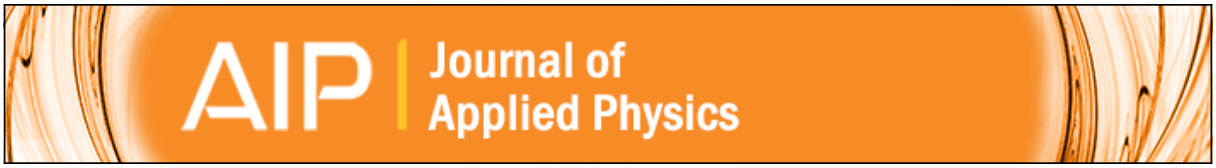

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Free-electronlike diffusive thermopower of indium tin oxide thin films

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We report our measurements of thermopower, $S(T)$, on a series of indium tin oxide thin films from 300 down to 5 K to extract the carrier concentration n. The temperature behavior of $S(T)$ below 300 K can be essentially described by a prevailing linear diffusive contribution. In this wide temperature interval, the phonon-drag thermopower is negligible relative to the diffusive thermopower. Therefore, the free-electronlike characteristic is clearly addressed. It should be stressed that linearity in S_d from liquid-helium temperatures all the way up to room temperatures is seldom seen even in simple metals. © *2010 American Institute of Physics*. [doi:10.1063/1.3524522]

I. INTRODUCTION

Indium tin oxide (Sn-doped indium oxide or ITO) films exhibiting high visible transparency and low electrical resistivity, ρ, have been extensively utilized in optoelectronic applications. The resistivity of high-quality ITO films can be made to be as low as $\sim 100-200$ $\mu\Omega$ cm at room temperature, while the carrier concentration, n, can be raised to be as high as $\sim 10^{20}-10^{21}$ electrons/cm^3 and essentially independent of temperature.[1–4] Surprisingly, this seemingly complex and doped oxide material is actually theoretically predicted to possess a *free-carrierlike* (i.e., parabolic) energy band structure.[5,6] Therefore, in addition to the technological aspects and applications, ITO is scientifically alluring and simple for the investigations of fundamental physics problems. Conventionally, the free-carrierlike, and thus metallic, behavior of ITO has often been studied by comparing the measured $\rho(T)$ with the Bloch–Gruneisen law derived from the Boltzmann transport equation.[7] This experimental approach, while confirming the metallic feature (i.e., decreasing ρ with decreasing temperature) of ITO, does not explicitly illustrate the free-carrierlike characteristic of the electronic energy band structure. In this work, we report our measurements of thermopower (Seebeck coefficient), $S(T)$, on a series of 21-nm-thick ITO films from 300 down to 5 K to explicitly demonstrate this unique and novel material property. It should be noted that recent thermopower measurements on ITO had focused on temperatures above 320 K,[8,9] and did not aim to address this fundamental question. Notice that our films are very thin (as compared with those previously studied by other groups,[1–4] yet they are of high metallic quality.

II. EXPERIMENTAL METHOD

Our 21-nm-thick ITO ($In_{91.8}Sn_{8.2}O_{150-\delta}$) films were deposited by rf sputtering on glass substrates and were supplied by the AIMCORE TECHNOLOGY Corporation (Hsinchu, Taiwan). They had room temperature resistivities of ≈ 210 $\mu\Omega$ cm. The as-grown films were thermally annealed in either air or a flowing oxygen gas for 1 h at several different temperatures between 100 and 500 °C. After annealing, the samples were cooled down to room temperature at a rate of 5 °C/min in air or O_2 gas. The thermopowers of our ITO films were measured by a steady dc technique, as described previously.[7] Four-probe Hall effect measurements were performed on a standard closed-cycle refrigerator equipped with a 1.2 T electromagnet. Rectangular samples of 4×13 mm^2 were cut from the wafers. In order to eliminate the effect due to any Hall probe misalignment, measurements were carried out by applying both positive and negative currents. For the Hall resistances, we confirmed that a linear characteristic holds between -1 and 1 T.

