Spectral selectivity of doped zinc and aluminium oxide thin films prepared by spray pyrolysis for solar energy applications

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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 in the ultraviolet, visible near infrared and infrared ranges have been performed in spectrophotometers in the NIR-VIS and infrared. Structural characterization has been performed using the Atomic Force Microscope and the Tencor Alpha Step IQ Profiler. The 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 percent has been achieved for Al-doped zinc oxide (ZnO:Al) films whereas 71.94 per cent has been obtained for Zn-doped aluminium oxide (Al_2O_3:Zn). The film thicknesses fall in the range 0.14 - 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 -$11.80 \times 10^{-4}\,\Omega$m have been achieved. These film properties have been related to applications in thin film solar cells.

Key words: spectral selectivity, 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. The choice of zinc and aluminium oxides is based on the fact that they are readily available and can be obtained cheaply as opposed to the previously used indium tin oxide (ITO) which is expensive and rarely available[1, 2].

2. Theoretical considerations

2.1 Spray pyrolysis

Spray pyrolysis is a simple and reliably cheap method of chemical vapour film deposition. It is a process in which an aqueous solution of metal oxides or halides is dispersed and transported by means of a carrier gas to a suitable substrate where a thin film forms. Figure 2.1 shows the apparatus setup.

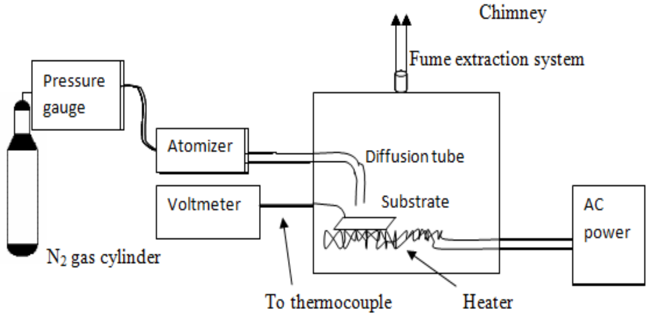


Figure 2.1 Schematic diagram of the modified spray pyrolysis unit.

The apparatus comprises an atomizer, a substrate heater, a reaction chamber, a diffusion tube, a temperature sensor (thermocouple), a carrier gas cylinder and pressure gauges. 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 it immediately evaporates leaving a solid thin film. [3]. In this particular setup the carrier gas used was nitrogen (N_2).

2.2 Optical and electrical evaluation

At normal incidence, the reflectance is obtained from the relation

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \text{ or } R = \frac{(n-1)^2}{(n+1)^2} \quad \text{if the extinction coefficient } k = 0 \qquad (1)$$

The thickness of the film from reflectance and transmittance measurements can be obtained using the approximated absorption coefficient α_λ [4] for which the relation below holds when both reflectance and transmittance are not negligible. Thus

$$d = \frac{1}{\alpha_\lambda}\ln\left(\frac{1-R_\lambda}{T_\lambda}\right) \text{ or } d = \frac{1}{\alpha_\lambda}\ln\left(\frac{1}{T_\lambda}\right) \text{ if reflectance is negligible.} \qquad (3)$$

The resistance is calculated from the IV characteristic measurements as given in the relation

$$R = \frac{V}{2I} = \frac{\rho}{2\pi d}\ln 2\,. \qquad (4)$$

The current is considered to flow in rings as opposed to spheres in the case of a thick film [4]. The resistivity is obtained from

$$\rho = \frac{\pi d}{\ln 2}\left(\frac{V}{I}\right) \qquad (5)$$

2.3 Effective medium theories (EMTs)

We have used the Bruggemann effective medium theory and the Maxwell-Garnet effective medium theory, which is essentially a modification of the Lorentz-Lorentz formula [5].

2.3.1 *Maxwell-Garnett effective medium theory.*This theory was initially developed to model the effective permittivity of heterogeneous media consisting of single dispersed spheres arranged in a cubic lattice structure. It considers random unit cells A and B imbedded in an effective medium each having dielectric permeability ε_A and ε_B respectively. The unit cells are considered to be small spheres with radii *a* and *b*. In this limit, the Maxwell-Garnett effective dielectric permeability is given by

$$\bar{\varepsilon}^{MG} = \varepsilon_B \left(\frac{\varepsilon_A + 2\varepsilon_B + 2 f_A(\varepsilon_A - \varepsilon_B)}{\varepsilon_A + 2\varepsilon_B - f_A(\varepsilon_A - \varepsilon_B)} \right) \qquad (8)$$

where f_A is the volume fraction of the inclusions forming the effective medium given by $f_A = \frac{a^3}{b^3}$, here a denotes the radius of the inner sphere and b that of the outer sphere.

