FABRICATION AND CHARACTERISATION OF ORGANIC THIN-FILM TRANSISTORS FOR SENSING APPLICATIONS

By

Daniel Elkington

A THESIS SUBMITTED TO THE UNIVERSITY OF NEWCASTLE FOR THE DEGREE OF DOCTOR OF PHILOSOPHY DEPARTMENT OF PHYSICS MAY 2013



© Daniel Elkington, 2013.

Typeset in $\mathbb{A}_{\mathbb{E}} X 2_{\mathcal{E}}$.

This thesis contains no material which has been accepted for the award of any other degree or diploma in any university or other tertiary institution and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made in the text. I give consent to this copy of my thesis, when deposited in the University Library^{**}, being made available for loan and photocopying subject to the provisions of the Copyright Act 1968. **Unless an Embargo has been approved for a determined period.

Daniel Elkington

Acknowledgements

I would like to offer some thanks to the people who helped me during my time as a PhD student.

Firstly, I'd like to thank the University of Newcastle and the Australian Government for their financial support through the Australian Postgraduate Award program.

Secondly, as well as providing me with all the support and facilities to help me complete this thesis, the Centre for Organic Electronics has been a tremendously fun and interesting place to work and this positive atmosphere can be attributed to the qualities of its members. As such, I would like to thank some Centre members (past and present) for their guidance and friendship. Kathleen Sirois, for teaching me many things when I first started. Dr Glenn Bryant, for seemingly knowing everything about every piece of equipment I ever used. Dr Ben Vaughan, for showing me that electrical engineers can be successful in Physics! My fellow PhD students - Darma, Nathan, Garth, Nic, Ben, Kerry, Glen, Azzu and everyone else - thanks for being easy to get on with and so friendly. Dr Xiaojing Zhou, for her support and broad knowledge of organic electronics. Dr Warwick Belcher, for helping me with the basics of chemistry and always being easy to get on with. Finally, Professor Paul Dastoor, for being a fantastic motivator ans so generous with his knowledge - inspiring all us students to "save the world" through Physics.

To my friends who reminded me that life was not all about study, cheers!

My family has always been a deep and dependable support resource for me and I couldn't have got this far without them. To Mum, Dad and Lisa and all my extended family: thank you very much!

To Yuko, thanks for putting up with me and providing help and support when I needed it. I really appreciate everything.

List of Publications

- D. Elkington, D. Darwis, X. Zhou, W. Belcher, P.C. Dastoor *The fabrication and characterization of poly (4-vinylpyridine)-based thin film transistors exhibiting enhanced ion modulation.* (Organic Electronics) **13**, pp 153-158 (2012)
- D. Elkington, X. Zhou, W. Belcher, P. Dastoor. Investigations into Current Modulation Mechanisms in Low Operating Voltage Organic Thin Film Transistors and Their Relationship to the Materials Employed. 2011 MRS Spring Meeting
- X. Zhou, K. Mutkins, D. Elkington, K. Sirois, W. Belcher, P.C. Dastoor *Effects* of Device Architecture on the Performance of Organic Thin Film Transistors. 2008 MRS Fall Meeting
- D. Darwis, D. Elkington, E. Sesa, N. Cooling, G. Bryant, X. Zhou, W. Belcher, P.C. Dastoor *Surfactant Free P3HT/PCBM Nanoparticles for Organic Photovoltaics (OPV)*. The 4th Nanoscience and Nanotechnology Symposium (NNS2011) 2011
- D. Darwis, D. Elkington, S. Ulum, A. Stapleton, G. Bryant, X. Zhou, W. Belcher, P.C. Dastoor *High-Performance Thin Film Transistor from Solution-Processed P3HT Polymer Semiconductor Nanoparticles*. The 4th Nanoscience and Nanotechnology Symposium (NNS2011) 2011

Abstract

Organic thin-film transistors (OTFTs) are a family of devices in the area of organic electronics which are generating a large amount of interest due to the wide variety of potential applications for transistors which have all the benefits associated with using organic materials. These benefits include low-temperature and low-power fabrication possibilities, the use of flexible substrates and the low cost of materials.

Previous literature on OTFTs comprising poly-3-hexylthiophene (P3HT) semiconductor layers, poly(4-vinylphenol) (PVP) dielectric layers and poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) gate electrodes have reported on their relatively high performance at low operating voltages. However, there still remains the potential for further investigations to discover more about the nature of the current modulation mechanism(s) in these types of OTFTs. Several experiments were carried out to probe their operation mechanisms and determine their suitability for applications such as biosensors. The results of many of these experiments indicated that ions donated from the acidic PEDOT:PSS gate material as well as those liberated from water in air contribute to current modulation by doping and de-doping of the P3HT semiconductor.

Poly(vinyl-pyridine) (PVPy) was then introduced as a dielectric material to replace PVP. PVPy contrasts in its chemical properties with PVP: rather than allowing and contributing to the free movement of protons within it as the acidic PVP does, the chemically basic PVPy will tend to bind protons to its pyridal groups, restricting their movement. It was shown that this change in material reduces the off current (I_{OFF}) of the devices (by inhibiting any doping of P3HT which occurs upon PEDOT:PSS deposition), however the on current (I_{ON}) was also reduced and thus no real improvement in current modulation ration (I_{ON}/I_{OFF}) was achieved.

Whilst some aspects of device performance were improved when PVPy was used as the dielectric layer instead of PVP, the current modulation ratio remained low. Subsequent experiments showed that the addition of a dopant salt (LiClO₄) to the PVPy layer can substantially increase the current modulation ratio of the OTFTs. In fact, it was demonstrated that the current modulation ratio can be controlled by varying the amount of salt added to each device. The nature of the drain current (I_D) response to changes in gate voltage (V_{GS}) in the time domain indicates that electrochemical doping, and not an electrostatic mechanism, is the nature of the mechanism causing current modulation (similar to the previous un-doped devices). NaClO₄ was also trialled as a candidate for the dopant salt and, despite Na⁺ being larger than Li⁺, it appeared to move more freely within the device which is consistent with a hydration sphere model and therefore supports the idea that the dielectric layer is moisture-rich when operating in air.

Finally, OTFTs incorporating the enzyme glucose oxidase (GOX) were fabricated for use as glucose sensors. GOX selectively oxidises glucose and it was hypothesised that the ions liberated in this oxidation reaction could contribute to the ionic processes which contribute to current modulation in the devices and therefore a relationship between the quantity of glucose exposed to the device and the I_D level could be established. The results presented here show that devices with embedded GOX do indeed show a relationship between glucose concentration and I_D when an analyte solution is deposited onto the device.