

## Aluminium doped zinc oxide thin film contacts for use in dye sensitized solar cells

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### Abstract

Aluminium doped zinc oxide films are deposited for use in dye sensitized solar cells. High temperature stability is achieved by varying the sputtering conditions, whilst maintaining high transmission. The most stable film of the set deposited increased to only 9.4  $\Omega$ /sq after heating in air at 400°C from 5.1  $\Omega$ /sq. Initial solar cells are made with encouraging efficiencies of 8.2% reported

### Introduction

Over the last 15 years, dye sensitized solar cells (DSCs) have emerged as a realistic, cheaper alternative to conventional inorganic, p-n junction type solar cells, with state of the art efficiencies reaching over 11% on small scale devices [1]. Abundant, low toxicity materials, as well as low production costs has attracted much academic and commercial interest as a viable route towards low cost power generation.

Figure 1 shows a schematic of a typical, 'laboratory scale' device. A mesoporous  $\text{TiO}_2$  layer is deposited on a transparent conducting oxide (TCO) layer coated on a glass substrate. The nanocrystalline and mesoporous  $\text{TiO}_2$  layer is then coated with a monolayer of a sensitizing dye, which typically absorbs light in the visible up to 720nm [2]. The circuit is then completed with an electrolyte containing an iodide/ triiodide redox couple in a solvent, in contact with another TCO coated with platinum particles, acting as counter-electrode.

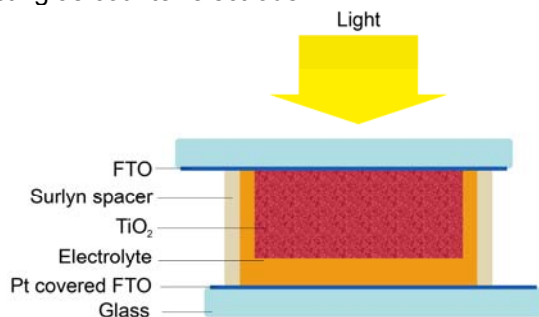


Figure 1 – Schematic of a DSC.

The TCO is an important part of the DSC since it governs both the amount of photons which are able to pass through to the dye, as well as contributing greatly to the series resistance of the device. Generally, fluorine doped tin oxide (FTO) is the TCO of choice when designing DSCs since it is both chemically and thermally very stable. It is able to withstand the high annealing temperatures (~450°C), without loss of conductivity, and is able to survive the, at times, acidic nature of the DSC manufacture process [3]. FTO however suffers from low conductivity compared to other TCOs, as well as low transmission, and so the present investigation is driven by the need to address an alternative transparent conductor.

Indium oxides based TCOs, such as tin doped indium oxide have good transparency in the visible, coupled with high conductivity, largely as a result of a large carrier concentration. The high transmission in the infrared of high mobility transparent conductors (HMTCOs) such as titanium doped indium oxide (ITiO) has recently shown to provide a method to improve the transmission of photons through a top DSC, for a bottom CIGS cell in a tandem structure [4]. Although promising, such TCOs are not a commercially viable alternative to FTO because of the high cost of indium, and so another alternative should be explored.

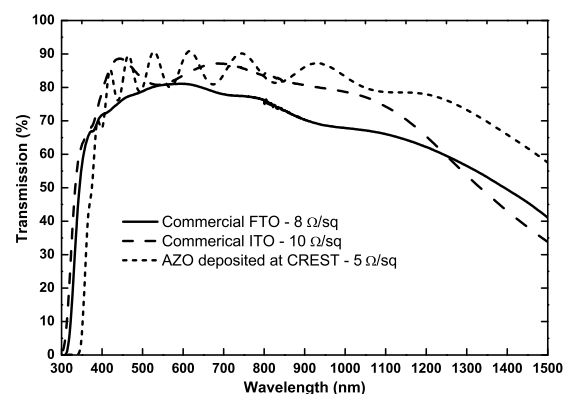


Figure 2 – Comparison of transmission spectra for different TCOs. AZO has high transmission whilst retaining good sheet resistance.

Zinc oxide based TCOs offer an interesting compromise between indium and tin oxide based systems. Aluminium doped zinc oxide (AZO) is already widely used in various thin film photovoltaic technologies, particularly with CIGS based systems [5], as well as amorphous silicon solar cells [6]. Utilising abundant materials, as well as providing high conductivity and high transmission (Figure 2), they offer a possible alternative to the current monopoly of FTO within DSC research.

This paper focuses on the deposition of AZO films for use with DSCs. Specifically, high transmission and high conductivity are needed to provide the best substrate possible for fabricating highly efficient devices. Initial work has been performed to combine these requirements with good heat stability, since the fabrication of a DSC involves at least one high temperature sintering step in air. Finally, preliminary trials have been made to solve the low chemical stability of these films, by the addition of a chemically stable oxide on the AZO surface.

