

**REACTIVE PULSED LASER ABLATION
DEPOSITION (RPLAD) OF INDIUM TIN OXIDE
(ITO), TITANIUM DIOXIDE (TiO₂) THIN FILMS
AND GOLD (Au) NANOPARTICLES FOR DYE
SENSITISED SOLAR CELLS (DSSC)
APPLICATIONS**

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**A Thesis submitted to the Faculty of Science, University of the
Witwatersrand, Johannesburg, South Africa. In fulfillment of the
requirements for the degree of Doctor of Philosophy**

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DECLARATION

I declare that this thesis is entirely my own unaided work, except for the advice and assistance mentioned in the acknowledgements. This thesis is being submitted for the degree of Doctor of Philosophy in the University of the Witwatersrand, Johannesburg, South Africa. It has not been submitted as an exercise for a degree in any other university.

Signature of Candidate

_____ day of _____

ABSTRACT

The focus of this work was the study possible ways to improve the efficiency of solar cells. To this end, the main aim was to investigate the deposition process of Indium Tin Oxide (ITO), Titanium Dioxide (TiO_2), multi-layers ITO/ TiO_2 on quartz SiO_2 substrates under different conditions (oxygen pressure, laser fluence and wavelength, and temperature) and later gold nanoparticles by the Reactive Pulsed Laser Ablation Deposition (RPLAD) technique. It was intended to investigate their electrical structural and optical properties under selected conditions for possible application to Dye Sensitised Solar Cells (DSSC).

Under optimised conditions, maximum deposition rates of 12nm/min for ITO and 21nm/min for TiO_2 thin films were achieved. Rutherford Backscattering Spectrometry (RBS) with 2MeV He^+ ions was used to measure the films thickness. Uniform thicknesses over a large area were found to be about 400nm and 800nm for ITO and TiO_2 films, respectively. Crystalline properties were studied via x-ray diffraction and Raman spectroscopy. X-ray Diffraction (XRD) analysis revealed that the ITO films are highly orientated nanocrystals with their a-axis normal to the glass substrate surface. The average particle size of the precipitated nanocrystals was calculated to be 10-15nm.

The structure of the films was characterised via Atomic Force Microscopy (AFM) imaging of the top surface of the film. The films have a rough surface with average roughness of 26-30nm. Pores were observed with a density of 144 and 125 pores/ mm^2 and average size of 150 and 110nm for ITO films deposited at 200 and 400°C, respectively. TiO_2 films deposited on the prepared ITO films were less crystalline. Annealing was performed at 300 and 500°C for 3 consecutive hours and the XRD results show that the transformation of TiO_2 film into anatase phase was almost complete with a crystal size of ~ 6-7nm.

Scanning Transmission Electron Microscopy (STEM) of the surfaces was also performed. The TiO_2 films deposited onto the prepared ITO films present a

relatively high pore size with an average pore diameter of $\sim 40\text{nm}$ and excellent uniformity. It is interesting to note that the pores are randomly arranged. The random arrangement of the pores network may actually be beneficial for producing a uniform electrode. In addition, STEM cross-sectional analysis of the films showed a columnar structure but no evidence of voids in the structure. The large surface area produced suggests applications in DSSC.

The electrical properties of the films were investigated and an estimation of resistivity and Hall mobility was made. Low values of resistivity and high values of mobility were observed for ITO films. The resistivity of the film increases with increasing thickness while it decreases when increasing the deposition temperature. The lowest value was found to be $1.5 \times 10^{-6} \Omega\text{m}$ for ITO films deposited at 400°C . Hall mobility was found to increase with substrate temperature. In this investigation, the highest Hall mobility at room temperature was estimated to be $22.3\text{cm}^2/\text{Vs}$ under ambient O_2 pressure (PO_2) of 1Pa and 52.1 and $51.3\text{cm}^2/\text{Vs}$ for films deposited at 200 and 400°C , respectively. But the best ITO film was deposited at 200°C , since this film combines good resistivity, good Hall mobility and good transmittance.

UV-VIS-IR transmission spectra were recorded on a Perkin Elmer Lambda 900. From the transmission data, the energy gap as well as the optical constant was estimated. A high transmission for ITO films in the visible (Vis) range was observed which was above 88% for films produced at room temperature and above 95% for those deposited at 200°C . The transmission for the films produced in oxygen was about 90% above 400nm , whereas it lies between 70 and 80% for films produced in rare gases. An increase in the band gap was observed by increasing the oxygen pressure and substrate temperature for ITO films. Increasing the quartz SiO_2 substrate temperature from room temperature to 400°C resulted in an increase of the transmission of TiO_2 films, mostly in the Visible Near Infrared (Vis-NIR) from about 70% to 92% . After annealing at 500°C for 3 consecutive hours, the transmission of TiO_2 film further sharply decreases toward shorter wavelengths.

Analysis of the transmittance curve of TiO₂/Au shows a decrease of about 6% of the transmission in the Ultraviolet Visible (UV-Vis) range.

Optical absorption edge analysis showed that the optical density could be used to detect the film growth conditions and to correlate the film structure and the absorption edge. The TiO₂ films deposited present a direct band gap at 3.51eV and 3.37eV for TiO₂ as deposited and after annealing, respectively, while the indirect band gap was found to be 3.55eV and 3.26eV for TiO₂ films as deposited and after annealing, respectively. There was a shift of about 0.1eV between as deposited ITO monolayer films and ITO/TiO₂ bilayers deposited at 200°C. A small shift towards shorter wavelengths has been observed for multilayer ITO/TiO₂/Au. In this case, the increase of E_g was ascribed to a reduction of the oxygen vacancies with increasing substrate temperature at which the ITO film was deposited.

The change in the shape of the fundamental absorption edge is considered to reflect the variation of density and the short range structural modifications undetected by structural characterisations. Enlargement of band-gap energies of semiconductors may be advantageous when used in DSSC to suppress the charge recombination between the reduced electrolytes and the photo-excited holes in the valence band of TiO₂ substrates and enhance the open-circuit potential of the cell. When ITO/TiO₂ bilayers were annealed before depositing Au, the gap energy remained constant.



This thesis is entirely dedicated to my son,

Romar Johann Kenfack-Fotsa

*Whose love, patience, and sacrifice have always been an
inspiration for me. May this scientific undertaking and
the effort required to complete it serve as motivation for his
academic future and life endeavours.*

And to my husband

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For his unconditional love and invaluable support!

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