

Temperature dependence of the resistance of antimony nanowire arrays

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2001 J. Phys.: Condens. Matter 13 2955

(<http://iopscience.iop.org/0953-8984/13/13/309>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.226

The article was downloaded on 16/05/2010 at 11:45

Please note that [terms and conditions apply](#).

Temperature dependence of the resistance of antimony nanowire arrays

M Barati¹, J C L Chow, P K Ummat and W R Datars²

Department of Physics and Astronomy, McMaster University, Hamilton Ontario,
Canada L8S 4M1

E-mail: datars@mcmaster.ca

Received 9 October 2000, in final form 23 February 2001

Abstract

The resistance of arrays of antimony hollow nanowires in porous anodic aluminum discs with channel diameters of 20 nm, 100 nm and 200 nm is reported. The structure was determined by x-ray diffraction and scanning electron microscopy. The Sb was deposited in a closed system by a vapour-phase method. The arrays were annealed at temperatures between 100 °C and 200 °C. This post annealing crystallized amorphous regions and decreased the resistivity with an annealing temperature of 150 °C. The resistance of all the arrays increased with decreasing temperature. This temperature dependence is described by an excitation energy which depends on the channel diameter and the temperature of the annealing.

1. Introduction

Anodic alumina has recently been used as a template to synthesize a variety of metal and semiconductor nanowires composed of Bi, Ni, Au, Pt and CdS. They were prepared by different chemical and electrochemical processes [1–7]. Zhang *et al* [5,8] fabricated Bi nanowires by injecting liquid Bi under pressure into the nanochannels of an alumina anodisc. The individual Bi nanowires were found to be crystalline. Heremans *et al* [6] filled the nanochannels of the anodisc with Bi by condensing Bi vapour in the channels where the Bi solidified.

Nanometer-sized amorphous Sb particles were prepared by a flowing gas evaporation technique [9] and were crystallized by a post-annealing procedure by Tanaka *et al* [10,11]. The crystallization depended on the annealing temperature, the annealing duration and the particle diameter. The fraction of crystalline, 30 nm particles was the largest (80%) with an annealing temperature of 150 °C. Antimony films condensed on a substrate from Sb vapour were also found to be amorphous up to a critical thickness [12].

The aim of this work is to form Sb in the channels with nanometer dimensions in alumina anodiscs and to study the effect of post annealing of the Sb nanowires at different temperatures.

¹ Permanent address: Department of Physics, Shiraz University, Shiraz, Iran.

² Corresponding author. Tel: 905-525-9140 ext. 24173; Fax: 905-546-1252.

The filling of the channels is determined with scanning electron microscopy. The crystallinity is tested by x-ray diffraction and the properties of the nanowires are determined by resistivity measurements. The temperature dependence of the resistivity is studied in detail between room and liquid nitrogen temperatures.

2. Experimental details

The templates consisted of porous alumina anodiscs obtained from the Whatman company. The pore density was 10^9 pores cm^{-2} for the 100 and 200 nm channels and 10^{12} pores cm^{-2} for the 20 nm channels. The thickness of all the discs was $60\ \mu\text{m}$. Attempts to fill the channels with Sb by the vapour transport technique used for Bi by Heremans *et al* [6] were not successful. Thus, a vapour-phase method in a closed system was employed. Crystalline Sb with a purity of 99.9999% and pieces of an anodisc were sealed in a evacuated quartz vessel. It was heated in a box furnace at $630\ ^\circ\text{C}$ for two days and then cooled. The anodiscs filled with Sb were taken from the reaction vessel and put into pyrex tubes which were evacuated and sealed for annealing. The samples were annealed for two days at a temperature between $100\ ^\circ\text{C}$ and $200\ ^\circ\text{C}$.

Filled discs were examined with a scanning electron microscope operating at 20 kV by breaking them into pieces and looking at the broken edges positioned at an angle to the electron beam. The electron micrograph of a 100 nm disc in figure 1 indicates a number of features. The channels are straight and of a uniform diameter along their length. The broken ends indicate that the channels are not filled completely. However, the bright edges and sides show that the inner surfaces are covered with Sb. This was confirmed by comparing micrographs of discs with and without previous exposure to Sb. Figure 1 also shows that most of the channels walls are covered with Sb. Thus, there are Sb hollow nanowires rather than solid wires. It was also established by scanning electron microscopy that the layer of antimony on the surfaces of the disc was very thin.

