

UNIVERSITY OF EXETER

# Phase Differential Surface Plasmon Imaging

by

Ciarán Stewart

A thesis submitted in partial fulfillment for the  
degree of Doctor of Philosophy

in the

Engineering, Mathematics and Physical Sciences  
School of Physics

August 2010

---

# Phase Differential Surface Plasmon Imaging

Submitted by Ciaran Stewart, to the University of Exeter  
as a thesis for the degree of  
Doctor of Philosophy in Physics  
**in August 2010**

This thesis is available for library use on the understanding that it is copyright material and that no quotation from the thesis may be published without proper acknowledgement

I certify that all material in this thesis which is not my own work has been identified  
and that no material has been previously submitted and approved for the award of a  
degree by this or any other University

Signature: .....

*“I not only use all the brains that I have, but all that I can borrow. ”*

Woodrow Wilson

UNIVERSITY OF EXETER

# *Abstract*

Engineering, Mathematics and Physical Sciences  
School of Physics

Doctor of Philosophy

by Ciarán Stewart

Surface Plasmon Resonance (SPR) has been utilised in various forms in sensors for many years. It is usually based on angular or wavelength interrogation of the reflectivity minimum found with Transverse Magnetic (TM) light. However, as the SPR is traversed there is also a very rapid change in the phase of the reflected TM light there being no such change in the Transverse Electric (TE) light. Presented in the thesis a new SPR sensor has been developed that exploits this rapid change in optical phase. Linearly polarised light of mixed TM/TE polarisation is passed through a polarization modulator, which adds a small amplitude modulation to the polarisation. This modulated light is incident on a gold film 40 nm thick evaporated onto the base of a SF2 prism in the Kretschmann-Raether, configuration. The coupling of the TM polarised light to the SPR is dependant on the properties of the dielectric medium adjacent to the gold film. The SPR shifts when this sensed medium undergoes a change in refractive index (or index or thickness if it is a bound analyte layer). This in turn causes a change in the reflected elliptically polarised light. The change of the resultant modulated polarisation dither is interrogated through the use of a phase sensitive detectors. Initially a simple photo diode coupled with a lock-in amplifier was used to monitor the modulated signal. This was expanded into an imaging technique by using two cameras (64 by 64 pixels) fabricated with the equivalent of a lock-in amplifier on each of the 4096 pixels. The spatial map of the modulation amplitude gives an optical phase differential image. By imaging in this way it is possible to produce a multi channel differential sensor.

# *Acknowledgements*

Firstly I must thank my supervisor Roy Sambles, without his persistent encouragement and his enthusiasm for science I would never have finished any project. He was always my first source of ideas. I am also very lucky to have extremely supportive parents, without their continuing support I would never have been able to undertake this PhD. I must also thank my CASE award supervisor Elaine Perkins for her support and for a different view point from that of pure academics.

Over the past few years the electromagnetic materials group has been more like a home than a work place. There have been a number of people who have helped me during my PhD. First mention must go to Dr Ian Hooper; especially during my first year, he was my first port of call for anything that I didn't understand. He was always willing to lend a hand in experiment. He has the infuriating but incredibly useful ability to know why an experiment will fail before it has started. My next mention should be to Dr Matt Lockyear who from the beginning was always there to give perspective on any problem, I hope that there will be more than one rad stations Ireland. Dr James Parsons and I started our projects in the same week. We sat next to each other for more than a year. He was always happy to talk about all forms of science, though he sometimes seemed close to the edge of sanity, 90% of my memories of the first year of my PhD are due to James. Andy Murray and Chris Burrows, whom I shared an office with while writing up, should get some credit as they had to put up with me for so long. Bill Barnes always had an open door ready to discuss science or sign blue forms. I also must thank Helen who I share a desk with in G31, she thankfully thought my humming and singing to jazz as I worked on some analysis was funny (I hope). Baptist the French man was a great help in debugging some of my earlier MATLAB scripts and I am ashamed to say that I still use nested loops. Sharon gave me guidance when I foolishly dabbled in making liquid crystal cells. Dennis from Nottingham must get a special mention for all his optimism 'it will be OK' something I don't think I will ever forget. Caroline I will miss for all the fruit she was willing to share with me. EEEEEVgeny was very helpful as a writing buddy. Matt B, Celia, James E, Lizzy, Alfie, Stephen, Ed, Mel and the rest of the electromagnetic materials group all get my thanks for being such great people to work with and be around.

There have been a number of people who have had a great and small influence on me and my PhD, not all of whom have been involved directly with science. A big mention must go to Gracie B and Laurence B, who throughout my studies were always a great source of friendship and cooked me too many amazing meals to count.

There have been a number of people I have lived with over the years who have made living in Exeter so much better during my PhD. Thank you Emma for putting up with me living opposite the prison. Pete BURNS, living in Mansfield road was the most chilled place I have ever lived, I think Peter will stay in Exeter long after everyone else has left. Finally the house of doom. Living with Chris, Pete and Tom was certainly an experience; there was always something going on. I will continue to draw cards to see who needs to buy milk and make tea long after I leave Exeter.

