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Yuki Yoshida, David M. Wood, Timothy A. Gessert, and Timothy J. Coutts

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# High-mobility, sputtered films of indium oxide doped with molybdenum

Yuki Yoshida[a)] and David M. Wood
*Department of Physics, Colorado School of Mines, Golden, Colorado 80401*

Timothy A. Gessert and Timothy J. Coutts
*National Renewable Energy Laboratory, Golden, Colorado 80401*

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Thin films of molybdenum-doped indium oxide, an *n*-type transparent conducting oxide, were deposited on glass substrates by a large-area deposition technique, radio-frequency magnetron sputtering, and their electrical properties were examined. Molybdenum content was varied from 1 to 4 wt%, and the highest mobility achieved was 83 $cm^2 V^{-1} s^{-1}$ at a carrier concentration of $3.0 \times 10^{20}$ $cm^{-3}$ without any postdeposition treatment for one of the films made from the target with 2 wt% Mo. Temperature-dependent Hall analysis indicated that this high mobility is limited by phonon scattering, whereas the method of four coefficients analysis showed that the conduction band is parabolic. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1687984]

In recent years, the research community has increased efforts to develop new transparent conducting oxides (TCOs) with electrical and optical properties superior to those of conventional TCOs (e.g., $SnO_2$, $In_2O_3$:Sn, and ZnO). In addition, the emergence of *p*-type TCOs has further stimulated the community because of the feasibility of developing devices for transparent electronics and ultraviolet emitters.[1] The widespread consensus on the best approach for developing higher-quality TCOs is to improve the mobility of free carriers,[2] which can be achieved by making films with longer relaxation time due to fewer defects, and/or by reducing the effect of charge scattering by ionized impurities. Meng *et al.* reported high-mobility films of indium oxide doped with molybdenum (IMO).[3,4] Their films were fabricated using evaporation onto glass substrates, and mobilities >100 $cm^2 V^{-1} s^{-1}$, at least three times greater than those typical of commercial TCO materials, were achieved. In the present work, we sought to duplicate their high-mobility results using radio-frequency (rf) magnetron sputtering, a process inherently better suited to high-volume manufacture of TCOs. We have also studied fundamental electrical properties of sputtered IMO films (e.g., relaxation time, effective mass, and charge scattering mechanisms) using the method of four coefficients[5,6] and temperature-dependent Hall measurements.

Films were prepared using rf magnetron sputtering at 13.56 MHz in a sputter-down configuration from 2-in.-diam planar targets of 99.99% purity. All IMO targets were hot pressed using fully oxidized $In_2O_3$ and Mo metal. The targets were purchased from Cerac, Inc. (Milwaukee, WI) and had nominal Mo contents of 0, 1, 2, 3, and 4 wt%. Sputter deposition was performed in a sputtering system capable of automated control of both substrate orbit and rotary motion to enhance the uniformity. Base pressures of $5 \times 10^{-8}$–$2 \times 10^{-7}$ Torr were established using a cryopump prior to each deposition. Sputtering gases were 99.993% purity oxygen and/or 99.999% purity argon, and partial pressures were set using needle valves prior to throttling to the sputtering pressures of 10 mTorr. Sputtering was conducted at a constant power of 120 W.

All depositions reported here were performed on cleaned glass substrates (Corning 7059) at a temperature of ~450 °C, the highest substrate temperature permitted by the current configuration. The source-substrate separation was ~1.27 cm. Following deposition, the samples were maintained in the sputtering ambient and temperature for 1 h, after which the gases and heater were shut off, and the substrate was allowed to cool under vacuum for 1 h. This postdeposition procedure was critical for both high-mobility samples and reproducibility of film electrical parameters.

The thickness of the ~0.5-1-$\mu$m-thick films was measured using stylus profilometry (Veeco Dektak 3). The film resistivity, mobility, and carrier concentration were obtained at room temperature from Hall analysis using the van der Pauw method (BioRad HL5500 System). Temperature-dependent Hall measurements (105–365 K) were performed in a similar system using a liquid nitrogen cryostat. A four-coefficient measurement system of in-house design was used to measure transport properties of the films.[7]

Previous studies showed that the electron concentration ($n$) in IMO increases as the amount of oxygen in the sputtering ambient decreases, and that higher substrate temperature improves the electrical properties of the films.[8] Consistent with previous studies, films produced from all target compositions studied here attain the highest electron mobility when a small amount of oxygen is added to the Ar sputtering ambient. The visible transmittance of the ~100-nm-thick films produced in this study is ~80%, regardless of Mo content. This level of transparency is consistent with previous optical studies of films containing 4 wt% Mo,[8] and compares well with $In_2O_3$:Sn films produced with this same system.

