

Making electrical contacts to nanowires with a thick oxide coating

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Received 24 July 2002, in final form 27 August 2002

Published 16 September 2002

Online at stacks.iop.org/Nano/13/653

Abstract

Techniques are presented for making ohmic contacts to nanowires with a thick oxide coating. Although experiments were carried out on Bi nanowires, the techniques described in this paper are generally applicable to other nanowire systems. Metal electrodes are patterned to individual Bi nanowires using electron beam lithography. Imaging the chemical reaction on the atomic scale with *in situ* high-resolution transmission electron microscopy shows that annealing in H₂ or NH₃ can reduce the nanowires' oxide coating completely. The high temperatures required for this annealing, however, are not compatible with the lithographic techniques. Low-resistance ohmic contacts to individual bismuth nanowires are achieved using a focused ion beam (FIB) to first sputter away the oxide layer and then deposit Pt contacts. By combining electron beam lithography and FIB techniques, ohmic contacts stable from 2 to 400 K are successfully made to the nanowires. A method for preventing the burnout of nanowires from electrostatic discharge is also developed.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The fabrication of nanowires within porous alumina templates has recently become a very popular area of research. During the past few years, researchers have filled these templates with a number of materials ranging from carbon nanotubes to superconductors and magnetic materials [1–3]. Our motivation for studying the Bi nanowire system is based on the unique properties of bulk Bi. In particular, the very long mean free path in bulk Bi (~0.4 mm at 4 K and 100 nm at 300 K) makes the Bi nanowires a suitable system for the study

of low-dimensional transport phenomena. Since the diameter of the nanowires is much smaller than the mean free path of the electrons, the electrons will be confined by the boundary of the nanowire, thereby resulting in a reduction in mean free path as the wire diameter decreases. Also, the small effective masses of Bi (which are as small as $0.001m_e$) result in very pronounced quantum size effects [4]. For these reasons, the Bi nanowire system is attractive for the fundamental investigation of classical and quantum size effects that are becoming more and more relevant to the semiconductor industry as devices become smaller and smaller.

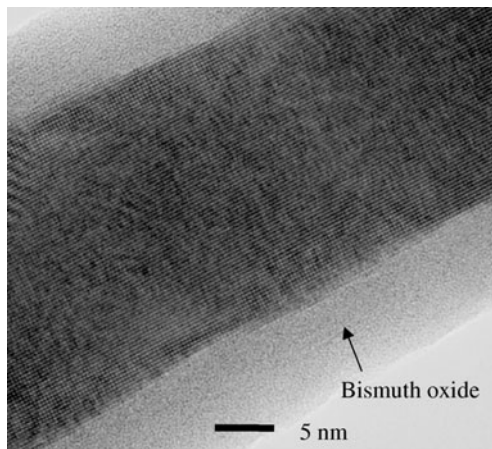


Figure 1. A HRTEM image of a 40 nm nanowire with a 25 nm crystalline Bi core and a 7 nm thick amorphous oxide coating.

2. Background

The nanowires used in this work were prepared by filling a porous alumina template [5–7] with molten bismuth and allowing the bismuth to crystallize through slow cooling. When the nanowires were removed from the template by dissolving the template in a solution of CrO_3 and H_3PO_4 [8], a thick oxide layer was formed on the nanowires. A HRTEM (high-resolution transmission electron microscope) image of this oxide is shown in figure 1. As can be seen from this figure, the crystalline Bi core of the nanowire is 25 nm and the amorphous oxide layer is 7 nm thick.

Metal electrodes were first attached to the nanowires using electron beam lithography [9]. Because of the thick oxide coating on the nanowires, the contacts were non-ohmic and highly resistive ($\sim 1 \text{ M}\Omega$). The non-linearity in the measured I - V curve can be understood on the basis of tunnelling transport through the oxide. This non-linearity is such that for very small currents the resistance is extremely high. Since there is very little current flowing through the two inner electrodes of a four-point measurement, the high resistance results in an extremely noisy voltage signal. This noise is found to be larger than the signal of the voltage drop across the nanowire, making the desired measurement unviable. Improving the contacts by annealing is not feasible because of the low melting point of Bi (271 °C). We cannot anneal at a high enough temperature for significant diffusion of the electrode material (i.e. chromium) through the oxide coating.

