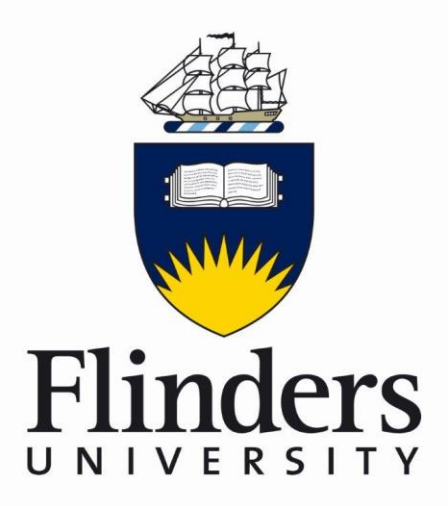
Electronic and Chemical Properties of Interfaces in Organic Photovoltaic Devices



Thesis Presented to the School of Chemical & Physical Sciences, Faculty of Science & Engineering of Flinders University in Candidacy for the Degree of

Doctor of Philosophy

July 2014

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Master of Nanotechnology

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श्रीश्री गुरु-गौराङ्गौ जयतः ।

कर्मण्येवाधिकारस्ते मा फलेषु कदाचन ।

मा कर्मफलहेतुर्भुर् मा ते संगोऽस्त्वकर्मणि ॥ ४७॥*

*Śrīmad Bhagavad Gītā, Chapter 2, Verse 47

"We are at the very beginning of time for the human race. It is not unreasonable that we grapple with problems. But there are tens of thousands of years in the future. Our responsibility is to do what we can, learn what we can, improve the solutions, and pass them on."

- *Richard P. Feynman*

In Loving memory of my beloved chacu late

Mr. Anuj Sharma (1966- 1988)

Dedicated to my grandparents late Mr. C. L. Sharma (1923- 2004) and Mrs. C. V. Sharma (1930-2003)

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Abstract

Organic Photovoltaics is a promising technology, which can potentially be a cheap source of clean and renewable energy in the near future. Despite tremendous research and development efforts in this field, organic solar cells still take a back stage in the mainstream photovoltaic market. Though the efficiencies have gradually increased to up to 12 %, device stability still remains a challenge limiting large-scale commercialization of this technology.

This dissertation is devoted primarily to the study of stability and performance-limiting electronic properties of device interfaces in both conventional and inverted OPVs. Given the importance of electrode workfunction in interfacial charge transport in devices, special focus was on better understanding the workfunction measurements on heterogeneous surfaces and precise measurement of lateral variations in workfunction on a nanoscale.

In particular, the interfacial instability of ITO-PEDOT:PSS interface in conventional OPVs was investigated and it was shown for the first time that the migration of indium and tin into the PEDOT:PSS was strongly driven by the presence of moisture and is not merely a diffusive process, as prior beliefs. It was systematically demonstrated that indium and tin contaminants can adversely affect the device performance by increasing the interfacial dipole at the ITO-PEDOT:PSS interface.

For inverted OPVs, a strong correlation between the processing conditions of ZnO and the device performance has been established. Changes in the electronic or structural properties of ZnO were demonstrated to be the driving force behind the strong dependence of device performance on the processing conditions of ZnO.

ZnO prepared via a range of techniques was studied and for all cases a minimum of 25 nm layer thickness was found to be essential to achieve optimum device performance. For sol-gel prepared ZnO, the workfunction was found to be independent of the layer thickness, whereas for ZnO layer casted from a colloidal solution, post annealing temperature was found to be critical and a minimum temperature of 200 °C was found to be essential in order to achieve desirable workfunction and electron affinity. As in case of pulsed laser deposited ZnO, stoichiometric ratio of Zn and O was also found to be dependent on the layer thickness and thicker layer (up to 100 nm) were found to get oxygen deficient with

increasing thickness. A fully evolved band structure of ZnO was found to be absent for layers of thickness 12 nm or less, which explains the poor performance of such devices.

This work also establishes a clear understanding of workfunction measurements of heterogeneous surfaces with UPS. Surfaces with heterogeneity on a nanoscale were artificially created with a combination of energetically different materials. It was demonstrated that materials having relatively low workfunction have an enhanced secondary electron emission, which can be misleading in deriving absolute workfunction values from UPS measurements. This behaviour was found to be valid even for polycrystalline materials with nanoscale variations in workfunction such as ZnO. While nano-domains of different workfunctions across a nano-roughned ZnO surface were clearly demonstrated using KPFM, UPS results were found to be more representative of the domains corresponding to low workfunction regions.

Declaration

I certify that this thesis does not incorporate without acknowledgement any material previously submitted for a degree or diploma in any university; and that to the best of my knowledge and belief it does not contain any material previously published or written by another person except where due reference is made in the text.