Figure 1 shows that the maximum mobilities for the films produced from targets containing 1, 2, 3, and 4 wt% Mo are 75, 83, 64, and 61 $cm^2 V^{-1} s^{-1}$, at $n = 1.6 \times 10^{20}$, $3.0 \times 10^{20}$, $3.0 \times 10^{20}$, and $4.6 \times 10^{20}$ $cm^{-3}$, respectively. Figure 1 also shows that while $n$ decreases systematically with increasing oxygen in the sputtering ambient, the mobility

[a)]Author to whom correspondence should be addressed; electronic mail: yuki_yoshida@nrel.gov

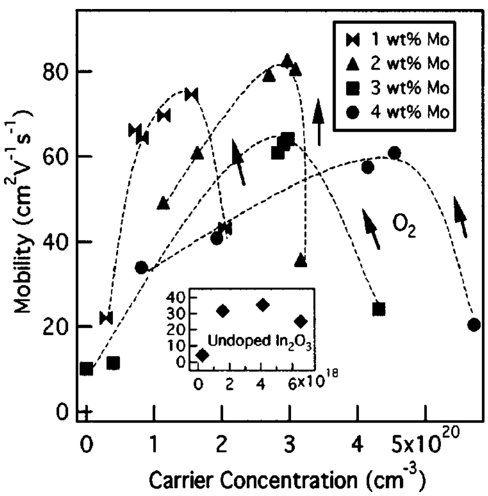


FIG. 1. Room-temperature mobility vs carrier concentration of IMO thin films with 0, 1, 2, 3, and 4 wt% Mo content. Direction of arrows indicates increase in oxygen concentration during deposition.

attains a maximum value at low $O_2$/Ar ratios of ~0.0035. The highest carrier concentrations for films with various Mo contents shown in Fig. 1 are all obtained when the films were grown in 100% Ar environment, which is summarized in Fig. 2, showing that $n$ increases linearly as Mo concentration increases. It should be noted, however, that the optical properties of these Ar-only IMO films are much poorer than when a small amount of $O_2$ ambient is present.

Taken together, the data in Figs. 1 and 2 suggest that the roles of Mo and oxygen in both carrier generation and scattering are interdependent. The fact that films containing Mo attain significantly higher mobility than undoped $In_2O_3$ films may imply that Mo participates in suppressing scattering by oxygen interstitials. However, the fact that the mobility is lower for films containing more than ~2 wt% Mo suggests that Mo itself can become a dominant scattering center.

The mobility is directly proportional to relaxation time and inversely proportional to the effective mass. Therefore, a longer relaxation time and/or smaller effective mass can yield higher mobility. To explore the reasons for the observed high mobility of IMO, the method of four coefficients was used to measure the relaxation time and effective mass of the as-deposited films shown in Fig. 3. The equipment used permits simultaneous measurement of the conductivity,

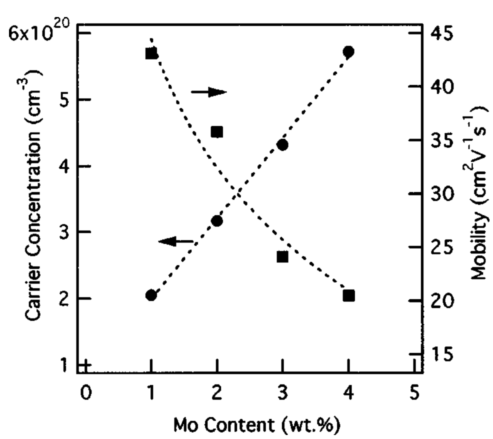


FIG. 2. Carrier concentration and mobility vs Mo content for films grown in 100% Ar environment.