The thick oxide coating on the nanowires prevents good electrical measurements from being taken. As the sample temperature is lowered, the contact resistance increases from $\sim 1 \text{ M}\Omega$ at room temperature to $\sim 1 \text{ G}\Omega$ at 250–275 K. In order to make reliable transport measurements, the contacts must be improved by reducing the thickness of the oxide coating. This may be achieved by several methods, including chemical etching of the oxide layer (see section 3.2), oxide reduction in a hydrogen environment (see section 3.3), and focused ion beam (FIB) sputtering (see section 3.4). Section 3 also describes how electrodes are attached to the Bi nanowires, and section 4 discusses the reliability of the techniques used to make ohmic contacts to these heavily oxidized nanowires.

3. Experimental methods

3.1. Electron beam lithography

In this work, metal electrodes are patterned on top of individual Bi nanowires using electron beam lithography. A grid of gold dots, 2 μm in diameter, is first patterned on an insulating substrate (Si with 100 nm of SiO_2) using photolithography, and serves as the reference markers. Nanowires are then deposited by applying a drop of nanowire-containing solution onto the substrate and allowing the solution to dry. We then locate a single isolated nanowire relative to the photolithographically defined grid of points using an optical microscope, SEM (scanning electron microscope), or AFM (atomic force microscope). A layer of PMMA (poly(methyl methacrylate)) is then spin coated on top of the wires. PMMA is chemically sensitive to electron radiation, and will serve to define the electrode pattern. In this work, an IBM VS2A electron beam writing system was used to expose the electrode pattern in the PMMA. Before exposing the electrode pattern with electron beam radiation, however, we first align our coordinate system to the grid of points on the substrate by using the electron beam of the VS2A as a SEM. Care is taken not to expose the resist in the area near the nanowire, as the SEM electron beam will also expose the PMMA resist. This is avoided by first finding reference markers in the photolithographically defined grid of points near the edge of the substrate, away from the selected nanowire. We then turn off the electron beam and move the sample stage by the relative distance between the reference point and the desired nanowire, which has been recorded in the optical microscopy step, so that the electron beam will be centred on top of the wire. A computer file containing the desired electrode pattern is then loaded into the VS2A. This file controls the deflection of the electron beam, and traces out the desired electrode pattern, writing the pattern into the PMMA. After the electron beam exposure, the PMMA is developed using a solution of 2:1 isopropanol:MIBK (methyl-iso-butyl-ketone), which dissolves the exposed PMMA while leaving the unexposed PMMA in place. We then evaporate the metal for the contacts, using 100 nm gold with a 5 nm adhesion layer of chromium. Finally, the remaining unexposed PMMA is removed using NMP (1-methyl-2-pyrrolidinone) at 90 °C. At this point, all that is left on the substrate is the evaporated metal in those regions which had been exposed to the electron beam, and the desired Bi nanowire underneath these electrodes [4, 9].

Because of the small diameter of the nanowires and low melting point of Bi (271 °C), care is taken to prevent the nanowires from being burnt out by unwanted electrical currents. The nanowires are therefore shorted at all times, even on the substrate. The shorts are removed before the measurements are taken with a small diamond scribe [4, 9].

