Spectrally selective doped zinc and aluminium oxide thin films prepared by spray pyrolysis for solar energy applications

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Abstract. Metal oxide thin films have been used in thin film solar cells and other solar energy applications for many years. The concern has been to improve their physical, electrical and optical properties in order to increase their efficiency and lower their production costs. Zinc oxide doped with aluminium (ZnO:Al) and aluminium oxide doped with zinc (Al_2O_3:Zn) thin films have been produced by a spray pyrolysis process onto standard microscope glass slides at different substrate temperatures and for different solution concentrations, spray times and pressure. The main objective was to produce single, double and triple layer thin films and characterized them for their optical, electrical and structural properties. The spectral selectiveness of these oxide thin films and their applicability in producing efficient solar cells has been investigated. Optical measurements have been performed in spectrophotometers in the visible-to-near infrared (NIR-VIS) and infrared (IR) ranges. Structural characterization has been performed using an Atomic Force Microscope and a Tencor Alpha Step IQ Profiler. A four-point resistance square probe was used for electrical characterization. The transmittance, reflectance, thickness and the film resistance have been experimentally obtained. The solar transmittance of 88 % has been achieved for Al-doped zinc oxide (ZnO:Al) films whereas 71.94 % has been obtained for Zn-doped aluminium oxide (Al_2O_3:Zn). The film thicknesses fall in the range 0.14 µm to 87.7 µm. The wavelength-dependent refractive index of the films has been evaluated from reflectance and transmittance measurements. The refractive indices ranged from 1.28 to 2.0 for the probed wavelength range. The properties of these thin films have been modelled using the Bruggemann and Maxwell-Garnett effective medium theories. The film resistivity values of $2.43 \times 10^{-4}\,\Omega$m to$11.80 \times 10^{-4}\,\Omega$m have been achieved. These film properties have been related to applications in thin film solar cells.

Key words: spectrally selective, spray pyrolysis, thin film, characterization.

1. Introduction

The utilization of solar technologies requires the development of materials that can be used to make this source of energy cheap and reliable. One such need involves the development of transparent conducting solid thin films that are spectrally selective. Spectral selectiveness is an important property in solar cells because the spectrum of interest for this application is restricted to the visible and near infrared regions and so the unwanted wavelength regions must be selectively rejected. This research focuses on producing mutually doped transparent conducting thin films of zinc and aluminium oxides which are characterized and modelled for efficient solar energy applications in thin film solar cells and other solar energy systems. Thin film solar cells are a good choice in terms of the device design and fabrication process and offer an interesting alternative to p-n junction silicon based photovoltaic devices. The choice of zinc and aluminium oxides was based on the fact that they are readily available and can be obtained cheaply as opposed to the previously used indium tin oxide which is expensive and rarely available [1, 2].

A thin film solar cell is comprised of several layers of different thin film materials. It is typical that a cell is made up of a substrate, a transparent conducting oxide (TCO), a window layer, an absorber layer and a metal contact layer all of which have different physical, chemical, optical and electronic properties. Individual properties of the cell components each affect the overall performance of the cell. With this in mind, it is important to understand the behaviour of these solar cell components. Transparent conducting oxides (TCOs) are generally n-type semiconductor metal oxides which exhibit high transmittance of the visible (VIS) and near infrared (NIR) radiation and have high conductivity for efficient charge carrier transport when used as thin film electrodes or contacts in solar cells. It is important that TCOs have high transparency in the solar region and high electrical conductivity because enough light must be allowed to pass through them onto the absorbing layer

2. The Experimental Methodology

Zinc chloride ($ZnCl_{2)}$ doped with a trace of aluminium chloride hexahydrate ($AlCl_3.6H_2O$) were dissolved in distilled water, forming aqueous solutions of different concentrations and doping levels. A little hydrochloric acid was added to the solution to prevent precipitation to hydroxide. In a similar manner, $AlCl_3.6H_2O$ aqueous solutions doped with zinc were prepared. A locally constructed pneumatic spray pyrolysis set up was used to prepare the oxide coatings. The process starts with production of small droplets of the precursor solution in the atomizer by way of a carrier gas pumped from a gas cylinder at controlled pressure by a system of pressure gauges. These droplets of the spray solution are transported by the carrier gas through a diffusion tube into the reaction chamber and onto a heated substrate where they immediately evaporate leaving a solid thin film [3]. In this particular setup the carrier gas used was nitrogen (N_2).