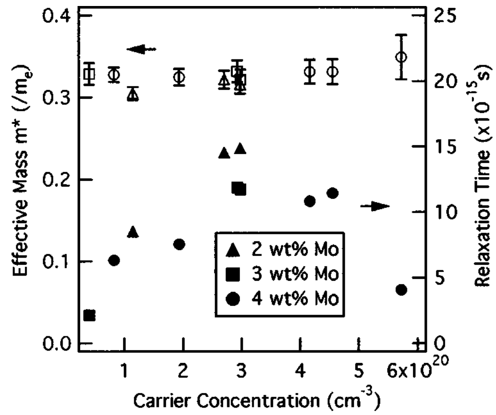


FIG. 3. Effective mass (open symbol) and relaxation time (closed symbol) as a function of carrier concentration of IMO thin films with 2, 3, and 4 wt% Mo content.

Hall, Nernst, and Seebeck coefficients for both thin films and bulk materials.[7] From this analysis, one can obtain the density-of-states effective mass ($m^*$), Fermi-level position relative to the conduction-band minimum (CBM), relaxation time, and an indication of the dominant scattering mechanism.[5,6,9,10]

Most TCOs are degenerate (i.e., the Fermi energy lies above the CBM), and $m^*$ is inversely proportional to the curvature of the conduction band. Therefore, measuring $m^*$ at different $n$ provides insight into the shape of the conduction band. As shown in Fig. 3, the effective mass of as-deposited IMO films does not vary significantly with Mo content (from the value of $0.32\pm0.01\, m_e$), even though the carrier concentration varies from $\sim4\times10^{19}$ to $\sim6\times10^{20}$ cm$^{-3}$. This indicates that the conduction band is parabolic, at least over the range associated with the level of degeneracy probed (i.e., Fermi energy located ~0.1–0.7 eV above the CBM), and within the experimental uncertainty of this method ($\pm0.016\, m_e$). This degree of parabolicity of the conduction band has not been observed in any other TCO,[5,9,10] but $m^*$ is in good agreement with theoretical calculations for the (direct) conduction-band minimum in $In_2O_3$.[11] The higher mobility correlates well with longer relaxation time, as shown by comparing Figs. 1 and 3, which is similar to other TCOs.

To investigate further the carrier scattering mechanisms, temperature-dependent Hall measurements were performed. Scattering rates predicted from Fermi's Golden Rule calculations associate distinct temperature dependences with specific scattering mechanisms.[12] As shown in Fig. 4, high-mobility films deposited in a low $O_2$/Ar ratio ambient demonstrate significant change in mobility with temperature. This trend is consistent with phonon scattering. In contrast, for films with high carrier concentration deposited in pure Ar, the minimal change in mobility with temperature suggests that these films are limited by ionized-impurity scattering. The observation that carrier concentration decreases with temperature for the films deposited in pure Ar has not been explained.

In summary, we have fabricated IMO films by rf magnetron sputtering that demonstrate a mobility exceeding 80 cm$^2$ V$^{-1}$ s$^{-1}$. This is twice the value of commercially available TCOs, which suggests that understanding the role of Mo

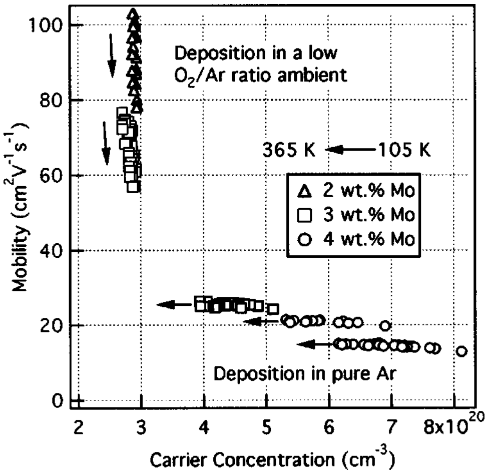


FIG. 4. Temperature-dependent Hall measurement of IMO films with 2, 3, and 4 wt% Mo. Direction of arrow indicates increasing temperature.

in $In_2O_3$-based TCOs may have significant commercial relevance. The method of four coefficients and temperature-dependent Hall measurements has shown that the highest-mobility films demonstrate longer relaxation time and contain fewer charged scattering centers.

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