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OPTIMIZATION OF CONDUCTIVITY AND TRANSPARENCY IN AMORPHOUS IN-ZN-O TRANSPARENT CONDUCTORS

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ABSTRACT

Amorphous mixed metal oxide TCOs are of increasing interest due to the excellent opto-electronic properties and smoothness ($R_{\text{RMS}} < 0.5$ nm) obtained for sputtered films deposited at less than 100 °C. In particular, for amorphous In-Zn-O (a-IZO) films grown from a ceramic target with 10 wt. % ZnO in In_2O_3 , the current industry standard, conductivities $\sigma \geq 2500$ S/cm are common. Here, we have investigated the combined materials phase space of oxygen stoichiometry and metals composition (In:Zn ratio) and made two key discoveries. First, that high conductivity a-IZO thin films can be made with substantially less indium provided that a corresponding change is also made in the oxygen content. And second, that for all compositions of a-IZO, the electron mobility (μ) and carrier concentration (N) fall on a single common curve when plotted as μ vs N.

INTRODUCTION

Transparent conducting oxides (TCOs) can serve a variety of important functions in thin film photovoltaics such as transparent electrical contacts, antireflection coatings and chemical barriers [1]. An area of particular interest and active development is amorphous mixed metal oxide transparent conductors which can be grown by sputtering at low, or even ambient, temperature. For example, amorphous In-Zn-O (a-IZO) films grown from a ceramic target with 10 wt. % ZnO in In_2O_3 , the current industry standard, commonly have conductivities $\sigma \geq 2500$ S/cm and are extremely smooth as well with $R_{\text{RMS}} < 0.5$ nm [2,3]. Here, we report on two experiments two experiments aimed at determining the relative roles of metals and oxygen stoichiometries on the opto-electronic properties of a-IZO thin films.

EXPERIMENTAL APPROACH

First, using co-sputtering from In_2O_3 and ZnO targets, compositional gradient samples spanning the amorphous composition range (50 – 85 at.% In) were deposited at a substrate heater temperature $T_{\text{S}} = 100$ °C in Ar containing 0, 2, 4 or 6 % O_2 onto 2"x2" Corning 1737 glass substrates. For each composition gradient sample, 11 spots were measured along the composition gradient to obtain data for different metals compositions. The typical measurement spot size is ~ 1 mm. X-ray diffraction was used

to determine if the samples were amorphous or crystalline. A mapping 4-point probe system was used to determine the sheet resistance. Optical reflection and transmission spectra were measured from 300 – 1100 nm using fiber optically coupled CCD array spectrometers. The sample thickness was determined on a spot by spot basis from the thin film interference oscillations in the reflection and transmission spectra [4].

RESULTS AND DISCUSSION

Figure 1 uses a color intensity scale to show the conductivity of a-IZO as a function of both the oxygen content of the sputter gas (left axis) and the relative metals composition (bottom axis). Yellow spots indicate a high conductivity, $\sigma > 2000$ S/cm. Starting from the bottom of the graph, a band of high conductivity angles up and to the right. The solid black line shows the ridge of maximum conductivity. The fact that this line runs diagonally in this (O_2 , %In) plot shows that the optimization of conductivity in a-IZO is a coupled process with the best metals composition depending upon the oxygen content of the sputter gas.

In addition to conductivity, transparency is a critical property for thin film transparent conductors. Figure 2

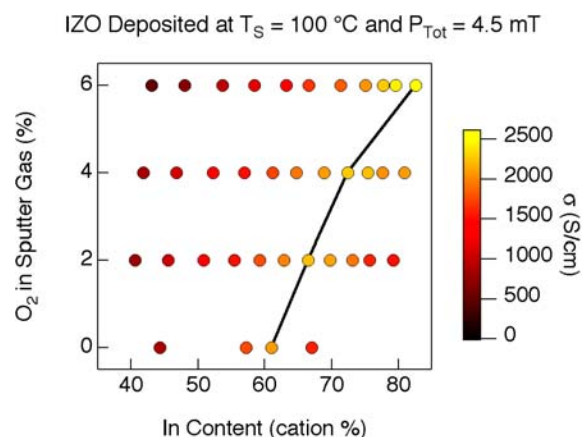


Fig. 1: Conductivity of as-deposited IZO as a function of oxygen content in the sputter gas (left axis) and relative metals composition (bottom axis).

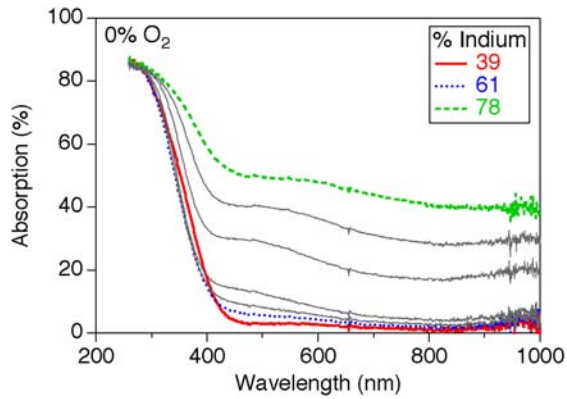


Fig. 2: Optical absorption spectra of IZO samples with varying In content. All samples grown in pure Ar (0% O₂)

