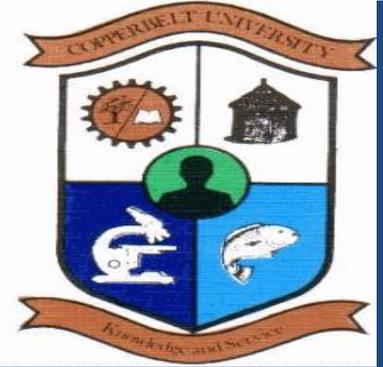


# Spectral selectivity of doped zinc and aluminium oxide thin films prepared by spray pyrolysis for solar energy applications



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# OUTLINE

- INTRODUCTION
- THEORY
- METHODOLOGY
- RESULTS AND DISCUSSION
- CONCLUSION
- ACKNOWLEDGEMENTS

# 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

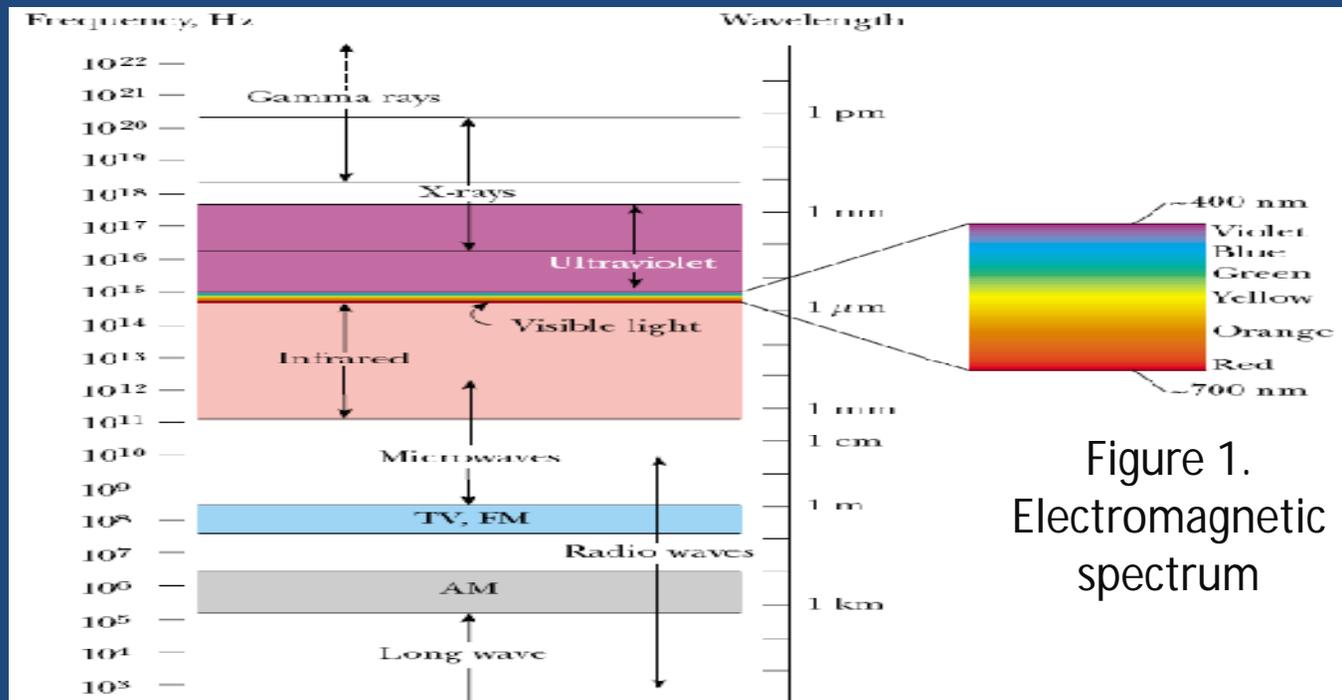


Figure 1.  
Electromagnetic  
spectrum

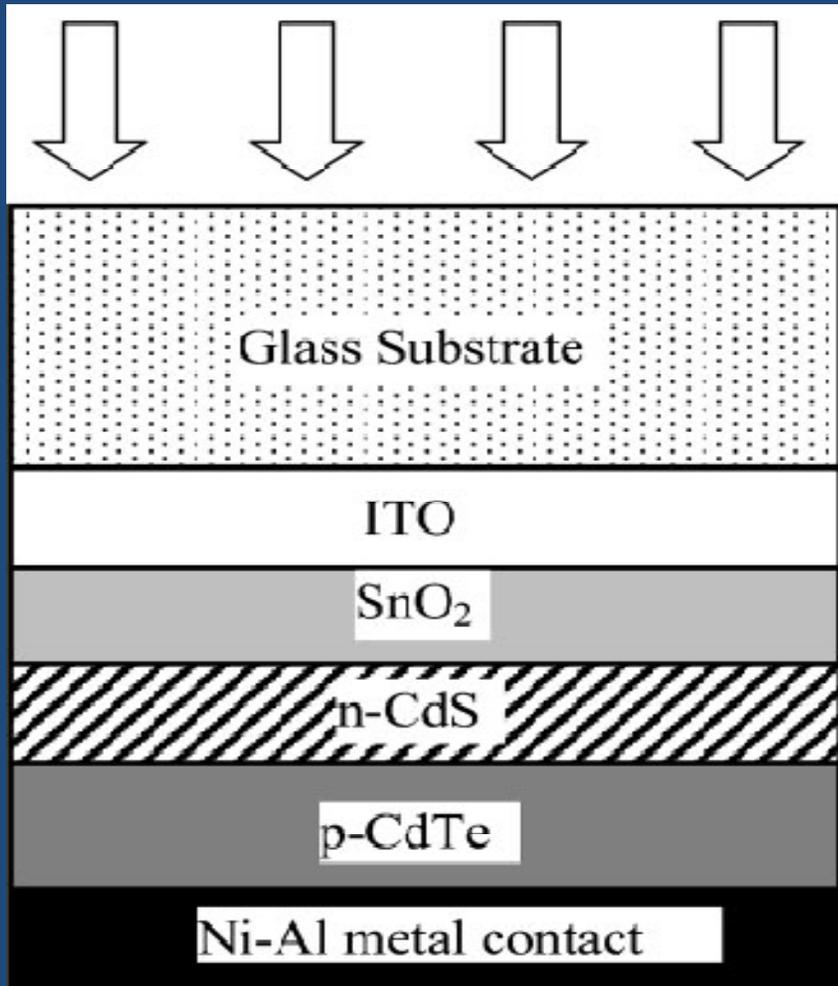


Figure 2. Typical thin film solar cell utilizing ITO as a TCO

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/SnO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub>O<sub>3</sub>
- ✓ investigated optical, electrical and structural properties
- ✓ theoretically modeled these properties
- ✓ tailor them for applications in efficient solar energy structures