Anirudh Sharma

Acknowledgement

The last four years have been an incredible phase of my life, which witnessed a transition of an inquisitive student to an independent scientist. My PhD journey was full of stirring experiences with fascinating science around me. As this enriching and unique PhD journey comes to an end, I would like to take this opportunity to acknowledge and thank all those who helped me either towards the completion of this dissertation or those who made my Australian odyssey, a memorable journey.

Firstly, I am deeply thankful to my advisor, Prof. David Lewis, for his invaluable guidance throughout my PhD journey and for his intellectual contribution, which helped me compile this work. I joined David's group as a Master's student and since then he has always been a constant source of support and inspiration for me. I sincerely appreciate him for showing confidence in me and giving me the right opportunities. I would like to equally thank my co-advisor Prof. Gunther Andersson for supporting me not only academically but also through the emotional ups and downs of a PhD life. His selfless time and support were sometimes all that kept me going, not to mention the sweet birthday cards on my desk which Gunther never forgot to surprise me with.

I owe my deepest gratitude to my co-advisor at Commonwealth Scientific and Industrial Research Organisation (CSIRO), Dr. Scott E. Watkins for his time and guidance during my various trips to CSIRO's fabrication facility at Clayton, Melbourne. I would also like to thank Dr Rüdiger Berger at Max Planck Institute for Polymer Research (MPIP) for his valuable supervision during my visiting study in Germany. I feel privileged to have got an opportunity to work and gain invaluable experience at MPIP, one of the world's most accomplished research institutes.

I am also indebted to Dr. Mihail Ionescu from Australian Nuclear Science and Technology Organisation (ANSTO) for helping me with Rutherford backscattering experiments and Dr. Joseph Franklin from Imperial College, London for his collaboration on PLD ZnO study. I must also acknowledge my colleagues at CSIRO, Dr Birendra Singh for his assistance with device fabrication, Dr. Jacek Jasieniak for providing ZnO particle ink and Dr. Gerry Wilson, for fruitful discussions.

I would like to extend my special thanks to Prof. Colin Raston for many stimulating

discussions and mentoring that has greatly benefited me in structuring this thesis in its current form. I would also like to show my gratitude to all my past and present colleagues in all the groups I have worked with, for their help and support especially Marie-Clare Hermant, Natalya Schmerl, Ben Chambers, Chris Ridings, Daniel Mangos, Daniel Gruszecki, Ashley Johns, Sean Clark, Sian La Vars at Flinders University and Dan Lee, Victor Bergmann, Anna Domanski, Dominic Pilat, Uwe Rietzler, Maria Untch and Prince Ravat at MPIP.

I gratefully acknowledge the funding sources, which made my PhD work possible. I was awarded a research scholarship from Flinders University for three and half years of my PhD candidature and a full fee waiver during my PhD candidature from the Faculty of Science and Engineering. I am thankful to the CSIRO Future Manufacturing Flagship for awarding me with a PhD top-up research scholarship, Australian Nanotechnology Network (ANN) for a travel grant towards an international conference and a visiting scholarship from Max Planck Institute for Polymer Research, Mainz, towards my study trip to MPIP in 3rd year of my PhD. I would not have been able to attend over six international conferences and study trips without these fellowships.

I would like to thank my family for all their love and encouragement and especially my *Mom* and *Dad* who raised me with a love of science and constantly supported me in various capacities throughout this long journey. Most of all, I really appreciate my loving girlfriend not only for her love and support but also for patiently bearing with me in those final and stressful days of my PhD. I love u!

Lastly, many thanks to the almighty for bestowing upon me his choicest blessing in form of such wonderful mentors, colleagues, parents, friends, family and all the right opportunities that came my way!

Anirudh Sharma

Flinders University

July 2014

List of Publications

Refereed Journal Articles

1. ***Anirudh Sharma***, Rüdiger Berger, Gunther Andersson, David A. Lewis. Nanoscale heterogeniety and workfunction variations in ZnO thin films, *Submitted.*

2. ***Anirudh Sharma***, Joseph B. Franklin, Birendra Singh, Gunther Andersson, David A. Lewis. Electronic and chemical properties of ZnO in inverted OPV's, *Submitted.*

3. ***Anirudh Sharma***, Rüdiger Berger, Gunther Andersson, David A. Lewis. Invisible high workfunction materials on heterogeneous interfaces. *Applied Surface Science, Accepted.*

4. ***Anirudh Sharma***, Scott Watkins, Gunther Andersson, David Lewis. Effect of annealing temperature of ZnO on the energy level alignment in inverted organic photovoltaics (OPVs). *Energy Technology, 2014,* 2 (5) pp. 462-468.

