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Title	Electrical characterization of bismuth sulfide nanowire arrays by conductive atomic force microscopy
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Publication date	2008-11-14
Original Citation	Birjukovs, P., Petkov, N., Xu, J., Svirksts, J., Boland, J. J., Holmes, J. D. and Erts, D. (2008) 'Electrical Characterization of Bismuth Sulfide Nanowire Arrays by Conductive Atomic Force Microscopy', The Journal of Physical Chemistry C, 112(49), pp. 19680-19685. doi: 10.1021/jp805422k
Type of publication	Article (non peer-reviewed)
Link to publisher's version	https://pubs.acs.org/doi/full/10.1021/jp805422k - 10.1021/jp805422k
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ELECTRICAL CHARACTERIZATION OF BISMUTH SULFIDE NANOWIRE ARRAYS BY CONDUCTIVE ATOMIC FORCE MICROSCOPY

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Abstract

A new method for determining the resistivity of templated Bi_2S_3 nanowires by conductive atomic force (C-AFM) microscopy is described in this paper. Unlike other vertical C-AFM approaches, in our method resistance measurements were carried out along the lengths of the nanowires. Nanowires embedded within anodic alumina membranes were exposed for contact by etching away the alumina template to form an open array of parallel nanowires. From these measurements the contact resistance between the gold electrodes and the C-AFM probe could be determined and subtracted to give the intrinsic resistivity of the nanowires. The resistivity of the nanowires determined in such a horizontal configuration was 10 to100 times lower than the resistivity determined when the same nanowires when contacted in a vertical configuration.

Introduction

Semiconductor nanowires are promising candidates as building blocks for the bottom-up assembly of nanosized devices and circuits[1]. Individual semiconductor nanowires have been exploited for a number of nanoscale applications that include high-speed field effect transistors (FETs)[2-4], light emitting devices[5], single electron memory devices[6], nanoelectromechanical devices[7], chemical and biological sensors[8] and logic circuits[9]. However, the successful incorporation of nanowires into optical and electronic devices will require their assembly into electrically addressable high-density architectures so that their unique transport properties, either individually or collectively, can be utilized. Several research groups have reported the synthesis of ordered arrays of semiconducting nanowires, such as within the pores of ordered templates[10-14], where nanowire densities of up to $2 \cdot 10^{12}$ cm^{-2} can be achieved[15]. Much work has focused on the deposition of ordered arrays of nanowires, *e.g.* ZnO[16], Ge[17-20], Si[21-23], and Bi_2S_3[13] inside anodized aluminium oxide (AAO) membranes. However, finding reliable methods for the fast screening and electrical characterization of individual nanowires within

these arrays is a challenge. In previous reports nanowires have been characterized as groups of nanowires by using macrocontacts on both sides of a templating membrane[16,18,19,21-23], or individually by liberating nanowires from the template and positioning a single nanowire between metal contacts. We have developed methods for determining the conductive properties of individual nanowires within a matrix using conductive atomic force microscopy (C-AFM)[17,18,20]. In this approach, the nanowires are contacted in their vertical orientation within the membrane by depositing a macrocontact on one side of the membrane and contacting the exposed ends of the nanowire at the other end of the membrane using a C-AFM tip. With this methodology, both topography and conductivity maps can be obtained simultaneously giving evidence of an ordered arrangements of conductive nanostructures. We have also used the vertical C-AFM method to determine whether nanowires run continuously throughout the membrane, from top to bottom. Nonetheless, all of the C-AFM measurements undertaken in the vertical configuration are 2-point contact measurements and a lot of effort is required to eliminate the contact resistance contribution. This can be achieved by using different sized contact pads and thinning of the nanowire-template samples.

In this paper we describe the use of polishing and etching techniques to access arrays of Bi_2S_3 nanowires, in their longitudinal direction, and employ C-AFM techniques to determine the resistance along the full lengths of the nanowires. We are interested in studying Bi_2S_3 nanowires as they have numerous potential applications as a material for photovoltaic[24,25] and thermoelectric[26] devices. However, the horizontal C-AFM technique described in this paper could be applied to other nanowires materials. Using this new technique have been able to determine the intrinsic resistivity of the nanowires of single crystalline, highly oriented nanowires within a templating matrix. The nanowire resistivity data obtained using the horizontal C-AFM technique were compared to those obtained using the vertical C-AFM method.

