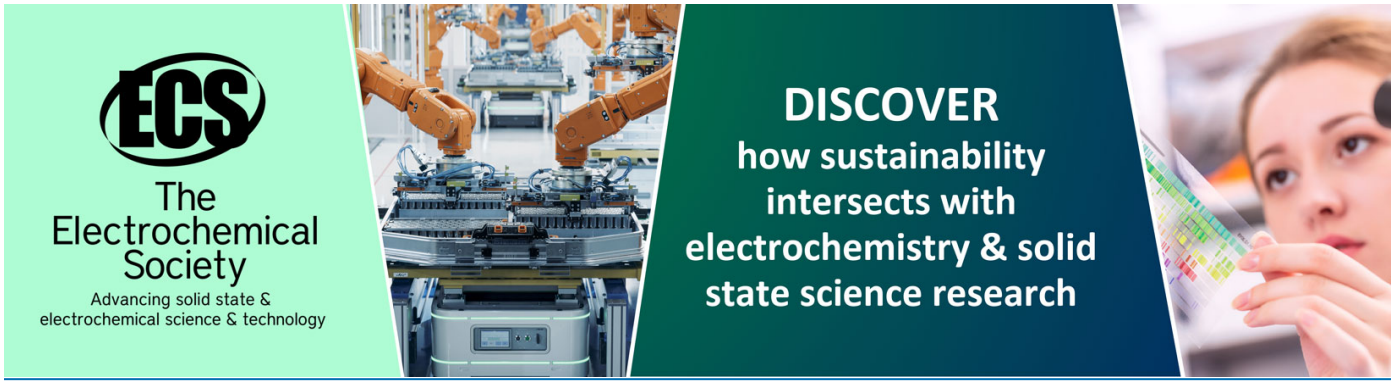
Electrical Properties of Electrospun Sb-Doped Tin Oxide Nanofibers



IOP Publishing Journal of Physics: Conference Series **61** (2007) 683–687
doi:10.1088/1742-6596/61/1/137 International Conference on Nanoscience and Technology (ICN&T 2006)

Electrical Properties of Electrospun Sb-Doped Tin Oxide Nanofibers

Neliza León-Brito[1], Anamaris Meléndez[1], Idalia Ramos[1], Nicholas J. Pinto[1], Jorge J. Santiago-Avilés[2]

[1]Department of Physics and Electronics, University of Puerto Rico at Humacao, CUH Station, Humacao, PR, 00791

[2]Department of Electrical and Systems Engineering, University of Pennsylvania, Philadelphia, PA, 19014

E-mail: iramos@mate.uprh.edu

Abstract. Transparent and conducting tin oxide fibers are of considerable interest for solar energy conversion, sensors and in various electrode applications. Appropriate doping can further enhance the conductivity of the fibers without loosing optical transparency. Undoped and antimony-doped tin oxide fibers have been synthesized by our group in previous work using electrospinning and metallorganic decomposition techniques. The undoped tin oxide fibers were obtained using a mixture of pure tin oxide sol made from tin (IV) chloride : water : propanol : isopropanol at a molar ratio of 1:9:9:6, and a viscous solution made from poly(ethylene oxide) (PEO) and chloroform at a ratio of 200 mg PEO/10 mL chloroform. In this work, antimony doped fibers were obtained by adding a dopant solution of antimony trichloride and isopropanol at a ratio of 2.2812 g antimony trichloride/10 ml isopropanol to the original tin oxide precursor solution. The Sb concentration in the precursor solution is 1.5%. After deposition, the fibers were sintered 600°C in air for two hours. The electrical conductivity of single fibers measured at room temperature increases by up to three orders of magnitude when compared to undoped fibers prepared using the same method. The resistivity change as a function of the annealing temperature can be attributed to the thermally activated formation of a nearly stoichoimetric solid. The resistivity of the fibers changes monotonically with temperature from 714 Ω-cm at 2 K to 0.1 Ω-cm at 300 K. In the temperature range from 2 to 8 K the fibers have a positive magnetoresistance (MR) with the highest value of 155 % at 2 K and ±9 T. At temperatures of 10 and 12 K the sign of MR changes to negative values for low magnetic fields and positive for high magnetic fields. For higher temperatures (15 K and above) the MR becomes negative and its magnitude decreases with temperature.