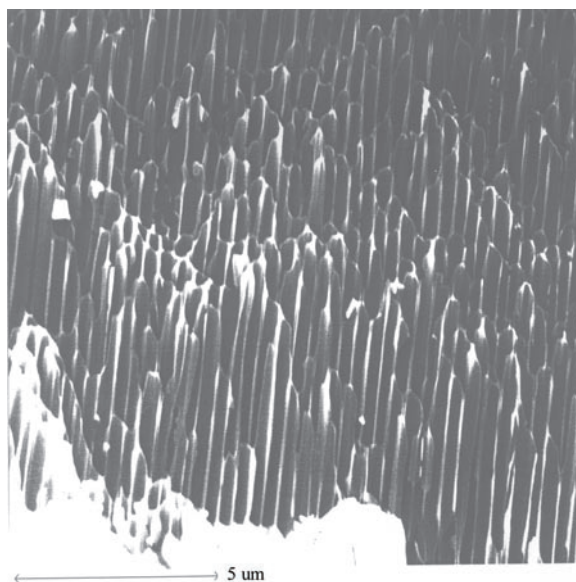


Figure 1. A scanning electron micrograph of an anodisc that had been exposed to Sb.

There is other evidence that the surface layer did not contribute significantly to our measurements. The surface resistance of a typical sample was 190 k Ω at 155 K and 82 k Ω at 300 K. This was a factor of 80 greater than the resistance across the sample so that the current was not shorted out by the surface. Also, the temperature dependence of the surface resistance was different from that across the sample. There is also no reason for getting a significant contribution from the Sb surface layer in the way we made our samples. They were prepared by cutting a piece from a section far from the edge of the anodisc and electrical contacts on the two sides made sure that the current passed through the nanowires.

A two-probe method was used to measure the resistance of the nanowire arrays. One side of a filled anodisc was connected to a copper electrode and the other side was connected to a copper wire with silver paste. The applied current was 0.1 mA. The potential difference between the two sides was measured with a computer-controlled system with nanovolt sensitivity and the temperature was monitored with platinum and carbon-glass thermometers. The area of the silver paste contacts on the specimen was measured under an optical microscope.

The resistance R that was measured resulted from the parallel resistances of the membrane and the nanowire array. Since the former was very large, the measured resistance R is the resistance of the array. The surface resistance of an individual nanowire is

$$\rho_s = \frac{ADR2\pi r}{d} \quad (1)$$

where A is the area of the silver contact, D is the density of the pores in the anodisc, d is the thickness of the anodisc and r is the radius of the pores. It was shown that R is inversely proportional to A by measuring R for different values of A in a range of a factor of 10. The surface resistance is a useful quantity for the comparison of the tubes with different sizes and annealing because the electron micrographs showed a similar thickness in all of them.

The resistance of all the samples was measured as the temperature was changed continuously between liquid nitrogen temperature and room temperature in a liquid-nitrogen cryostat. The resistance of some samples was also measured down to 4.2 K in a liquid helium cryostat.

3. Results and discussion

The resistance of a 20 nm Sb nanowire as a function of temperature for an annealing temperature of 175 °C is shown in figure 2. This figure represents the general behaviour of all Sb nanowires made with three diameters and annealed at different temperatures. The resistance increases with decreasing temperature with the resistance of the order of few hundred ohms at room temperature and a value between 10³–10⁶ ohms, depending on the size and the annealing process, at liquid nitrogen temperature.

The resistance of the Sb nanowires with different annealing treatments is characterized by an exponential $e^{E/kT}$ where e is the characteristic excitation energy. Such a characterization has been applied in the study of the semiconducting properties of antimony amorphous thin films by Cohen [13]. He reported a temperature dependence of the above form with excitation energies of 70 meV and 130 meV for temperatures below and above 125 K, respectively. The resistance and the excitation energy of the Sb nanowires are highly affected by the size and the annealing procedure. In order to study the effect of post annealing on the Sb nanowires, the resistance as a function of the temperature of samples with different annealing temperatures and the x-ray diffraction patterns of the wires with different annealing temperatures are studied in detail.