Experimental Section

Porous AAO membranes were purchased from Whatman, under the commercial name Anodisc filters, with a nominal pore size of about 200 nm. Porous AAO membranes with a pore diameter of 80 nm were synthesized in-house using a well-known procedure described previously[27,28].

A single source precursor, bismuth bis(diethyldithiocarbamate) [$Bi(S_2CNEt_2)_3$] complex, was prepared by the reaction of Bi_2O_3 with carbon disulfide and diethylamine in methanol and was thoroughly purified by repeated recrystallization[13]. The synthesis of arrays of single crystal Bi_2S_3 nanowires was carried out in a flat bottom glass tube (inner diameter 14 cm). In a typical experiment, the organometallic precursor (~300 mg) was placed on the surface of the AAO membrane in the glass tube and heated to 200 °C under vacuum. After the precursor melted, the temperature was maintained for another 30 minutes. The vacuum was then disconnected and the glass tube containing the sample was placed on to a hot plate at 300 °C for 30 minutes until the Bi_2S_3 precursor had completely decomposed.

The crystal structure of the Bi_2S_3 nanowires was examined by selected area electron diffraction (SAED) and HRTEM combined with fast Fourier transforms (FFTs) on a JEOL 2010 HRTEM equipped with Oxford Instrument EDX system. X-ray diffraction (XRD) data were collected on a Phillips Xpert PRO diffractometer using Cu K_α radiation, an anode current of 40 mA and an accelerating voltage of 40 kV. Data was collected in a range of 10÷90 2Θ degrees with a step size of 0.005° and a scan rate of 0.2 s per step. The AAO samples were polished, etched and then placed on a glass slide that minimized incoherent background scattering contributions.

In order to access the electrical properties of the nanowires, the AAO membranes containing the Bi_2S_3 nanowires were treated in a way similar to that described previously[18] prior to the AFM measurements. The surfaces of the AAO membranes were mechanically polished with diamond paste with grain sizes of 1 μm, 250 nm and 50 nm in order to remove any Bi_2S_3 film from both sides of the membrane. Additionally the bottom surface was chemically etched with 9 % H_3PO_4. SEM images of the membrane

surface before and after etching showed that the ends of the nanowires were liberated from the membrane exposing their tips (figures 1(a), (b)).

Before the gold macroelectrode was deposited on to the bottom of a membrane the surface was cleaned with Ar ions at energy of 5 keV and current of 120 μA for 5-10 s, using a precision etching coating system (Gatan), to remove contamination. The surface of the membrane was then coated with a 50 nm thick layer of Au metal film in the same chamber without breaking the vacuum at 10^{-6} Torr and a coating speed of 1-1.5 Å s^{-1}.

To perform resistance measurements in a horizontal configuration (along the longitudinal axis of the nanowires) the membranes, with the deposited bottom electrode, were glued inside an epoxy in between two glass slides. The samples were then mechanically polished to expose the nanowires in the sample plane. Afterwards polishing the surface of the samples was chemically etched with 9 % H_3PO_4.

The surfaces of the membranes and the contacts were visualized using a scanning electron microscope Hitachi S4800. An AFM (MFP-3DTM, Asylum Research) in contact mode was used for topography and current mapping. Conductive Pt-coated silicon AFM tips (NT-MDT CSC12/Pt) and boron doped diamond tips (NT-MDT DCP20) were used in the experiments described in this paper.

Results and discussion

The electrical properties of the individual Bi_2S_3 nanowires within the AAO matrix were analyzed in two different configurations throughout the study: (i) with the conductive AFM probe in contact with the ends of individual nanowires oriented vertically (figure 2 (a)) and (ii) with a C-AFM probe in contact with individual nanowires along their longitudinal axis (figure 2 (b)).