Prior to spraying, the substrates were cleaned in acetone and dried. Different films were obtained for different spray parameters. Optimization of film properties was achieved by varying substrate temperature, solution concentration, carrier gas pressure, doping levels, and spray times and multi-laying of films. Optical characterization in the ultraviolet, visible and infrared (UV/VIS/IR) were conducted using the Perkin Elmer Lambda 19 spectrophotometer and Perkin Elmer Spectrum BX FT-IR system. Electrical characterization was conducted using a four-point resistance probe whereas the surface and thickness characterization were done using an atomic force microscope and a Tencor Alpha Step profiler respectively.

3. Results and discussion

The temperature in the oven and that of the substrate were monitored with a calibrated chromium-nickel thermocouple.

3.1 Film thickness

The thickness of a thin film depends much on the growth parameters and conditions. Different thicknesses were obtained for films grown using different growth parameters such as spray time, pressure, concentration of precursor solution and to some extent, substrate temperature. It was observed that more concentrated solutions gave thicker films as compared to less concentrated ones under the same conditions.

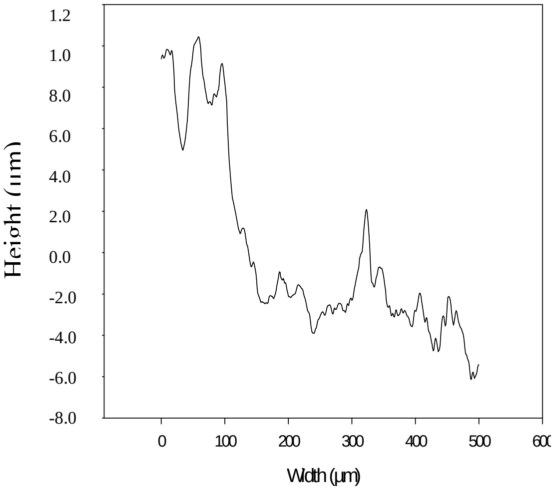

Figure 1. Thickness profile of single layer ZnO thin film.

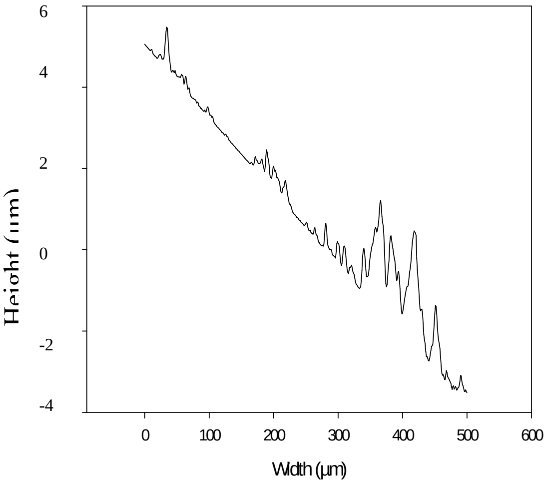

Figure 2. Thickness profile double layer aluminium oxide thin film.

The interesting result was that the edges of the thin film resulting from spray pyrolysis tend not to give a step ending but rather steadily reduce in height from the top to the surface of the substrate as seen from figure 1 and figure 2. In the two figures above, the vertical represents the thickness of the thin film whereas the horizontal represents the width of the profiled film section. In spray pyrolysis process, you obtain non-distinct edges but rather a steady decrease in thickness towards the edge. Thicknesses ranging from 0.14 µm to 87.7 µm have been achieved in this research. It has been noted that time of spray had the greatest influence on the thickness of the resulting coating film.

