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Zinc oxide-doped indium oxide (IZO): an amorphous transparent conducting oxide for use in tandem solar cells

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Abstract

Zinc oxide-doped indium oxide (IZO) is an amorphous transparent conducting oxide (TCO) exhibiting excellent properties for use in tandem solar cells. Similar to high mobility TCOs, it has a reduced absorption of near IR photons leading to an increased transmission to the bottom cell in a tandem stack. As a result, IZO is a potential replacement of traditional TCOs used as the top contact in the Cu(In,Ga)Se2 cell when used in a tandem solar cell. A monolithically fabricated dye-sensitized Cu(In,Ga)Se2 tandem solar cell suffers from corrosion of the Cu(In,Ga)Se2 absorber by the DSC electrolyte. This paper reports the successful use of IZO to reduce the rate of etching compared to AZO of similar thickness, when used to prevent the etching of an Au substrate.

Introduction

The combination of one or more solar absorbers into a single device has been shown to deliver a single cell with a step jump in efficiency, higher than that of either single cell. Currently the most efficient device is a triple junction InGaP/GaAs/InGaAs solar cell. [1] In order for a tandem cell to be effective, each absorber must have overlapping EQE spectra such that all light entering the device is absorbed. The dye-sensitized solar cell (DSC) and Cu(In,Ga)Se2 (CIGS) solar cell have been combined in the past into a tandem cell, due to their unique ability to tune their performance parameters. [2]

This DSC/CIGS tandem device demonstrated efficiencies up to 15%, an improvement over both individual cells. Despite this increase in performance, the device measured was a mechanically stacked combination of both individual cells. An attempt to fabricate a monolithic cell was successful, with an efficiency of 12.2%. [3] It was discovered that after 2 hours of the device being assembled and measured that the performance would rapidly decline, due to corrosion of the CIGS layer by the \( \Gamma^+I_3^- \) electrolyte used in the DSC top cell. It was postulated that the electrolyte was able to percolate through pinholes in the TCO of the CIGS cell.

It is therefore crucial that the elimination of corrosion should be prevented in the monolithic cell to make this technology of use. By either changing the surface of the TCO to reduce pinholes or covering the surface of the TCO with a buffer layer, it was theorised that percolation may be impeded.

The TCO is deposited on the CIGS cell by a magnetron sputtering process. It is possible to vary the temperature of the substrate during the deposition, with higher temperatures often leading to higher quality films, due to the reduction of pinholes and the higher crystallinity. CIGS poses a problem in that it is sensitive to high temperatures, causing the p-n junction to breakdown. To prevent this, the temperature during the deposition of the TCO is limited to room temperature.

Zinc oxide-doped indium oxide (IZO) is an amorphous TCO which may be deposited at low/room temperature. [4] IZO may potentially prevent the electrolyte percolation, due to the lack of grain boundaries in an amorphous material. This may provide an excellent replacement to the TCOs commonly used as the top contact on CIGS: aluminium doped-zinc oxide (AZO) and tin-doped indium oxide (ITO). IZO is a viable replacement to AZO and ITO due to its equivalent optical and electronic performance. The transmission of IZO compared to AZO and ITO can be seen below in Fig 1.

To determine the suitability of using IZO as a protective barrier against the electrolyte corrosion, gold was chosen as a replacement to CIGS in this study. Gold is readily etched by a typical DSC electrolyte and much easier to prepare. A 50 nm Au sample can be fully etched in under 60 seconds.
*Experimental*

To ensure adhesion of Au to the substrate, a ~200 nm thick layer of iSnO₂ was RF magnetron sputtered (Orion 8, AJA International) at 200°C onto a 5 x 5 cm soda-lime glass substrate at a working pressure of 0.13 Pa, with a power of 180 W and oxygen content of 10 %. Next a layer of gold is sputtered via DC sputtering (Quorum Technologies) at room temperature onto the glass/iSnO₂ substrate. An aluminium mask with 36 0.5 x 0.5 cm square holes is placed on top of the substrate prior to deposition. 36 ~50 nm Au squares are therefore deposited on the iSnO₂ surface. These are cut into individual squares before TCO deposition.

*iSnO₂ Deposition*

A ~400 nm layer of iSnO₂ was deposited onto the glass/iSnO₂/Au samples. This layer is deposited using identical parameters as outlined before.

*Au Etching Study*

Gold is rapidly etched upon immersion in an I⁻/I₃⁻ electrolyte. An electrolyte solution commonly used in DSCs was prepared, consisting of 0.6M 1-butyl-3-methylimidazolium iodide, 0.03M I₂, 0.5M tert butylpyridine and 0.1M guanidine thiocyanate in a 85:15 volume ratio of acetonitrile and valeronitrile. [5]

Each sample was immersed into an electrolyte solution face up for a maximum of three hours. At 1 hour intervals the sample was removed, cleaned with DI H₂O and isopropyl alcohol and examined under an optical microscope at a magnification of 50x. After examination the sample was again immersed into the electrolyte bath.