3.2. Chemical etching

The Bi nanowires were etched in an acid solution in an attempt to remove the oxide layer. Figure 2 shows HRTEM images of 40 nm Bi nanowires after they were dipped in 10:1 diluted HCl for 3 s. The image shows that Bi was dissolved while leaving the oxide shell intact. Several other acids, HF, H_2SO_4 , H_3PO_4 , and HNO_3 , were tried at various concentrations, but all yielded similar results. Basic solutions of KOH and NaOH

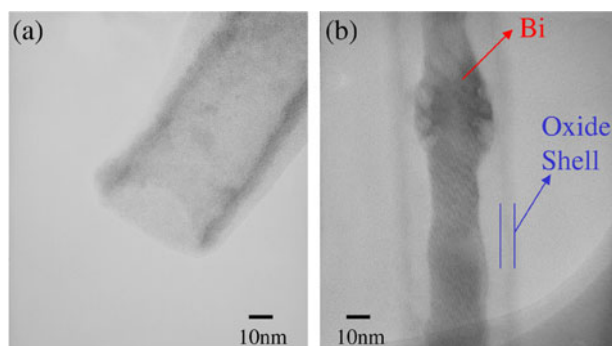


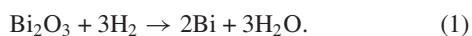
Figure 2. HRTEM images of 40 nm Bi nanowires after a 3 s etching in 10:1 diluted HCl, (a) showing the remaining oxide shell and (b) showing a partially dissolved Bi core inside an oxide shell.

were also used, but again were found to dissolve the Bi core and not the oxide coating. From these studies, we conclude that the Bi nanowires are very sensitive chemically and are stable only in a narrow range of pH, while the oxide is highly chemically resilient. Thus, it has been very difficult to find a chemical reaction that can reliably remove the bismuth oxide coating without damaging the enclosed bismuth nanowire [12].

3.3. High-temperature gas-phase reaction

As a second attempt to remove the surface oxide, we annealed the nanowires in hydrogen gas. An environmental HRTEM⁷ was employed to flow hydrogen gas through the sample chamber at elevated temperatures, while imaging the sample on an atomic scale. Hydrogen flow at 130 °C for 6 h completely reduced the surface oxide of bismuth nanowires. Figure 3 shows that the amorphous bismuth oxide layer was successfully removed upon hydrogen annealing, leaving behind the crystalline bismuth nanowire. The same result was also achieved when the sample was annealed in ammonia gas flow instead of hydrogen gas flow in the environmental HRTEM chamber [12, 15].

From a thermodynamics standpoint, the reduction of bismuth oxide can be understood by considering the following chemical reaction:



By comparing the sums of the energies of formation of the products and reactants, we find the products to be more stable than the reactants. Therefore, there must be a high activation energy prohibiting this reaction from occurring at room temperature. From the long time required for the removal of the oxide layer (6 h), we conclude that the activation energy is significantly larger than 35 meV ($=k_B T$ at 130 °C).

In this work, an electron beam evaporator was modified to flow hydrogen through the sample chamber while the sample was mounted on a heated stage. It was important to carry out the metal evaporation immediately after the hydrogen annealing without breaking the vacuum to avoid sample re-oxidation. It was found after some testing that

⁷ The environmental HRTEM in this work was developed in the DuPont Research and Development Center by Dr Pratibha Gai.

the lithographic mask cannot withstand the prolonged high-temperature treatment required for oxide reduction. That is, the lithographic process of patterning four electrodes on top of a Bi nanowire is incompatible with this annealing process. Several alternative lithographic processes have been proposed—for example, using a SiO₂ transfer layer—to overcome this temperature limitation. However, these approaches were not feasible because only chemicals with a pH \sim 7 could be used without damaging the nanowires. Thus, the extreme chemical instability of the Bi nanowires severely limited the lithographic processes that could be applied.

Hydrogen annealing has also been used successfully to remove the surface oxide from many materials other than Bi [16, 17]. Since the limitation of lithographic processes arises from the chemical instability of bismuth nanowires, this scheme of hydrogen annealing with a lithographic mask in place may work for other nanowire systems.

3.4. Focused ion beam techniques

Ion beam techniques have been used to improve electrical contacts to nanowires [10, 11]. In our third approach, we used a FIB to make contacts to the Bi nanowires. The FIB was employed to first sputter off the oxide coating and then to deposit platinum by introducing some Pt–hydrocarbon gas (methylcyclopentadienyl) in the path of the Ga-ion beam. Both steps were carried out *in situ* without breaking the vacuum.