3.2 Transmittance and reflectance

A UV transmittance cut-off appears to take effect at wavelength near 325 nm. This coincides with a UV transmittance cut-off for a pure clean glass substrate. Similarly, infrared attenuation was observed at wavelength 2700 nm and at 4100 nm where the transmittance falls steadily to zero. Figure 4 compares the cut-off transmittance for the uncoated substrate and two substrates coated with ZnO and Al_2O_3. It was generally observed that ZnO films allow more of the incidence beam to be transmitted as compared to the aluminium films, transmitting nearly as much as the uncoated substrate. The highest transmittance was achieved for ZnO doped with aluminium. The average solar transmittance was 88.03 % for ZnO and 71.94 % for Al_2O_3.

The achieved transmittance of 88.02 per cent for ZnO films grown using spray pyrolysis method means that the thin films are suitable for use as window layers for heterojunction solar cells. It means that more light is admitted to improve the performance of the solar cell. We suggest that the use of these coatings would improve the efficiency of solar cells sufficiently.

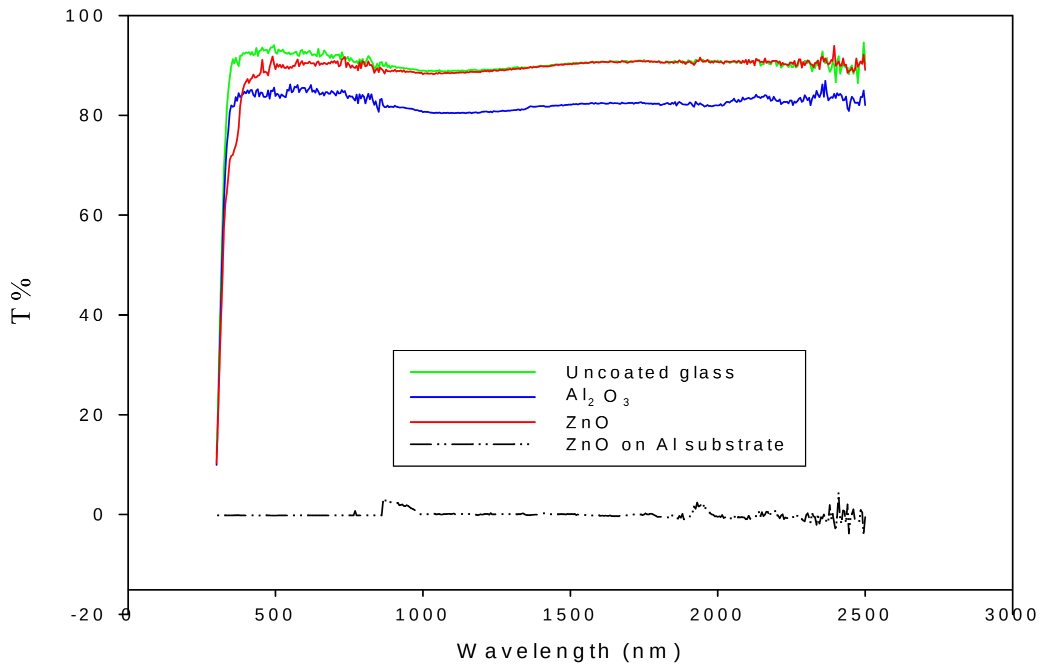

Figure 3. Comparative transmittance curves for aluminium and zinc oxides thin films UV-VIS-NIR grown under same conditions.