5. ***Anirudh Sharma***, Mihail Ionescu, Gunther Andersson and David Lewis. Role of zinc oxide thickness on the photovoltaic performance of laminated organic bulk hetero-junction solar cells. *Solar Energy Materials and Solar Cells,* 2013, 115 pp. 64-70.

6. ***Anirudh Sharma***, Scott Watkins, David Lewis and Gunther Andersson. Effect of indium and tin contamination on the efficiency and electronic properties of organic bulk hetero-junction solar cells. *Solar Energy Materials and Solar Cells*, 2011, 95(12) pp. 3251-3255.

7. ***Anirudh Sharma***, Gunther Andersson and David Lewis. Role of humidity on indium and tin migration in organic photovoltaic devices. *Physical Chemistry Chemical Physics,* 2011, 13 pp. 4381-4387.

8. Lee Hoffman, Gunther Andersson, ***Anirudh Sharma***, Stephen Clarke, and Nicolas Voelcker. New insights into the structure of PAMAM dendrimer/gold nanoparticle nanocomposites. *Langmuir,* 2011, 27(11) pp. 6759-6767**.**

Conference Proceedings

1. ***Anirudh Sharma***, Gunther Andersson and David Lewis. Effect of ZnO layer thickness on the photovoltaic performance of laminated solar cells. *Nanomaterials for Green Technology,* Proceedings of the *3rd ISESCO International Workshop and Conference on Nanotechnology* (IWCN 2012) Selangor, Malaysia. Dec 2012, pp. 57-57.

2. ***Anirudh Sharma***, Scott E. Watkins, Gunther Andersson, and David Lewis. Instability of ITO-PEDOT:PSS interface in organic bulk hetero-junction solar cells and its effect on the efficiency and electronic properties of the device. *Thin Films and Nanomaterials* (Macmillan Advanced Research Series, India) edited by S. Jayakumar, M.D. Kannan, R. Balasundaraprabhu, S. Prasanna, Proceedings of the *International Conference on Advanced Materials* (ICAM 2011) Coimbatore, India. Dec 2011, pp. 212-215.

Presentations and Seminars

1. [Oral] ***Anirudh Sharma***, Rüdiger Berger, Gunther Andersson, David Lewis. Workfunction measurement of heterogeneous surfaces. *Flinders Centre for Nanoscale Science and Technology (FCNST) Annual Conference, June 18, 2014, Adelaide, Australia.*

2. [Oral] ***Anirudh Sharma***, Rüdiger Berger, Gunther Andersson, David Lewis. Nanoscale surface electronic properties of zinc oxide. *International Conference on Nanoscience and Nanotechnology (ICONN 2014)*, February 2- 6, 2014, Adelaide, Australia.

3. [Invited Oral] ***Anirudh Sharma***, Scott Watkins, Gunther Andersson and David Lewis. ZnO buffer layer for OPV's: Interfacial energetics and its influence on device performance. *International Workshop and School on Nanotechnology (NanoS-E3 2013)*, September 15-20, 2013, Airlie Beach, Australia.

4. [Seminar] ***Anirudh Sharma***, Scott Watkins, Gunther Andersson and David Lewis. Role of interfacial layers on the performance of OPV's. *Physics at Interfaces Research Group, Max Planck Institute for Polymer Research*, June 3, 2013, Mainz, Germany.

5. [Poster] ***Anirudh Sharma***, Gunther Andersson and David Lewis. Role of ZnO layer thickness on the photovoltaic performance of OPV's. *Hybrid and Organic Photovoltaics Conference (HOPV 2013)*, May 5-8, 2013, Sevilla, Spain.

6. [Oral] ***Anirudh Sharma***, Gunther Andersson and David Lewis. Effect of ZnO layer thickness on the photovoltaic performance of laminated OPV's. The *3rd ISESCO International Workshop and Conference on Nanotechnology (IWCN2012)*, December 5-7, 2013, Universiti Kebangsaan (UKM) Malaysia.

7. [Seminar] ***Anirudh Sharma***, Scott Watkins, Gunther Andersson and David Lewis. Role of interfaces on the photovoltaic performance of organic bulk hetero-junction solar cells. *South Australian Physical Chemistry Symposium*, December 3, 2012, University of Adelaide, Australia.

8. [Poster Prize] ***Anirudh Sharma***, Gunther Andersson and David Lewis. Understanding the morphological and electronic properties of zinc oxide buffer layers used in inverted organic photovoltaic cells. *International Organic Excitonic Solar Cell Conference (IOESC 2012),* September 3-7, 2012, Coolum Beach, Australia.