## THEORY

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

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

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

Absorption coefficient for negligible reflectance

$$R = \int_{x_1}^{x_2} \rho \frac{dx}{2\pi x d} = \int_s^{2s} \rho \frac{dx}{2\pi x d}$$

$$R = \frac{V}{2I} = \frac{\rho}{2\pi d} \ln 2$$

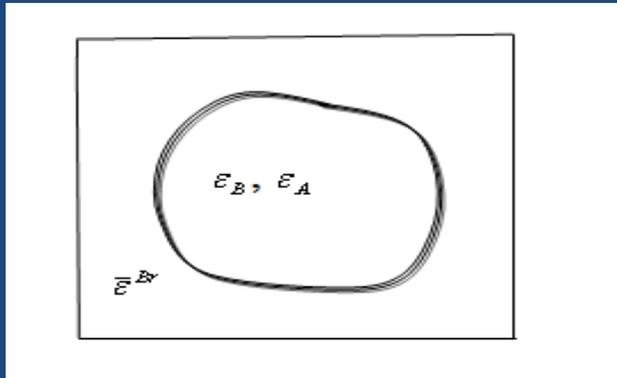
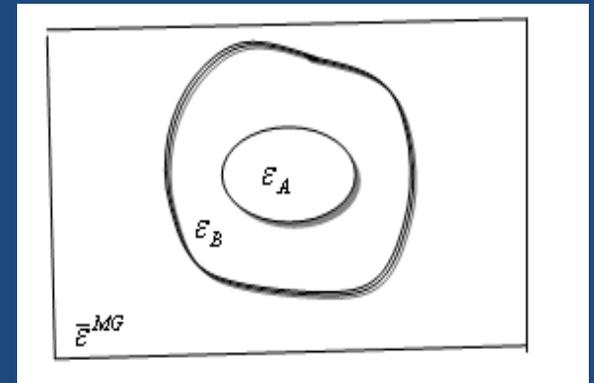
Electrical resistance

For an effective medium.

$$\bar{\epsilon}^{MG} = \epsilon_B \left( \frac{\epsilon_A + 2\epsilon_B + 2f_A(\epsilon_A - \epsilon_B)}{\epsilon_A + 2\epsilon_B - f_A(\epsilon_A - \epsilon_B)} \right)$$

Maxwell-Garnett effective medium having respective dielectric permeability  $\epsilon_A$  and  $\epsilon_B$

$$f_A = \frac{a^3}{b^3}$$



Bruggemann effective medium

$$f_A \left( \frac{\epsilon_A - \bar{\epsilon}^{Br}}{\epsilon_A + 2\bar{\epsilon}^{Br}} \right) + (1 - f_A) \left( \frac{\epsilon_B - \bar{\epsilon}^{Br}}{\epsilon_B + 2\bar{\epsilon}^{Br}} \right) = 0$$

## METHODOLOGY

### Raw materials:

- ✓ zinc chloride ( $\text{ZnCl}_2$ )
- ✓ aluminium chloride hexahydrate ( $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ )
- ❖ The  $\text{ZnCl}_2$  and  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  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