1. Introduction

Metal oxide nanostructures are of considerable interest for the development of nanoelectronic devices and gas sensors. Of these metal oxides, tin oxide is interesting because it is a binary semiconducting oxide with a large bandgap (Eg=3.6 eV) that can be modulated using of a doping material. It is an ideal candidate for gas sensing applications since its conductivity changes considerably when exposed to a reducing gas [1-5]. The sensitivity of tin oxide is expected to increase when it is in the form of fibers due to the increase in the surface to volume ratio. As the active element in chemical or biological sensors, metal oxide one-dimensional nanostructures can be configured either as resistors

whose conductance is altered by charge-transfer processes occurring at their surfaces or as field-effect transistors whose properties can be controlled by applying an appropriate potential to its gate [6]. Sensors based on SnO_2 wires on these configurations have been reported [7-10] with good electrical and photoconduction properties. Several dopants have been studied to enhance the electrical properties of tin oxide while maintaining the optical characteristics. Many reports have been made of the use of antimony as tin oxide dopant, particularly thin films [11, 12].

Of the methods used to fabricate metal oxide nanostructures, electrospinning is especially interesting in that it is easy and inexpensive. The electrospinning technique was invented in the 1930s [13], and was rediscovered about a decade ago to synthesize ultrafine polymer fibers. In a previous work, our group obtained a fluid with the appropriate viscosity to electrospun fibers using a pure SnO_2 solution mixed with a poly(ethylene oxide) (PEO)/chloroform ($CHCl_3$) solution at an appropriate ratio [14]. Then simple thermal decomposition yielded SnO_2 fibers. In a subsequent research, antimony was added as a dopant with the objective of increasing the conductivity of the fibers. For the doping, our original tin oxide precursor solution was modified by removing the water of the previous solution and adding a solution made from antimony trichloride ($SbCl_3$) and isopropanol ($2\text{-}C_3H_7OH$). The fibers electrospun with this precursor solution were followed by a heat treatment for two hours at 600°C to produce the antimony doped tin oxide (ATO) fibers. The electrical conductivity of the ATO fibers increases by three orders of magnitude when compared to the undoped fibers fabricated using the same method [15].

In this work further characterization of the electrospun ATO nanofibers is performed to study the electrical properties of the fibers at low temperatures from 300 down to 2 K. The resistivity of the fibers is measured without and in the presence of a transverse magnetic field that varies form – 9 T to 9 T and the magnetoresistance of the fibers is studied for the temperature range from 2 K to 40 K.

2. Experimental

The fibers were fabricated using a precursor solution based on a pure SnO_2 sol made using tin (IV) chloride anhydrous $SnCl_4$ (ACROS Organics), propanol (C_3H_7OH, Fisher Scientific), and isopropanol ($2\text{-}C_3H_7OH$, Fisher Scientific) at a molar ratio of 1:9:6. To reach the appropriate viscosity for the electrospinning process the SnO_2 solution was mixed with a viscous solution made from poly(ethylene oxide) (PEO) ($[\text{-}CH_2CH_2O\text{-}]n$ molecular weight 900,000, Aldrich) and chloroform ($CHCl_3$, Sigma) at a ratio of 200 mg PEO/10 mL $CHCl_3$. The details of this process are described elsewhere [14]. The doping solution was made from 2.2812 g of antimony trichloride ($SbCl_3$) dissolved in 10 mL of isopropanol ($SbCl_3$). All three solutions are combined in a volume ratio of 1:1.5:0.5 [15].

The electrospinning was done at room temperature using a homemade setup reported in detail previously [16]. Single crystal silicon wafers with an oxidized surface layer of 150 nm in thickness were used as substrates to collect single fibers. The samples were sintered at 600°C in air for two hours using a Sentry 2.0 Digital Temperature Controller made by Paragon Industries, Inc. The sintered fibers were observed under a JEOL JSM-6360 scanning electron microscope (SEM). The height and horizontal diameter of the fibers were measured using an Alpha Step 500 Tencor profilometer. A Digital Instruments Dimension 3000NS-III atomic force microscope (AFM), operated in tapping mode, was used to record the height and amplitude images of the fibers as data files. Offline image processing software was used to obtain the average cross-section profile, from which the cross-section area was evaluated. The electrodes for the electrical measurements were made by evaporating silver over a metallic grid. Then the grid was removed and the connections were made using gold wires and silver paint.