The growth, structure and encapsulation of the Bi_2S_3 nanowires within the pores of the AAO membranes were determined by XRD, HRTEM and SAED. A detailed description of the crystallography and growth mechanism of the Bi_2S_3 nanowire arrays within the AAO membranes is presented elsewhere[13]. Briefly, highly oriented single crystalline arrays of Bi_2S_3 nanowires within AAO membranes were obtained by growing them exclusively along the [002] growth direction. Figure 3

shows TEM images of Bi_2S_3 nanowires that have been isolated from each other within AAO pores with a mean diameter of 80 nm. The corresponding fast Fourier transforms (FFT) of the HRTEM image (figure 3 (a)) verifies their single crystalline nature indicated by the sharp diffraction dots. The SAED patterns were taken with the electron beam along the [010] direction and confirmed that the nanowires were grown along the [002] direction. All of the nanowires studied by SAED and FFTs of the HRTEM images, isolated from the AAO, showed growth directions along the [002] zone axis. Detailed crystallography studies showed that this type of material is among the few examples of highly oriented and aligned single crystalline nanowires deposited as high density arrays within an electrically isolating matrix[29].

Figure 4 shows the topography and current maps of the surface of vertically oriented Bi_2S_3 nanowires, with a mean diameter of 200 nm, measured through a 20 μm thick membrane. 90 % of the nanowires contacted using the vertical C-AFM approach were observed to be conductive and these nanowires ran the entire length of the membrane. The resistivities of the Bi_2S_3 nanowires, with mean diameters of 200 and 80 nm, determined using this technique were found to be in the interval 3-20 and 30-120 Ω m respectively. These resistivity measurements are orders of magnitude higher than the reported resistivity of bulk Bi_2S_3 ($5 \cdot 10^{-5}$ Ω·m)[26], but are in the range, or higher, compared to resistivity values obtained for individual Bi_2S_3 nanowires grown by template-free methods and measured in a two-terminal configuration, *e.g.* 0.06-12.1 Ω·m[30] and 0.012 Ω·m[31]. We have previously shown that the ends of the nanowires can be damaged during the mechanical polishing process, thus being source of enormous contact problems[18]. In fact the defects created at the ends of the nanowires can lead to non-uniform nanowire-probe interaction increasing the resistances of nanowires to a large extend.

In order to avoid contact to the damaged ends of nanowires, resistance measurments were performed on the longitudinal axes of the exposed nanowires. In this configuration, the conductive probe can contact a nanowire at different distances from the macroelectrode (figure 2 (b)). Moreover, it will allow a single nanowire to be scanned to perform “quasi” multi-probe electrical measurement, thus allowing the contact resistance to be determined. Critical to these experiments is the degree of removal of the

AAO matrix during the planarization process. As the grain size of the diamond pastes used for polishing were comparable to or larger than the diameters of the nanowires, most of the open nanowires were damaged during this process. Therefore the samples were polished under angle and only small surface areas of nanowires were exposed (figure 5 (a)). Only areas containing intact nanowires were subjected to subsequent chemical etching of the AAO matrix with 9 % H_3PO_4. The resistance measurements were conducted on the areas exposed by chemical etching.

The length of the open ended parts of the nanowires could be further adjusted by varying the etching time in 9 % H_3PO_4 (figure 5 (b)-(d)). For etching times longer than 120 minutes, completely open nanowires were obtained (figure 5 (c), (d)). Since such nanowires are no longer isolated by the templating matrix they can contact each other, thus the measured current when the AFM probe is not in contact to a single nanowire and effectively reflects the current through a group of an unknown number of nanowires. Therefore, the resistivity was determined on samples with partly opened nanowires (see figure 5 (b) as an example) where the possibility of forming electrical contacts between neighboring nanowires is diminished.

