AIP | Journal of Applied Physics

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Citation: Journal of Applied Physics **96**, 5918 (2004); doi: 10.1063/1.1801153
View online: http://dx.doi.org/10.1063/1.1801153
View Table of Contents: http://scitation.aip.org/content/aip/journal/jap/96/10?ver=pdfcov
Published by the AIP Publishing

JOURNAL OF APPLIED PHYSICS VOLUME 96, NUMBER 10 15 NOVEMBER 2004

Electrical resistivities and thermopowers of transparent Sn-doped indium oxide films

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(Received 17 May 2004; accepted 3 August 2004)

We have systematically measured the electrical resistivities and thermopowers of transparent tin-doped indium oxide films. We found that the resistivities obey the Bloch-Grüneisen law between 25 and 300 K, whereas below 25 K, the resistivities slightly increase logarithmically with the decreasing temperature due to the weak-localization and electron-electron interaction effects. The thermopowers are negative and decrease linearly with temperature from 300 K down to 1.8 K. Our results strongly indicate that the tin-doped indium oxide films behave as a good, free-electron-like conductor while being transparent. © *2004 American Institute of Physics*.

[DOI: 10.1063/1.1801153]

Transparent conducting oxide films have been extensively studied in recent years, because they not only exhibit high optical transparency in the visible range of light spectrum but also possess high electrical conductivities.[1] These unique features made them very useful in many optoelectronics applications, including flat panel displays, photovoltaic electrochromics, solar cells, and energy-efficient windows. Among the various transparent conducting films, the tin-doped indium oxide (ITO) films with a resistivity of the order of 10^{-4} Ω cm are probably the most widely used ones. Hence, it is not surprising that there have been numerous experimental and theoretical investigations on this material system.[2] However, previous studies of ITO have mainly focused on the deposition techniques for high-quality films and the optical and electrical-transport properties at room temperatures. The temperature dependence of the resistivity represents a key element for the understanding of the conduction mechanisms in the materials. Surprisingly, there have been few reports on the temperature behavior of the resistivity in ITO in the literature.[3–5] Besides the electrical-transport studies, there have been essentially no heat transport measurements on ITO thus far. In this work, we have measured the thermoelectric powers (thermopowers) of several ITO films from 300 K down to 1.8 K. We have also measured the resistivities from 300 K down to 0.4 K. We report the systematic studies of both the electrical and heat transport properties of this important transparent conductor in the following discussions.

The high-quality ITO thin films prepared by the standard rf sputtering technique were provided by Merck Display Technologies Ltd. (Taiwan). Two thicknesses (125 nm and 240 nm) of the films were chosen for this experiment. The structures of the films were determined by a Rigaku x-ray diffractometer (D/max-2500×) with a Cu K_α radiation. The measurements indicated that the films were single phased with a cubic structure characteristic to that of the undoped In_2O_3 (powder-diffraction file number: 06-0416). Our deduced lattice constants were 1.0204 nm and 1.0210 nm for the 125-nm and 240-nm-thick films, respectively. These two values are in reasonably good agreement. The atomic fractions were determined by using an electron-probe microanalysis, and the results indicated that the atomic ratio of Sn to In was 1:23.23 in both types of films. This observation is strongly suggestive of the high reproducibility of the sputtering deposition of the films, because our films differed only in the thickness. The resistivities were measured by a standard four-probe method. The samples were typically 2–3 mm wide and about 1 cm long. Electrical leads were attached to the samples using a silver paste. The temperature backgrounds were provided by a standard ^{4}He dipper and a ^{3}He cryostat. In the ^{4}He dipper, the temperature was monitored using a calibrated AlGaAs thermometer. In the ^{3}He fridge, a calibrated carbon-glass thermometer was used for monitoring the temperatures above 7 K, whereas a calibrated RuO_2 thermometer was used for monitoring the temperatures below 7 K. The Seebeck coefficient or thermopower S was measured by a standard dc technique. A temperature gradient (usually chosen to be less than 5% of the sample temperature below 50 K) across the sample was provided by a 10-Ω resistor, and the temperatures in the cold and hot ends were measured by a calibrated carbon-glass thermometer. Thin Pb wires were used for our voltage leads because Pb has a high superconducting transition temperature of 7.19 K and the thermopower of Pb in the normal state has been well tabulated in the literature.[6]

Figure 1 shows the normalized resistivities, $\rho(T)/\rho(300\text{ K})$, as a function of the temperature for a 125-nm and a 240-nm-thick ITO films from 300 K down to liquid-helium temperatures. Clearly, both films reveal electrical-transport characteristics of a typical metal, i.e. the resistivities decrease as the temperature decreases. Our measured resistivities can be well described by the Bloch-Grüneisen formula[7]

