REACTIVE PULSED LASER ABLATION DEPOSITION (RPLAD) OF INDIUM TIN OXIDE (ITO), TITANIUM DIOXIDE (TIO_2) THIN FILMS AND GOLD (AU) NANOPARTICLES FOR DYE SENSITISED SOLAR CELLS (DSSC) APPLICATIONS

Fernande Fotsa-Ngaffo

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

November, 2006

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 ~ 40nm 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 $1.5 \times 10^{-6} \Omega m$ 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 $22.3 cm^2/Vs$ under ambient O_2 pressure (PO_2) of 1Pa and 52.1 and $51.3 cm^2/Vs$ 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 TiO_2/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 TiO_2 films deposited present a direct band gap at 3.51eV and 3.37eV for TiO_2 as deposited and after annealing, respectively, while the indirect band gap was found to be 3.55eV and 3.26eV for TiO_2 films as deposited and after annealing, respectively. There was a shift of about 0.1eV between as deposited ITO monolayer films and ITO/TiO_2 bilayers deposited at 200°C. A small shift towards shorter wavelengths has been observed for multilayer ITO/TiO_2/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 TiO_2 substrates and enhance the open-circuit potential of the cell. When ITO/TiO_2 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

Aurelien Kenfack-Jiotsa

For his unconditional love and invaluable support!

ACKNOWLEDGEMENTS

Adversity is often one of our best teachers. Even the people that somehow gripped our meanest imagination, violated us in some way, even those people are due their honour for what they have taught us. I wish to acknowledge all for their role in my life; however, this page is specifically designed to note my appreciation of those people who stand out most notably in my mind as contributing to the content of this thesis

Foremost, I would like to render my deepest gratitude to the One I owe allegiance to, my Shield, my Strength, and my very Present Help in times of need, the Almighty God, without whom this thesis would not have seen the light of day, to Him be all the glory.

Although I was registered to the University of the Witwatersrand in Johannesburg, South Africa, this work was conducted in the Lecce Laser Laboratory (LLL) in the University of Lecce in Italy. From the formative stages of this thesis, to the final draft, I owe an immense debt of gratitude to my external local advisor, Professor Armando Luches who has been the best supervisor I have ever met. I am highly indebted to him for boosting my confidence at a time it was desperately needed. His seemingly unlimited belief in me, his total availability, sage advice and careful guidance aided the writing of this thesis in innumerable ways.

It is also the occasion for me to thank his entire group members and particularly, Professor Maurizio Martino, Manuel Fernandez, Anna Paola Caricato and Francesco Romano whose steadfast support of RPLAD deposition was greatly needed and deeply appreciated. Numerous fruitful and valuable discussions with them had a tremendous impact on completing this thesis

I am very grateful to Professor Alessio Perrone, Professor Sergio Fonti and Professor Leonid V. Zhigilei whose general advice, helpful suggestions and kind encouragement made an indirect nonetheless positive impact on this work.

My profound gratitude also goes to Professor John Carter for agreeing to serve as my faculty advisor. His help and advice were indispensable to this work, and will always be deeply appreciated. Here is the occasion to thank Professor B. J. Cole and Professor J.A.P Rodrigues for their administrative help and assistance toward the completion of this thesis.

I would like to thank Dr. Malik Maaza for initiating me into the ideas and literature of the subject. Thanks to Dr. O. Nemraoui for his fruitful discussions.

I am grateful to the Third World Organisation for Women in Science (TWOWS) as well as the University of the Witwatersrand through the Postgraduate Merit Award for their financial support as PhD student in the University of the Witwatersrand, Johannesburg, South Africa. The generous financial support received enabled me to focus and concentrate on my work.

The experimental work was conducted in the Lecce Laser Laboratory (LLL) in the University of Lecce in Italy. Thanks for the three months support of the Department of Science and Technology (DST) from South Africa and for the rest of the time by the International Centre for Theoretical Physics (ICTP) through the Training and Research in Italian Laboratory (TRIL). None of the work done in the frame work of this thesis would have been possible without them thus this support is acknowledged with deepest and sincerest thanks.

The Raman, STEM and some optical and electrical measurements of the films were performed in the Bologna National Research Centre (CNR) labs. It is the occasion to express my sincere thanks to Professor Rita Rizzoli and Professor Giampiero Ruani for their effort and assistance in making the above mentioned measurements, for their fruitful discussions and priceless suggestions.

Professor Sean R. Agnew is acknowledged for his skilful XRD measurements performed in the University of Virginia. This is the occasion to express my profound gratitude for his helpful suggestions.

In my daily life, I have been blessed with a cheerful family. I would like to express my deepest thanks and profound and warm gratitude to my lovely Father, Mother and to my entire family for their unflinching LOVE, support and endless encouragements since I was born. The sacrifices they made to grow me up have always been a great source of inspiration and motivation. I love you so much.

Invaluable support from my son, who sleeps the whole night and never cries even during the day, from the very day he was born, so that I can work in peace and confidence is greatly acknowledged with much love.

Unconditional love and priceless support from my husband is acknowledged with lots of love. For accepting me the way I am, for the countless ways he ensured that I finished it in one piece, in every aspects of our together life, I will be always indebted to him.

Thanks to my family in law whose moral support is acknowledged with many thanks and deepest affection. I would like to thank particularly my mother in law for her steadfast support in taking care of my son when I could not physically do it, for her encouragement and advice in many aspects of my life, merci Maman

Thanks to all my friends and colleagues, I hesitate to list them because I do not wish to leave anyone out, for our constructive discussions, which in one way or another has made me improved on my best!

Last but not least, I am extremely very grateful to the School of Physics of the University of Witwatersrand and all the staff members for welcoming me and for my years of study as a PhD student. Many thanks to all of them!

Glory be to the LORD!!!

TABLE OF CONTENTS

CONTENTS **Page**

LIST OF FIGURES

LIST OF TABLES