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Thermoelectric properties and thermal tolerance of indium tin oxide nanowires

Jose A Hernandez¹, Jennifer Carpena-Nunez², Luis F Fonseca¹, Michael Thompson Pettes³, Miguel Jose Yacaman⁴ and Alfredo Benitez⁴

¹ Department of Physics—University of Puerto Rico—Rio Piedras Campus, San Juan, PR 00931, United States of America
² Department of Physics—University of Puerto Rico—Rio Piedras Campus. Now at Brookhaven National Laboratory, United States of America
³ Department of Mechanical Engineering and Institute of Materials Science, University of Connecticut, Storrs, CT 06269-3139, United States of America
⁴ Department of Physics—University of Texas—San Antonio Campus, San Antonio, TX 78249, United States of America

E-mail: luis.fonseca@upr.edu

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Abstract
Highly crystalline indium tin oxide (ITO) nanowires were grown via a vapor–liquid–solid method, with thermal tolerance up to ~1300 °C. We report the electric and thermoelectric properties of the ITO nanowires before and after heat treatments and draw conclusions about their applicability as thermoelectric building blocks in nanodevices that can operate in high temperature conditions. The Seebeck coefficient and the thermal and electrical conductivities were measured in each individual nanowire by means of specialized micro-bridge thermometry devices. Measured data was analyzed and explained in terms of changes in charge carrier density, impurities and vacancies due to the thermal treatments.

Supplementary material for this article is available online

Keywords: thermoelectrics, nanowires, thermal tolerance, ITO, indium tin oxide

(Some figures may appear in colour only in the online journal)

Introduction
The synthesis of multifunctional nanomaterials has received great attention in the last few years due to the possibility of integrating multiple functionalities into individual building blocks to enable the fabrication of novel and powerful devices. Transparent conducting oxides (TCO) combining high transparency and electrical conductivity are widely used in important technological applications. Indium tin oxide (ITO) is one of the most used TCO and plays an important role in diverse technologies [1] that include solar cells [2–5], light emitting diodes [6, 7], gas sensors [8] and smart windows [9]. Due to the high crystallinity, large grains size, and high transparency in the visible spectral region ITO films are also used as transparent electrodes [8, 9]. In the last few years, reports show high performance synthesis of ITO nanowires, which makes these nanostructures a promising electrode material due to their exceptional properties, such as large surface area, high crystallinity, low resistivity and reproducible synthesis via different techniques including carbothermal evaporation process [10], vapor transport method [11–15], pulsed laser ablation [6, 16, 17], thermal metal co-evaporation [18, 19], electron beam evaporation [20], co-precipitation-annel method [21], electrospinning [22], DC sputtering [23], and electrochemically assisted deposition in template membranes [24].

The thermoelectric properties of ITO and its thermal tolerance expand the potential use of ITO nanowires, especially for applications in harsh and high temperature environments. In general, thermoelectric nanomaterials are receiving great attention in recent years because they can interconvert thermal gradients and electric fields for power generation, waste heat recovery, or solid state refrigeration [25–29] with high efficiencies. The energy conversion efficiency figure of merit...
(ZT) can be expressed in terms of the material’s thermoelectric parameters as \( ZT = S^2\sigma T/\kappa \), where \( S \) is the Seebeck coefficient or thermoelectric power, \( \sigma \) and \( \kappa \) are the electrical and thermal conductivity, respectively, and \( T \) is the absolute temperature. This expression shows that for high-ZT values a material should possess large \( S \) and \( \sigma \) values, and low \( \kappa \) values. Nanostructured materials with moderate densities of charge carriers show ZT higher than bulk values because of the different size-dependent scaling trends for the electrical and thermal conductivities allowing for the reduction of the long wavelength phonon mean free path by enhancing the surface scattering, thus reducing \( \kappa \) without affecting \( \sigma \) as strongly [30–34]. An example of the improvement of the thermoelectric properties is nano-structured Si. Si has a thermal conductivity \( \sim 148 \text{ W m}^{-1}\text{K}^{-1} \) in bulk but Yu et al [35] reported a decrease to \( 1.9 \text{ W m}^{-1}\text{K}^{-1} \) in Si nanomesh structures. Boukai et al [36] reported a ZT \( \sim 1 \) at 200 K and Hochbaum et al [37] reported a ZT \( \sim 0.6 \) at room temperature in Si nanowires, compared with ZT \( \sim 0.01 \) in bulk, at room temperature. ZT \( \sim 3 \) at 550 K has been reported in Bi-doped n-type PbSeTe/PbTe quantum-dot superlattice [38].