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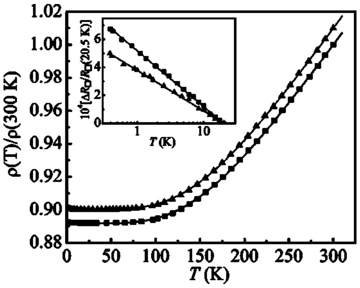

FIG. 1. Normalized resistivities vs temperature for a 125-nm (squares) and a 240-nm (triangles) thick ITO film. The symbols are the experimental data and the solid lines are the theoretical predictions of Eq. (1). For clarity, the data for the 240-nm-thick film has been shifted by +0.01. Inset: Sheet resistances as a function of the temperature for the same two ITO films below 25 K. The solid lines are the least-squares fits to Eq. (2).

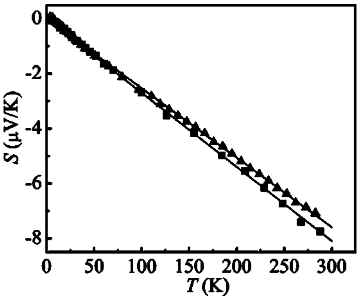

FIG. 2. Variation of the thermopowers S with temperature for a 125-nm (squares) and a 240-nm (triangles) thick ITO film. The straight solid lines are the least-squares fits to Eq. (3).

$$\rho = \rho_0 + \beta T\left(\frac{T}{\theta_D}\right)^4 \int_0^{\theta_D/T} \frac{x^5 dx}{(e^x - 1)(1 - e^{-x})}, \tag{1}$$

where ρ_0 is a residual resistivity, β is a constant, and θ_D is the Debye temperature. The theoretical predictions of Eq. (1) are least-squares fitted to our experimental data and are shown by the solid curves in Fig. 1. The fitted values for the relevant parameters are listed in Table I. Figure 1 clearly indicates that the experimental data are well described by the Bloch-Grüneisen law, implying that the ITO possesses conduction characteristics of typical metals. It should be noted that, from 300 K down to 25 K, the resistivities drop by only ~13%, suggesting the presence of significant amounts of residual resistivities in these films. A large residual resistivity reflects the presence of a high level of disorder in the film. Indeed, close inspection reveals that the resistivities increase slightly with decreasing temperature below 25 K (see the inset of Fig. 1). More precisely, the resistance rise obeys a logarithmic temperature dependence over a decade of temperature from 25 K down to 0.4 K. Such a resistance rise at low temperatures can originate from the weak-localization and electron-electron interaction effects in a disorder conductor. In quasi-two-dimensional systems, the change in the sheet resistance due to the weak-localization and electron-electron interaction effects is given by [8]

$$\frac{\Delta R_\square(T)}{R_\square(T_0)} = -\frac{e^2}{2\pi^2\hbar}\left[\alpha p + \left(1 - \frac{3}{4}F\right)\right] R_\square(T_0) \ln\left(\frac{T}{T_0}\right), \tag{2}$$

where α is a constant of the order unity, T_0 is an arbitrary reference temperature, and F is an electron screening factor. The theoretical predictions of Eq. (2) are compared to the experimental results and are represented by the straight solid lines in the inset of Fig. 1. The fitted values of the adjusting parameter $\alpha p + 1 - (3/4)F$ are listed in Table I. We notice that the fitted values of $\alpha p + 1 - (3/4)F$ in these two films are identical. As for a further check, we have also compared our measured $\Delta\rho(T)$ with the temperature variation $\Delta\rho(T) \propto -\sqrt{T}$ predicted for a three-dimensional disordered system. [9] We found that our results could not be described by such a variation, suggesting that our films are quasi-two-dimensional with regard to the weak-localization and electron-electron interaction effects.

Figure 2 shows a plot of the variations of the thermopowers S with temperatures from 300 K down to 1.8 K for the two ITO films. This figure clearly indicates that the thermopowers are negative and vary essentially linearly with temperature over our entire measuring temperature range. Such a linear temperature behavior of S can be ascribed to the diffusion thermopower due to the free-electron-like carriers. The diffusion thermopower at temperatures well below the Debye temperature θ_D in a typical metal is given by[10]

$$S = -\frac{\pi^2 k_B^2 T}{3e\xi_0}, \tag{3}$$

where e is the electronic charge and ξ_0 is the Fermi energy. Apart from the diffusion thermopower, a phonon-drag contribution to S usually exists in the clean samples having long phonon mean free paths. The phonon-drag thermopower is generally highly nonlinear in temperature. Such a nonlinearity is obviously not observed in our ITO films. In fact, the phonon-drag term is expected to be suppressed in our ITO films due to the presence of disorder in the films.[10] Indeed, that our films contain a noticeable level of disorder has been fully confirmed from the electrical-transport studies discussed earlier.