shows optical absorption spectra for several representative a-IZO with differing metals compositions but all grown in pure Ar (0% O₂). The a-IZO samples with 39 cation% In (red line) and 61 cation% In (dashed blue line) show almost no absorption for wavelengths longer than about 450 nm. However, for the a-IZO samples with higher indium content, a nearly wavelength independent absorption increases with increasing indium content. For the sample with 78 cation% indium, the visible wavelength absorption is nearly 50%. Examination of the absorption spectra for a-IZO samples grown in 2 to 6% O₂ (not shown) show that this broad visible wavelength absorption occurs when the relative indium content is higher than the indium content to obtain the best conductivity for the given amount of oxygen used (see Figure 1).

Subsequently, constant composition IZO films were sputter deposited onto ambient temperature fused silica substrates from single composition targets with $x = 0.6, 0.7, 0.8$ and 0.84 ($\text{In}_x\text{Zn}_{1-x}\text{O}_y$). The oxygen content of the Ar sputter gas was varied from 0 to 10 %, yielding a varia-

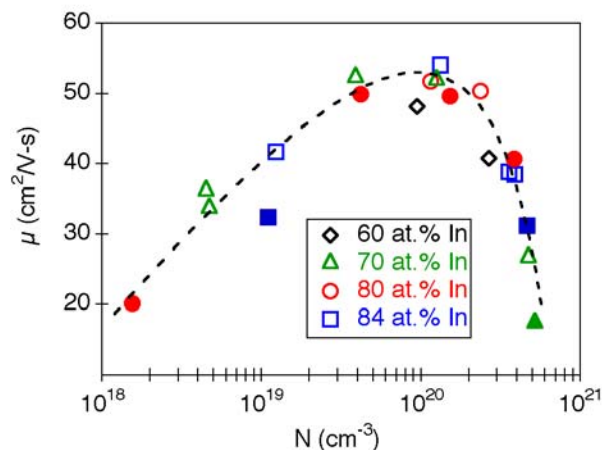


Fig. 3: Mobility vs. carrier concentration for IZO samples grown from single fixed composition sputter targets as indicated in the legend.

tion in the conductivity from $\sigma \approx 2 \times 10^3$ S/cm down to $\sigma \approx 10^{-6}$ S/cm. For these samples, additional Hall effect measurements were done to determine the carrier concentration (N) and electron mobility (μ). Figure 3 shows the mobility as a function of the carrier concentration for the a-IZO samples with $N \geq 10^{18}/\text{cm}^3$. Surprisingly, for all these a-IZO samples, the mobility as a function of the carrier concentration is given by a common curve, independent of the differing metals compositions [5]. This supports the results shown in Figure 1. At $N \approx 10^{20}/\text{cm}^3$, the mobility maximum with $\mu \approx 50$ cm²/V-s, the mobility increased upon cooling to 100 K indicating metallic conduction for the highest mobility a-IZO materials. At low carrier concentration, $N < 10^{19}/\text{cm}^3$, the mobility is thermally activated and at very high carrier concentration, $N \approx 5 \times 10^{20}/\text{cm}^3$, the mobility is nearly temperature independent suggestive of screened ionized impurity scattering.

SUMMARY

In summary, amorphous In-Zn-O (a-IZO) thin film transparent conductors with good TCO properties can be easily deposited at near-ambient temperatures. The a-IZO thin films are also extremely flat. Taken together, these attributes make sputtered a-IZO thin film TCOs an attractive choice for many PV applications.

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REFERENCES

- [1] D.S. Ginley and C. Bright, "Transparent Conducting Oxides", *MRS Bulletin* **25**, 2000, pp. 15.
- [2] M.P. Taylor, D.W. Readey, C.W. Teplin, M.F.A.M. Van Hest, J.L. Alleman, M.S. Dabney, L.M. Gedvilas, B.M. Keyes, B. To, J.D. Perkins and D.S. Ginley, "The electrical, optical and structural properties of $\text{In}_x\text{Zn}_{1-x}\text{O}_y$ ($0 \leq x \leq 1$) thin films by combinatorial techniques.", *Measurement Science and Technology* **16**, 2005, pp. 90.
- [3] T. Minami, T. Kakumu, Y. Takeda and S. Takata, "Highly transparent and conductive $\text{ZnO-In}_2\text{O}_3$ thin films prepared by dc magnetron sputtering", *Thin Solid Films* **291**, 1996, pp. 1-5.
- [4] J.D. Perkins, C.W. Teplin, M. Van Hest, J.L. Alleman, X. Li, M.S. Dabney, B.M. Keyes, L.M. Gedvilas, D.S. Ginley, Y. Lin and Y. Lu, "Optical analysis of thin film combinatorial libraries", *Applied Surface Science* **223**, 2004, pp. 124-132.
- [5] A.J. Leenheer, J.D. Perkins, M. Van Hest, J.J. Berry, R.P. O'hayre and D.S. Ginley, "General mobility and carrier concentration relationship in transparent amorphous indium zinc oxide films", *Physical Review B* **77**, 2008, 115215

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