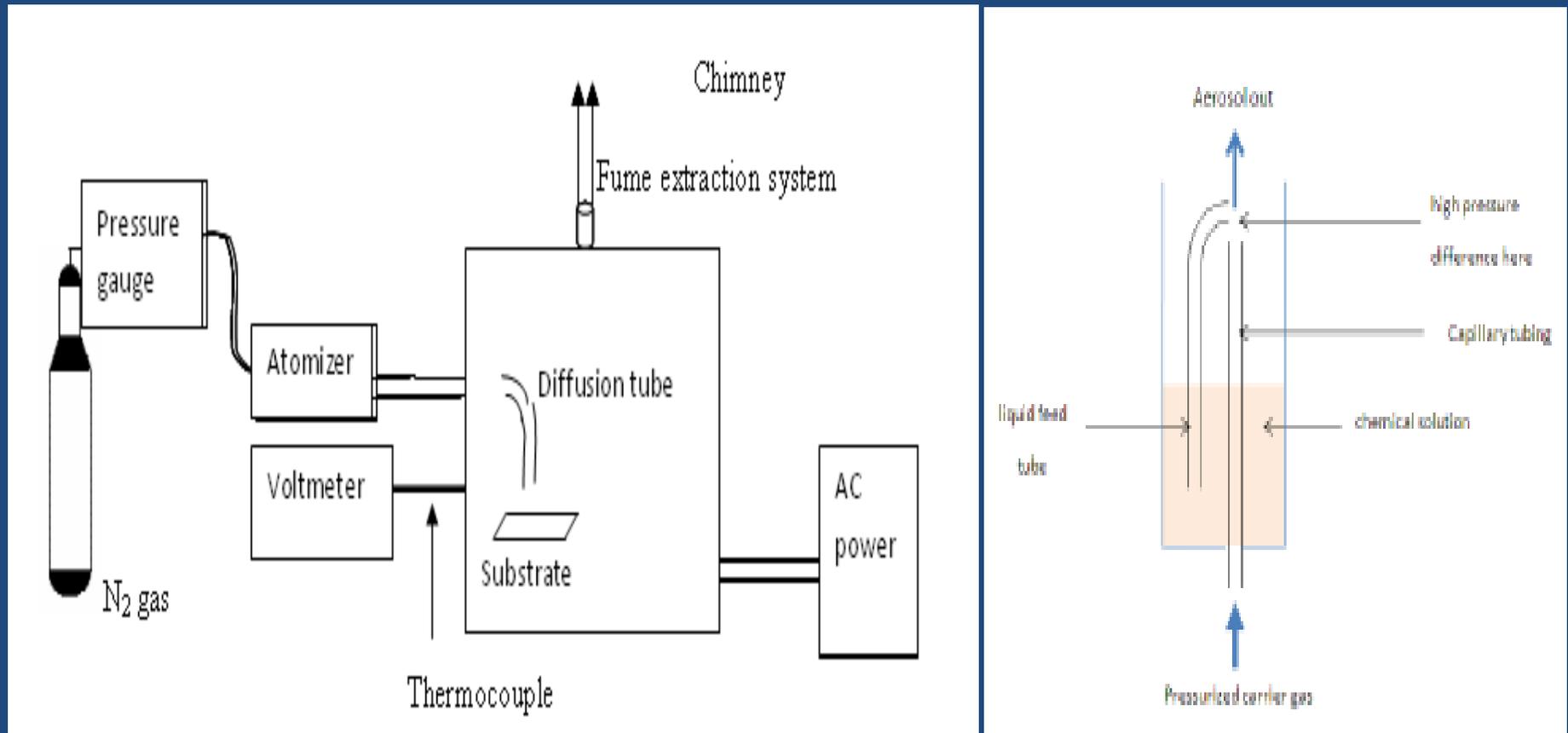


Figure 3. Spray pyrolysis unit

## Transmittance and reflectance measurements

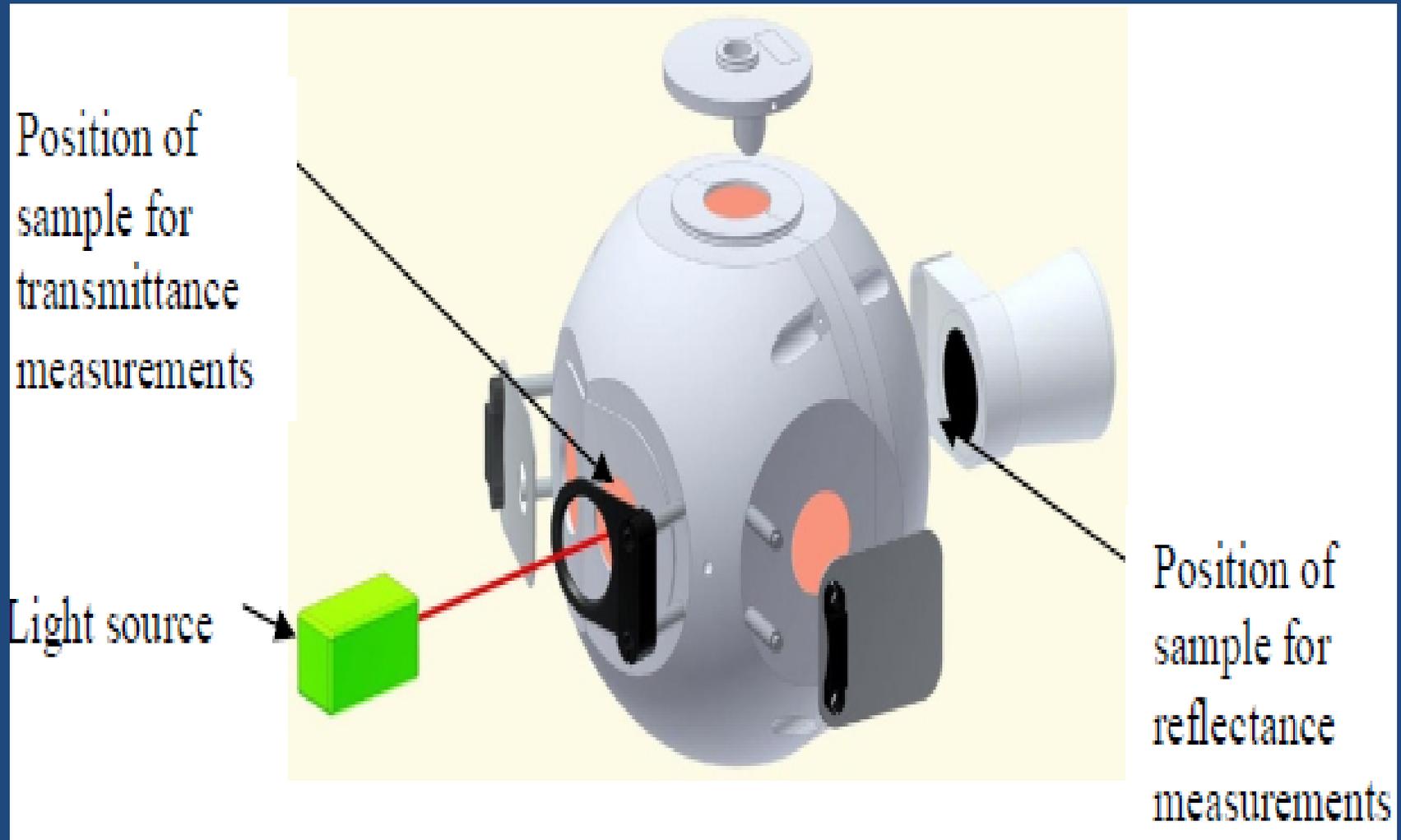


Figure 4. Integrating sphere of a spectrometer

# Thickness measurements

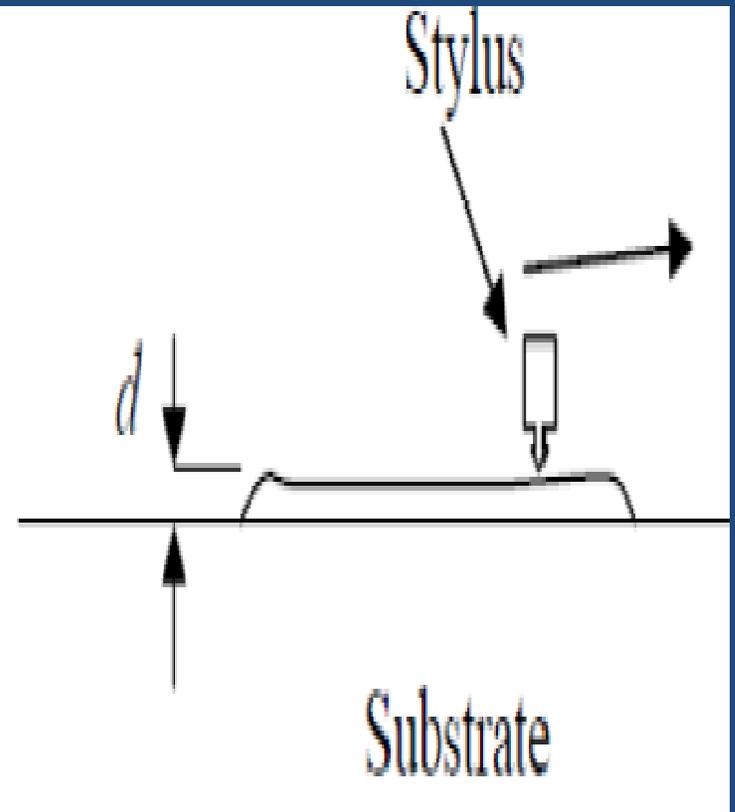


Figure 5. Tencor Alpha Step profiler

# Film surface characterization

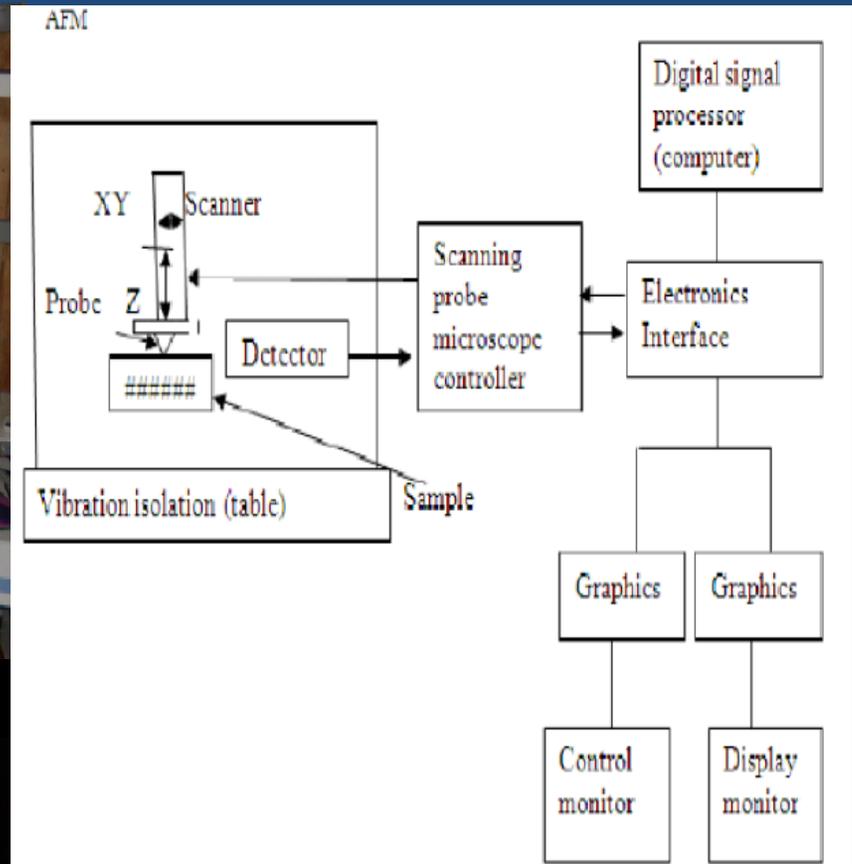


Figure 6. System components of the AFM: electronics interface, microscope, objective lens, Optical lighter, control monitor, display monitor and CPU.