The linear dependence of S on temperature over a wide range of temperature is strongly supportive of the free-electron-like behavior of the carriers in the ITO films. For

TABLE I. Values for the relevant parameters for the two representative ITO films. The fitted values of ρ_0, β and $\theta_D$were obtained according to Eq. (1), the fitted values of $\alpha p + 1 - (3/4)F$ were obtained according to Eq. (2) and the fitted valuies of ξ_0 were obtained according to Eq. (3). l is the electron elastic mean free path at 10 K. $R_\square$is the sheet resistance at 10 K.

Thickness (nm)	ρ(300 K)(Ω cm)	ρ_0(Ω cm)	β(Ω Cm/K)	θ_D(K)	ξ_0(ev)	$\alpha p + 1 - (3/4)F$	l (nm)	$R_\square$(Ω)
125	1.89×10^{-4}	1.68×10^{-4}	4.69×10^{-7}	984	0.905	0.813	7.3	13.9
240	2.63×10^{-4}	2.34×10^{-4}	6.60×10^{-7}	979	0.943	0.813	5.1	9.95

our films, the Fermi energies deduced according to Eq. (3) are listed in Table I. The values for these two films are in reasonably close agreement, as would be expected. It should be noted that the validity of Eq. (3) in describing our experimental results in Fig. 2 is also consistent with our electrical-transport measurements, where we extracted the values of $\theta_D \sim 1000$ K in the ITO films. In fact, the diffusion thermopower should reveal a change in the slope as the temperature increases to above θ_D, i.e., the theory[10] predicts $S = -\pi^2 k_B^2 T/(e\xi_0)$ at $T > \theta_D$. Our observation of a single slope in Fig. 2 is certainly inconsistency with our experimental values of $\theta_D \gg 300$ K.

In the free-electron-like model, the Fermi energy is given by $\xi_0 = \hbar^2 k_F^2/(2\,m^*)$, where m^* is the effective mass of the carrier and k_F is the Fermi wave number. For ITO, it is well established that the carriers have an effective mass $m^* \approx 0.4\,m$, where m is the free-electron mass.[11] Using our experimental value of $\xi_0 \approx 0.9$ eV, we estimate the carrier concentration $n = k_F^3/(3\pi^2)$ in our films to be $\approx 9.8 \times 10^{20}$ cm^{-3}. This value is in good agreement with those previously reported by other groups.[11–13] Furthermore, the ITO is generally accepted as an n-type semiconductor.[14,15] This assertion is also confirmed by our observation of negative thermopowers in Fig. 2. Having the values of n, the magnitude of the electron mean free paths can be estimated (see Table I).

Recently, Odaka *et al.*[16] have performed first-principles band-structure calculations for Sn-doped In_2O_3. They found that the conduction electrons in ITO possess free-electron-like characteristics. Mryasov and Freeman[17] have also calculated the band structure of ITO using the local-density full-potential linear muffin-tin orbital method. Their results are consistent with that of Odaka *et al.* Our experimental observations of the transport properties characteristic to typical metals in both the electrical resistivities (Fig. 1) and thermopowers (Fig. 2), therefore, provide strong supports for the validity of these theories. Together with these theoretical calculations, our experimental assertion of the free-electron-like behavior of the electrons in ITO establishes a key element for the optoelectronics applications of this material.

In summary, we have systematically investigated the electrical resistivities and thermopowers of ITO films. The resistivities of these films reveal metallic behavior from 300 K down to 0.4 K. The thermopowers vary linearly with temperature between 300 K and 1.8 K and are negative. Our results provide strong evidences that free-carrier-like electrons are responsible for the electrical and heat conduction in this transparent conductor.

The authors are grateful to Professor. H. F. Meng for bringing ITO to their attention and to J. B. Lee for his involvement in the early stage of this experiment. This work was supported by the Taiwan National Science Council through Grant No. NSC 92-2120-M-009-007. One of the authors (Z. Q. L.) acknowledges the Taiwan NSC for supporting his visit to the NCTU through Grant No. NSC 92-2816-M-009-0004-6.

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