Figure 6 shows current maps of the surfaces of partially opened Bi_2S_3 nanowires with mean diameters of 200 and 80 nm. Dark areas are corresponding to presence of open parts of nanowires on the surface. These nanowires are running parallel to each other, corresponding to orientation within the membrane as shown schematically in figure 2 (b). Nanowires that were completely 'open' were observed to be continuous between both contacts without breaks. The open lengths for 200 nm diameter nanowires was in the interval 1 – 3 µm (Figure 6 (a)) but for 80 nm diameter wires is much shorter (Figure 6 (b)). As shown in figure 7, the current values are almost equally distributed across the nanowires. After exposure of the nanowires, the AFM probe was positioned on single nanowire and its I(V) characteristics were obtained. The I(V) characteristics of individual Bi_2S_3 nanowires were non-linear and exhibited a nonconductive gap for both the 200 and 80 nm diameter nanowires (figure 8 (a)). The nonconductive gap may be related to the presence of a thin amorphous layer on the nanowire surface[31,32] and/or a Shottky barrier[33]. The slope of the linear part of the I(V) curve at higher bias is related directly

to the resistance of the nanowire[32,33]. Figure 8 (b) shows I(V) characteristics of a single 200 nm diameter nanowire measured along its length. The slope in the linear part of the I(V) curve is decreasing when the distance from the electrode is increasing and provides a direct indication that the contact resistance of a single nanowire can be readily extrapolated by performing length dependent measurements along the longitudinal axes of the nanowires.

The contact resistance was determined by measuring the nanowire resistance at different probe-macroelectrode separations. The length of a nanowire was determined by scanning from the open end along the length of the nanowire until the contact point was reached, at which a sharp increase in the current was observed due to the metallic conductivity of the macroelectrode. Figure 9 shows that the resistance decreases as the separation between the probe and the macroelectrode is decreased, and becomes constant at separations below 1 μm. The increase in the nanowire resistance close the bottom electrode may be due to the formation of a depletion layer in the nanowires. However, for Bi_2S_3 nanowires the depletion distance is shorter, *i.e.* does not exceed 200 nm, than our electrode separation, even at voltages 4 orders of magnitude higher than we used in the measurements (2 mV)[32]. This data therefore suggests that the overall resistance (sum of nanowire and contact resistances) for probe-macroelectrode separations that are below 1 μm is determined by the contact resistance. The contact resistance may be determined by the presence of an amorphous oxide layer on the nanowire, the presence of insulator layer on the AFM tip or a Shottky barrier.

Contact resistance depends on tip conditions and may change from sample to sample. For example, boron doped diamond tips used on two different Bi_2S_3 nanowire samples yielded contact resistances of 15 and 3 MΩ (figure 10). In some measurements with Pt coated tips, the contact resistance reached values higher than 100 MΩ. We speculate that in these cases the Pt layer that covers the AFM tip is damaged and that most likely tunneling instead of an ohmic contact is occurring. For metal contacts deposited on individual semiconductor nanowires the contact resistance is suggested to be around 1 MΩ[33]. A factor that may play a substantial role in explaining the increased contact resistances in the C-AFM measurements, in comparison to measurements performed using deposited electrodes, is the

difference in the size of the contacts. Effectively the contact area between the C-AFM probe and the nanowires is much smaller than the size of the deposited contact. This argument is supported by the fact that the contact resistivity and I(V) characteristics both depend on the size of the contact area as shown in recent papers[32,34].

The resistivities of the Bi_2S_3 nanowires were determined by subtracting the contact resistance from the overall resistance. The resistivity for the 200 nm diameter nanowires was measured for approx. 470 nanowires on four different samples using two different AFM tips and was in the range between 0.4 to 1.2 Ω·m. The weighted average resistivity for the 80 nm diameter nanowires measured for 200 nanowires on two different samples by using two different AFM probes was 50 Ω·m. This is an order of magnitude higher than the resistivity measured for 200 nm diameter nanowires. The higher resistivity of 80 nm diameter nanowires can be explained by the greater influence of surface traps as seen with Ge nanowires[18].

Additionally, it should be noted that the resistance measurements obtained along the nanowires longitudinal axis are 10 to 100 times lower than the values obtained when the measurements were conducted with the vertical C-AFM configuration. These data therefore suggest that the horizontal C-AFM method used for contacting arrays of nanowire within AAO membranes can be used to estimate the 'true' intrinsic resistivity of the nanowires and also presents a valuable way of contacting aligned arrays of nanowires.

Conclusions

Whilst the electrical properties of individual nanowires have been intensely investigated, there are relatively few studies of the conductive properties of ordered arrays of semiconductor nanowires within defined architectures. Until now, most of the investigations for determining the resistivity of nanowires within channeled matrices have been realized by contacting exposed ends of vertically oriented nanowires. Alternatively, the other well investigated approach utilizes nanowires that are released from

the matrix and contacted by fabricating metal contacts with focused ion-beam or electron beam lithography.