Electronic transport properties were measured using a Model 6000 Physical Measurement System by Quantum Inc, equipped with a Keithley 237 high-voltage source measurement unit. The resistance of a single fiber was measured using a four point probe setup without any applied magnetic field at temperatures from 300 K down to 2 K and back to 300 K. Each voltage sweep was repeated three times. Then, the current was measured while the applied magnetic field was increased or decreased

continuously between -9 T to 9 T. To suppress possible heating effects, the total measuring power was limited to 50 nW.

3. Results

The I/V curves for the ATO fibers with no magnetic field applied and for temperatures 300 K down to 2 K demonstrated the ohmic nature of the contacts as shown in figure 1. The resistance of the fibers was obtained from the slope of I/V curves. The corresponding resistivity ρ was calculated using the resistance R, the length l, and cross sectional area A for the fibers as $\rho = RA/l$.

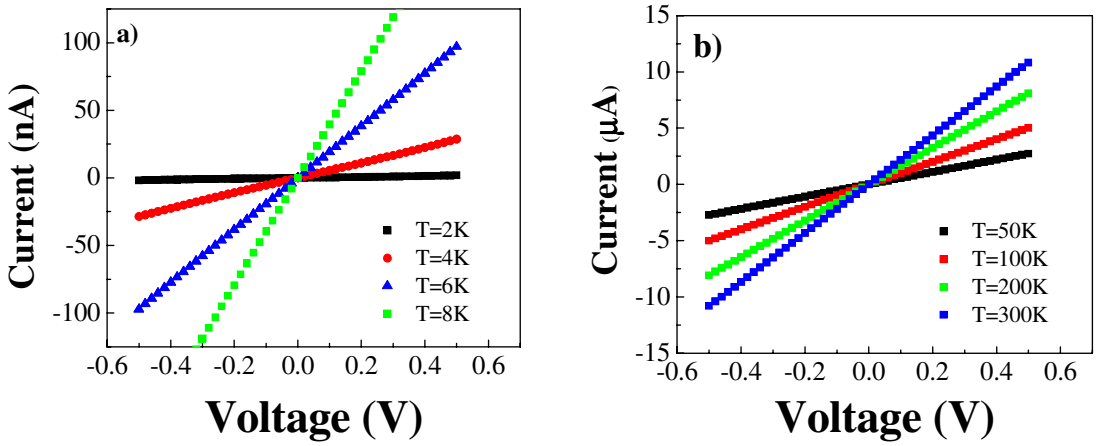


Fig 1 I-V characteristics of single ATO fiber in the a) lower and b) higher temperature limits, showing ohmic behaviour

Figure 2 shows the temperature dependence of the fiber's resistivity from 300 K to 2 K. The resistivity decreases monotonically with increasing temperature from 714 Ω-cm at 2 K to 0.1 Ω-cm at 300 K. These values are comparable to those reported on literature for a low percentage of antimony doping [11, 17]. The conductivity is expected to increase with the addition of more antimony.

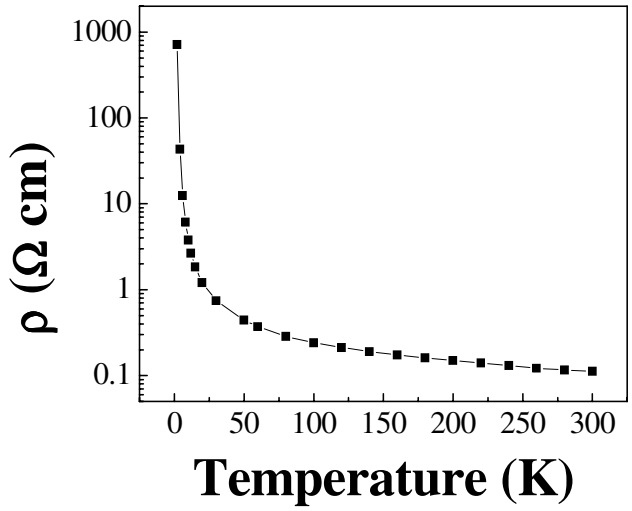


Figure 2 Temperature dependence of resistivity of ATO electrospun fiber

The magnetoresistance (MR) of ATO fibers were studied as shown on figure 3. The MR at low temperatures (2 K to 6 K) is positive, increases with decreasing temperature, and has a maximum value of 155 % at a magnetic field of ± 9 T. At 8 K the MR is small and negative for magnetic fields smaller than ± 4 T and becomes high and positive for higher magnetic field values. At 10 K the MR is negative for magnetic field values of ± 8 T or lower and becomes positive for higher magnetic fields. At 12 K the MR is negative for all magnetic fields. For higher temperatures, MR remains negative and its magnitude decreases with increasing temperature. These results differ from those reported by Kimura et. al. [17] in their study of $Sn_{1-x}Mn_xO_2$:Sb films. They measured negative and small MR values for SnO_2:Sb films for the range of 5 K to 50 K. They obtain positive MR only with the addition of Mn. In a related work with Mn doped ZnO Fukumura et. al. [18] reports a switch in the sign of the MR similar to our results. Switching signs is attributed to Mn doping providing localized spins interacting with conducting carriers in ZnO. Currently, our group is conducting more research to better explain this behavior in our ATO nanofibers.

