Ultrasonically Sprayed Aluminium-doped Zinc Oxide Layers for Transparent Conductive Oxide in Thin Film Solar Cells

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Abstract

Aluminium-doped zinc oxide (AZO) thin films have been deposited on glass substrates using ultrasonic spray deposition whilst varying the operational parameters. Electrical and optical properties were investigated as a function of the deposition parameters and the optimum conditions were defined. The optimum parameters result to films with a sheet resistance of ~6kΩ/□ when they are as deposited and to ~1kΩ/□ for annealed films in vacuum. The resulting transparency ranges from 80 to 85% for optimum films.

Introduction

Transparent conducting oxide (TCO) films are used in an increasing number of optoelectronic devices, such as displays, smartphones, as well as solar cells. Zinc oxide (ZnO) is highly investigated because of its non-toxicity and high abundance and as a consequence, lower material cost. When doped with aluminium, ZnO has improved electrical properties and it is ideal for TCO applications [1]. Among the methods for thin film deposition, spray pyrolysis is a low cost, atmospheric deposition technique which is simple in operation and allows easy adjustment of the spray characteristics. The use of spray deposition, as it is an atmospheric process, is an alternative to the conventional, vacuum-based techniques such as sputtering, for thin film deposition. There is on-going research for sprayed films in copper, indium and selenium-based (CIS) solar cells [2-4] since the use of spray deposition can effectively reduce the manufacturing costs.
In the present work, AZO thin films have been deposited by ultrasonic spray pyrolysis, with varying deposition parameters. Some of the variable parameters are the type of precursor salts, solvent type, solution concentration, sprayed solution flow rate, substrate temperature and process parameters such as atomization power and carrier gas flow.

Experimental

The system consists of the precursor solution, a syringe pump for the liquid delivery, a substrate heater, a spray nozzle and an atomizer, which oscillates at ultrasonic frequencies. The solution is first atomized and the formed droplets are transported to the heater using nitrogen as the carrier gas.
The precursor used was a solution of zinc acetate and aluminium chloride. Different precursors were used (hydrated and anhydrous compounds), dissolved in methanol, or water (or a mixture) and in various concentrations. Spraying conditions were also varied, including the distance between the nozzle and the heater, the atomization power and the flow of the precursor solution and carrier gas.
The conditions for the deposition of AZO thin films with the highest conductivity obtained so far in this study are reported here. It was observed that in order to obtain conductive films, methanol instead of water should be used, a moderate flow rate of the carrier gas, low solution flow, low precursor concentration and high temperatures. Electro-optical characterisation has been carried out on as-deposited and annealed AZO films using UV-Vis-NIR spectrophotometry, 4 point probe and Hall effect measurements, whilst the structural properties of the films were investigated using SEM and XPS techniques.

Results and Discussion

Ultrasonic spray deposition is a versatile technique for depositing thin films. However, as a result, a wide variety of parameters must be optimised in parallel to produce films of high conductivity and high transmission. The following section describes the optimisation of each parameter, and its effects on the film quality and the deposition process.

Atomization power: A narrow band of input power (1.3 to 1.4 Watts) to the spray head is ideal for the formation of a fine, low viscosity mist. Lower power results in an inefficient atomization of the drops, whilst higher power leads to droplet cavitation within the nozzle.
Precursor concentration: The optimum concentration of the solution is in the range of 0.1-0.2M. At higher concentrations, the obtained films are powdery, whilst at lower concentrations the deposition rate is very low.

Solvent: The use of methanol as a solvent leads to AZO films of higher conductivity compared to water alone. The lower density and surface tension of methanol enables the formation of smaller atomized droplets [5]. A solvent with increased viscosity will delay the fluid breakup, which will result in the increase of the average droplet size [6]. Higher surface tension also results in a higher droplet size.
Carrier gas: High carrier gas flow rates lead to the cooling of the heated substrate, whilst low flow rates do not deliver the droplets efficiently to the substrate surface. An optimum value of 6 litres per minute (LPM) was used. The cooling effect of the carrier gas was observed by using a thermographic camera (VarioCAM). The cooling effect is illustrated in a thermal image, shown in Figure 1. It was concluded that a gas flow rate of 10LPM can cause an approximate 40°C drop in the substrate temperature, which can lead to significant temperature uncertainties during deposition.