2.3.2 *The Bruggemann effective medium theory*. The Bruggemann approach differs with the Maxwell-Garnett by way of arrangement of the composite microstructure and the fact that no particular phase constituent of the composite is preferred. It assumes a structure that comprises random spherical unit cells embedded in an effective medium. One phase of the composite will have a dielectric function ε_A while the other is assigned the dielectric function ε_B and the result is a medium with an effective dielectric permeability $\bar{\varepsilon}^{Br}$. Each unit cell has the probability f_A to have dielectric permeability ε_A or 1- f_A to have ε_B .
The equation for the effective Bruggemann dielectric permeability is obtained by solving

$$f_A\left(\frac{\varepsilon_A - \bar{\varepsilon}^{Br}}{\varepsilon_A + 2\bar{\varepsilon}^{Br}} \right) + (1 - f_A)\left(\frac{\varepsilon_B - \bar{\varepsilon}^{Br}}{\varepsilon_B + 2\bar{\varepsilon}^{Br}} \right) = 0 \qquad (9)$$

To apply the effective medium theory according to Maxwell-Garnett and Bruggemann, we make the assumption that the volumes of the medium constituents are the atoms of the ZnO and Al for the doped samples. We assign the permeability constants ε_A to aluminium atoms and ε_B to ZnO as $1.7 < \varepsilon_B < 2.5$ and $\varepsilon_A = 9$ respectively.

3.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. Using nitrogen as the carrier gas, respective solutions were sprayed through an atomizer onto standard microscope glass substrate slides to form solid thin films. 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, spray time 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 the atomic force microscope and the Tencor Alpha Step profiler respectively.

4. Results and discussion

The temperature in the oven and that of the substrate were monitored with a calibrated chromium-nickel thermocouple. Figure 9 is a calibration curve of the used thermocouple.

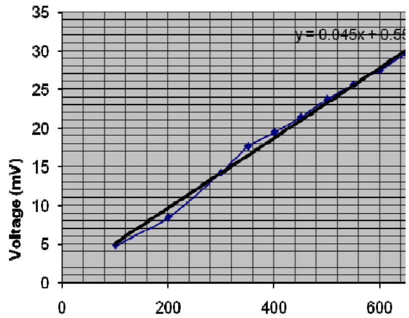


Figure 4.Thermocouple temperature calibration curve.

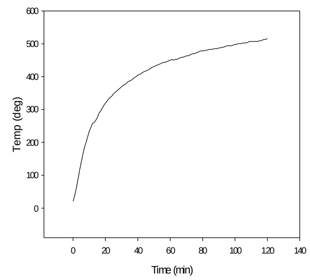


Figure 5. Oven temperature as a function of time.

4.1 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.

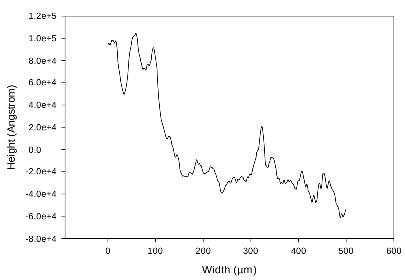


Figure 6.Thickness profile of single layer ZnO thin film.

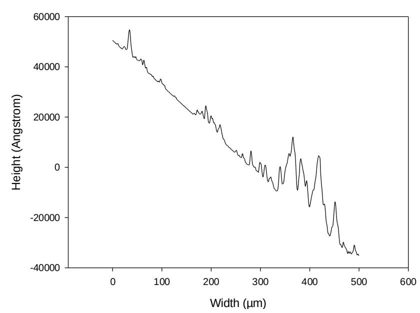


Figure 7. Thickness profile double layer aluminium oxide thin film.

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 reduces in height from the top to the surface of the substrate. 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.

4.2 Transmittance and reflectance

A UV transmittance cut-off appears to take effect at wavelength near 325 nm and a sharp infrared attenuation was observed at wavelength 2700 nm and at 4100 where the transmittance falls steadily to zero. It has generally been observed that ZnO films allow more of the incidence beam to be transmitted as compared to the aluminium films. The highest transmittance was achieved for ZnO doped with aluminium. The average percent solar transmittance was 88.03 for ZnO and 71.94 for AlO.

