens focal difference between the Gaussian focus condition for the STM tip and the selected whisker. This procedure requires a very sharp STM tip with a thickness small enough to produce a significant amount of phase contrast. The height aligning process has to be repeated several times starting far away from the object with the coarse movement (inertia slider) and then closer to the object with the fine, piezo movement. It must be taken into account that the inertia slider does not give a unidirectional movement. When approaching the object in the z direction, the STM tip will also move in the x and y directions.

Alternatively a potential of about 400 mV can be applied between the STM tip and the sample. The tip current output from the control box can then be amplified and connected to a tone generator giving a signal to a loudspeaker. The contact current will modulate the amplitude of the tone, which will basically give an audio signal of the contact between the tip and the sample. This gives a practical advantage when operating the microscopes.

Electrical Characterization of InAs Nanowhiskers

The sample holder with a mounted tip and sample is cleaned for 30 s in a Fischione Instruments Inc. Model 1020 Plasma Cleaner. The Plasma Cleaner is using a high frequency oxygen/argon plasma with an energy of 12 eV at a gas pressure of 15 mTorr (Isabell et al., 1999). A single freestanding nanowhisker is selected in the TEM and the STM tip is connected to the top gold particle. A small bias of about 300 mV is applied between the tip and the sample and the electron beam is focused on the interface between the tip and the gold particle. This will increase the mobility of gold atoms on the two gold surfaces and "fuse" them together, forming a contact with a much lower resistance. The beam is spread out again as soon as the current reading stabilizes. The gold–gold contact is strong enough to sustain stress, sometimes up to the point where the nanowhisker breaks before the joint. The range of the I–V measurements differs depending on the thickness of the whisker and how good a contact is obtained. A typical I–V measurement is recorded as an average of 10 runs ranging from -200 mV to 200 mV with an acquisition time of 500 ms, a settling time of 100 ms between each measurement, and a settling bias of -200 mV.

Results and Discussion

The major challenge with these measurements is to create a point contact with a low resistance between the tip and the whisker. Several factors are affecting the quality of the point contact, where the cleanliness of the two surfaces that are to be connected has the greatest influence on the measurement. The sample and the tip of the nano manipulator (the STM tip) are often exposed to air and will quickly develop an insulating oxide layer, which has to be removed before contacting. Residual hydrocarbons in the low-pressure atmosphere ($<3 \times 10^{-5}$ Pa) inside the TEM is also an important factor, introducing a carbon deposition on everything that is exposed to a focused electron beam. This amorphous carbon deposition acts as an insulating layer, preventing a good electrical contact. Other contaminants on the STM tip are introduced during the production of the tip, for example, a tungsten oxide sheeting of the W tips. All these factors, together with the actual point contact resistance, will give a varying range of measured resistances, ranging from megaohms down to only a few kiloohms, on nanowhiskers with similar dimensions. Some approaches have been suggested on how to improve the electrical contact in these types of measurements, mainly on how to make a sharp and clean STM tip, using postetching and sputtering techniques to cleanse the tip (Ekvall et al., 1999; Guise et al., 2002). Other approaches have been to glue the STM tip to the structure using low-melting-temperature metals (Shimizu et al., 2002) or by pulsing currents through the contact, stimulating diffusion of atoms to create a better contact (Kizuka, 1998). We have found that it is possible to clean the STM tip inside the TEM by crashing the tip in a controlled manner into the substrate. Any oxide or contamination on a STM tip can be removed, together with a part of the tip, by moving the STM tip in contact with the substrate and applying a high voltage with a high current (approx. 5 V and 1 mA). The contaminated outermost edge of the tip will melt and display a fresh surface. This method works well for cleaning of the tip but not for cleaning samples such as nanowhiskers, which can be contaminated from remnants of the growth procedure as well as carbon contamination in the electron microscope.

The gold catalyst at the top of the whisker can be fused together with the gold STM tip by focusing the electron beam at the interface between the tip and the whisker. This will fuse the two surfaces together and create a good electrical connection. The downside of this is that the focused electron beam will introduce a severe carbon deposition on all surfaces in that area. Plasma cleaning of the entire sample holder with the tip and sample mounted will remove most of the carbon depositions and also prevent it from developing at all. We have found that the method giving the best contact is a combination of using plasma cleaning together with the electron beam fusing technique.