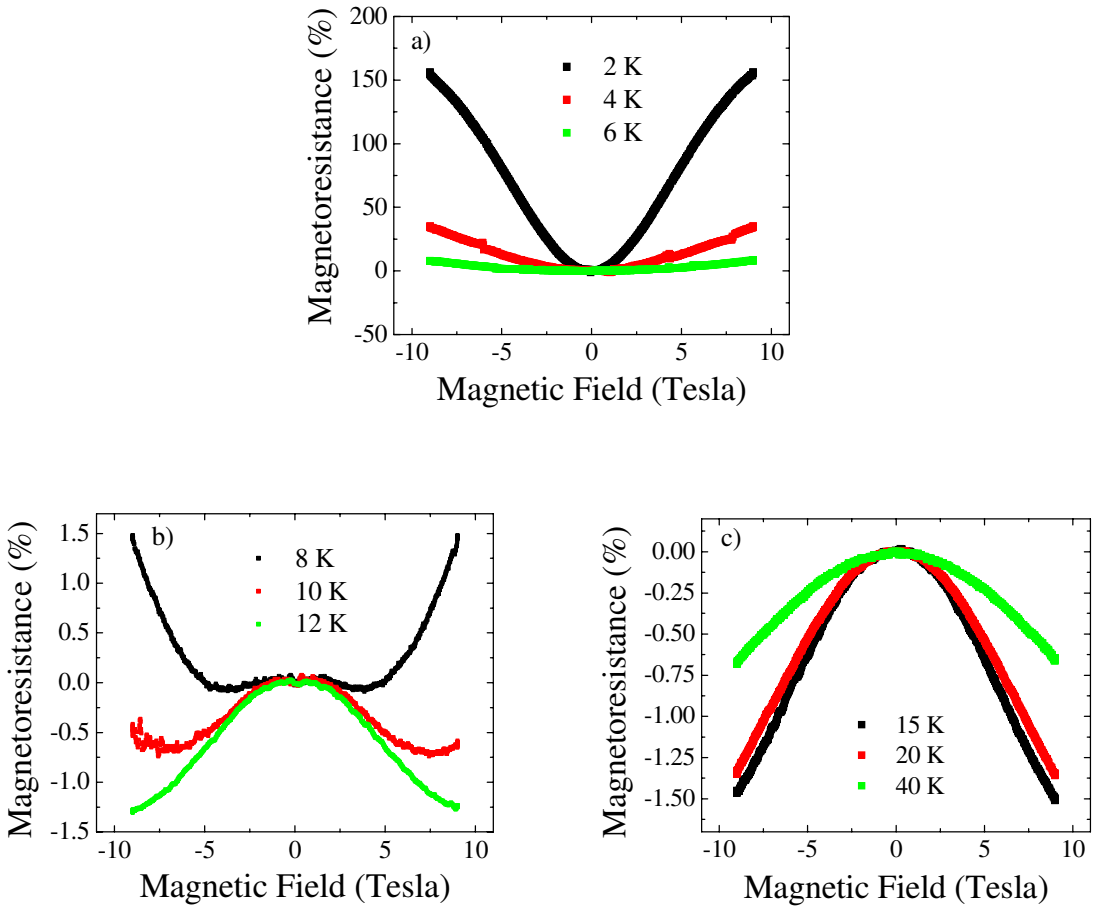


Figure 3 MR measurements a) positive MR for temperature of 2, 4, and 6 K b) switching in MR sign for temperatures of 8, 10 and 12 K c) negative MR for temperatures higher than 12 K.

