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

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OUTLINE

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INTRODUCTION

- Hydro and fossil energy prices are rising rapidly with chance to double in a space of five years (Skyways, July 2013, pg 38).
- Electricity load shedding is a norm rather than an exception – Eskom knows
- Battle to meet country or regional energy demand
- Utilization of solar technologies offer nearly an immediate solution for cheap, reliable green energy.
- Looking to the skies for our energy requirements
Metal oxide thin films are used for thin film solar cells (TFSCs)

Development of cheap transparent conducting solid thin films –replacement of rare, expensive ITO.

These must be spectral selective

Spectral selectiveness is an important property in TFSCs

Figure 1. Electromagnetic spectrum
A typical TFSC 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 affect the overall performance of the cell.
Focus in this study is on the TCOs.
✓ generally n-type semiconductor metal oxides
✓ exhibit high transmittance of the visible (VIS) and near infrared (NIR) radiation
✓ have high conductivity for efficient charge carrier transport when used as thin film electrodes or contacts in solar cells
✓ In figure 2, ITO/SnO₂ transparent conducting oxides bi-layer were used ........expensive
We propose a new innovation
✓ to have a combination of mutually doped zinc and aluminium oxides making a bi-layer in a solar cell
✓ acting as the transparent oxides replacing the ITO/SnO$_2$ combination used in a typical solar cell in figure 2.
✓ ……cheaper approach

We have
✓ produced mutually doped spectrally selective solid thin films of ZnO and Al$_2$O$_3$
✓ investigated optical, electrical and structural properties
✓ theoretically modeled these properties
✓ tailor them for applications in efficient solar energy structures
THEORY

Reflectance as a function of reflective index for air-substrate interface

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

Absorption coefficient for negligible reflectance

$$\alpha_\lambda = \frac{1}{d} \ln\left(\frac{1}{T_\lambda}\right)$$

Electrical resistance

$$R = \frac{V}{2I} = \frac{\rho}{2\pi d} \ln 2$$
For an effective medium.

\[
\bar{\varepsilon}_{MG} = \varepsilon_B \left( \frac{\varepsilon_A + 2\varepsilon_B + 2f_A(\varepsilon_A - \varepsilon_B)}{\varepsilon_A + 2\varepsilon_B - f_A(\varepsilon_A - \varepsilon_B)} \right)
\]

Maxwell-Garnett effective medium having respective dielectric permeability \(\varepsilon_A\) and \(\varepsilon_B\).

\[
f_A = \frac{a^3}{b^3}
\]

\[
f_A \left( \frac{\varepsilon_A - \varepsilon_{Br}}{\varepsilon_A + 2\varepsilon_{Br}} \right) + (1 - f_A) \left( \frac{\varepsilon_B - \varepsilon_{Br}}{\varepsilon_B + 2\varepsilon_{Br}} \right) = 0
\]
METHODOLOGY

Raw materials:

✓ zinc chloride (ZnCl₂)
✓ aluminium chloride hexahydrate (AlCl₃·6H₂O)

❖ The ZnCl₂ and AlCl₃·6H₂O were weighed on an electronic balance
❖ Mutual doping was done by adding a determined amount to either chloride
❖ Mixture was dissolved in distilled water, forming aqueous solutions of different molar concentrations and doping levels
❖ hydrochloric acid was added to the solution to prevent precipitation to hydroxide
Spray pyrolysis technique was employed for coating thin films

Figure 3. Spray pyrolysis unit
Transmittance and reflectance measurements

Figure 4. Integrating sphere of a spectrometer
Thickness measurements

Figure 5. Tencor Alpha Step profiler
Film surface characterization

Figure 6. System components of the AFM: electronics interface, microscope, objective lens, Optical lighter, control monitor, display monitor and CPU.
Electrical measurements

Figure 7. Physical arrangement of the four point resistance probe
RESULTS AND DISCUSSION

Figure 8. Thermocouple temperature calibration curve

Figure 9. Oven temperature as a function of time.
Figure 9. Thickness profile of double layer Al$_2$O$_3$ thin film

Figure 10. Thickness profile of single layer ZnO thin film

Figure 11. Transmittance curve for uncoated glass slide in UV-VIS-NIR region

Figure 12. Transmittance curve for uncoated glass slide in the IR region
Figure 13. Solar transmittance curves for ZnO:Al films of thicknesses 1.67 μm and 1.28 μm fabricated at 320°C and 340°C.

Figure 14. NIR and IR transmittance curves for ZnO:Al films of thicknesses 1.67 μm and 1.28 μm fabricated at 320°C and 340°C.

Figure 15. NIR and IR transmittance curves for ZnO:Al films of thicknesses 2.7 μm and 3.6 μm fabricated at 340°C and 290°C.

Figure 16. NIR and IR transmittance curves for Al₂O₃ coatings.
Spectral selectivity of the thin films is established. The thin films are therefore suitable for use as TCOs in RFSCs.
Figure 19. Refractive index as a function of reflectance, effective media effect applied to figure 19 (d)
### Table 1. Wavelength-dependent refractive indices of selected thin films in the VIS-NIR and FIR wavelength regimes.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Resistance (Ω)</th>
<th>Average resistance (Ω)</th>
<th>Resistivity (10^4 Ωm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25B</td>
<td>0.75</td>
<td>5.24</td>
<td>0.0959</td>
</tr>
<tr>
<td>26A</td>
<td>9.54</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Table 2. Calculated electrical values for ZnO: Al

<table>
<thead>
<tr>
<th>Sample</th>
<th>Resistance (Ω)</th>
<th>Average resistance (Ω)</th>
<th>Resistivity (10^4 Ωm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>5.56</td>
<td>8.78</td>
<td>11.8</td>
</tr>
<tr>
<td>10-03A</td>
<td>12</td>
<td></td>
<td>4.47</td>
</tr>
</tbody>
</table>

### Table 3. Calculated electrical values for Al₂O₃:Zn
CONCLUSION

- We have utilized a simple and cheap process of fabricating spectrally selective thin solid films by way of the spray pyrolysis process.
- The films’ optical, electrical and structural properties have been investigated.
- A solar transmittance of 88 per cent was obtained for doped zinc oxide and 71.9 per cent for aluminium oxide films.
- This result is good for thin film application in solar cell manufacture.
- Reflectance peaks were observed in the wavelength range 8,000-13,000 nm.
Film resistivities obtained were to the order of $10^{-4}$ m. This result was good for possible application in thin film solar cells.

The Maxwell-Garnett and Bruggeman effective medium theories were applied to obtain effective dielectric permeabilities of the film coatings.

A new transparent conducting thin film combination of a ZnO:Al/Al$_2$O$_3$:Zn TCO combination has been proposed to replace the ITO/SnO$_2$ combination as a cheaper alternative.

**SAVE THE ENVIRONMENT BY PROMOTING GREEN ENERGY**
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