Many oxide semiconductors are chemically and thermally stable in air at high temperatures, which makes them good candidates for high temperature thermoelectric applications [26, 39–41]. Thermoelectric studies on ITO thin films show a dependence of ZT on Sn concentration, growth conditions and doping. The thermopower in ITO is negative indicating n-type behavior [42–45], Guillemau et al [46] tuned the ITO-bulk transport properties through doping In sites with \( \text{Tl}^{4+}, \text{Z}^{+} + e^{-}, \text{Sn}^{4+}, \text{Ta}^{3+} \), and \( \text{Nb}^{5+} \), finding a thermopower at room temperature of \( \sim 41 \mu \text{V K}^{-1} \) in case of \( \sim 1\% \) Sn; Zhu et al [47] found a maximum ZT of 0.15 at 1000 K using 5\% Lu and 0.1\% Sn concentrations. Other similar studies used Co [48], Zn and Nd [49], Ge [50] and Ga [51] as dopants but none of these works have investigated size effects on the thermoelectric properties. ITO is also a biocompatible material for implantable microelectrodes [52], what makes it attractive in applications for micro and nanoscale power sources using thermopower waves-based energy generation devices that has been studied with promising results with nanotubes [53], some tellurides, [54] and some oxides with similar thermoelectric figure of merit than ITO, such as ZnO [55] and MnO$_2$ [56].

Here we report successful synthesis of high quality crystalline ITO nanowires with high temperature tolerance up to 1300 °C. We explain the correlation between the structural and thermoelectric properties of single nanowires with and without heat treatment and the corresponding changes in \( S \), \( \sigma \) and \( \kappa \) values. The high temperature tolerance of ITO nanowires is then clarified for their potential use as building blocks in new thermoelectric devices that can operate in harsh environments.

**Experimental section**

ITO nanowires were synthesized using a catalyst-assisted thermal CVD-VLS process, using sapphire substrates coated with 1–3 nm thick Au films, into a quartz reactor (MTI 1200XL). High purity powders of tin oxide (99.998% purity, Sigma-Aldrich) and indium oxide (99.995%, Sigma-Aldrich) and graphite were used as source materials. The mixed powders were loaded at one end of an alumina boat with a sapphire substrate at 1 in. of distance downstream. The temperature was increase to 840 °C at a rate of 10 °C min$^{-1}$. The target temperature was kept for 1 h. During the synthesis the system was kept at atmospheric pressure, using 100 sccm of Ar as the carrier gas. After synthesis, the samples were loaded in a MTI GSL-1700X oven to perform the thermal annealing treatments up to 1400 °C, at atmospheric pressure in air. The crystal structure, morphology and chemical composition of as-synthesized and annealed ITO nanowires were characterized by x-ray diffraction—XRD (Rigaku, Cu-K$_\alpha$ radiation with \( \lambda = 1.5406 \AA \)), scanning electron microscopy—SEM (JEOL 7500 F), and SEM (Hitachi 5500) equipped with an energy dispersive x-ray spectrometer (EDS) (see figures S1, S2 and table S1 in the supplementary information, which is available online at stacks.iop.org/NANO/29/364001/mmedia). Transmission electron microscopy TEM (Zeiss Leo EM922) was used for imaging and SAED of one measured sample.