The natural logarithm of the resistance of a 200 nm Sb wire array that had not been annealed is shown in figure 3 as a function of $1/T$. The resistivity has excitation energies of 60 meV at

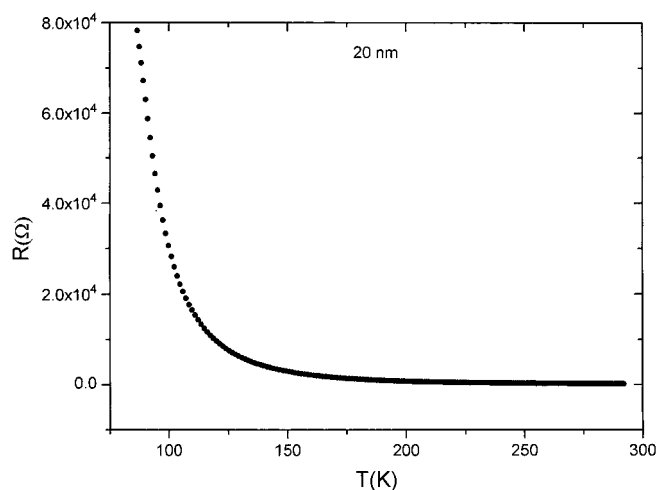


Figure 2. Temperature dependence of the resistance of an Sb nanowire array with a diameter of 20 nm post annealed at 175 °C.

high temperatures and 130 meV at low temperatures. These values are similar to the excitation energies reported by Cohen in the study of the antimony amorphous thin films. The annealing treatment changes the resistance so that it is described by a single excitation energy. The value depends on the annealing temperature and the diameter of the Sb nanowires. The highest excitation energy is observed in the samples annealed at 150 °C. This is the temperature for which the crystalline phase is formed in nanometer-sized antimony particles with a maximum ratio of crystallization [11]. The natural logarithm of the resistance as a function of $1/T$ of 20, 100 and 200 nm wire arrays that were annealed at 150 °C is shown in figure 4. The resistance and the excitation energy depend on the size of the wire and, in contrast with the sample without an annealing treatment, the slope is constant with an uncertainty of less than 5% between room and nitrogen temperatures. The excitation energy also depends on the annealing temperature. The result of this investigation is presented in table 1. As is seen from the table, the excitation energy has the lowest value of 23 meV for the 200 nm wire annealed at 175 °C and the highest value of 109 meV for the 20 nm wire annealed at 150 °C.

Table 1. The excitation energy of Sb nanowires annealed at 125 °C, 150 °C and 175 °C.

Diameter (nm)	E (meV)		
	125 °C	150 °C	175 °C
200	27	33	23
100	66	84	67
20	50	109	65

The effects of two different annealing processes on the crystalline formation in the Sb nanowires were also studied. The x-ray diffraction patterns of 100 nm samples annealed at 100 °C and 150 °C were analysed. The x-ray diffraction with $\text{CuK}\alpha$ radiation from the sample annealed at 100 °C for two hours indicates broad diffraction peaks with a full width of 4 ° at scattering angles 2θ of 16 ° and 24 °. The broad diffraction peaks were reduced in amplitude from a sample annealed at 150 °C. However, with this sample a narrow diffraction peak at 28.5 °, which is at the scattering angle of the strongest Bragg diffraction peak of crystalline

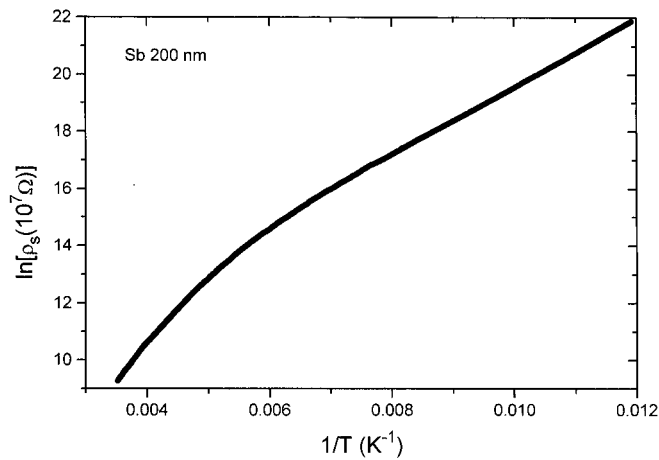


Figure 3. Natural logarithm of the surface resistance of an annealed 200 nm Sb nanowire array as a function of $1/T$.