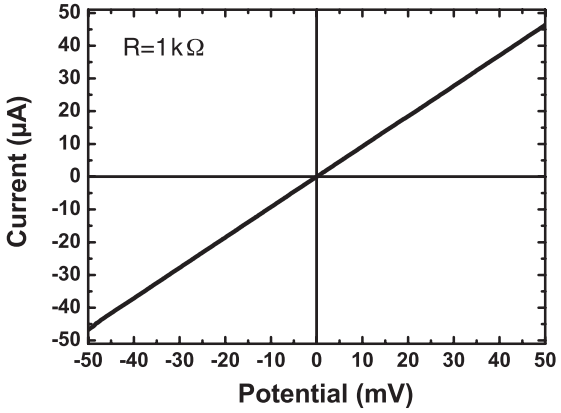


Figure 4. An I–V measurement of a tungsten STM tip in contact with the InAs layer on top of the GaAs substrate.

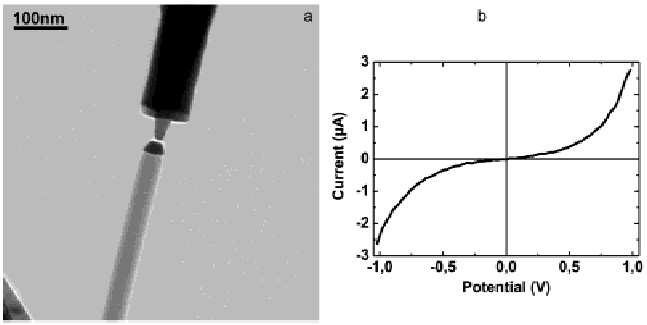


Figure 5. a: A tungsten tip with the outermost oxide layer removed has been maneuvered in contact with an InAs nanowhisker. **b**: An I–V measurement of an InAs nanowhisker in contact with a tungsten STM tip. The curve shows an average of 10 measurements.

The InAs nanowhiskers are electrically connected to the back contact via the thin, bulk grown, InAs layer and the silver paint. The resistance from the InAs layer to the back contact is measured by pressing the clean STM tip in contact with the substrate. Figure 4 shows an I–V curve from such a measurement where the resistance is measured to 1 kΩ.

Figure 5a shows the edge of a tungsten STM tip in contact with the gold catalyst of an InAs nanowhisker. The tip, at the top half of the image, has a shell of tungsten oxide. The composition was verified by electron energy loss spectroscopy (EELS). At the very end, the oxide has been removed with the method described above, displaying a smaller tip of tungsten metal. The width of the nanowhisker can, in the TEM image, accurately be determined to 41 ± 1 nm. The tip and sample have not been cleaned by plasma cleaning. The corresponding I–V measurement is shown in Figure 5b. The I–V curve in Figure 5b is an average of 10 measurements from −1 V to 1 V with an acquisition time of 500 ms and a settling time of 100 ms between each measurement, and a settling bias of −1 V. The length of the

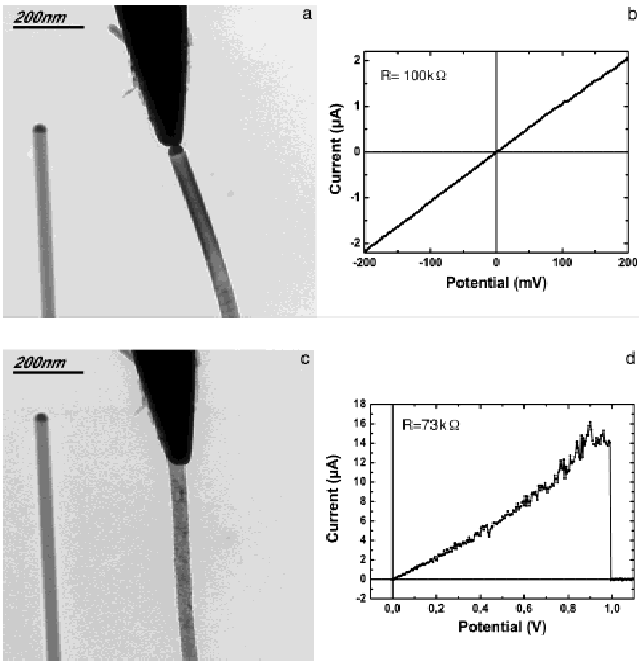


Figure 6. **a**: A gold STM tip in contact with an InAs nanowhisker. The strain contrast from the bending of the whisker can be seen as two darker bands on each side of the whisker. **b**: I–V measurement of an InAs nanowhisker in contact with a gold STM-tip (corresponds to a). The gold tip and the gold particle on the whisker have been fused together with the electron beam to get a good contact. The curve shows an average of 10 measurements. **c**: The nanowhisker after a high current has been passed through the whisker (the gold particle is now obscured by the tip). The structure has changed and the contact to the substrate has melted off. **d:** An I–V measurement of an InAs nanowhisker in contact with a gold STM tip. The applied bias has been increased until the nanowhisker melts off.

whisker is approximately 1 μm. The I–V curve is nonlinear, indicating a potential barrier in the system, most likely coming from a very thin remaining oxide layer on the edge of the tungsten tip. This oxide layer is too thin to be detected by EELS or seen with this microscope. With an oxide layer on the tip, the properties of the I–V curve will be totally determined by the tunnel current or the point contact resistance.

