Near-Field Scanning Optical Lithography for Nanostructuring Electroactive Polymers

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DECLARATION

This work 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.

(Signed): ....

Daniel Cotton

ACKNOWLEDGEMENTS

In preparing to write this passage it occurred to me that it may be appropriate to quote Sir Isaac Newton, specifically “If I have seen further it is by standing on ye shoulders of Giants.” Yet on further reflection I realised that Newton’s words are not as accurate for the modern scientist. For, whilst I do indeed owe some credit to the greats in providing my present vantage point, it has taken more than a few relative giants of the field to provide this view. Today it is more appropriate to describe, metaphorically, the contributions of my fellows as a human pyramid. A pyramid, perhaps, that has been added to so consistently often that it has become a mountain.

Just as a climber of tall mountains must have support to reach the summit, so must the student of science have help. The most important help comes in the form of a guide; my supervisors Paul Dastoor and Chris Fell have each climbed their own mountain in the past and their experience and time in showing me the easier paths to take has been beyond precious. Paul and Chris, I thank you. Likewise the help of my family, my parents and brothers, who have provided for me a base camp, at the foot of the mountain, from which to make the assault has been invaluable. Mum and Dad, I especially want to thank you.

Of course there are many others to thank as well. To continue the analogy: a mountaineer has the help of a logistical crew and the company of fellow climbers to ease their journey; and so there is a litany of friends and colleagues that I wish to thank here. In particular I want to thank Warwick Belcher, Ben Watts, Chris Foster, Ben Duck, Chris Duckett, Tania Ritchie, Colin Waters, Lars Thomsen, David Green, Ben Vaughan, Kate Wagner, Erica Wanless, John Holdsworth, Jordan Downs, Chris Harris, Chris McNeill, Steve Morley, Steven Schofield, Kathleen Sirois, Jamie Quinton, Neil Curson, Feridoun Samavat, Stephan Steiss and too many more to name here. To everyone who has aided me during this period, you have assisted me in my endeavour and I thank you.

CONTENTS

ABSTRACT

The photochemistry of poly{*p*-phenylene[1-(tetrahydrothiophen-1-io)ethylene chloride]} (PPTEC), a water soluble precursor of the semiconducting polymer, poly{*p*-phenylenevinylene} (PPV), has been studied both under atmospheric conditions and in environments devoid of oxygen. UV-visible spectroscopy and photoluminescence data has been used to provide a picture of the mechanistic pathways involved in UV irradiation of the PPTEC material. A new quantitative model for the effect of UV irradiation upon film morphology is presented.

The technique of near-field scanning optical lithography (NSOL) has been used to produce arbitrary structures of the semi-conducting polymer poly{*p*-phenylenevinylene} at sizes comparable with optical wavelengths. Structures on this scale are of interest for integrated optical devices and organic solar cells. The structures are characterised using AFM and SEM and examined in the context of the electric field distribution at the NSOM tip. The Bethe-Bouwkamp model for electric field distribution at an aperture has been used, in combination with the developed model for precursor solubility dependence on UV energy dose, to predict the characteristics of lithographic features produced by NSOL. Fine structure in the lithographic features that are characteristic of the technique are investigated and their origins explained. Suggestions for the improvement of the technique are made.

Presented here for the first time is a device manufactured by the technique of NSOL functioning as an optical device. The technique of NSOL is used to manufacture an optical transmission phase grating (or phase mask) of PPV, this was done as a proof of concept for device manufacture by this method and to demonstrate the potential usefulness of the unique characteristics of the technique. The phase mask was characterised using AFM and SEM and examined in the context of how well a diffraction pattern matches with theoretical calculations.