This ion sputtering technique for oxide removal was repeated at four areas along the nanowire where electrodes were to be attached. Once the oxide had been significantly removed from the nanowire in the contact areas, a small amount of Pt–hydrocarbon gas was introduced above the sample, and Pt electrodes were deposited by rastering the Ga-ion beam to form the electrode pattern. A SEM image of a 200 nm bismuth nanowire prepared using this technique is shown in figure 4(b). The stick-like lines are the Pt electrodes and the wide strips attached to the Pt wires are gold electrodes, which in turn are attached to four large bonding pads (not shown) patterned by photolithography.

The nanowire sample of figure 4(b) has a diameter of 200 nm and the distance between the inner electrodes is 6.9 μm . The contact resistance was found to be 4 k Ω and the sample resistance was found to be 413 Ω by the four-point method, yielding a resistivity of $1.9 \times 10^{-4} \Omega \text{ cm}$ for this 200 nm diameter nanowire. This result is only slightly higher than the resistivity of bulk Bi, $1.2 \times 10^{-4} \Omega \text{ cm}$, indicating that at 300 K there is no significant increase in the carrier scattering due to wire boundary or defect scattering relative to bulk Bi. This very low resistivity indicates that the crystal quality of the bismuth nanowires is very high, as observed also in transmission electron microscopy (figure 1).

Electrodes were patterned on another 200 nm diameter Bi nanowire using the same technique. Again, low-resistance ohmic contacts were achieved across all four electrodes. The four-point resistance of this sample was found to be 570 Ω , yielding a resistivity of $2.9 \times 10^{-4} \Omega \text{ cm}$, which is considerably higher than that of the previous sample. This raises the question of whether or not this discrepancy is due to sample-to-sample variation or to some systematic error in the measurement. This topic will be addressed in detail in the discussion section (section 4.1).

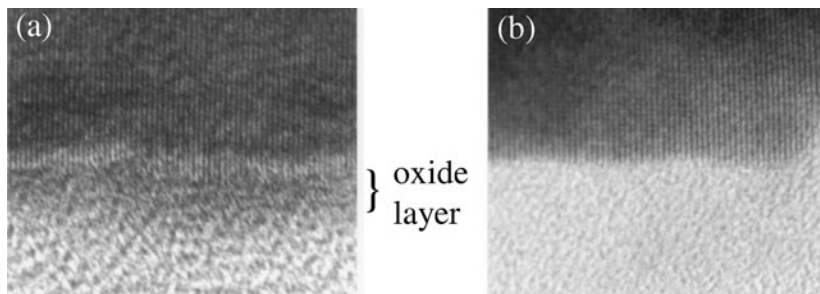


Figure 3. HRTEM images of a Bi nanowire (a) before and (b) after annealing under hydrogen flow at 130°C for 6 h.

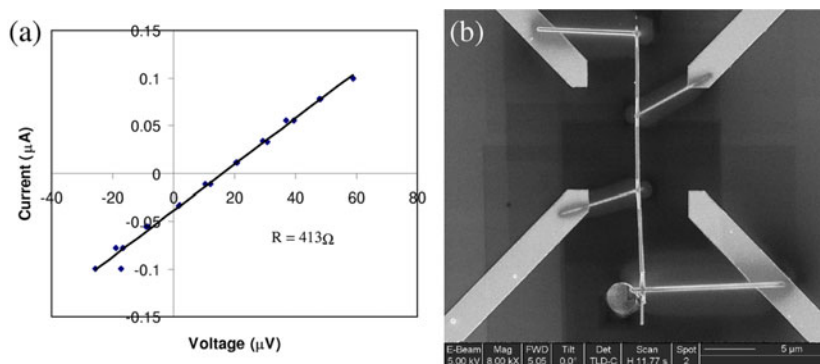


Figure 4. (a) A four-point $i(V)$ curve taken at room temperature for the sample on the right. (b) A SEM image of a 200 nm Bi nanowire with four platinum electrodes prepared using FIB.