# Electrical measurements

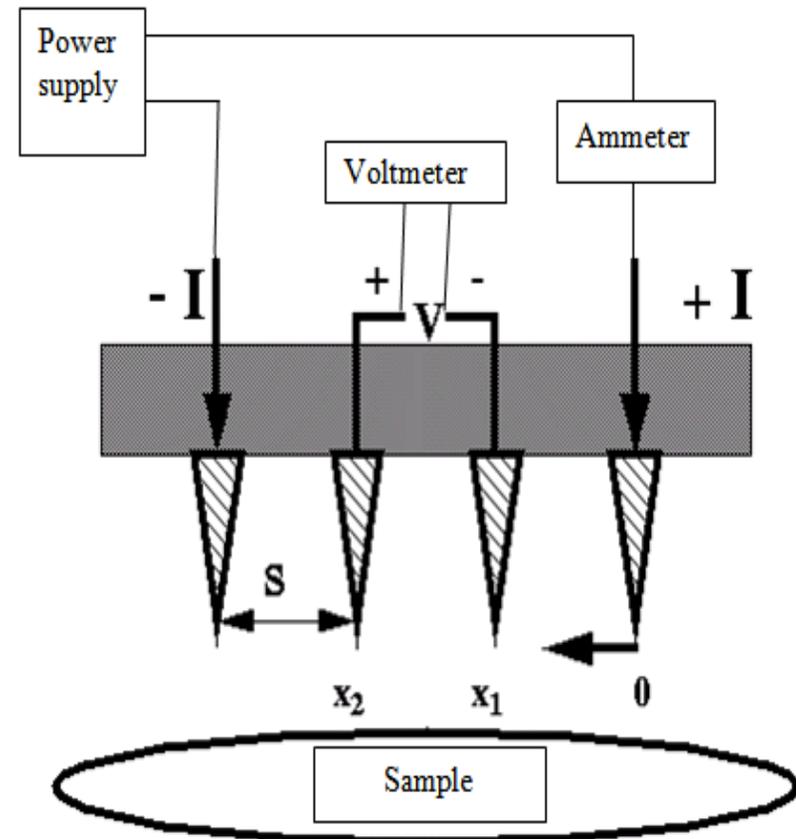


Figure 7. Physical arrangement of the four point resistance probe

# RESULTS AND DISCUSSION

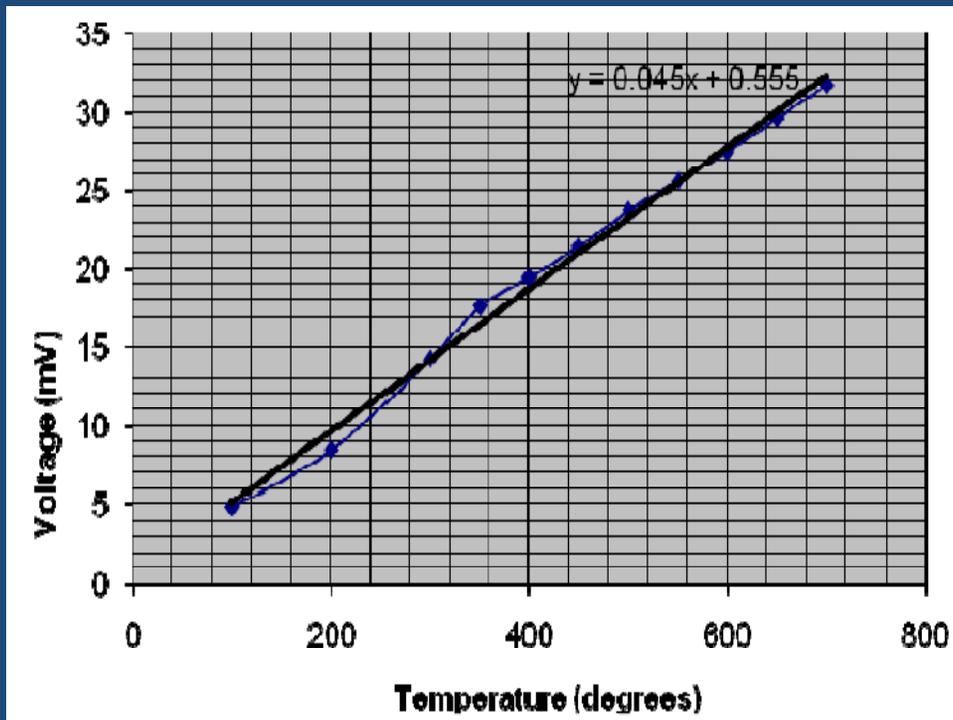


Figure 8. Thermocouple temperature calibration curve

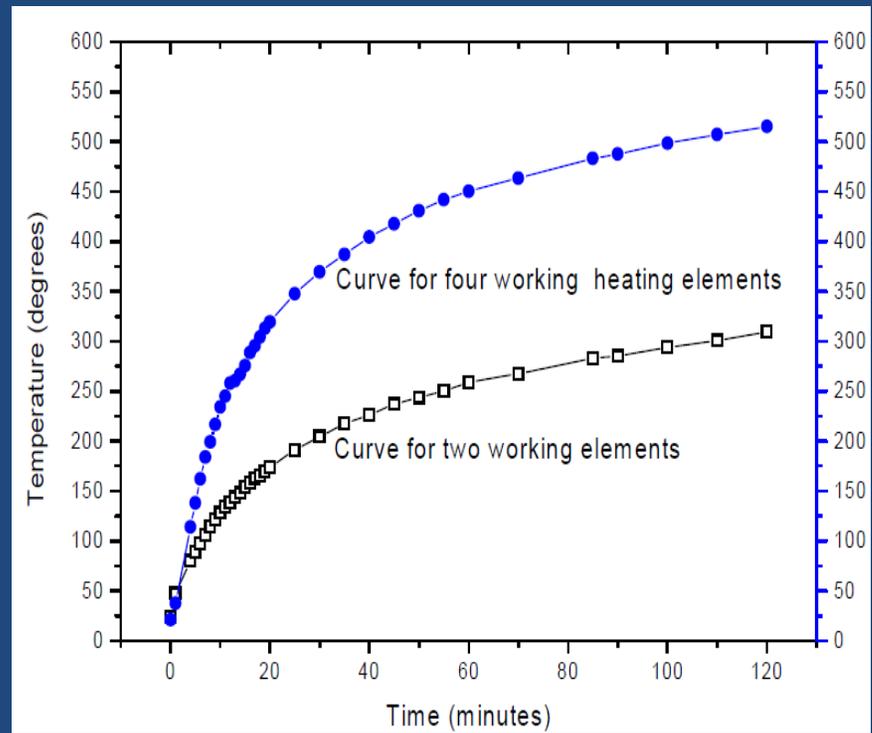


Figure 9. Oven temperature as a function of time.