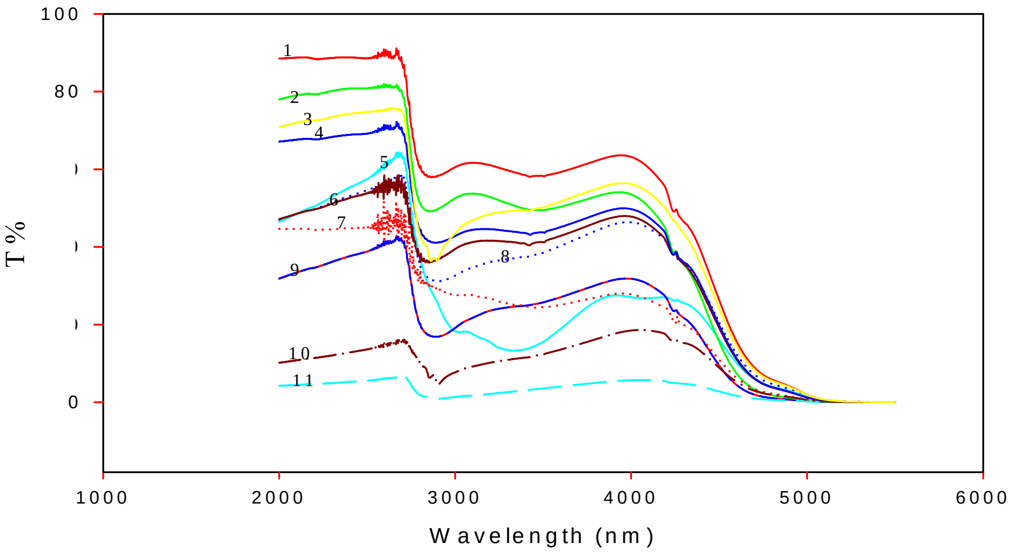

Figure 4. Comparative transmittance curves for aluminium and zinc oxides thin films in NIR region for thin films grown under same conditions.

Figure 5 shows how the transmittance of the different thin film coatings compares in the infrared. The curve labelled 1 is for the uncoated glass substrate, curves 2 to 7 represent the transmittance of the ZnO thin films, giving a trend of reduced transmittance with film thickness. Similarly the curves 8 to 10 represent transmittance curves for Al_2O_3 thin films. The transmittance for ZnO films is higher compared to the Al_2O_3 thin films.

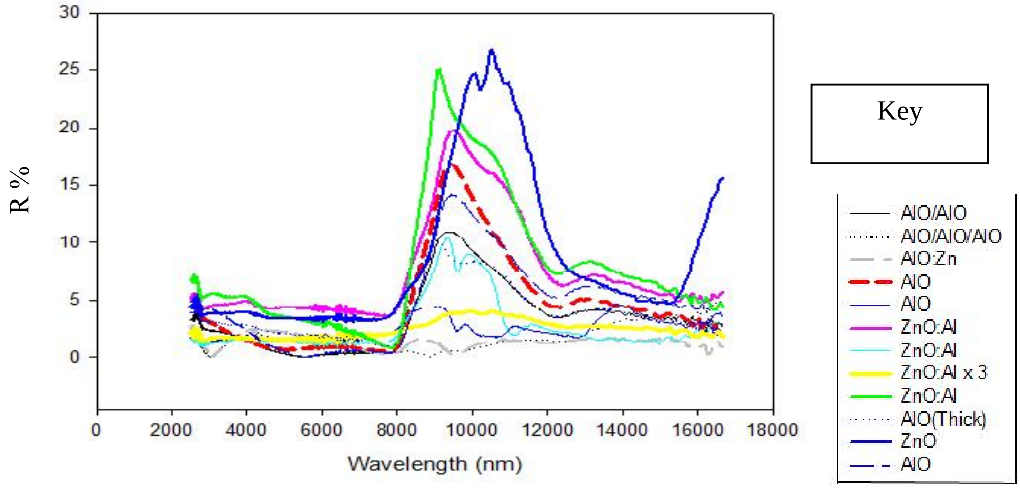

Figure 5. Transmittance curves in the IR region for different ZnO and Al_2O_3 films.

3.3 Surface characterization

The analysis with AFM revealed interesting structures of the film coatings. We present here the features of each of the samples with main emphasis being set on surface roughness, surface cross-section and particle size and distribution. The AFM micrograph presented below reveals the surface structure of the ZnO:Al thin film. The analysis indicated that the mean roughness for this particular coating was 14.11 nm. Figure 7 shows the surface roughness of the thin film and figure 8 is a surface profile of a section from figure 7. We associate the surface roughness to the effect this has on transmittance. It is expected that a rough surface tends to scatter the incident radiation resulting into poor solar energy yield for a solar thin film. The smoothness of the film is improved by coating the substrate with double or more layers.