4. Conclusions

ATO fibers produced by electrospinning and subsequent heat treatment at 600°C have a monotonically decreasing temperature dependence of resistivity that varies from 714 Ω-cm at 2 K to 0.1 Ω-cm at 300 K. In the temperature range from 2 to 8 K the fibers have a positive MR with the highest value of

155 % at 2 K and ±9 T. A switch on the sign of MR appears at 8 and 10 K, when the MR is negative for small and positive for large magnetic fields. After 10 K, the MR is negative for all magnetic fields. Further experiments are being conducted to explain this behavior.

5. Acknowledgements

This work was supported by NSF-DMR-353730, and NSF-SBE-0123654 and MARC UPR-Humacao, NASA Training Grant NNG05GG78H. The authors would like to express their gratitude to Maria Taku, Christopher Rodd, Daniel Milkie and Jay Kikkawa from the University of Pennsylvania.

References

1. Dai ZR, Gole JL, Stout JD, and Wang ZL 2002 Tin Oxide Nanowires, Nanoribbons, and Nanotubes *J. Phys. Chem. B* **106** 1274
2. Amin N, Isaka T, Yamada A, and Konagai M 2001 Highly efficient 1 μm thick CdTe Solar Cells with textured TCOs *Solar Energy Materials and Solar Cells* **67** (1-4) 195
3. Seal S and Shukla S 2002 Nanocrystalline SnO Gas Sensors in view of Surface Reactions and Modifications *Journal of Metals*, **54**(9) 35
4. Mishra S, Ghanshyam C, Ram N, Singh S, Bajpai RP, and Bedi RK 2003 Alcohol Sensing of Tin Oxide Thin Film prepared by Sol-Gel Process *Bull. Mater. Sci*, 25(3) 231
5. Xu C, Xu G, Liu Y, Zhao X, and Wang G 2002 Preparation and characterization of SnO_2 Nanorods by Thermal Decomposition of $SnCl_2O_4$ Precursor *Scriptia Materialia*, **46** 789
6. Kolmanov A and Moskovitz M 2004 Chemical Sensing and Catalysis by One-Dimensional Metal-Oxide Nanostructures *Annu. Rev. Mater. Rese.* 34 151
7. Liu Z, Zhang D, Han S, Li C, Tang T, Jin W, Liu X, Lei B, and Zhou C 2003 Laser Ablation Synthesis and Electro Transport Studies of Tin Oxide Nanowires *Advanced Materials*, **15**(20) 1754
8. Kolmakov A, Zhang Y, Cheng G, and Moskovits M Detection of CO and CO_2 using Tin Oxide Nanowire Sensors 2003 *Advanced Materials* **15** (12) 997
9. E. Comini E, Faglia G, Sberveglieri G, Pan ZW, and Wang ZL 2002 Stable and highly sensitive Gas Sensors based on Semiconducting Oxide Nanobelts *Appl. Phys. Lett*. **81** 1869
10. Arnold NS, Avouris P, Z. Pan ZW, and Wang ZL Field Effect Transistors based on Single Semiconducting Oxide Nanobelts 2003 *J. Phys. Chem*. B **107** 659
11. Terrier C, Chatelon JP and Roger JA 1997 Electrical and optical properties of Sb:SnO_2 thin films obtained by the sol-gel method 1997 *Thin Solid Films* **295** 95
12. Elangovaan E and Ramamurthi K 2005 A study of low cost-high conductivity fluorine and antimony doped tin oxide thin films 2005 *Applied Surface Science* **249** 183
13. Formhals 1934 US Patent **1**(975) 504
14. Wang Y, Aponte M, León N, Ramos I, Furlan R, Evoy S, and Santiago-Avilés JJ 2005 Synthesis and Characterization of Tin Oxide Micro/Nano Fibers using Electrospinning *Journal of the American Ceramics Society* **88**(8) 2059
15. León N 2006 Electrical Characterization of Electrospun Sb-doped SnO_2 Nanofibers *Proceedings of the National Conference on Undergraduate Research* Asheville NC
16. Wang Y, Serrano S and Santiago-Avilés J 2003 Raman characterization of carbon nanofibers prepared using electrospinning *Synthetic Metals* **138** 423
17. Kimura H, Fukumura T, Kawasaki M, Inaba K, Hasegawa T and Koinuma H 2002 Rutile-type oxide-diluted magnetic semiconductor: Mn-doped SnO_2 *Applied Physics Letters* **80** (1) 94
18. Fukumura T, Zhengwu J, Ohtomo A, Koinuma H and Kawasaki M 1999 An oxide-diluted magnetic semiconductor: Mn-doped ZnO *Applied Physics Letters* **75** (21) 3366