After synthesis and heat treatment, annealed and non-annealed nanowires were detached from the substrates by sonication in 2-propanol and spread onto quartz substrates. After evaporation of the solvent, individual nanowires were selected, transferred by micromanipulation (Narishige MMO203) with a 50 nm diameter tungsten tip, and finally mounted on specialized micro-devices for thermoelectric characterization. Figure 1 shows the SEM images of an ITO nanowire assembled onto a microdevice and connected to a four-electrode array. The specialized devices consisted of two adjacent \( 20 \times 20 \mu \text{m}^2 \) low-stress silicon nitride SiN$_{x}$ membranes, each suspended with six \( 420 \mu \text{m} \) long and \( 2 \mu \text{m} \) wide SiN$_{x}$ beams. One serpentine platinum resistor was patterned on each membrane which acted as a thermometer and connected to four Pt electrodes. Two additional Pt electrodes were patterned on each membrane to connect the sample. Below the two membranes a through substrate hole was made for TEM inspection. The device fabrication process and use is reported in earlier works [57–63]. Four Pt contacts were made in the nanowire using a focused ion beam (JEOL JEM9310) to electrically connect the nanowire to the device. For the measurements, the devices were finally attached to chip carriers and electrically connected using wire bonding. The prepared samples were placed in a cryostat chamber, pumped with a turbomolecular pump to reduce pressure to \( \sim 5 \times 10^{-6} \) Torr to minimize convection heat losses. Using two locking amplifiers, a DC source, two voltages and one current amplifiers, a thermal gradient were created between the ends of the nanowire and the voltage drop was measured between the inner and outer contact electrodes, respectively. The temperatures at the ends and the two thermoelectric voltages were measured for different ambient temperatures between 150 and 370 K using liquid nitrogen and a temperature controller. From these measurements the contact thermal resistance, corrected thermal conductivity, the Seebeck coefficient, and the electrical conductivity of each nanowire were
obtained. The schematics of the measuring setup is shown in figure S3 in the supplementary information.

Results and discussion

As-synthesized samples exhibited homogeneous and straight morphological features with lengths of up to several tens of micrometers as shown in figures 2(a), (b). The samples were tested for high temperature tolerance by annealing them in air at different temperatures in 30 min intervals. As shown in the SEM images, the overall morphology is preserved in the temperature range up to 1300 °C as shown in figures 2(c), (d). Thermal treatment at higher temperatures resulted in evaporation and segregation of the material on the substrate. Figures 2(e), (f) shows the effect of 1400 °C heat treatment. According to these results, the thermal, electrical, and thermoelectric properties of three as prepared and three 1300 °C annealed samples were studied.

Indium, tin and oxygen concentrations were determined by analyzing quantitative EDS data from the measured nanowires. Figures 3(a), (b) shows a SEM image, selected area electron diffraction (SAED), and EDS elemental mapping from where the chemical composition is obtained. EDS were obtained by SEM results are similar in the thermally treated samples up to 1300 °C (see figures S1, S2 and table S1 in the supplementary information for EDS maps and atomic percent estimates of all measured samples). XRD patterns (figure 3(c)) show all the main peaks corresponding to the In₂O₃ cubic structure (JCPDS 89-4596), indicating the incorporation of Sn into the In₂O₃ lattice. Other small peaks are related to SnO₂ and catalytic Au. The lattice parameter a from PDF card is 10.12 Å, the calculated from XRD and SAED patterns are 10.1006 Å and 10.1003 Å before and after annealing respectively, confirming the thermal stability of the nanowires and discarding any obvious dislocation or clusters formation.
Figure 4 summarizes the thermoelectric measurements. The temperature-dependent Seebeck coefficient ($S$) is shown in figure 4(a), the thermal ($\kappa$) and electrical ($\sigma$) conductivities are shown in figures 4(b) and (c), respectively, and the figure of merit ($ZT$) is shown in figure 4(d), all of which has been corrected to consider the thermal and electrical contact resistance of each nanowire-device ensemble. Thermal contact resistance is an important parameter in nanostructure materials, because in some cases it can dominate the thermal transport, especially in cases of weak bonding between the

Figure 3. (a) SEM image, insert: SAED patterns for sample before annealing. (b) SEM-EDS mappings (c) XRD pattern for the ITO nanowires without substrate before and after 1300 °C annealing.