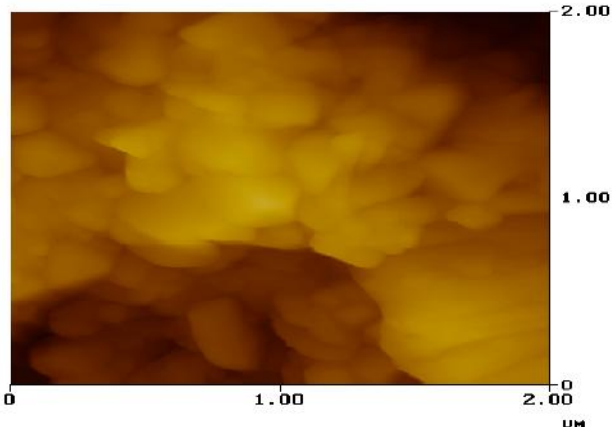

Figure 7. Surface roughness of 3.6 « m thick ZnO:Al film deposited at 290 ^oC.

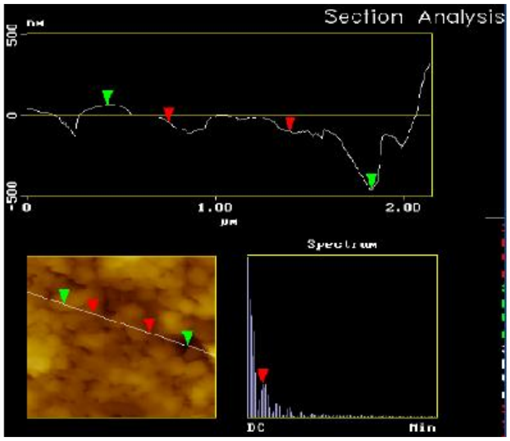

Figure 8. Section analysis of 3.6 « m thick ZnO:Al film deposited at 290 ^oC.

3.4 Modelling the experimental results

This section examines experimentally derived results and uses them into theoretical models that help us to fully understand these properties and how they fit into the theoretical expectations. The average refractive indices for the two wavelength regions were obtained from reflectance equation for normal incidence and presented in table 1.

$$R = (n-1)^2 (n+1)^{-2} \tag{1}$$

Knowing the refractive index of the material is useful in the fabrication of thin film solar cells as this determines the reflectance or transmittance of solar radiation from or into a solar panel in a given wavelength range.

Table 1. Wavelength-dependent refractive indices of selected thin films.

Spectrum	Average refractive index		
	ZnO	ZnO:Al	Al_2O_3
VIS-NIR	1.80	1.96	2.00
FIR	1.28	1.53	1.30

The resistivity of ZnO:Al thin film was on average 0.29 Ωm whereas that for Al_2O_3 was 0.58 Ωm. These values were obtained by applying the theory presented by Hirunlabh [4]. They are on the higher side of most reported values which are of order $10^{-4}\,\Omega$m. Reflectance and transmittance values have been used to calculate the absorption coefficients. The result for doped ZnO with thickness 1.2 « m was 662.6 and the highest value rising to 239 000. The absorption coefficient has an inversely relation to the thickness of the coating but is also greatly influenced by both transmittance and reflectance values. Effective dielectric permeability of the thin films were modelled using the Maxwell-Garnett effective medium theory (MGET) and Bruggemann effective medium theory (BEMT) [5] to yield values in the range 5 to 6.1 for the MGET and 4.4 to 8.5 for the BEMT.

4. Conclusion

This Study has utilized a simple and cheap process of fabricating spectrally selective thin solid films by way of spray pyrolysis process. Process parameters were easy to control with a chance to coat large surfaces. Characterization for solid film parameters was successfully conducted on the samples. Optical and micro-structural properties were determined both experimentally and theoretically. An average solar transmittance of 88 % was obtained for doped zinc oxide and 71.9 % for aluminium oxide films. In the infrared region, reflectance peaks were observed in the wavelength range 8 « m to 13 « m. Maxwell-Garnett and Bruggemann effective medium theories were applied to obtain effective dielectric permeability of the coatings. The Maxwell-Garnett EMT produced dielectric permeability range of 5 to 6.1 and the Bruggemann approximation yielded the permeability range 4.4 to 8.5. These values indicate that doping ZnO with aluminium raises it dielectric permeability and also raises the refractive index.

Acknowledgements

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