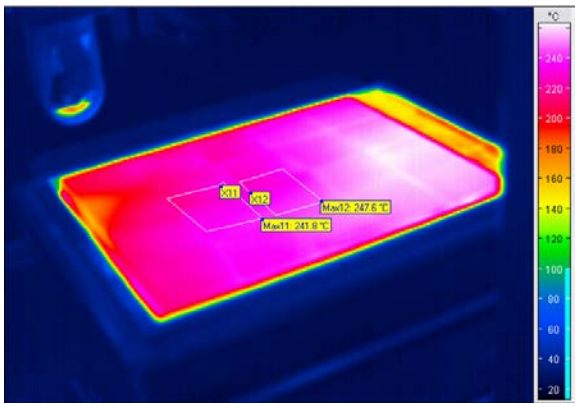

Figure 1: Thermal image of the hot plate showing the cooling effect of carrier gas (10LPM of nitrogen).

The combined cooling effect from the carrier gas and the atomized droplets is compensated by raising the substrate temperature. Thus, higher temperatures result in higher conductivity of the films. When high substrate temperatures are used (T_s>400 ^{o}C), the resulting films are conductive. However, at higher substrate temperatures (T_s>475^{o}C), the droplets are too dry when they arrive at the surface and some of the droplets form separate domains [6] as seen in Figure 2. As a result, the charge transport across the domain boundaries is impeded, which results in a higher sheet resistance. The optimum temperature (475°C) results in the lowest sheet resistance and smoothest surface. Also, films deposited at 475°C give the highest transmission as shown in Figure 3, for films of the same thickness. At temperatures lower than 450°C, the films are powdery due to incomplete pyrolysis of the solution. At temperatures higher than 500°C the nozzle is heated and there is rapid solvent evaporation inside the spray head, thus leading to clogging of the nozzle.

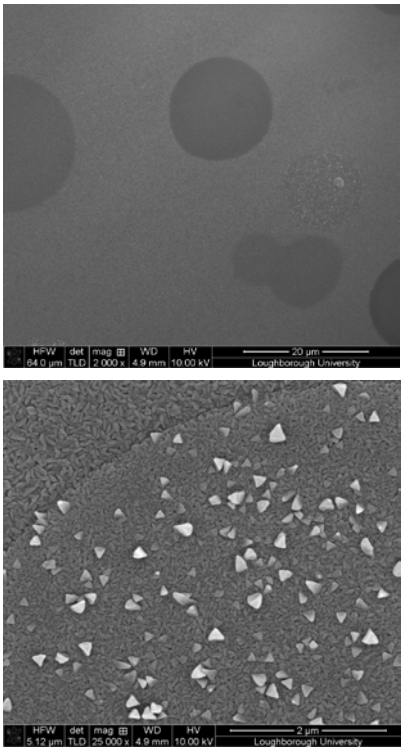

Figure 2: SEM images of the samples, deposited at 550°C. Stacking of dried droplets is shown (top). The image was magnified on the edge of the droplet (bottom).

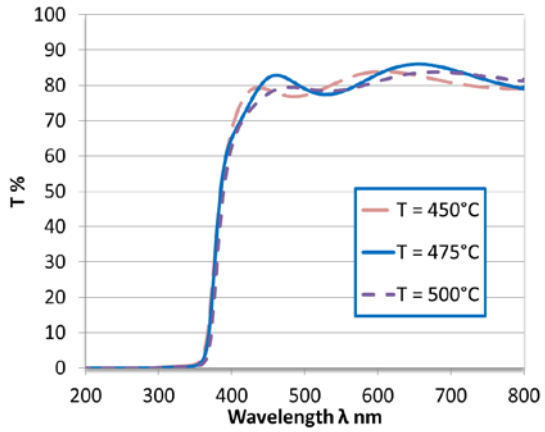

Figure 3: Transmission data of AZO thin films, as-deposited in different temperatures.

Annealing: The sheet resistance of the films is significantly decreased by annealing, as annealed samples have improved crystal quality. In addition, the high initial resistance can be attributed to the oxygen being adsorbed on the film surface, during deposition in an oxygen containing atmosphere [7]. The presence of adsorbed oxygen was presumed

by observing the composition-depth profile by X-ray photoelectron spectroscopy (XPS), shown in Figure 4. The fact that the oxygen concentration is higher than zinc shows that there is a decrease in the oxygen vacancies, which makes the film resistive [8]. However, the adsorbed oxygen is removed to some extend by annealing the sample in vacuum, resulting in a decrease of the sheet resistance by three orders of magnitude. Nevertheless, the compositional ratio of the oxygen appears to be lower in other films deposited under the same parameters. Therefore, the deposition parameters should be investigated into more detail, as minor factors seem to affect the results. For instance, the amount of time that the sample remains on the heater after the deposition should be carefully controlled.