## Experimental

AZO layers were deposited by RF magnetron sputtering (Orion 8, AJA International), using a 0.5 wt% Al<sub>2</sub>O<sub>3</sub> doped ZnO target on 1.1mm thick sodalime glass substrates, at 300°C. All films were deposited for 3 hours, in argon, and no post deposition heat treatment was performed. In one set of films, the working pressure was maintained at 0.5mTorr whilst the sputtering power was varied between 140 and 180W (films named PW), whilst in another set of films, the power was maintained at 180W and the pressure was varied between 0.5 mTorr and 10mTorr (films named PR).

DSCs were fabricated using a procedure similar to one previously reported [7]. The prepared AZO films were first deposited, by sputtering, with a thin SnO<sub>2</sub> layer to protect the AZO from being etched from the acidic properties of the deposited paste. The films were then cleaned using deionised water and IPA, and then a 13.3µm thick transparent TiO<sub>2</sub> (Dyesol, DSL 18NR-T) layer was deposited on the TCO by screen printing. This was then followed by the deposition of a 3.3µm opaque TiO<sub>2</sub> layer (Dyesol, DSL 18NR-AO) to aid absorption in the red part of the spectrum via light scattering. The films were then annealed at 400°C for 20 minutes, and immersed in a 0.5mM solution of N719 (Ruthenium 535-bisTBA, Solaronix SA) in 1:1 volume ratio of acetonitrile and tert-butanol for 20 hours. Counter electrodes were prepared by placing a solution of hexachloroplatinic acid in propanol on FTO substrates, and sintering in air at 500°C for 15 minutes. The counter and working

electrodes were then sealed together using a hot melt polymer gasket, before a solution of 0.6M 1-butyl-3-methylimidazolium iodide, 0.03M I<sub>2</sub>, 0.5M tert butylpyridine and 0.1M guanidine thiocyanate in a 85:15 volume ratio of acetonitrile and valeronitrile was introduced into the cell through a pre-drilled hole in the counter electrode.

Finally, transmission spectra were taken using a Cary 5000 (Varian) spectrophotometer and sheet resistance measurements were made using a 4 point probe (Jandel) connected to a source meter (Keithley 2440). Current-voltage characteristics of devices were taken using a Labview controlled Keithley 2425 source meter, under AM1.5G solar spectrum from a solar simulator (Sciencetech Inc). The intensity was adjusted to 1 sun using a silicon photodiode fitted with an optical filter (Schott, KG-5) to ensure a good spectral match between the reference diode and the DSC.

## Results and analysis

All solar cell technologies, regardless of type, require the maximum amount of photons possible to reach the absorbing layer of the solar cell for current generation. In the DSC, the TCO is the first layer which photons will pass through, and so, absorption and reflection losses need to be as small as possible. Figure 3a shows transmission spectra of selected AZO deposited films, varying pressure (the power was constant at 180W), whilst Figure 3b shows transmission spectra of the AZO films, varying power (the pressure was constant at 0.5mTorr).

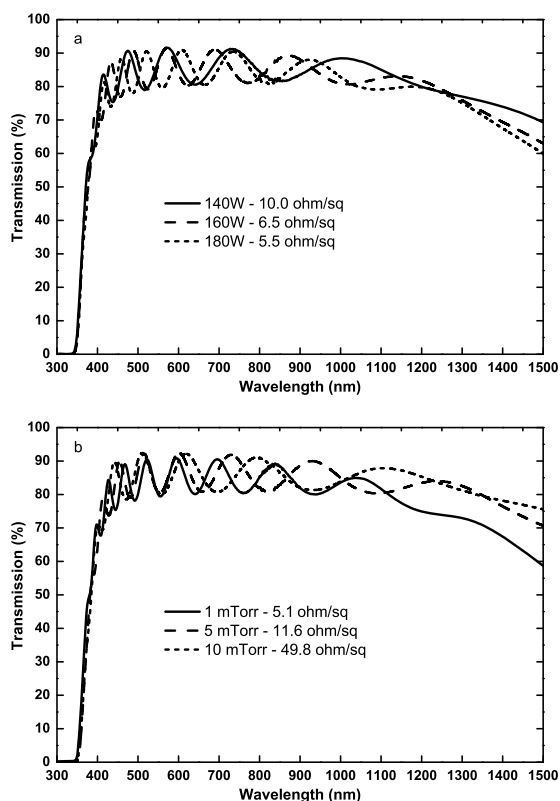


Figure 3 – Transmission spectra of films deposited varying a) power (pressure constant at 0.5mTorr) and b) pressure (power constant at 180W). Argon was used as the sputtering gas, and the temperature was 300°C.

In both sets of films, the transmission in the region associated with absorption by the sensitizing dye (from 350-750nm) is high, regardless of deposition condition. The main differences between the 6 sets of data is the location of the maxima and minima of the interference fringes as a result of the varying film thicknesses (all films are between 700 and 900nm thick), as well as the amount of light transmitted in the infra red. This can be attributed to a difference in the carrier concentration of the 6 sets of films. Films of higher carrier concentration exhibit lower NIR transmission due to increased absorption by the free carriers in the film. The variation in sheet resistance of these films is also shown in each figure and shows a high dependency on the sputtering conditions. Table 1 highlights this more clearly, for a larger set of samples.