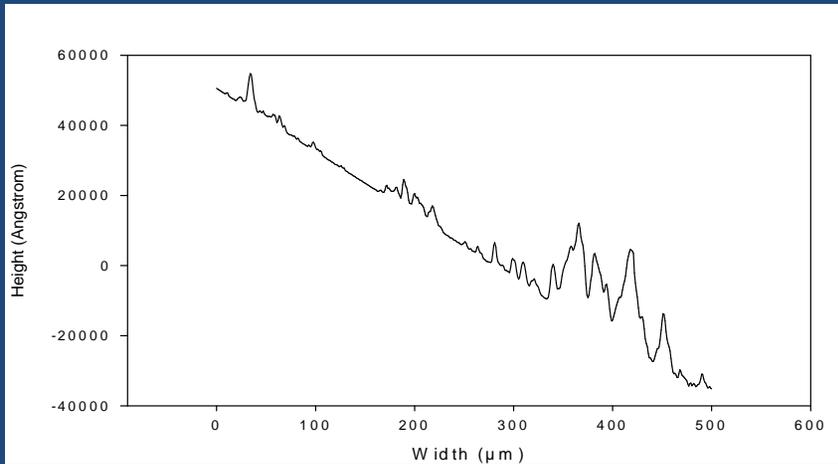


Figure 9. Thickness profile of double layer  $\text{Al}_2\text{O}_3$  thin film

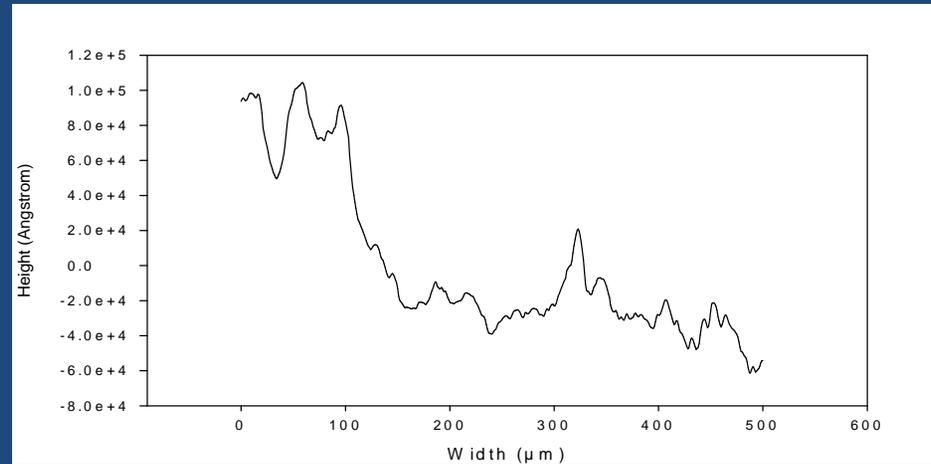


Figure 10. Thickness profile of single layer  $\text{ZnO}$  thin film

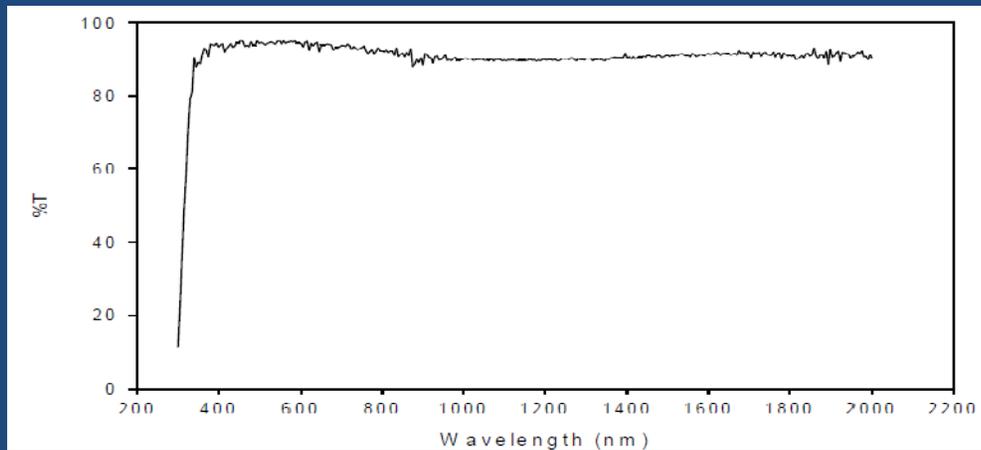


Figure 11. Transmittance curve for uncoated glass slide in UV-VIS-NIR region

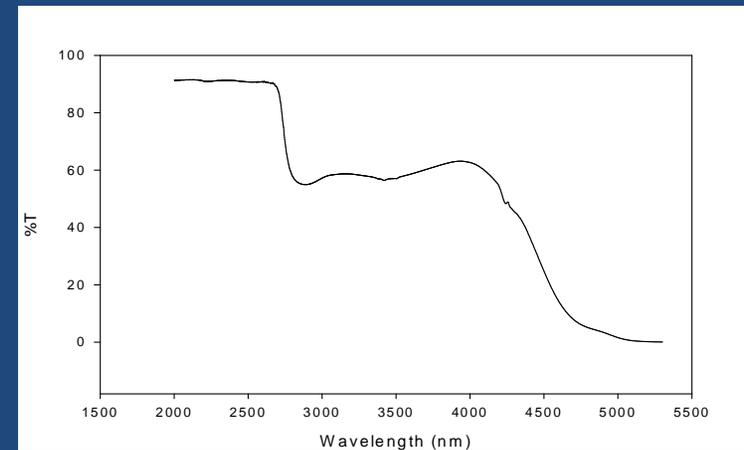


Figure 12. Transmittance curve for uncoated glass slide in the IR region

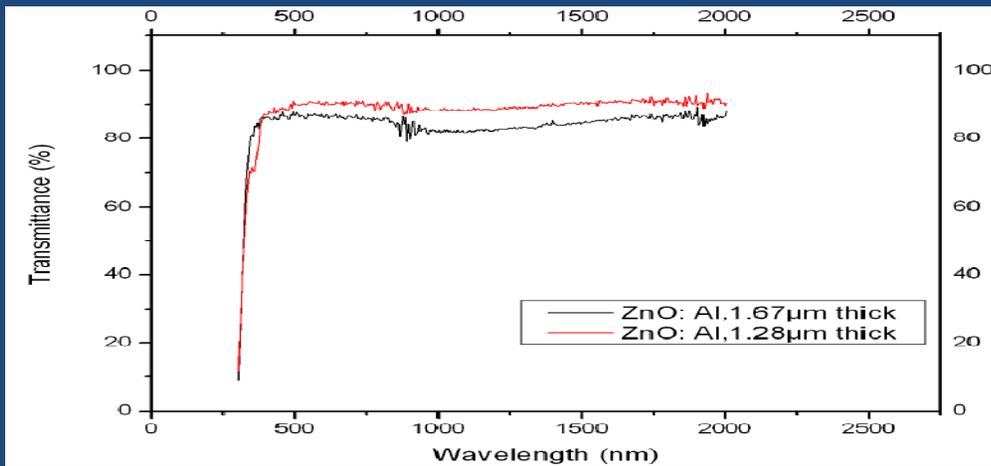


Figure 13. Solar transmittance curves for ZnO:Al films of thicknesses 1.67 μ m and 1.28 μ m fabricated at 320° C and 340° C.

