Temperature dependence of electron properties of Sn doped In$_2$O$_3$ nanobelts

Adenilson J. Chiquito$^{a,*}$, Marcia T. Escote$^b$, Marcelo O. Orlandi$^c$, Alexandre J.C. Lanfredi$^d$, Edson R. Leite$^d$, Elson Longo$^e$

$^a$Departamento de Física, Universidade Federal de São Carlos, CEP 13565-905, CP 676, São Carlos, São Paulo, Brazil
$^b$Centro de Engenharia, Modelagem e Ciências Sociais Aplicadas, Universidade Federal do ABC, Rua Catequese 242, CEP 09090-900, Santo André, SP, Brazil
$^c$Departamento de Física e Química, Universidade Estadual Paulista, CP 31, CEP 15385-000, Ilha Solteira, SP, Brasil
$^d$LIEC-CMDMC, Departamento de Química, Universidade Federal de São Carlos, Km 235, CP 676, CEP 13565-905, São Carlos, Brazil
$^e$Instituto de Química, Universidade Estadual Paulista – Araraquara, R. Prof. Francisco Degni, s/n, CEP 14801 907 Araraquara, SP, Brazil

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Abstract

This paper reports on the measurements of transport properties of high crystalline quality Sn doped In$_2$O$_3$ nanobelts. The samples presented metallic conduction in a large range of temperatures; however, at low temperatures, the resistivity showed a slight increase and the current–voltage curves showed a tendency to saturate even in the low-voltage range. From these observations, we discuss some arguments on the possibility of low dimensional conducting channels as the main responsible for the conduction at low temperatures. Additionally, we present an alternative technique for production of low resistance ohmic contacts, which can be further used in devices’ construction.

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1. Introduction

Oxide nanobelts have attracted much attention during the last years. These systems are synthesized using vapor–solid methods, and structures with characteristic rectangular cross section thickness of nanometers and widths of 5 nm–1 μm can be easily obtained. Potential uses of these structures, like field-effect transistors (FETs), transparent FETs and gas sensors, were proposed [1–4]. As an example, wide-band gap semiconductors, such as doped SnO$_2$ and In$_2$O$_3$, are transparent conducting oxides that have applications in optoelectronics due to their high electrical conductivity and optical transparency. When compared with carbon nanotubes and other kinds of nanobelts (based on usual semiconductors, such as GaAs, AlAs and InAs), the oxide nanobelts are obtained without the presence of a surface insulating layer of native oxides. For applications in electronic or optical devices, the knowledge of the electronic characteristics plays a fundamental role in order to optimize a particular device.

Due to their peculiar characteristics and size effects, oxide nanostructures often exhibit novel physical properties that are different from those of the bulk and of great interest for fundamental study. The issue here is to determine some properties of Sn doped In$_2$O$_3$ (ITO), such as the transport characteristics like resistivity and the type of the conductivity (insulating, semiconducting or metallic). Moreover, taking into account the dimensions of these structures, carrier transport takes place in a regime which ranges from the quantum limit (when the conductors have dimensions comparable with the characteristic mean free

*Corresponding author.
E-mail address: chiquito@df.ufscar.br (A.J. Chiquito).
path of the system) to the classical one. When in a quantum limit, the carriers do not exhibit fully wave-like behavior, but are sufficiently delocalized to exhibit also some particle-like properties [5].

We have measured some electrical properties of ITO nanobelts and the data obtained show a deviation of the linear ohmic conduction, presenting saturation of the current as a function of the applied voltage associated to the formation of low dimensional channels when the dimensions of the nanobelts were decreased.

2. Experiment

ITO nanobelts were grown by carbothermal evaporation process of In₂O₃ and SnO₂ powders in a tube furnace [6]. SnO₂ and In₂O₃ powders were mixed with 5 wt% of carbon black and placed inside two separate alumina crucibles (one for each powder), which were placed side by side in the hot zone of a tube furnace with controlled temperature and gas flux. The syntheses were carried out at 1150 and 1200 °C under a N₂ gas flux of 50 sccm for 2 h. The resulting material, which was collected from the coolest extremity of the tube, had a woolly appearance. Its structure was investigated by X-ray diffraction, scanning electron microscopy (SEM), X-ray spectroscopy (EDX and WDX) and transmission electron microscopy (TEM). The results and associated analyses have been published in Ref. [7].

The nanobelts presenting rectangular sections of 2.8 μm x 0.18 μm (sample A) and 1 μm x 0.06 μm (sample B) were placed on SiO₂ (500 nm thick) covered silicon substrates, and ohmic contacts were made by alloying small pieces of Indium (~200 μm) into the wire + substrate at 450 °C for 10 min in a tube furnace with an inert argon atmosphere. The Indium pieces provide mechanical adhesion of the wire to the substrate and electrical contacts for the experiments. Fig. 1 depicts an optical microscope image of the implemented device.

The transport measurements were carried out at different temperatures from 8 to 300 K using a closed cycle helium cryostat (Janis CCS 350) and at a pressure lower than 5 × 10⁻⁶ Torr. Both two probes current–voltage and resistivity were obtained using standard low frequency lock-in (AMETEK 7265) techniques (f = 13 Hz) and DC (Keithley 2400) techniques.