Here we describe a novel method for contacting horizontal arrays of nanowires that allowed us to access the full length of the nanowires. This technique employs precise polishing and selective etching steps to obtain exposed nanowires parallel to their longitudinal axes partially supported by the AAO membrane. The resistivities determined by this technique are 1 to 2 orders of magnitude lower than those measured by contacting the nanowires in a vertical configuration. Most importantly we demonstrated that this technique can be applied to reliably determine the contact resistance by performing quasi multi-point measurements. Additionally applying this contacting strategy large numbers (more than several hundred) of aligned and oriented single crystal nanowires were electrically contacted and screened. In summary, this paper presents a viable method for electrically characterizing arrays of semiconductor nanowires deposited within templating matrices such as AAO.

Acknowledgments. The authors acknowledge financial support from ERAF, Ministry of Education and Science of Latvia, the Centre for Research on Adaptive Nanostructures and Nanodevices (CRANN) and Science Foundation Ireland (Grant No.: 03/IN3/I375). We acknowledge K. Didriksone for the help with sample preparation.

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Figures

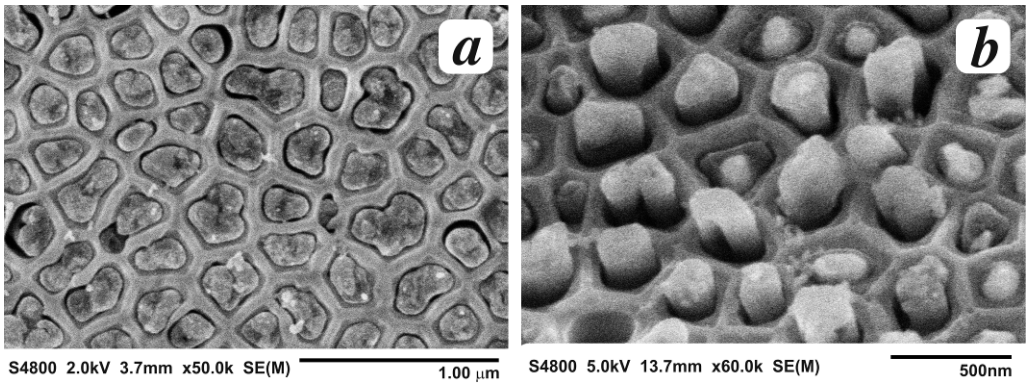


Figure 1. SEM images of perpendicular (a) and tilted (b) sample surface after being etched with 9 % H_3PO_4 for 40 min.

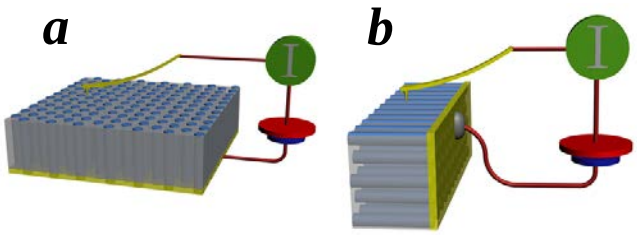


Figure 2. Schematics of conductivity measurements through individual nanowires by C-AFM: (a) vertical configuration where the AFM probe is contacting the ends of nanowires and (b) horizontal orientation where the AFM probe is contacting the nanowire along longitudinal nanowire axis.