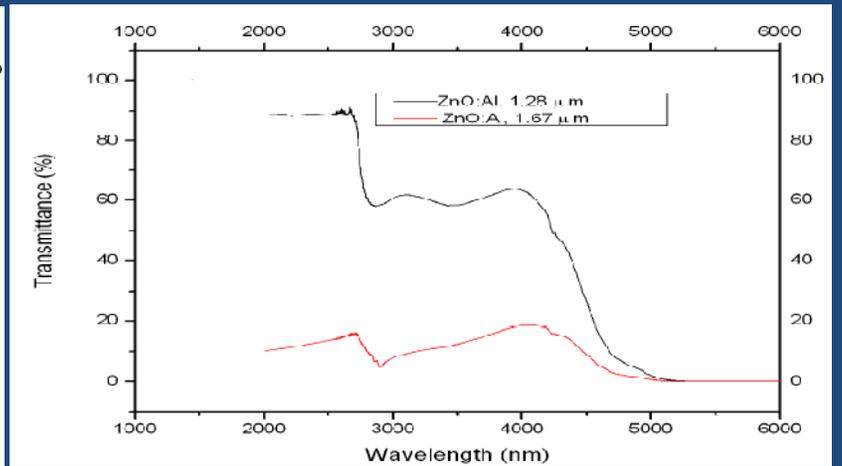


Figure 14. NIR and IR transmittance curves for ZnO:Al films of thicknesses 1.67 μ m and 1.28 μ m fabricated at 320° C and 340° C.

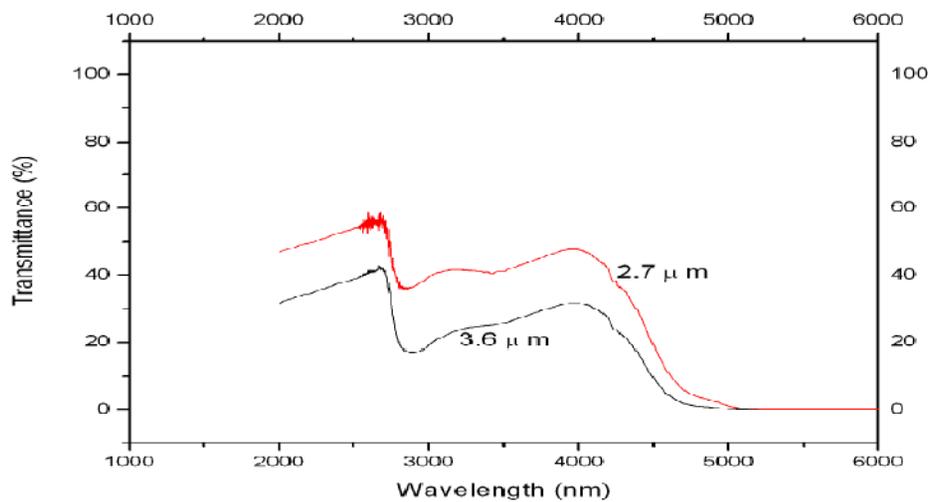


Figure 15. NIR and IR transmittance curves for ZnO:Al films of thicknesses 2.7 μ m and 3.6 μ m fabricated at 340° C and 290° C.

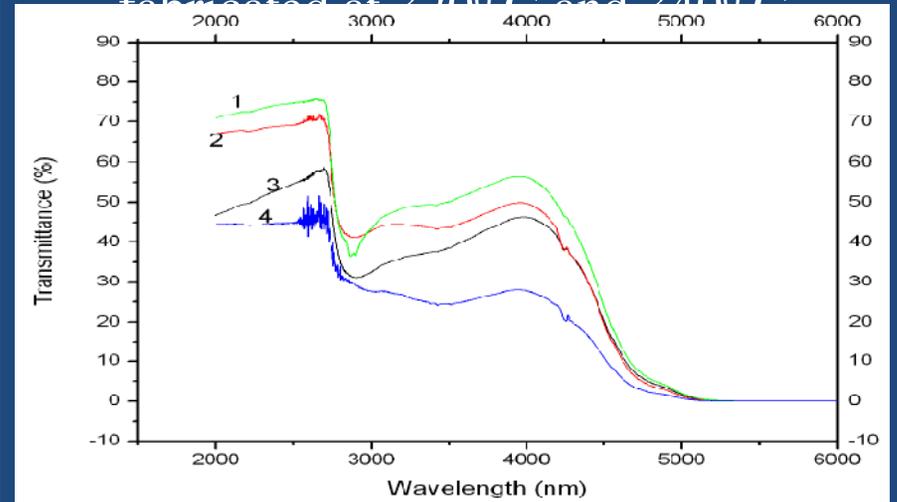


Figure 16. NIR and IR transmittance curves for Al<sub>2</sub>O<sub>318</sub> coatings

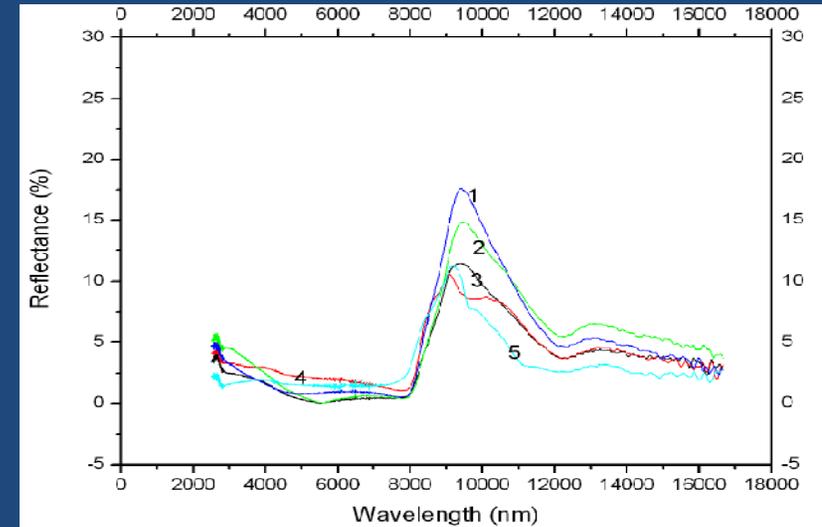
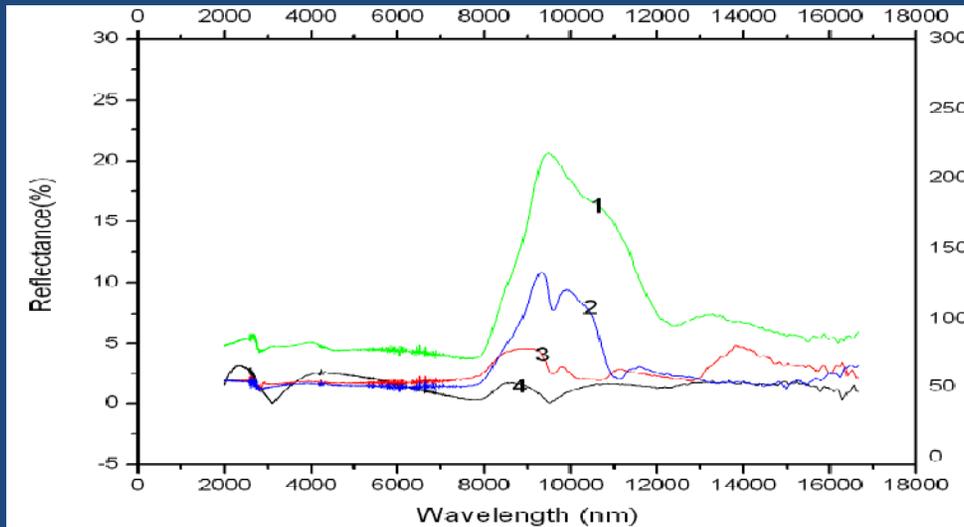