III. EXPERIMENTAL RESULTS

In an ideal metal with a spherical Fermi surface, S contains two contributions: the diffusive thermopower due to free carriers, S_d, and the phonon-drag thermopower, S_g, i.e.,

$$S = S_d + S_g = -\frac{\pi^2 k_B^2 T}{3|e|E_F} + BT^3, \tag{1}$$

where E_F is the Fermi energy and B is a material dependent constant. The asymptotic expression of the first term is valid when $T \ll \theta_D$ (θ_D is the Debye temperature), which is particularly pertinent to the present study because ITO has a relatively high value of $\theta_D \approx 1050$ K.[4] Notice that at $T > \theta_D$, the diffusion thermopower S_d will cross over to another linear regime given by $S_d = -\pi^2 k_B{}^2 T/(|e|E_F)$.[10] Therefore, for typical metals with Debye temperatures lying between ~ 200 and ~ 400 K,[11] the measured S_d will not be linear over the large temperature interval from liquid-helium temperatures up to 300 K.

Figure 1 shows our measured $S(T)$ for one as-grown and three representative O_2 annealed samples. (The samples annealed in air revealed similar $S(T)$ behavior to those annealed in O_2 gas.) The symbols are the experimental data and the solid lines are least-squares-fits to Eq. (1). It is clearly seen that the thermopowers are negative, indicating electron, but not hole, conduction in this material. In particular, it is noteworthy that $S(T)$ is essentially linear over the wide range of

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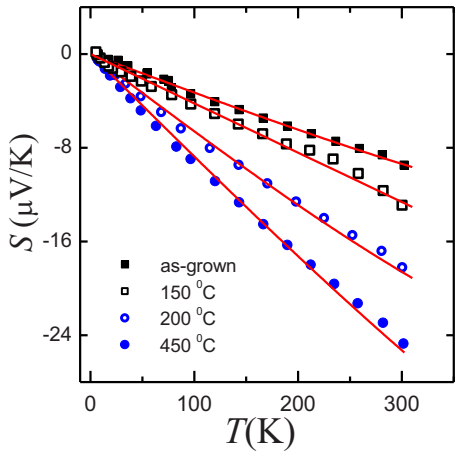

FIG. 1. (Color online) Thermopower as a function of temperature for one as-grown and three O_2 annealed ITO films, as indicated. The solid lines are least-squares fits to Eq. (1).

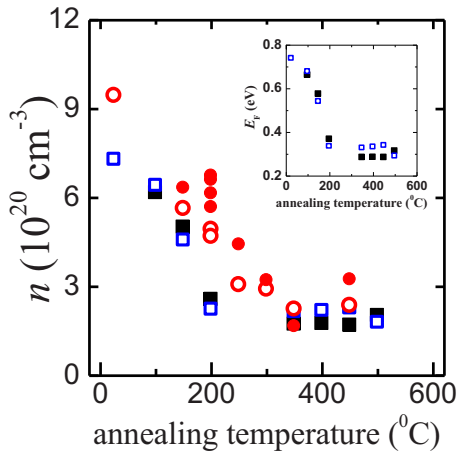

FIG. 2. (Color online) Variations in carrier concentration and Fermi energy with annealing temperature, as indicated. Open (closed) squares: thermopower carrier concentration n for air (oxygen) annealed films; open (closed) circles: Hall carrier concentration n_H for air (oxygen) annealed films.

our measurement temperature, which directly manifests the combined material effect of a high Debye temperature and a minute contribution from the phonon-drag term in ITO. Such kind of a prevailing linearity in S_d from liquid-helium temperatures all the way up to 300 K is seldom seen even in textbook simple metals.[10] This robust linearity provides a direct and strong proof of the free-electronlike energy band structure of ITO, as has recently been theoretically calculated by Mryasov and Freeman,[5] and Odaka *et al.*[6] In all cases, the phonon-drag term in our samples is very small (typically, $B \approx 5 \times 10^{-8}$ $\mu V/K^4$) and contributes less than 10% to the total S even at 300 K. This contribution is suppressed by the disorder effect in ITO films in which a non-negligible level of randomness can readily originate from Sn dopants, oxygen vacancies, and grain boundaries.