Figure 4. (a) Measured Seebeck coefficient ($S$), (b) total thermal conductivity ($\kappa$), with the error bars (c) electrical conductivity ($\sigma$), and (d) $ZT$ as a function of temperature for ITO nanowires as-grown (samples 1–3) and after thermal annealing at 1300 °C in air (annealed a–c).
nanostructure and the substrate. In our samples the corrected thermal contact resistance was found about: 9%–14% sample 1, 23%–26% in sample 2, 15%–25% in sample 3, 8%–18% in annealed a, 17%–25% in annealed b and 7%–16% in annealed 3 of the total thermal resistance [57].

The negative values of \( S \) confirm the expected n-type behavior. The absolute value of the Seebeck coefficient increases almost linearly with temperature in all studied samples, with a greater slope and values for thermally treated ones. Wu et al [44] and Li et al [42] found a similar behavior in ITO thin films with annealing temperatures between 150 °C and 450 °C. The lowest total thermal conductivity values for the ITO nanowires was between ~1 and ~1.5 W m\(^{-1}\) K\(^{-1}\) corresponding to the annealed samples (figure 4(b)), staying practically constant in the studied temperature range. In the case of non-annealed samples, the thermal conductivity was between ~1.8 and ~2.6 W m\(^{-1}\) K\(^{-1}\). The decrease of the total thermal conductivity in annealed samples can be attributed mainly to the reduced contribution of electronic thermal conductivity as will be discussed. These values are lower than the reported thermal conductivity for In\(_2\)O\(_3\)-based compounds (2.0–8.5 W m\(^{-1}\) K\(^{-1}\) for different doping) [47–49].

The temperature dependence of the electrical conductivity is dominated by the free carriers and decreases as the temperature increases, similarly to previous reports in thin films [42, 43, 45, 64] and nanowires [11, 17, 19]. Thermally treated samples show almost an order of magnitude lower electrical conductivity that is consistent with our observation of a large increase in \( S \) for all annealed samples, and a lowering of the carrier concentration due to reduction of oxygen vacancy sites as evidenced from the EDS results. The thermoelectric performance of the ITO nanowires is shown in figure 4(d). The ZT value have a maximum of 4.28 × 10\(^{-3}\) at 370 K in sample 1, and similar values were obtained in annealed samples with a maximum of 3.64 × 10\(^{-3}\) in the annealed b sample.

The total thermal conductivity (\( \kappa \)) can be separated into two terms, one is the contribution from the free charges and the other from the lattice vibrations, and expressed as, \( \kappa = \kappa_e + \kappa_L \), where \( \kappa_e \) is the electronic thermal conductivity and \( \kappa_L \) is the lattice thermal conductivity. The electronic contribution (figure 5(a)) was estimated according to the Wiedemann–Franz Law (\( \kappa_e = \sigma L T \)), where \( T \) refers to the absolute temperature and \( L \) is the Lorentz number. In the Sommerfeld limit of a free electron gas \( L \) can be derived as \( L_0 = \pi^2 k_B^2 / (3e^2) = 2.44 \times 10^{–8} \) W Ω K\(^{-2}\) where \( k_B \) is the Boltzmann constant and \( e \) is the elementary electron charge [65, 66]. The lattice contribution was calculated from the difference between the measured total thermal conductivity and \( \kappa_e \), assuming \( L_0 \) and is shown in figure 5(b). We note that \( L_0 \) is the metallic limit of \( L \), and for semiconductors an empirical expression has been developed for the non-degenerate regime as a function of Seebeck coefficient [67] \( L = 1.5 \times 10^8 \exp(–|S|/116 \times 10^{-6}) \). We note that in the limit of our measured Seebeck coefficients, \( L \) is ~2.35–2.42 × 10\(^{-8}\) W Ω K\(^{-2}\), for the as-grown samples and ~2.17–2.36 × 10\(^{-8}\) W Ω K\(^{-2}\) for the annealed samples. Thus by assuming \( L_0 \), the maximum uncertainty error propagated to \( \kappa_L \) is expected to be a 0.6%–3.43% overestimation for the as-grown samples, and a 3.4%–11.2% overestimation for the annealed samples according to Hyun et al [67]. Thus our reported \( \kappa_L \) and ZT values may be slightly overestimated and slightly underestimated, respectively. As expected, phonons were the main contributors to the thermal transport. Detailed modeling of \( \kappa_L \) was used to obtain more information about defect formation during the thermal treatment, where \( \kappa_L \) was calculated in terms of the dislocations and impurity density using a modified Debye–Callaway model [68] which also takes into account the contributions from umklapp processes and boundary phonon scattering [69–71].