Figure 17. Reflectance curves for ZnO:Al Figure18. Reflectance curves for Al<sub>2</sub>O<sub>3</sub>

- ❖ Spectral selectivity of the thin films is established.
- ❖ The thin films are therefore suitable for use as TCOs in RFSCs.

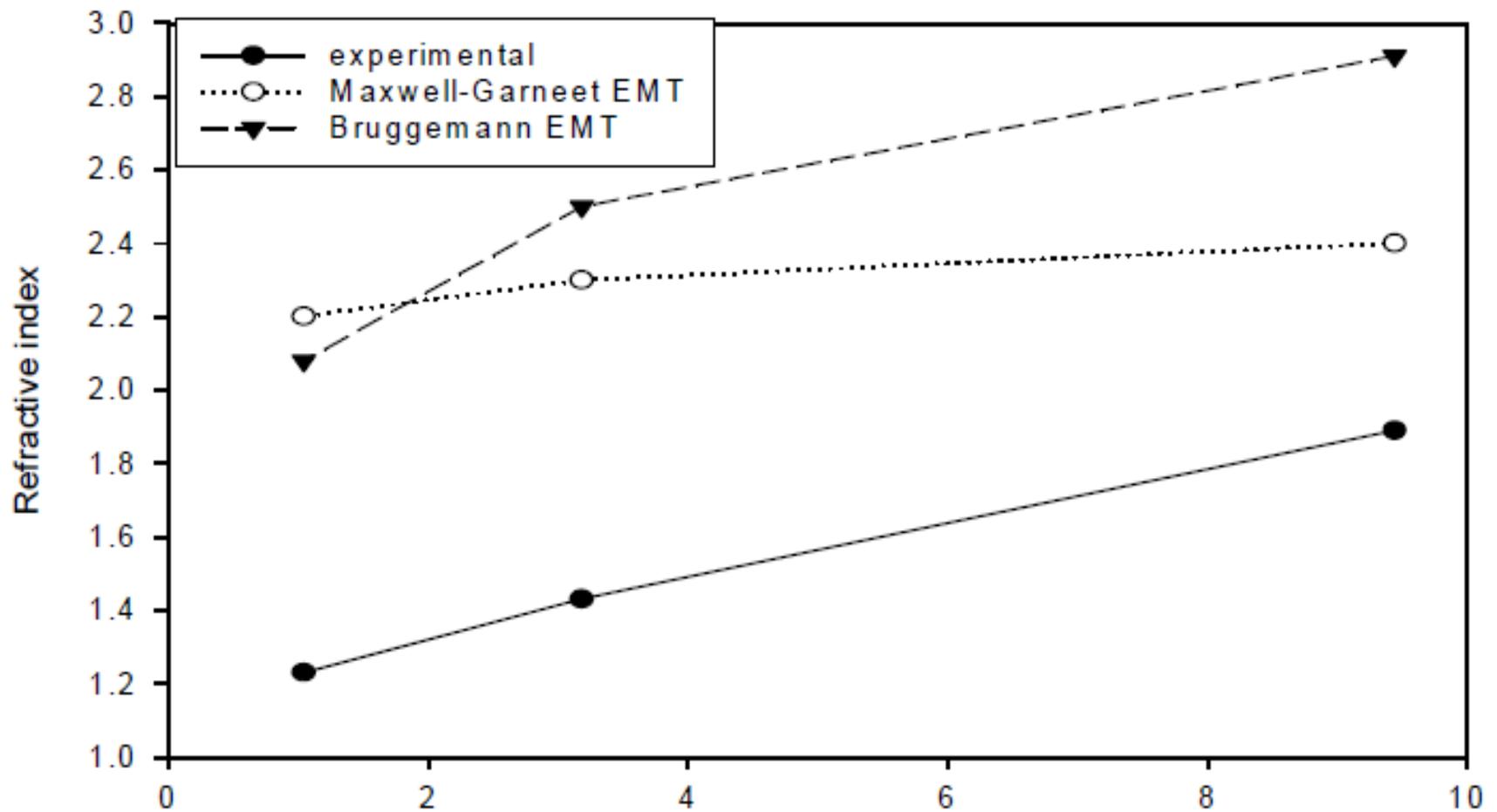


Figure 19. Refractive index as a function of reflectance, effective media effect applied to figure 19 (d)