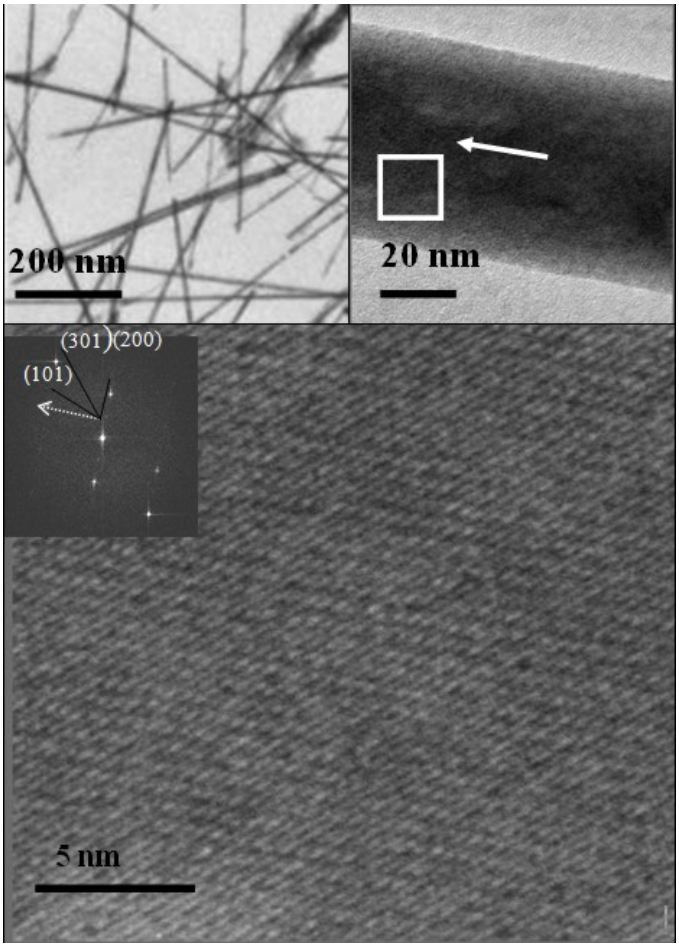


Figure 3. (a) TEM image of Bi_2S_3 nanowires isolated from 80 nm membranes, (b) TEM image of 80 nm single Bi_2S_3 nanowire and (c) HRTEM image of the same nanowire taken within the marked area with the corresponding growth direction shown with white arrows (inset: corresponding FFTs).

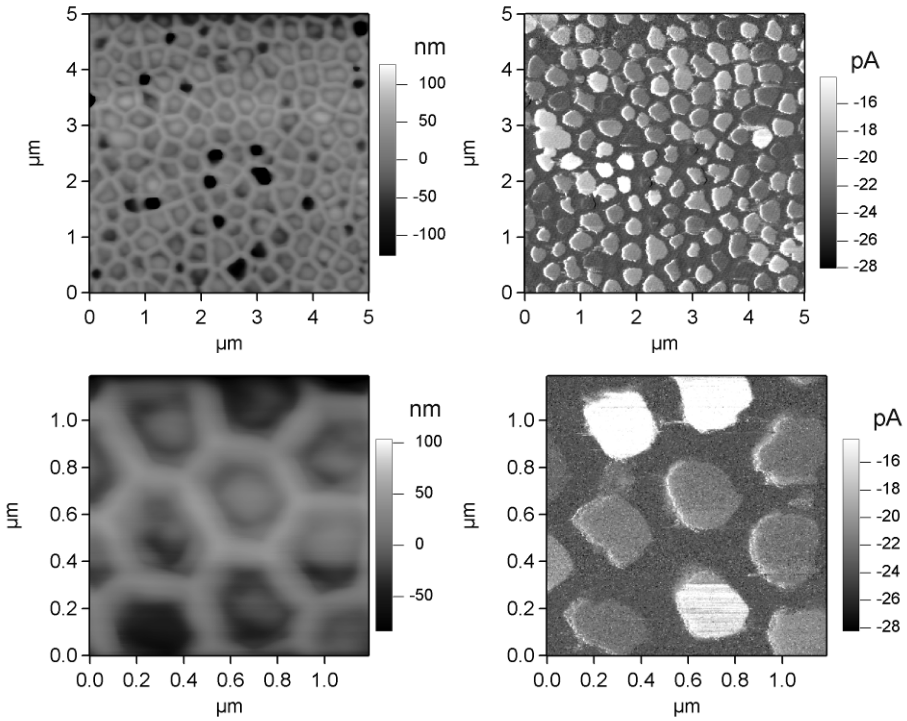


Figure 4. Vertically aligned 200 nm Bi_2S_3 nanowire within AAO topography (left) and current maps (right).