*Results and discussion*

*200 nm AZO and IZO Performance*

With most crystalline TCOs, such as ITO, AZO and ITiO heating the substrate during deposition will lead to more desirable opto-electronic properties. A deposition at room temperature typically gives smaller crystal grains, often with a larger number of pinholes in the film. Fig 2a) and Fig 2b) indicates the difference in the ability to resist the etching from the electrolyte, which is apparent. The gold layer beneath the AZO in Fig 2a) is almost completely etched from the substrate, with cracks in the top of the TCO visible. The amorphous IZO in Fig 2b) can be seen to provide a much more stable barrier against etching from the electrolyte, with no cracking of the TCO film.

A second set of samples were prepared, with a 1 micron thick AZO layer and a 500 nm thick IZO layer. By increasing the thickness of the TCO it was hoped that the longevity of the gold layer could be increased.

*AZO Deposition*

~200nm and ~1 μm thick layers of AZO was RF sputter deposited (Orion 8, AJA International) from an aluminium-doped zinc oxide ceramic target (99:1 wt ZnO:Al₂O₃, 3” dia, 0.125” thick) at room temperature onto a 5 x 5 cm soda-lime glass/iSnO₂/Au stacked substrate as prepared above. This was achieved at a working pressure of 0.13 Pa, an argon flow rate of 5 sccm and a power of 180 W.

*IZO Deposition*

~200 nm and ~500 nm thick layers of IZO was deposited from a ceramic zinc oxide-doped indium oxide target (90:10 wt In₂O₃:ZnO, 3” dia, 0.125” thick) onto the glass/iSnO₂/Au substrates prepared above. RF magnetron sputtering was used to deposit these films (AJA International) at room temperature with an oxygen content of 1%, argon/oxygen flow rate of 7 sccm, working pressure of 0.13 Pa and a power of 120 W.
Fig 2a). A 200 nm layer of AZO deposited onto the glass/iSnO₂/Au stack, submersed in an I⁻/I₃⁻ electrolyte for 60 mins.

Fig 2b). A 200 nm layer of IZO deposited onto the glass/iSnO₂/Au stack, submersed in an I⁻/I₃⁻ electrolyte for 60 mins.

1 μm AZO and 500 nm IZO Performance

Fig 3a). A 1 μm layer of AZO deposited onto the glass/iSnO₂/Au stack, submersed in an I⁻/I₃⁻ electrolyte for 60 mins.

Fig 3b). A 1 μm layer of AZO deposited onto the glass/iSnO₂/Au stack, submersed in an I⁻/I₃⁻ electrolyte for 180 mins.

Increasing the thickness of the AZO layer dramatically reduced the rate of the gold etching after 60 mins, which can be seen in Fig 3a. No visible cracks are present and considerably more gold is left on the substrate than the 200 nm IZO substrate in Fig 2b). Even after immersion in the electrolyte bath for 180 mins the AZO sample in Fig 3b) has more gold present than the 200 nm IZO. The gold under the 500 nm layer of IZO in Fig 4a) is clearly more corroded after 60 mins than under a micron of AZO. This would suggest that despite the improvement an amorphous layer gives to the reduction of etching, the thickness of the layer still has to be optimised. Again after immersion for 180 mins, IZO can be seen in Fig 4b) to be much worse than the micron thick AZO layer.

Fig 4a). A 500 nm layer of IZO deposited onto the glass/iSnO₂/Au stack, submersed in an I⁻/I₃⁻ electrolyte for 60 mins.
Despite these latter findings, initial results are promising in that an amorphous layer may be the key to preventing electrolyte corrosion of the CIGS layer in a tandem DSC/CIGS solar cell. Further investigation into the relationship between film thickness and etching rate is vital to the continuation of this study. Depositions at room temperature are always likely to cause pinholes in the sputtered layer, as such a 400 nm iSnO₂ was deposited onto a glass/iSnO₂/Au stack at 200°C and the result from immersion in the electrolyte bath for 60 mins can be seen in Fig 5. This film clearly offers better protection than any TCO presented regardless of thickness.

As this is not a conducting oxide it would not be suitable for use as the contacting layer in the CIGS cell prior to tandem cell assembly. However it may find use as a ‘capping’ layer, being deposited on top of the TCO, in a similar fashion reported when using ITiO in DSCs. [6] In addition the temperature used to heat the substrate would not be ideal for the CIGS cell.

Optimisation of the amorphous layer structure when deposited will be the scope of further work. Clearly pinholes exist in the film and need to be eliminated. Surface imaging on the nanometre scale through the use of SEM is vital to determine the structure of IZO. Elimination of these pinholes could be delivered through adjustment of the deposition technique, causing a potential change in the IZO structure and thus may block pinhole pathways to the CIGS surface.

Conclusion

From the results presented it can be concluded that for the same thickness (200 nm), IZO is a better barrier against electrolyte etching of the Au layer than AZO. The IZO layer however does not provide complete protection against etching. Increasing the thickness of either layer decreases the etching rate proportional to the thickness. Further investigation and understanding of the IZO surface via techniques such as SEM and TEM, should provide insight into the optimisation of IZO in order to prevent electrolyte etching through pinholes present in the film.

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