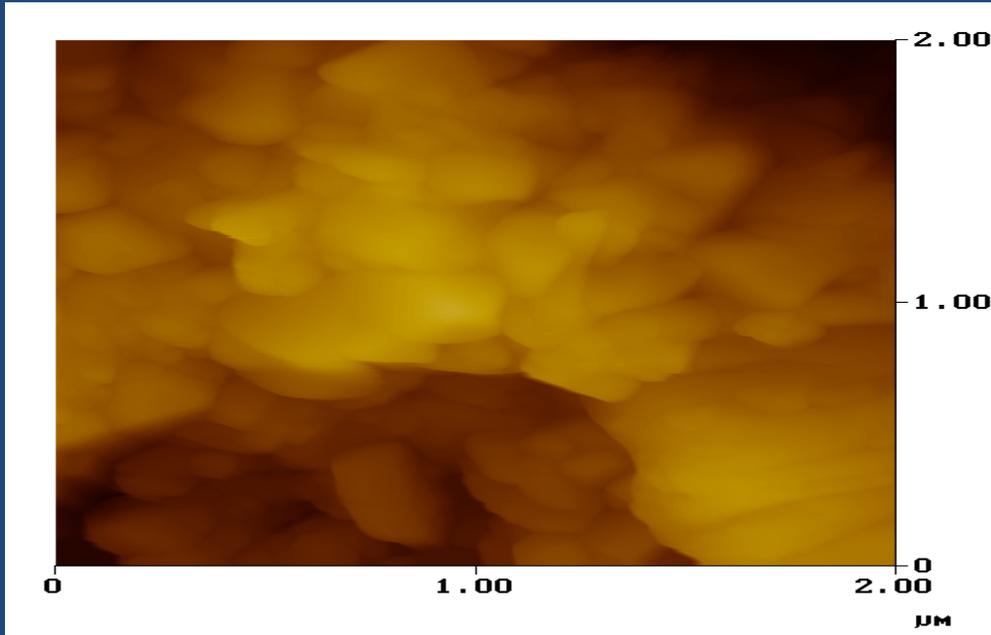


Figure 20. Surface roughness of ZnO:Al

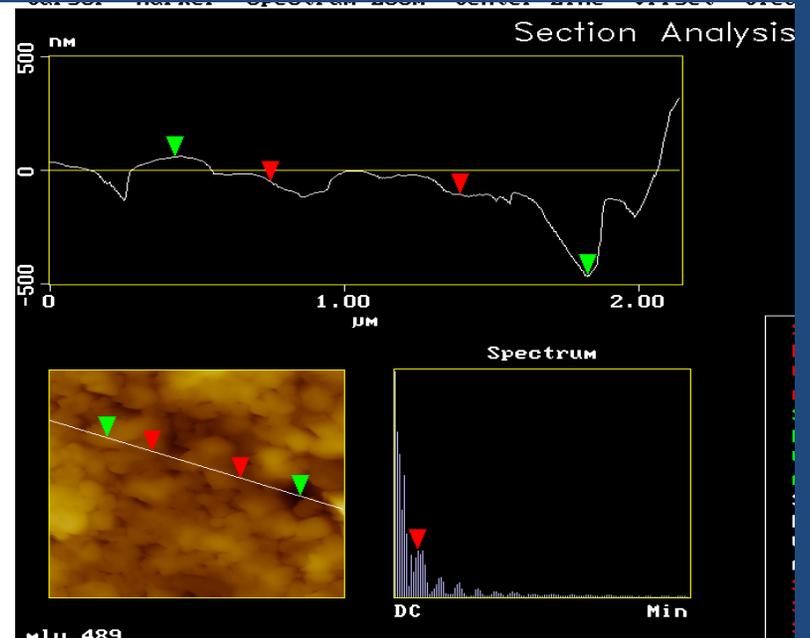


Figure 21. Section analysis

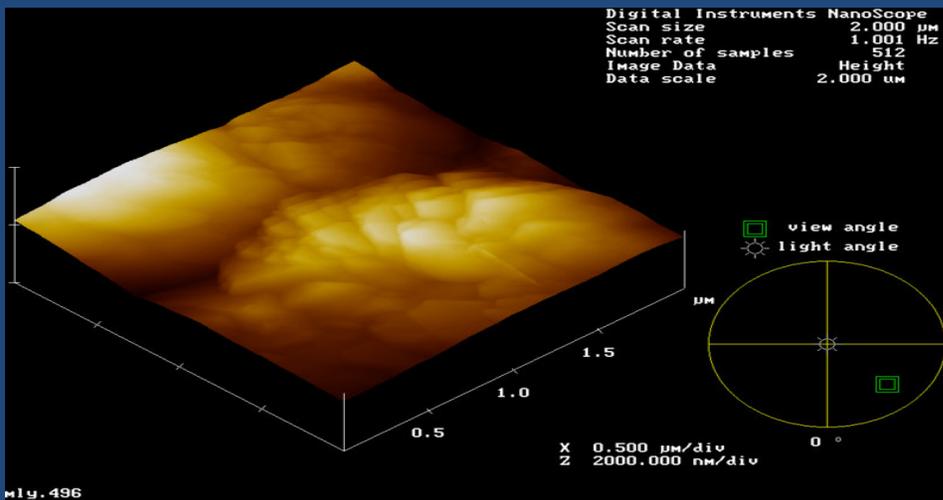


Figure 22. Surface plot for undoped ZnO thin film deposited at 340°C

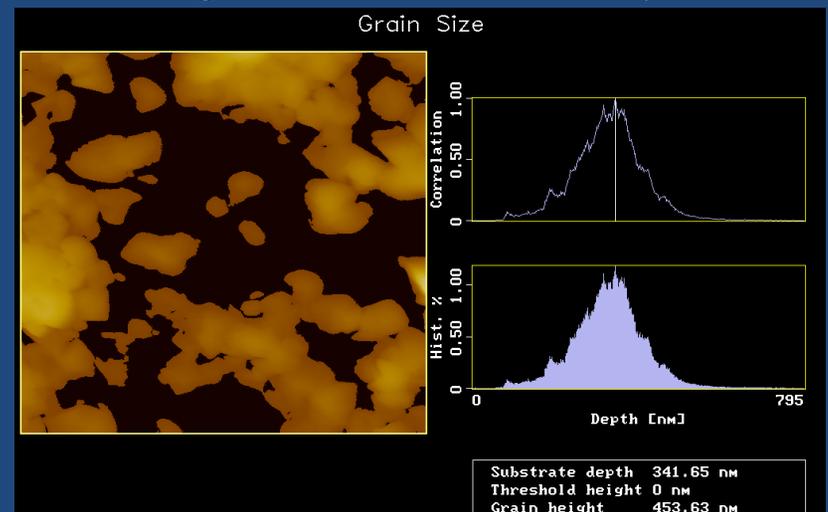


Figure 23. Distribution of grains in the thin film

| SPECTRUM       | AVERAGE REFRACTIVE INDEX |        |                                    |
|----------------|--------------------------|--------|------------------------------------|
|                | ZnO                      | ZnO:Al | Al <sub>2</sub> O <sub>3</sub> :Zn |
| <b>VIS-NIR</b> | 1.80                     | 1.96   | 2.00                               |
| <b>FIR</b>     | 1.28                     | 1.53   | 1.30                               |

Table 1. Wavelength-dependent refractive indices of selected thin films in the VIS-NIR and FIR wavelength regimes.

| Sample | Resistance<br>(Ω) | Average resistance<br>(Ω) | Resistivity<br>(10 <sup>-4</sup> Ωm) |
|--------|-------------------|---------------------------|--------------------------------------|
| 25B    | 0.75              | 5.24                      | 0.0959                               |
| 26A    | 9.54              |                           | 2.43                                 |

| Sample | Resistance (Ω) | Average resistance(Ω) | Resistivity<br>(10 <sup>-4</sup> Ωm) |
|--------|----------------|-----------------------|--------------------------------------|
| S5     | 5.56           | 8.78                  | 11.8                                 |
| 10-03A | 12             |                       | 4.47                                 |

Table 2. Calculated electrical values for ZnO: Al

Table 3. Calculated electrical values for Al<sub>2</sub>O<sub>3</sub>: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<sub>2</sub>O<sub>3</sub>:Zn TCO combination has been proposed to replace the ITO/SnO<sub>2</sub> combination as a cheaper alternative.

**SAVE THE ENVIRONMENT BY PROMOTING  
GREEN ENERGY**

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