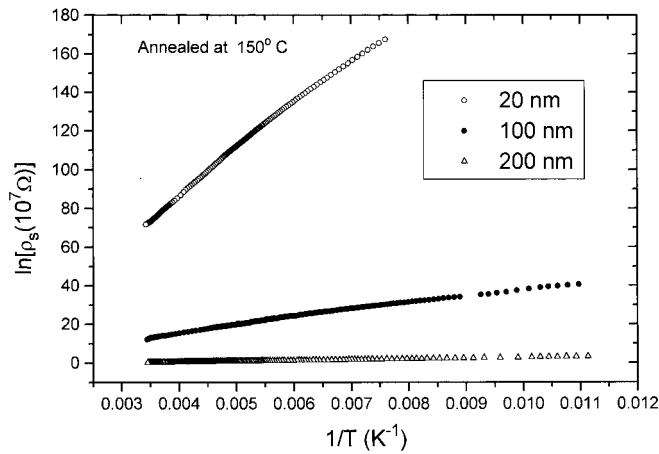


Figure 4. Natural logarithm of the surface resistance of 20, 100 and 200 nm Sb nanowire arrays as a function of $1/T$.

antimony, was observed as shown in figure 5. The broad diffraction peaks after annealing at 100 °C are attributed to amorphous antimony. Annealing at 150 °C reduces the amount of the amorphous phase as indicated by the reduced amplitude of these peaks and forms a crystalline phase as seen by the sharp diffraction peak at $2\theta = 28.5^\circ$. Thus, the crystalline phase is formed by annealing at 150 °C so that both phases are present from this annealing temperature. The proposed mechanism of crystallization is the instantaneous reconstruction of constituent atoms. It takes place very quickly so that two hours for annealing is plenty of time. Therefore, the resistance of the Sb nanowires is expected to depend on both the annealing temperature and the diameter of the nanowires. However, the way it depends on the size is not the same as that seen with the Bi wires that are crystalline for which the scattering of the carriers from the boundary and the appearance of quantization of the electronic energy levels are the major factors of the size dependence [8].

The natural logarithm of the resistance as a function of $1/T$ for the 20 nm wire arrays annealed at different temperatures is presented in figure 6. This figure represents the general behaviour of all the nanowires with the three diameters. The room temperature surface resistance of an individual hollow nanowire in the 20, 100 and 200 nm membranes is presented in table 2. The room-temperature resistance depends on the size and the annealing temperature and increases by decreasing the diameter of nanowire at a particular annealing temperature. The lowest room-temperature resistance was measured for the samples annealed at 150 °C. Therefore, as expected the resistance of the Sb nanowires is reduced with an increase in the amount of the crystalline formation.

The properties of the resistance of the 20 nm nanowires is especially interesting. The room-temperature resistance is reduced by only 25% by annealing at 150 °C. Thus, the resistance

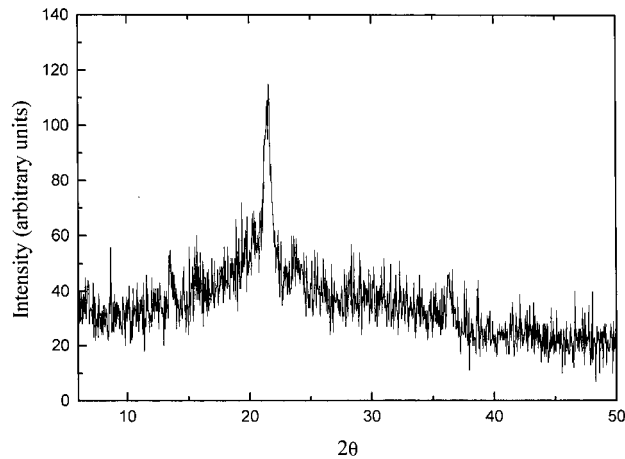


Figure 5. X-ray diffraction with $\text{CuK}\alpha$ radiation of a 100 nm nanowire array post annealed at 150 °C.