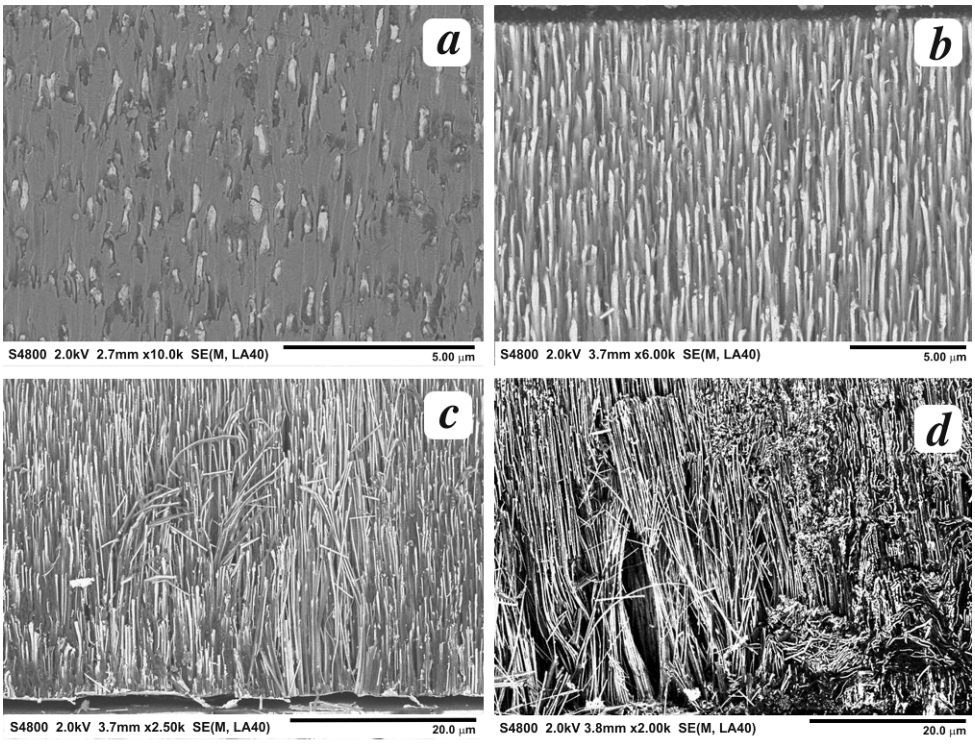


Figure 5. SEM images of cross-section of Bi_2S_3/AAO matrix etched with 9 % H_3PO_4 after (a) 0 min, (b) 120 min, (c) 180 min and (d) 220 min.

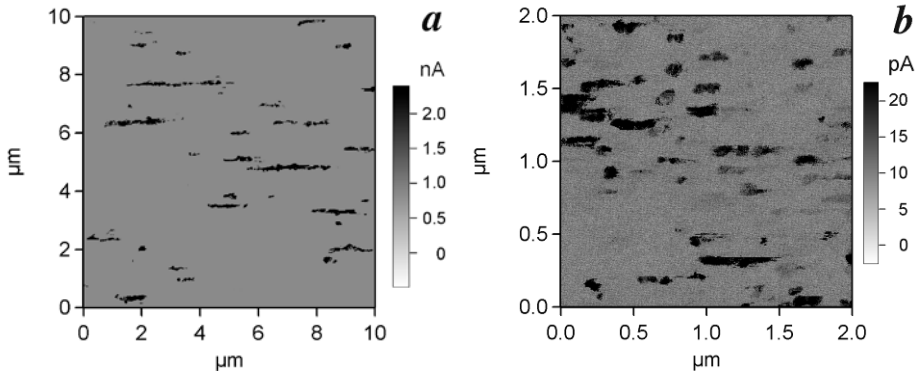


Figure 6. Bi_2S_3 nanowire within AAO cross sectional conductive AFM images showing current maps ((a) 200 nm and (b) 80 nm). For (a) distance from the macroelectrode was 12 µm, and for (b) - 8 µm.