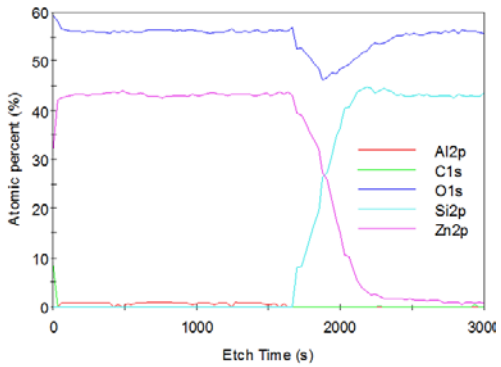

Figure 4: XPS depth profile of AZO thin film, as-deposited at 550°C. Doping level: 4% Al:Zn.

Nozzle-heater distance: An optimum distance of 10cm was used. When a longer working distance is used, the droplets follow a longer path and thus they absorb more heat. In this case, the reaction occurs in the gas phase [9] and the resulting films are powdery and more resistive.

Thickness: SEM surface images (Figure 5) of the films show that the grain shape and size change with the film thickness. When the thickness is increased, the grains are flake shaped, while in thinner films, the grains are rounded and elongated. Also, the resistivity of the films is improved with increased thickness, indicating an improvement in the film quality during extended growth times.

Doping level: The doping level used in the precursors was 4% atomic ratio Al:Zn. However, interestingly, the aluminium concentration in the film is much lower than in the precursor. This is evident from the depth profile of the sample (Figure 4), where the aluminium concentration is ~1%. The significant difference in the concentration can be attributed to the air extraction used in the enclosure of the spray deposition equipment. The air turbulence formed by the extraction is possibly causing some of the precursor not to be deposited on the glass substrate.

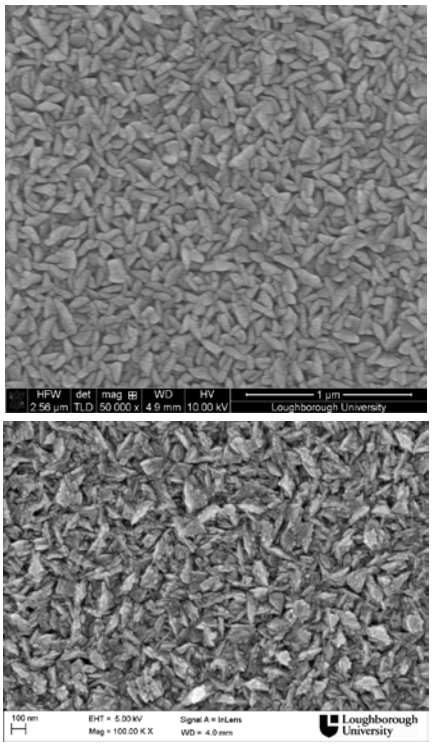

Figure 5: SEM surface images for films of different thickness. Films of ~200nm (top) and ~400nm thickness (bottom).

The optimum parameters are summarised in Table 1, while Table 2 shows indicative values of the sheet resistance measurements with varying substrate temperature.

Optimum Deposition Parameters			
Doping level	4% Al:Zn	Flow rate of precursor	0.3 ml/min
Concentration	0.2 M	Atomization power	1.3 W
Temperature	475 °C	Volume of precursor	18 ml

Table 1: Optimum deposition parameters used in this study.

	As-deposited	Annealed
550°C 0.3 ml/min 1.4 W 9 ml	1.06 MΩ/□	19 kΩ/□
500°C 0.6 ml/min 1.3 W 18 ml	437 kΩ/□	9 kΩ/□
475°C 0.6 ml/min 1.3 W 18 ml	6 kΩ/□	1 kΩ/□

Table 2: Obtain sheet resistance of indicative samples, before and after the deposition.

Future Work

The optimization was carried out based using solutions in 100% methanol. In future work, the process parameters have to be re-optimised for different solvents. A solvent mixture should be used, which will result in a combination of high homogeneity of the films, low surface roughness and high conductivity. Also, the effect of the doping level on the electrical properties should be investigated more thoroughly and the concentration of aluminium on the films can be compared with the precursor, for various doping levels.

Overall, even under the optimum deposition parameters the films are considerably resistive, with a sheet resistance of around 1kΩ/□. This is caused by the oxygen adsorption on the surface of the films, thus fewer oxygen vacancies, poor crystalline quality of the material and by the cooling effect on the substrate surface during the deposition. Further investigation will be carried out in order to eliminate these factors.

Conclusion

AZO thin films have been deposited by ultrasonic spray pyrolysis technique and the opto-electronic properties of the films have been investigated. The spray parameters for the deposition of transparent conductive films have been optimised. However, further work is now needed to improve resistivity and produce performance comparable with AZO thin films deposited by vacuum-based methods.

Acknowledgements

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