A clear trend can be seen with the two varying deposition conditions. With increasing power, the sheet resistance of each film decreases, reaching a minimum at 180W. The same can be seen for increasing sputtering pressure, although to a more exaggerated extent. Films sputtered at 10 mTorr show a very high sheet resistance, compared to films deposited at lower pressures. As previously noted, this may be due to a decreased carrier concentration in

these films compared to those sputtered at lower pressures, as is noted from the high transmission in the infrared of high pressure sputtered films. Hall Effect measurements would clearly indicate this, and will be explored in future work on these thin films.

Name	Power (W)	Pressure (mTorr)	R <sub>sheet</sub> (Ω/sq) before	R <sub>sheet</sub> (Ω/sq) after
PW01	140	0.5	10.0	51.7
PW02	150	0.5	7.9	39.8
PW03	160	0.5	6.5	23.7
PW04	170	0.5	5.8	16.2
PW05	180	0.5	5.1	13.9
PR01	180	1	5.1	9.4
PR02	180	2	7.2	21.3
PR03	180	5	11.6	35.7
PR04	180	10	49.8	OOR*

Table 1 – Sheet resistance measurements of different films before and after annealing in air at 400°C for 20 minutes. \* OOR= Out of range of measurement.

Table 1 also shows the change in sheet resistance of films, after annealing in air at 400°C for 20 minutes. Heat stability is one of the most important characteristics a TCO must have in DSC fabrication. The TiO<sub>2</sub> paste which is deposited needs a high temperature sintering step to burn off the organic part of the deposited film, and anneal the TiO<sub>2</sub> particles together to form an electrical pathway for electrons to travel to the front current collector. So, it is important that the TCO can undergo the high temperature process, without a significant loss in conductivity, ensuring as low a series resistance as possible. The variation in sheet resistance of the films is very large depending on the sputtering conditions. Low sputtering powers show relatively low thermal stability, however the most thermally unstable films are seen with the highest sputtering pressure (10mTorr), resulting in an immeasurable sheet resistance. Interestingly, although films PW05 and PR01 both start with initially the same sheet resistance, which is not unusual since the sputtering pressure is very similar, the films exhibit a different thermal stability, with the film sputtered at slightly higher pressure having a higher thermal stability. Work is on going to study the causes of these different thermal effects.

Following these results, DSCs were fabricated using films based on PR01, since this film was the most thermally stable of the set. Figure 4 shows the resulting J-V curve from the best fabricated cell, and shows the potential for use of AZO thin films as transparent conductors for DSCs.

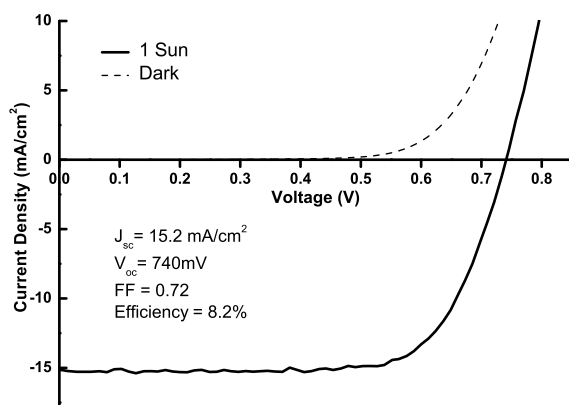


Figure 4 – J-V characteristics of a DSC fabricated on an AZO thin film. The active area was  $0.282\text{cm}^2$ .

This result is very encouraging considering no optimisation was performed on the  $\text{SnO}_2$  barrier layer, to protect the AZO underneath. The lower current may be associated with absorption by photons in the non-optimised  $\text{SnO}_2$  layer. The high temperature sintering process needed for use in DSCs clearly does not affect the performance of the device. This is highlighted in the very good fill factor associated with this device.

Further work is underway to optimise the process. Here the acidic  $\text{TiCl}_4$  treatment was not used in our preliminary trials, however  $\text{TiCl}_4$  has been shown to improve current collection in DSCs [8]. Optimisation of the  $\text{SnO}_2$  layer is needed to ensure an optimised protecting layer for the AZO from chemical attack, and also to improve overall transmission of the device.

## Conclusions

Preliminary trials on the use of AZO films in DSCs has been reported. High temperature stable films are able to be sputtered using high sputtering powers combined with low pressures. The transmission in the visible region of such films is not effected by varying the deposition conditions in this way. An initial device performance of 8.2% is reported which is encouraging. Further optimisation is needed to raise the efficiency higher, by improving the protective  $\text{SnO}_2$  layer deposited after deposition.

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