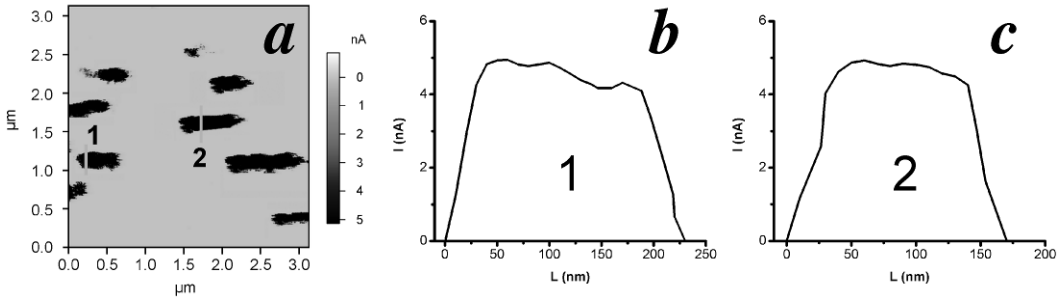


Figure 7. Current map of 200 nm Bi_2S_3 nanowires within AAO and corresponding current profiles (b),(c) across the nanowires as shown in (a).

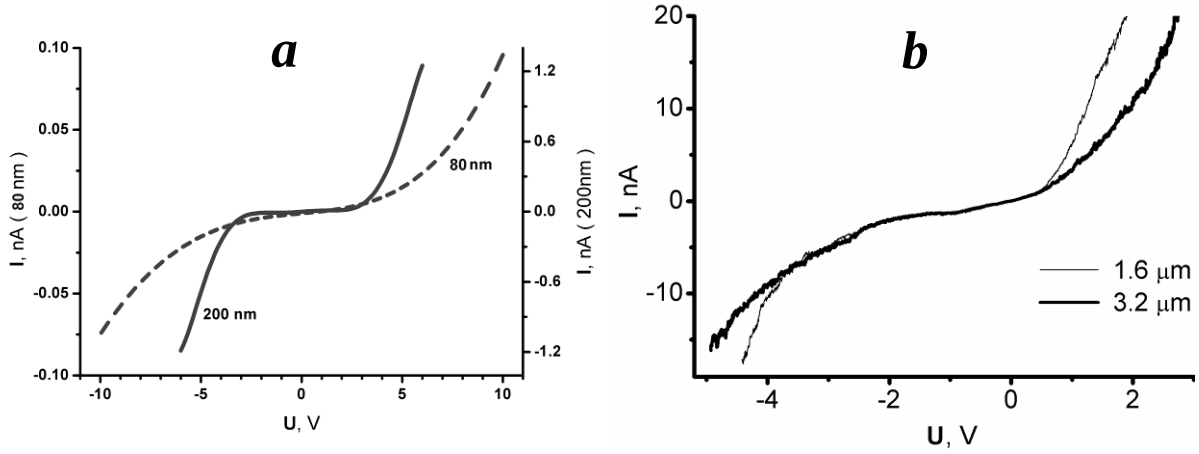


Figure 8. I(V) characteristics of Bi_2S_3 nanowires within AAO measured with doped diamond conductive AFM tip: (a) I(V) on 200 nm and 80 nm diameter nanowires; (b) I(V) on 200 nm diameter nanowires at different distances from the macroelectrode.

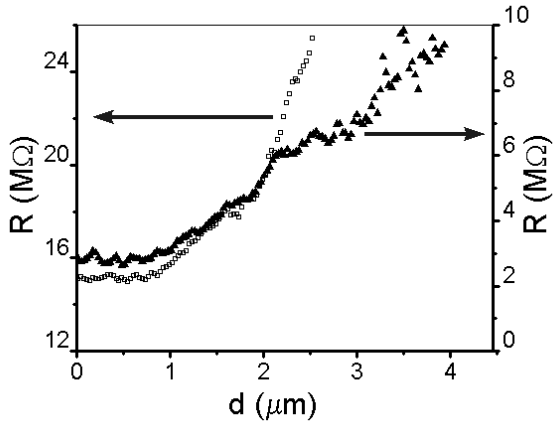


Figure 9. Resistance of two individual Bi_2S_3 nanowires within AAO matrix measured by single scan along the nanowire longitudinal axis with doped diamond tip as a function of the distance from the macroelectrode.