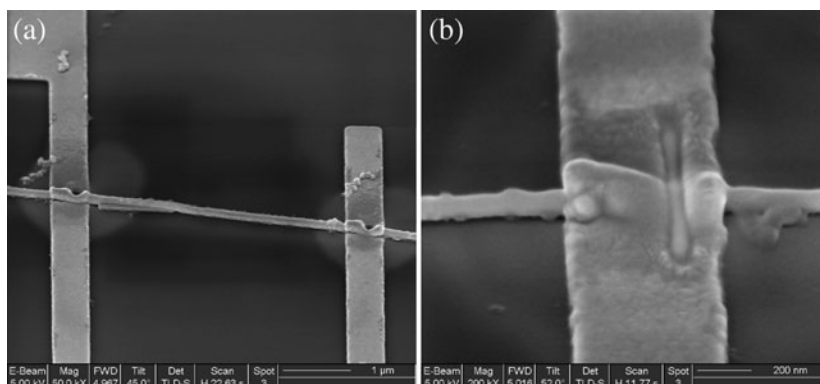


Figure 5. (a) A SEM image of two gold electrodes patterned on a 40 nm Bi nanowire using electron beam lithography after a hole has been milled in the contact region by a focused Ga-ion beam. (b) A SEM image at a higher magnification of the contact region after the hole has been filled with Pt.

We were unable to extend this technique of making contacts to nanowires with diameters smaller than 100 nm. For the finer nanowires (such as the 40 nm nanowires, which are in the semiconducting regime at 77 K), the oxide layer is a significant fraction of the wire diameter. And since the oxide is a relatively hard material and Bi a relatively soft material, the oxide will sputter at a much slower rate than Bi. In the case of a finer nanowire of <100 nm, once the oxide is significantly removed, the Bi core is depleted quickly.

To make contacts to nanowires with diameters smaller than 100 nm, we modified our technique by first patterning gold electrodes on top of the nanowire. We then ion milled a small hole in the contact region and filled the hole with Pt using the FIB. Figure 5 shows SEM images of these two steps in the preparation of contacts on a 40 nm diameter Bi nanowire.

This post-lithography ion-milling technique was first used to measure the four-point resistivity of a 200 nm Bi nanowire in the temperature range of 200–350 K. Two of the four contacts remained stable from 2 to 400 K. The resistivity is found to be more than three times that of bulk Bi, increasing the spread in the measured resistivity of samples of the same nominal wire diameter [13, 14].

4. Discussion and conclusions

4.1. Challenges with the FIB

The FIB is a very powerful tool that allows samples to be manipulated on the sub-micron scale without using lithography. However, the mechanisms involved in ion beam milling are complex, and it is important to know what is

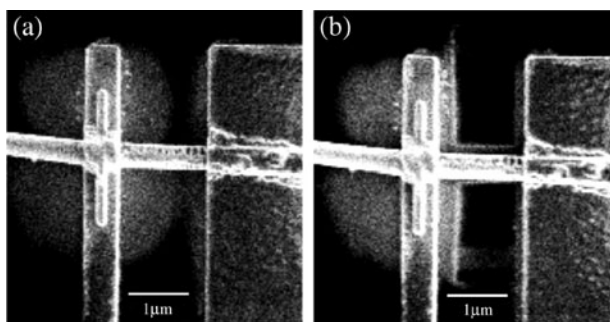


Figure 6. (a) A SEM image of two electrodes where the overlap of the Pt halos is significant. (b) A SEM image of the same contact area as in (a) after ion milling of the Pt overlap area.

happening at the atomic level in order to understand what it is that is being measured. Two phenomena occur in using the FIB that may potentially give rise to error in a transport measurement, especially on a delicate nanowire.