3. Results and discussion

The transport data are shown in Fig. 2. They reflect the geometry and the influence of the nanobelts' dimensions. Fig. 2(a) shows sample A’s current versus voltage (I–V) behavior in two probes geometry. The linear shape observed for a large voltage range (taking into account the physical dimensions of the nanobelts) is a clear indicative of the ohmic character of the nanobelts. This characteristic was observed at all the temperatures used in the experiments. From these results, it seems that the

![Fig. 1. Optical microscope image of the devices.](image1)

![Fig. 2. (a) Shows the current–voltage characteristics for the sample A. The resistivity as function of the temperature is plotted in panel (b). The behavior observed in (b) is related to the metallic character of ITO nanobelts. The insertion in panel (b) shows in detail the metallic character of the resistivity at low temperatures.](image2)
probed nanobelt presents a metallic conductivity, mainly determined by the Sn doping, as confirmed by X-ray wavelength dispersive spectroscopy measurements (Oxford WDS attached to a Zeiss DSM949A electron microscope).

The resistivity measurements (four probes geometry) as a function of the sample’s temperature are plotted in Fig. 2(b). The small resistivity values and the observed temperature dependence are in agreement with the metallic character of the ITO wire, as it was already seen in the $I–V$ curves [sample A, Fig. 2(a)]. At high temperatures ($T>77\,\text{K}$), electron–phonon scattering is the dominating process controlling the current conduction and we should expect the relaxation time to be inversely proportional to the temperature. Quantitatively, the temperature dependent behavior in Fig. 2(b) can be explained by taking into account the above mentioned electron–phonon scattering mechanism. As the temperature and phonon excitation increase, the amount of scattering events experienced by the conduction electrons is increased as well, resulting in a greater resistivity. In fact, for temperatures greater than $77\,\text{K}$ and at low disorder limits, the resistivity can be described by the Bloch-Grüneisen theory [8]

$$\rho(T) = \rho_0 + c \left( \frac{T}{\Theta_D} \right)^p \sigma_p(T), \quad (1)$$

where $c$ is a constant, $\Theta_D$ is the Debye temperature and $\sigma_p(T)$ is the Debye integral of order $p$ [8]. $\rho_0$ is a constant and $p$ ranges from 3 to 5 when the electron–phonon interaction is the main responsible for the scattering events [9]. The fitting of the experimental data using Eq.(1) revealed $p \approx 3.4$ and $\Theta_D = 1220\,\text{K}$ while theoretical calculations give $\Theta_D \sim 1200\,\text{K}$ [10]. From these results, the transport characteristics of the ITO nanobelts studied here are in agreement with the diffusive Drude theory: the electron conduction process is due to the diffusive three-dimensional bulk classical conductivity, $\rho = 1/nq\mu(T)$ for temperatures lying in the $77\,\text{K}<T<300\,\text{K}$ range [11]; here $n$, $q$ and $\mu$ are the density, charge and mobility of electrons. The electron–phonon interaction is the main scattering process leading to the mobility/resistivity dependence on temperature.

Similar measurements using $1\,\mu\text{m} \times 0.06\,\mu\text{m}$ nanobelts (sample B) have shown a very different and surprising behavior, as plotted in Fig. 3. The current–voltage curves show a tendency to saturate even in the low-voltage range [Fig. 3(a)]. This feature can be understood if we take into account that, decreasing the system’s physical dimensions, the electron-boundary collisions and quantum effects begin to contribute to its properties.

The resistivity measurements using this sample have also presented features that can be attributed to a different scattering mechanism in comparison to the larger sample [Fig. 3(b)]: in the low temperature range, the metallic characteristic was not observed as it was in sample A. Using the fitting procedures above described for the resistivity-temperature data and neglecting the low temperature range for sample B ($T>77\,\text{K}$), we obtain $n \approx 3.9$ and $\Theta_D = 1125\,\text{K}$. This result is twofold. It is an evidence that both samples present the same behavior for high temperatures, where the main scattering process is the electron–phonon interaction. In this range, the physical dimensions seem not be crucial; but at low temperatures, the difference in the dimensions of the samples may determine the observed characteristics (see the insertion in Fig. 3).

Due to the unexpected character of the observed transport properties, the experimental conditions should be carefully examined. The Joule heating was investigated as a possible responsible for the current saturation. The maximum measured current gives a current density of $J = 7 \times 10^3\,\text{A/cm}^2$ ($I–V$ curves), while the resistivity measurements were taken at a very low current ($1\,\mu\text{A},
would be quite surprising because we do not expect the section of the belt, the observation of quantum effects should be mentioned that, considering only the rectangular completely filled. In such a case, the current will saturate. It ohmic response will be obtained until the subbands are propagating subbands and in the absence of scattering, an saturation might be attributed to the band structure. If we suppose that the current in metallic nanobelts is carried by defects. The characteristics presented by both in large (macroscopic) sample, but without structural temperature dependence of ITO nanobelts' resistivity even in the low temperature range are an indication that a more detailed study on the electron structure of the samples is needed, taking into account different scattering mechan-

4. Conclusion

Electronic properties of self-assembled high crystalline quality tin-doped indium oxide were studied. The electron transport in the nanobelts was determined by the three-dimensional classical conductivity, as supported by the high temperature experimental data. The quantum size effects play an important role in determining the overall temperature dependence of ITO nanobelts’ resistivity even in large (macroscopic) sample, but without structural defects. The characteristics presented by both \( I-V \) curves in the low temperature range are an indication that a more detailed study on the electron structure of the samples is needed, taking into account different scattering mechanisms.

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References