# Contents

<b>Abstract</b>	<b>2</b>
<b>Acknowledgements</b>	<b>3</b>
<b>List of Figures</b>	<b>8</b>
<b>List of Tables</b>	<b>23</b>
<b>Abbreviations</b>	<b>24</b>
<b>1 Introduction</b>	<b>27</b>
1.1 Aim of this work . . . . .	27
1.2 Outline of thesis . . . . .	28
<b>2 Sensing with Surface Plasmon Resonance</b>	<b>30</b>
2.1 Introduction . . . . .	30
2.2 Surface Plasmon Resonance . . . . .	30
2.2.1 Introduction . . . . .	31
2.2.2 Intensity . . . . .	31
2.2.3 Angle . . . . .	31
2.2.4 Wavelength . . . . .	32
2.2.5 Phase . . . . .	33
2.3 Differential techniques . . . . .	34
2.4 Comparison of Techniques . . . . .	35
2.4.1 Characteristics of Comparison . . . . .	35
2.4.2 Sensitivity . . . . .	35
2.4.3 Linearity . . . . .	38
2.4.4 Dynamic Range . . . . .	38
2.4.5 Limit of Detection . . . . .	38
2.5 SPR Instrumentation . . . . .	38
2.5.1 SPR sensors based on prism coupling . . . . .	39
2.5.2 SPR sensing based on grating couplers . . . . .	46

---

2.5.3	SPR sensing based on optical waveguides . . . . .	50
2.5.4	Commercial systems . . . . .	53
2.6	SPR in Protein measurement . . . . .	63
2.7	SPR imaging in Biochips . . . . .	65
2.8	Differential SPR . . . . .	65
2.9	Differential SPR in biochips . . . . .	66
2.10	Summary . . . . .	67
<b>3</b>	<b>Materials and Methods</b>	<b>68</b>
3.1	Details of Cameras used in SPR imagaing . . . . .	68
3.2	Micro channel Fabrication . . . . .	69
3.3	Preperation of Reagents and Samples . . . . .	69
3.4	Calibration and Optomisation . . . . .	69
<b>4</b>	<b>Theory of Differential Surface Plasmon Resonance Bio-sensing</b>	<b>72</b>
4.1	Introduction . . . . .	72
4.2	Electromagnetic Theory of Surface Plasmon Resonance . . . . .	72
4.2.1	The Surface Plasmon Polariton . . . . .	73
4.2.2	Propagation Length of the SPP . . . . .	77
4.2.3	SPP field penetration . . . . .	78
4.2.4	Surface Plasmon Polariton Dispersion Relation . . . . .	79
4.2.5	The Effect of a Dielectric Overlayer . . . . .	81
4.3	Coupling to the SPP . . . . .	82
4.3.1	Prism coupling . . . . .	82
4.3.2	Grating coupling . . . . .	87
4.3.3	Waveguide coupling . . . . .	89
4.4	Sensing with SPR . . . . .	90
4.5	Pseudo First Order Kinetics . . . . .	92
4.6	Summary . . . . .	97
<b>5</b>	<b>Surface Plasmon Enhanced Differential Ellipsometry for Single and dual channel Bio-sensor</b>	<b>98</b>
5.1	Introduction . . . . .	98
5.2	Surface Plasmon Differential Ellipsometry . . . . .	99
5.2.1	Surface Plasmon Ellipsometry . . . . .	99
5.2.2	Polarisation Modulation . . . . .	102
5.3	Polarization Modulation . . . . .	117
5.3.1	Mechanically Oscillated Polariser . . . . .	117
5.3.2	Liquid crystal polarization modulator . . . . .	118
5.3.3	Photo Elastic Modulator . . . . .	118
5.4	Surface Plasmon Differential Ellipsometry . . . . .	120
5.4.1	Experimental Set-up . . . . .	120
5.4.2	Optimizing the Sensitivity by Tuning the Incident Angle . . . . .	120
5.4.3	Determining Sensitivity . . . . .	122
5.4.4	Linearity . . . . .	122



---

5.4.5	Sensitivity . . . . .	123
5.5	Dual channel . . . . .	125
5.6	Conclusions . . . . .	126
<b>6</b>	<b>Surface Plasmon Resonance Imaging - PC4</b>	<b>129</b>
6.1	Introduction . . . . .	129
6.2	Differential surface plasmon resonance imaging . . . . .	130
6.2.1	Basic Setup for imaging . . . . .	130
6.2.2	Light Source . . . . .	130
6.2.3	Phase sensitive pixelated detector . . . . .	133
6.3	Bulk index sensitivity - Divergent beam . . . . .	136
6.4	Magnesium fluoride spots . . . . .	139
6.4.1	$MgF_2$ spots polarisation rotation . . . . .	142
6.5	Imaging flow front between brix solution and silicone oil . . . . .	143
6.6	Bulk Sensitivity . . . . .	147
6.7	Proteins binding to functionalised surface . . . . .	151
6.8	Conclusions . . . . .	154
<b>7</b>	<b>Surface Plasmon Resonance Imaging with camera Atto1b</b>	<b>160</b>
7.1	Introduction . . . . .	160
7.2	The pixelated phase sensitivity detector . . . . .	160
7.3	LED testing . . . . .	161
7.4	Polarisation rotation . . . . .	163
7.5	Light source . . . . .	169
7.6	Bulk index change . . . . .	170
7.7	Summary . . . . .	176
<b>8</b>	<b>Conclusions and the future</b>	<b>179</b>
8.1	Conclusions . . . . .	179
8.2	Future Work . . . . .	181
8.3	Publications and patents . . . . .	182