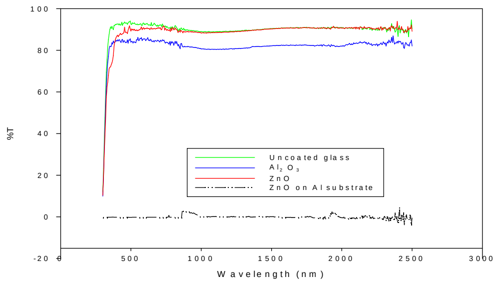


Figure 8. Comparative transmittance curves for aluminium and zinc oxides thin films UV-VIS-NIR grown under same conditions.

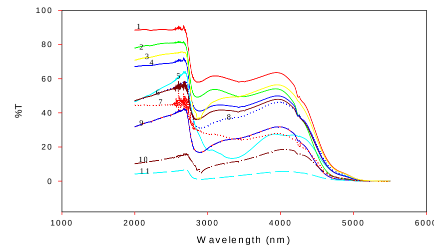
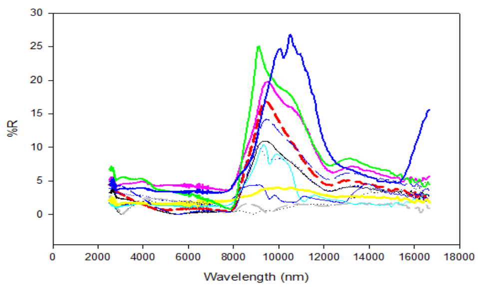
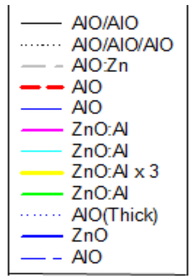


Figure 9. Reflectance curves in the IR region.



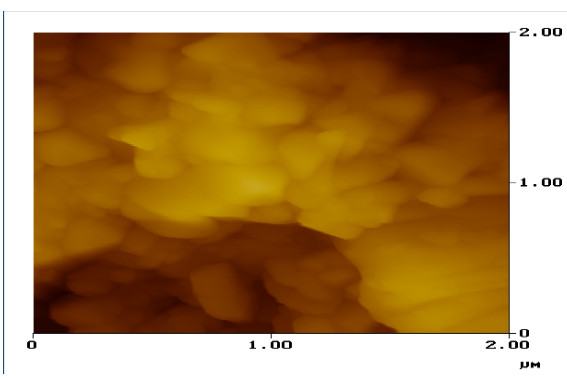


Key

Figure 10. Transmittance curves in the IR region for different ZnO and Al_2O_3 films.

4.3 Surface characterization

The analysis with the AFM reviewed 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 reviews the surface structure of the ZnO:Al thin film. The analysis indicated that the mean roughness for this particular coating was 14.11 nm.



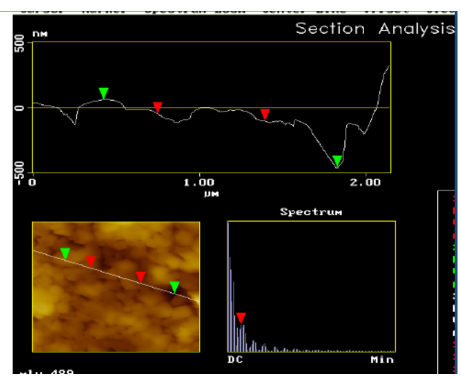


Figure 11.Surface roughness of ZnO doped with aluminium that is 3.6 μm and mean roughness 14.11 nm and grown at 290 ^{o}C.

Figure 12. Section analysis of 3.6 μm thick aluminium doped ZnO film deposited at 290 ^{o}C.

4.4 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 are obtained from equation (2.14). Table 4.1 gives the calculated values in the VIS-NIR-FIR regions.

Spectrum	Average refractive index		
	ZnO	ZnO:Al	AlO
VIS-NIR	1.8	1.96	2.0
FIR	1.28	1.53	1.3

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

The resistivity of ZnO:Al thin film was on average 0.29 Ωm whereas that for AlO was 0.58 Ωm. These values 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 μm was 662.6 and the highest value rising to 239000. The absorption coefficient has an inversely relation to the thickness of the coating but is also greatly influenced by both transmittance and reflectance values.

5. 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 per cent 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 8,000-13,000 nm. Maxwell-Garnett and Bruggemann effective medium theories were applied to obtained effective dielectric permeability of the coatings. The Maxwell-Garnett EMT produced dielectric permeability of 5-6.1 and the Bruggemann approximation yielded 4.4-8.5. These values indicate that doping ZnO with aluminium raises it dielectric permeability and also raises the refractive index.

Acknowledgements

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