Amorphous Indium-Zinc-Oxide Transparent Conductors for Thin Film PV

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ABSTRACT
Amorphous InZnO’s (a-IZO) basic PV applicability has now been demonstrated in prototype CIGS, Si Heterojunction (SiHJ) and organic photovoltaics (OPV). However, to move beyond initial demonstration devices, improved TCO properties and processibility of the a-IZO films are needed. Here, RF-superimposed DC sputtering was used to improve the reliable deposition of a-IZO with conductivity $\sigma > 3000$ S/cm.

INTRODUCTION
Amorphous InZnO (a-IZO) films sputter deposited at ambient temperature have excellent opto-electronic properties and smoothness (R$_{RMS} < 0.5$ nm) [1]. Further, the optical transparency and electrical conductivity of optimized a-IZO do not change in damp heat at 85°C, 85%RH [2]. In addition, a-IZO’s basic PV applicability has now been demonstrated in prototype CIGS, Si Heterojunction (SiHJ) and organic photovoltaics (OPV) [2]. However, to move beyond initial demonstration devices, improved TCO properties and processibility of the a-IZO films are needed. For example, for DC sputtering, the % of O$_2$ in the Ar sputter gas which yields optimized a-IZO for a 200 nm thick film, yields grey 1000 nm thick films due to oxygen depletion from the target during film growth. The use of RF-superimposed DC sputtering [3] eliminates this problem and a-In$_{0.8}$Zn$_{0.2}$O$_x$ (87 wt.% In$_2$O$_3$ / 13 wt.% ZnO) films with $R_S < 4$ Ω/sq. and $T_{VIS} = 88$ % (vs glass) were grown.

EXPERIMENTAL APPROACH
Amorphous InZnO (a-IZO) thin films were deposited at ambient temperature onto 2”x2” Eagle 2000 glass substrates by RF-superimposed DC sputtering from an In$_2$O$_3$/ZnO ceramic target in varying Ar/O$_2$ gas mixtures. Three different In:Zn target compositions were used (70:30, 80:20, 87:13 In$_2$O$_3$/ZnO wt%). Thickness was determined by ellipsometry. Typical film thicknesses were 300 nm. Optical reflection and transmission spectra were measured from 300 – 1100 nm using fiber optically coupled CCD array spectrometers. Sheet resistance was measured with a linear 4-pt probe method. Amorphous structure of the films was confirmed by X-ray diffraction (XRD). For each metals composition, the electrical conductivity was optimized with respect to variation of the %O$_2$ in the sputter gas and the RF:DC power ratio.

RESULTS AND DISCUSSION
Figure 1 shows the electrical conductivity for amorphous In$_{0.8}$Zn$_{0.2}$O$_x$ (87:13 In$_2$O$_3$/ZnO wt%) films deposited by RF-superimposed DC sputtering with equal RF and DC power as a function of the %O$_2$ in the Argon sputter gas. As the total power (RF+DC) is increased from 50W to 100W to 150W, the %O$_2$ necessary for maximum conductivity increases. Here, the %O$_2$ is the measured gas composition during deposition and hence oxygen sourced from the target sets a lower limit on %O$_2$ even when no additional oxygen is added. A common maximum conductivity of ~ 3200 S/cm is found for both the 100W depositions (red) and the 150W depositions (black) albeit at different %O$_2$. For the 50W depositions (blue), the conductivity increases monotonically with decreasing %O$_2$ but does not reach a maximum even at the lowest %O$_2$, ~ 0.3%. This suggests that at this lower power, 50W, the residual oxygen sourced from the InZnO sputter target was already too high to achieve the optimized conductivity.

To determine if the film properties were constant with changing thickness, two films with differing thickness were grown by changing only the total deposition time. The conductivity for these two films is shown in Figure 1 using an open red circle for the 1200 nm thick film and a solid red circle for the standard 300 nm thick film. The near overlap of the two data points in Figure 1 shows that the conductivity of the films deposited by RF-superimposed DC sputtering is not changing with film thickness. This
was not the case with pure DC sputtering due to gradual reduction of the InZnO sputter target surface with increasing deposition time. This improved deposition stability achieved by RF-superimposed DC sputtering is important in that it now allows a-IZO film thickness to be treated as a device engineering variable without having to re-optimize the deposition parameters for each different thickness of interest.

Figure 2 compares the optical transmission spectra normalized to a bare glass substrate for the 300 nm thick (blue spectra) and 1200 nm thick (red spectra) a-IZO films just discussed above. With the improved deposition stability of RF-superimposed DC sputtering, the 1200 nm thick film has a low sheet resistance of $R_s = 3.2 \, \Omega/sq$. coupled with a high average transparency of $\sim 85\%$ across the visible and near-IR.

Figure 3 compares the maximum conductivity achieved with optimized RF-superimposed DC deposited a-IZO films (red triangles) with best obtained by DC-only deposition (black circles) [4]. For the RF-superimposed this corresponds to optimization across both the RF:DC mixture and the $%O_2$ but for a fixed total deposition power (RF+DC) of 100W. The RF-superimposed DC sputtering process yields about a 20% increase in conductivity for the three different compositions tested. In addition, the optimized conductivity increases monotonically with indium content from about $\sigma = 2500$ S/cm at 58 at % In to 3200 S/cm at 80 %. To make clearer how the conductivity scales with In content, Figure 4 shows the maximum conductivity for RF-superimposed DC deposited a-IZO films normalized to their relative In content, showing that the conductivity/In-content is nearly constant at $\sim 40$ (S/cm)/(at.% In). This suggests that a-IZO may be essentially diluted and structurally stabilized amorphous indium oxide which is itself a good TCO but is challenging to deposit and crystallizes easily at 180 °C [5]. In contrast, a-IZO containing 20 – 40 at.% Zn does not crystallize until 500 °C or higher [1].

FIGURE 2: Optical transmission of 300 and 1200 nm thick a-IZO thin films.

FIGURE 3: Comparison of conductivity vs indium content for differing levels of process optimization.

FIGURE 4: Maximum conductivity normalized to indium content for optimized a-IZO.

SUMMARY

In summary, a-IZO thin film transparent conductors with excellent TCO properties can be easily deposited at ambient and near-ambient temperatures. By using RF-superimposed DC sputtering, conductivities of $\sigma = 3200$ S/cm can be reliably achieved for $In_{0.8}Zn_{0.2}O_x$ films. Further, prior work has shown that a-IZO is optically and electrically inert for up to 40 days in damp heat (85°C, 85% RH) and also is an effective water vapor transport barrier making it a very promising TCO for thin film PV applications.
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