To avoid the problems that arise with oxide layer formation on the tungsten tips, we decided to use gold tips instead. The mechanically cut gold tips were all very blunt and also frequently bent. The positioning of the tip in the y direction in the microscope was difficult to do with a blunt tip having no sharp edge to focus on. This type of STM tip was found to be useless for high precision TEM-STM work and will not be discussed any further. The electrochemically etched gold tips were, on the other hand, very sharp and well suited for TEM-STM work. Figure 6a shows a nanowhisker connected to a gold STM tip, and Figure 6b shows the corresponding IV curve. The tip and the sample have both been cleaned in a plasma cleaner and fused together

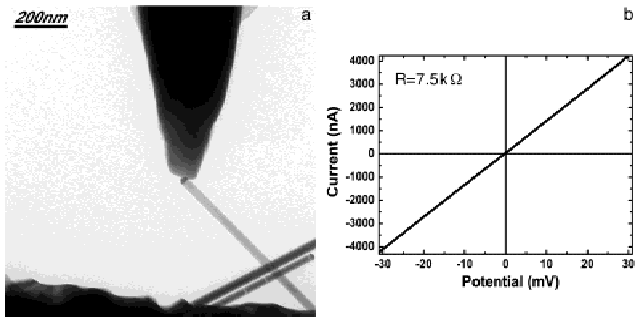


Figure 7. **a**: An InAs nanowhisker in contact with a gold STM tip. The gold tip and the gold particle on the whisker have been fused together with the electron beam to get a good contact. **b**: The corresponding I–V measurement. The curve shows an average of 10 measurements.

with the method described above. The whisker diameter is 51 nm and the resistance of the nanowhisker measured as the slope (di/dv) is 100 kΩ. This is a fairly high resistance for such a thick whisker. We believe that the resistance is determined by the point contact resistance and not by the resistance in the whisker.

The best electrical contacts have been achieved by fusing a gold STM tip to the gold particle on the nanowhisker by focusing the electron beam onto the contact area. It is still difficult to get a contact area corresponding to a full contact over the diameter of the whisker. A nonlinear I–V curvature with very high resistances in the MΩ range indicates that the resistance is totally determined by the point contact at the gold–gold connection. Figure 7b shows a measurement with a very good contact resulting in a resistance of 7.5 kΩ, a measurement that corresponds well to previous measurements on InAs nanowhiskers of the same size and length (Björk et al., 2002*a*), in which lithographic contacting techniques were used. We have also seen that the gold particle at the top of the nanowhisker is essential for the TEM-STM electrical measurements. We have not been able to make an electrical contact to nanowhiskers where the gold particle is missing.

The point contact with the tip seems to determine the resistance of the system. However, thinner whiskers have a lower resistance and will easily melt off when the current is too high. Some measurements have been performed where we intentionally increased the applied bias slowly until the whisker melts off. Figure 6a and 6c show a whisker before and after a melt-off; we also present an I–V curve in Figure 6c from a similar measurement. The whisker breaks at about 16 μA for a 51-nm-thick InAs whisker and this corresponds to 800 kA/cm^2. Still, some whiskers melt and break off at much lower currents, and we suggest that this is due to stress induced by the bending force of the whisker from the STM tip.

The InAs nanowhiskers are highly flexible and can easily be bent 90°, sometimes even more, without breaking. The STM tip has to be pressed quite hard to the whisker to

get a good electrical contact; this procedure will bend the whisker and induce strain in the whisker, which is clearly visible as dark bands. When the STM tip is retracted, the nanowhisker will immediately recoil completely and the strain pattern will shortly after disappear. No permanent structure change or induced stacking fault has been observed as a result from bending and relaxing of nanowhiskers. The bending has not been seen to affect the electrical measurements as long as the currents are well below the critical melt-off current.

Conclusions

Accurate and reproducible electrical measurements on nanowhiskers can be performed with the TEM-STM giving results well comparable with measurements using lithographic contacting techniques. The most severe problems with the measurements are the contamination of both the sample and the STM tip, and a point contact effect when the contact area is too small. The first problem can be solved by using systems with good vacuum and clean samples from plasma cleaning to remove carbon deposits, and the described tip-melting technique, where the STM tip is placed in contact with the bulk substrate and the voltage is increased so that a part of the tip is melted and removed. The second problem was dealt with by fusing the STM tip together with the gold particle on the nanowhisker by focusing the electron beam at the interface. We have also demonstrated the ability to controllably deform the nanowhiskers using the STM tip as a bending device, and were able to image the development of strain-induced dark features in the TEM images during such deformation.

Acknowledgments

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