In the modified Debye–Callaway model, \( \kappa_{ph}(T) \) can be expressed as:

\[
\kappa_{ph}(T) = \frac{k_B}{2\pi\nu_J} \left( \frac{k_BT}{\hbar} \right)^3 f_0^{\pi_0/T} \frac{x^4 e^x}{\tau_{ph}^4 (e^x - 1)^2} \quad (1a)
\]

with

\[
\tau_{ph}^{-1} = \tau_I^{-1} + \tau_D^{-1} + \tau_U^{-1} + \tau_B^{-1} + \ldots
\]

\[
= A \alpha^2 T^4 x^4 + RTx + B \alpha^2 T^3 x^3 e^{-T/D} + \frac{V_J}{D} + \ldots \quad (1b)
\]
Table 1. Values of impurities (A) and boundary (D) parameters used in the modified Debye–Callaway model given in equation (1).

<table>
<thead>
<tr>
<th>Sample</th>
<th>A (s^3)</th>
<th>D (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>1.25 × 10^{-41}</td>
<td>230</td>
</tr>
<tr>
<td>Sample 2</td>
<td>4.80 × 10^{-42}</td>
<td>320</td>
</tr>
<tr>
<td>Sample 3</td>
<td>2.70 × 10^{-42}</td>
<td>180</td>
</tr>
<tr>
<td>Annealed a</td>
<td>1.30 × 10^{-41}</td>
<td>330</td>
</tr>
<tr>
<td>Annealed b</td>
<td>1.00 × 10^{-41}</td>
<td>330</td>
</tr>
<tr>
<td>Annealed c</td>
<td>5.80 × 10^{-42}</td>
<td>220</td>
</tr>
</tbody>
</table>

where $\chi = \frac{h \nu}{k_B T}$ is the reduced phonon frequency, $h$ is the reduced Planck constant, $k_B$ is the Boltzmann constant, $\nu$ is 6400 m s$^{-1}$ the speed of sound, $T_D = 700$ K is the Debye temperature [69] and $T$ is the absolute temperature. The fitting parameters are: $A$ for point defects, $R$ for dislocations, and $B$ for the umklapp processes. The parameter $D$ is related to the scattering at the boundaries and in our case is identified as the diameter of the nanowires. $D$ was obtained from the electron microscopy inspection of each sample. The best fitting of the observed $\kappa_v$ values gave $R$ and $B$ parameters practically unchanged for all the samples, with assigned values of $1 \times 10^9$ s$^{-1}$ K$^{-1}$ and $8 \times 10^{-18}$ s K$^{-1}$, respectively. The values for $A$ and $D$ used for each sample are summarized in table 1. Figure 5(b) includes the results from the model calculations as continuous lines. The comparison in table 1 between the values of coefficient $A$ before and after 1300 °C thermal treatment shows an overall increase of the contribution from point defects upon annealing, but within the same order of magnitude.