9. [Poster Prize] ***Anirudh Sharma***, Scott Watkins, Gunther Andersson and David Lewis. Air-processed organic bulk hetero-junction solar cells fabricated with hot press lamination: A step towards roll-to-roll processing. *Flinders Centre for Nanoscale Science and Technology (FCNST) Annual Conference*, June 13, 2012, Adelaide, Australia.

10. [Oral] Jonathan Campbell, ***Anirudh Sharma***, David Lewis, Thermomechanical behaviour of conducting polymer blends. *33rd Australian Polymer School,* February 12-15, 2012, Hobart, Australia.

11. [Oral] ***Anirudh Sharma***, Scott Watkins, David Lewis and Gunther Andersson. Instability of ITO-PEDOT:PSS interface in organic bulk hetero-junction solar cells and its effect on the efficiency and electronic properties of the device. *International Conference on Advanced Materials (ICAM) / Indo-Norwegian Workshop on Solar Energy Materials and Applications*, December 12-16, 2011, Coimbatore, India.

12. [Oral] ***Anirudh Sharma***, Scott Watkins, Gunther Andersson and David Lewis. Degradation of OPV's due to interfacial instability and an alternative approach towards roll-to-roll device fabrication. *Flinders Centre for Nanoscale Science and Technology (FCNST) Annual Conference*, July 18, 2011, Adelaide, Australia.

13. [Poster] ***Anirudh Sharma***, Gunther Andersson and David Lewis. Stability of ITO-PEDOT:PSS interface in bulk hetero-junction solar cells. *Australian Research Network for Advanced Materials & Australian Research Council Nanotechnology Network Joint Annual Workshop (ARNAM/ARCNN 2010)*, July 19-23, 2010, Adelaide, Australia.

Awards and Prizes

2014: **Best Presentation Award**

Flinders Centre for Nanoscale Science and Technology (FCNST) Annual Conference, Australia.

2013: **Visiting Research Fellowship**

Max Planck Institute for Polymer Research (MPIP), Germany.

2012: **Conference Travel Grant**

Australian Nanotechnology Network (ANN), Australia.

2012: **Poster Prize**

International Organic Excitonic Solar Cell Conference (IOESC), Coolum Beach, Australia.

2012: **University Finalist (2nd prize- Faculty of Sci. & Eng.)**

Flinders University 3MT Competition, Australia.

2012: **Poster Prize**

Flinders Centre for Nanoscale Science and Technology (FCNST) Annual Conference, Australia.

2011: **Chancellor's Letter of Commendation for Academic Excellence**

Flinders University, Australia.

2011: **Tuition Fee Waiver**

Faculty of Science & Engineering, Flinders University, Australia.

2010: **Postgraduate Research Top-up Scholarship**

Future Manufacturing Flagship, Commonwealth Scientific and Industrial Research Organization (CSIRO), Australia.

2010: **Privately Funded Postgraduate Research Scholarship**

Flinders University, Australia.

2009: **Summer Research Scholarship**

Faculty of Science & Engineering, Flinders University, Australia.

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Abbreviations

AFM	Atomic force microscope
ALD	Atomic layer deposition
AM	Air mass index
BHJ	Bulk hetero-junction
CPD	Contact potential difference
CSIRO	Commonwealth scientific and industrial research organization
DI	De-ionized
FWHM	Full-width-half-maxima
HOMO	Highest occupied molecular orbital
ITO	Indium tin oxide
IMFP	Inelastic mean free path
KPFM	Kelvin probe force microscope
LUMO	Lowest occupied molecular orbital
MEH-PPV	Poly(2-methoxy-5-2(2'-ethyl-hexyloxyl)-p-phenylene vinylene)
NICISS	Neutral impact collision ion scattering spectroscopy
nm	Nanometer
OPV	Organic photovoltaic
PEDOT:PSS	Poly(3,4-ethylenedioxythiophene): poly(4-styrenesulfonate)
P3HT	poly (3-hexylthiophene)
PCBM	[6,6]-phenyl-C61-butyric acid methyl ester
PPM	Parts per million
PESA	Photoelectron spectroscopy in air

p-LED	Polymer light emitting diodes
PET	Polyethylene terephthalate
PLD	Pulsed laser deposition
PEN	Polyethylene naphthalate
RH	Relative humidity
RBS	Rutherford backscattering spectroscopy
SPM	Surface probe microscopy
S. E.	Secondary electron
SKPM	Scanning kelvin probe microscopy
TEM	Transmission electron microscope
TOF	Time of flight
TW	Terawatt
UV	Ultraviolet
UHV	Ultra-high vacuum
UPS	Ultraviolet photoelectron spectroscopy
VBM	Valence band maxima
XPS	X-ray photoelectron spectroscopy
ZnO	Zinc oxide