One problem with platinum deposition using the FIB is the very large spatial spread in the beam. The Ga-ion beam can be focused very finely by using charged particle optics. Since the Pt beam is generated by the interaction of the Ga-ion beam with a stationary Pt-hydrocarbon gas, there is a large spatial spread in the Pt beam, which leads to a thin halo of Pt deposited around the Pt-written features. Figure 6 shows that this Pt halo can extend over $1\ \mu\text{m}$ beyond the intended location of the deposition. For electrodes that are very close to one another, these halos can overlap, shorting the electrodes. In the case of overlapping halos, we typically do post-deposition ion milling of the overlapped area, as shown in figure 6(b). Although this milling does decrease the amount of shorting between electrodes, there is still an area very close to the nanowire that is not milled and this halo area can result in significant shorting, which will lead to an underestimation of the nanowire resistivity.

Other sources of error in the measurements are the defects and Ga impurities along the length of the nanowire due to the highly energetic Ga ions incident on the nanowire away from the contact areas, causing an increase in the resistivity and resulting in an overestimation of the actual resistivity. In order to perform ion milling that is precisely aligned with the nanowire, the nanowire must first be imaged with the Ga-ion beam in much the same way that a SEM image is produced, which requires several scans to be made of the entire nanowire. The true extent of the damage caused by Ga-ion exposure of the nanowire is unknown, but it is believed to be significant since the resistivity of Si nanowires can be increased by three orders of magnitude by Ga-ion exposure. It was also found that the photoluminescence of InP nanowires is completely destroyed by just one scan of the Ga-ion beam. We believe that these competing effects give rise to the errors in the measurements and account for the spread in the measured resistivity of bismuth nanowires with the same diameter [14].

The resistivity of a 100 nm Bi nanowire was also measured by the FIB technique and found to be $7 \times 10^{-4}\ \Omega\ \text{cm}$, approximately six times the resistivity of bulk Bi. We can estimate the defect density from this measurement. The effect of quantum confinement is expected to reduce the carrier density of the Bi nanowires at 300 K to half that of bulk Bi.

This implies that the mean free path of the carriers must also be reduced by a factor of three, to account for the sixfold increase in resistivity. Thus, the mean free path in Bi is expected to be decreased from its bulk value (100 nm at room temperature) to 33 nm in the nanowire. Assuming a defect separation of 33 nm, the defect density is $2.7 \times 10^{16}\ \text{cm}^{-3}$. This defect density is of the same order of magnitude as the impurity density estimated from the temperature dependence of resistance of Bi nanowire arrays [18].

One possible solution to the problems in using a FIB is to pattern a protective lithographic mask that would only expose the area of the contact region. After ion milling and Pt deposition, this mask could be removed along with the undesired Pt halo. The protective mask may prevent the shorting of adjacent electrodes and reduce the Ga-ion exposure along the length of the nanowire.

4.2. Conclusions

In spite of the rather delicate chemical and mechanical nature of Bi nanowires, we have established a technique for making ohmic contacts to these nanowires with thick surface oxide layers. The techniques developed in this work are general and can be applied to nanowire systems other than Bi ones. State-of-the-art FIB techniques were used to first sputter through the oxide and then deposit metal contacts on the nanowires. By combining the FIB techniques with electron beam lithography, we achieved low-resistance ohmic contacts to nanowires that were stable from 2 to 400 K. The large variation in the measured resistivity of nanowires with the same diameter was attributed to the errors created by the FIB rather than to sample-to-sample variation. A method for preventing the burnout of nanowires by electrostatic discharge was also developed.

Annealing in H_2 flow or NH_3 flow was found to reduce the surface oxide layer of the nanowire completely. However, the high temperatures required for this gas-phase reaction were not compatible with the lithographic techniques. Since the incompatibility is specific to Bi, this approach may be applicable to other nanowire systems that are less chemically sensitive.

Acknowledgments

We thank Dr Gene Dresselhaus, Professor Ray Ashoori and Dr Laurent Vila for valuable discussions, Michael Frongillo for assistance with the electron microscopy, Mark Mondol and Professor Henry Smith for allowing the use of the electron beam lithography equipment, and Professor Charles Lieber and Dr Thomas Rueckes for allowing the use and operation of the FIB apparatus. The support from MURI subcontract 0205-G-7A114-01, NSF grant DMR-01-16042, and US Navy contract N00167-98-K0024 is gratefully acknowledged.

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