A predominant linear $S \approx S_d$ over a wide range of temperature renders the extraction of E_F very accurate, according to the expression of Eq. (1). The difference in the slopes of the solid lines in Fig. 1 implies a change in E_F as a result of thermal annealing. Our extracted values of E_F, together with n, are shown in Fig. 2 [open (closed) squares for air (oxygen) annealed films]. Here the values of n were deduced through the free-electron-gas relation $E_F=(\hbar^2/2m^*) \times (3\pi^2 n)^{2/3}$, by taking an effective mass $m^*=0.4m$,[7] where m is the free electron mass. Our obtained values of n [$\approx (2-7) \times 10^{20}$ electrons/cm^3] are in good accord with those values reported in the literature for ITO thick films[2] and single-crystalline nanowires[12] with compatible resistivities. Figure 2 reveals that n decreases by a factor of ~ 4 as the annealing temperature was raised to above 200 °C, with a seemingly sharp drop in n occurring at an annealing temperature of ~ 150 °C. (Close inspection indicates that the values of n for the oxygen annealed samples still decrease slightly until an annealing temperature of 350 °C.)

We have also carried out the Hall effect measurements on several samples to compare with the n values deduced from S measurements. The open (closed) circles in Fig. 2 indicate the Hall carrier concentration, n_H, for the air (oxygen) annealed samples.[13] This figure demonstrates that n_H reveals a similar trend to that of the thermopower carrier concentration, i.e., a decrease in n_H with increasing annealing temperature. The values $n_H \approx (2-9) \times 10^{20}$ electrons/cm^3 are somewhat larger than the corresponding n. Nevertheless, it is very encouraging to see that the difference is within a factor of 1.3, except for the films annealed at 200 °C (see below). We notice that a slight difference between n and n_H is not unexpected and had previously been observed in, for instance, In–Ti–O bulk ceramics.[9] One possible origin for such a discrepancy may arise from the simplified expression of S_d in Eq. (1). Theoretically, the expression of the diffusion thermopower is more accurately written as $S_d=[-\pi^2 k_B{}^2 T/(3|e|E_F)] \times \xi$,[14] where the value of the thermoelectric parameter ξ, may differ somewhat from unity in real metals and alloys. On the other hand, the widely used Hall coefficient $R_H=1/(n_H e)$ is also a simplified expression. In short, the carrier concentrations in ITO reported in the literature have been extracted from the Hall effect measurements thus far.[1–4,15] The present work demonstrates that $S(T)$ measurement can provide a particularly reliable and alternative method for determining this important material quantity.

Finally, we notice that the extracted n and n_H magnitudes for the 200 °C annealed films vary somewhat (four of them were cut and measured), although the annealing conditions were nominally the same. This result suggests that some subtle changes in the chemical content and/or the structural homogeneities of the sample might occur around this annealing temperature. However, such subtle changes are difficult to detect experimentally, since our films are very thin and, for example, the energy-dispersive x-ray spectroscopy signals are very weak. This issue requires further detailed investigations.

IV. CONCLUSION

In conclusion, we have studied the temperature dependent thermopowers of a series of ITO thin films annealed under various conditions. The temperature behavior of $S(T)$ below 300 K can essentially be described by a prevailing linear diffusive contribution. This observation provides a di-

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rect and explicit experimental proof of the free-electronlike characteristic of the energy band structure of ITO. The extracted carrier concentrations are within a factor of ~1.5 of those determined from the Hall effect measurements.

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