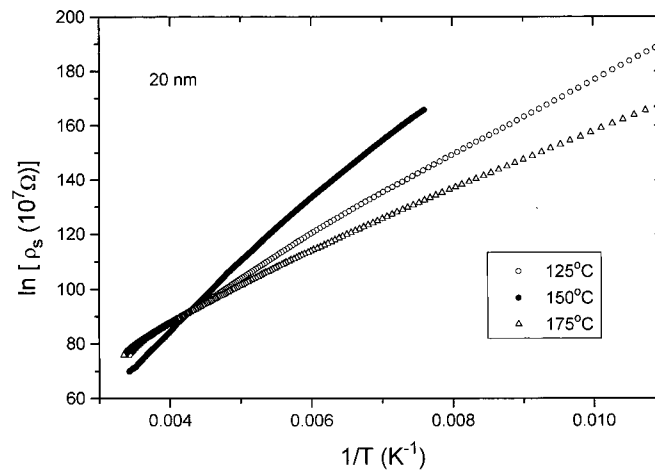


Figure 6. Natural logarithm of the surface resistance as a function of $1/T$ for 20 nm Sb nanowires for three different post-annealing temperatures.

Table 2. The room-temperature resistance of a hollow Sb nanowire annealed at 125 °C, 150 °C and 175 °C.

Diameter (nm)	$\rho_s (10^7 \Omega)$ 125 °C	$\rho_s (10^7 \Omega)$ 150 °C	$\rho_s (10^7 \Omega)$ 175 °C
200	16	1.2	6.6
100	29.6	1.2	8.0
20	440	330	440

is not affected greatly by the crystallinity of the wires. In contrast, the room-temperature resistance of the 200 nm is reduced by more than a factor of 10. Thus, the resistance of the 20 nm nanowires is controlled by its small dimension or by surface scattering.

The second interesting property of the 20 nm nanowires is the excitation energy. It is increased by more than a factor of two by annealing at 150 °C. It is thus increased significantly by the crystallinity. The increase due to the crystallinity is much smaller in the larger nanowires. Thus there is a size dependence of the excitation energy. The origin of this energy is not known at present.

4. Conclusions

Antimony hollow nanowire arrays embedded in porous alumina discs can be made in a closed system by a vapour-phase method. The technique allows one to produce Sb microcylinders with a thin wall and a well defined diameter and length. The diameter is the diameter of the channels and the length is the thickness of the disc. The Sb is prepared in an amorphous phase part of which can be crystallized by annealing at 150 °C for two hours. The resistance increases monotonically with decreasing temperature between liquid nitrogen and room temperatures. The temperature dependence can be described by a characteristic excitation energy which depends on the annealing temperature and the nanowire diameter. The room-temperature resistance is much larger than that of the bulk and depends on the post-annealing temperature and the nanowire diameter.

Acknowledgments

The research was supported financially by the Natural Sciences and Engineering Research Council of Canada. The x-ray diffraction measurements were taken by W Gong in the Brockhouse Institute of Materials Research. Research leave from Shiraz University was granted to M Barati. Dr J Heremans provided useful information about the vapour-phase method of sample preparation. The assistance of J Mativetsky in the analysis and electron microscopy is gratefully acknowledged.

References

- [1] Saito M, Kirihara M, Taniguchi T and Miyagi M 1989 *Appl. Phys. Lett.* **55** 607
- [2] Konno M, Shindo M, Sugawara S and Saito S 1988 *M. Mem. Sci.* **37** 193
- [3] Martin C R 1994 *Science* **266** 1961
- [4] Routkevitch D, Bigioni T, Moskovits M and Xu J M 1996 *J. Phys. Chem.* **100** 14 037
- [5] Zhang Z, Gekhtman D, Dresselhaus M S and Ying J Y 1999 *Chem. Mater.* **11** 1659
- [6] Heremans J and Thrush C M 1999 *Phys. Rev. B* **59** 12 579
- [7] Brumlik C J, Menon V P and Martin C R 1994 *J. Mater. Res.* **9** 1174
- [8] Zhang Z B, Ying J Y and Dresselhaus M S 1998 *J. Mater. Res.* **13** 1745

-
- [9] Iwami S and Mihama K 1995 *Nano. Str. Mater.* **6** 305
 - [10] Tanaka K and Iwama S 1997 *Nano. Str. Mater.* **9** 121
 - [11] Tanaka K, Iwama S and Mihama K 1998 *Japan. J. Appl. Phys.* **37** L669
 - [12] Hashimoto M, Niizaki T and Kambe K 1980 *Japan. J. Appl. Phys.* **19** 21
 - [13] Cohen J 1954 *J. Appl. Phys.* **25** 798