The comparison between the results from XRD, EDS, electrical and thermal transport between as-grown samples and 1300 °C heat treated samples confirms high overall thermal stability of ITO nanowires with diameters in the 180–330 nm range that suggests applicability of these nanostructures to work in high temperatures in an expanded area of applications that includes thermoelectricity. Their high thermal tolerance will make these nanostructures preferred among other high performance thermoelectric materials, such as tellurides and selenides with melting temperatures below ~800 °C for high temperature applications.

The combination of increased Seebeck coefficients and reduced electrical conductivities after annealing suggests a reduction in the charge carrier density that is compatible with the change in defect density. From the point of view of thermoelectrical power generation, the increased $S$ and reduced $\kappa$ and $\sigma$ work against each other to finally produce little overall changes in $ZT$ upon thermal annealing.

Conclusions

We successfully measured the Seebeck coefficient, the thermal and the electrical conductivities to obtain the thermoelectric figure of merit of individual highly crystalline ITO nanowires with and without 30 min of thermal treatment in air at temperatures up to 1300 °C. ITO nanowires were synthesized by a VLS process with diameters in the 180–330 nm range. The comparison between the samples’ response with and without annealing showed relatively high thermal tolerance of the material at the nanoscale that encourages its use in applications designed to operate at high temperatures up to 1300 °C.

Despite the high crystallinity of the samples, their density of crystalline defects varies between as-synthesized nanowires. According to the model calculations the reducing diameter and the density of defects are the two main changing parameters to determine the final contribution of phonons to the total thermal conductivity of the nanowires. Annealing produces a reduction of the electrical and the thermal conductivity in all the studied samples. An increasing Seebeck coefficient related to the decrease of the electrical conductivity is also observed that keeps ZT in the same order of magnitude before and after annealing.

In general, the observed thermal stability shown in the XRD patterns before and after annealing and the thermoelectric response of the studied ITO nanowires makes them a promising candidate as an n-type thermoelectric building block to develop nanodevices to operate in harsh environments.

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ORCID iDs

Jose A Hernandez https://orcid.org/0000-0002-6544-3334
Luis F Fonseca https://orcid.org/0000-0001-5534-7202
Michael Thompson Pettes https://orcid.org/0000-0001-6862-6841

References

Supplementary Information: Thermoelectric Properties and Thermal Tolerance of Indium Tin Oxide Nanowires

Jose A. Hernandez\textsuperscript{a}, Jennifer Carpena-Nunez\textsuperscript{a}, Luis F. Fonseca\textsuperscript{a}\textsuperscript{*}, Michael Thompson. Pettes\textsuperscript{c}, Miguel Jose Yacaman\textsuperscript{d}, and Alfredo Benitez\textsuperscript{d}

\textsuperscript{(a)} Department of Physics - University of Puerto Rico - Rio Piedras Campus, San Juan PR 00931, USA.

\textsuperscript{(b)} Department of Physics - University of Puerto Rico - Rio Piedras Campus, San Juan PR 00931, USA. Now National Research Council Associateship.

\textsuperscript{(c)} Department of Mechanical Engineering and Institute of Materials Science, University of Connecticut, Storrs, CT 06269-3139, USA.

\textsuperscript{(d)} Department of Physics - University of Texas - San Antonio Campus, San Antonio TX, 78249, USA.

\textsuperscript{*} luis.fonseca@upr.edu
Supplementary Information:
Thermoelectric Properties and Thermal Tolerance of Indium Tin Oxide Nanowires

Summary of SEM-EDS Chemical characterization

Figure S 1: SEM images and EDS mapping for measured sample 1, 2 and 3 of ITO nanowires
Figure S 2: SEM images and EDS mapping for measured annealed sample a, b and c of ITO nanowires

Table S 1: Summary of atomic percent concentration approximation of measured ITO nanowires.
Figure S 3: Schematic of the experimental method for thermal conductance measurements of individual suspended ITO nanowire