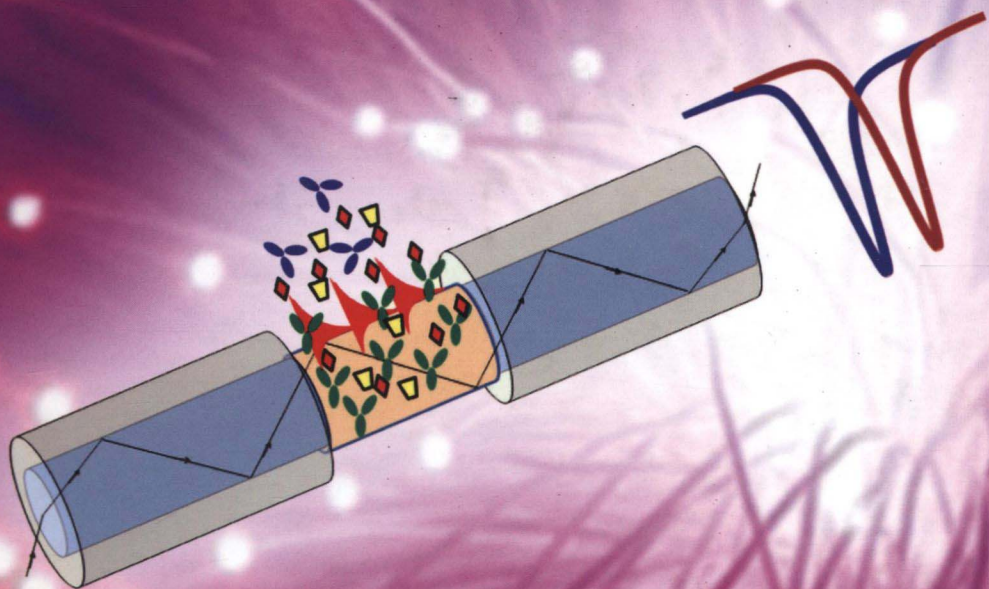
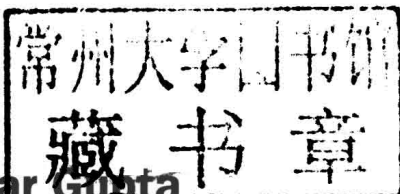
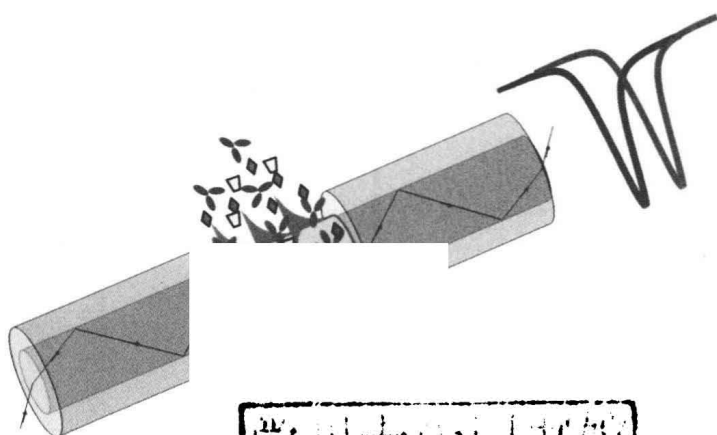


FIBER OPTIC SENSORS BASED ON PLASMONICS

Banshi Dhar Gupta
Sachin Kumar Srivastava
Roli Verma



FIBER OPTIC SENSORS BASED ON PLASMONICS



Banshi Dhar Gupta

Indian Institute of Technology Delhi, India

Sachin Kumar Srivastava

Ilse Katz Institute of Nanoscale Science and Technology, Israel

Roli Verma

Indian Institute of Technology Delhi, India

 **World Scientific**

NEW JERSEY • LONDON • SINGAPORE • BEIJING • SHANGHAI • HONG KONG • TAIPEI • CHENNAI

Published by

World Scientific Publishing Co. Pte. Ltd.

5 Toh Tuck Link, Singapore 596224

USA office: 27 Warren Street, Suite 401-402, Hackensack, NJ 07601

UK office: 57 Shelton Street, Covent Garden, London WC2H 9HE

British Library Cataloguing-in-Publication Data

A catalogue record for this book is available from the British Library.

FIBER OPTIC SENSORS BASED ON PLASMONICS

Copyright © 2015 by World Scientific Publishing Co. Pte. Ltd.

All rights reserved. This book, or parts thereof, may not be reproduced in any form or by any means, electronic or mechanical, including photocopying, recording or any information storage and retrieval system now known or to be invented, without written permission from the publisher.

For photocopying of material in this volume, please pay a copying fee through the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, USA. In this case permission to photocopy is not required from the publisher.

ISBN 978-981-4619-54-7

In-house Editor: Song Yu

Typeset by Stallion Press

Email: enquiries@stallionpress.com

Printed in Singapore by B & Jo Enterprise Pte Ltd

FIBER OPTIC SENSORS BASED ON PLASMONICS

Preface

This book is an effort of bringing a comprehensive book on fiber optic plasmonic sensors for undergraduate and graduate students. The idea resulted due to many enquiries to one of the authors, Banshi D. Gupta, for writing a text book on the subject. Though tremendous amount of literature is available on the research, hardly any text book is available on the subject. Few books have been edited on surface plasmon resonance (SPR)-based sensors, though, to present the advancement of research to the established researchers.

SPR is a phenomenon that can be dealt with a little primary knowledge of electromagnetic theory and hence can be introduced to undergraduate students with its possible applications. A book by Professor Stefan Meir successfully does a part of the job. However, when it comes to the fascinating world of the sensors and their integration with optical fiber, most of the available literature fails to provide a comprehensive collective knowledge of the subject. With this book, we aim to introduce the undergraduate students and early researchers to an overview of the fiber optic sensors based on the fascinating field of plasmonics, their working principles, and applications. The book helps the established researchers with an insight of the current trends in the fiber optic plasmonic sensors.

In the first chapter of the book we have provided a historical overview of the fiber optic sensors based on plasmonics. A chronological development has been presented, along with the remarks at

crucial stages of the development. Further, to build the foundation, the Physics of surface plasmons has been discussed in Chapter 2. The chapter comprises of a rigorous discussion and derivation of the wave-vector condition for surface plasmons from Maxwell's equations, issues related to the excitation of surface plasmons, various techniques of excitation, interrogation techniques, and SPR configurations. In the third chapter, we have presented a detailed description of the various components of a sensor, their characteristics, and roles in the sensor. The important characteristics of sensors have also been discussed. In chapter 4, we have presented a rigorous theoretical treatment of fiber optic SPR sensors. This chapter discusses how to incorporate various light launching conditions in optical fiber sensing. Chapter 5 discusses various methods of fabrication of fiber optic SPR sensors. It presents various surface functionalization strategies depending upon the analyte and the medium/ambience of interest. In Chapter 6, we present a number of studies on SPR-based fiber optic sensor using various surface immobilization techniques. Chapter 7 discusses the effect of some of the intrinsic and extrinsic factors, such as temperature, ions, dopants, etc. on the performance of fiber optic SPR sensors. In Chapter 8, we present an overview of the future trend of research and development in the field of fiber optic SPR sensors. We have added two appendices at the end of the book to provide the treatment of the dielectric functions of the metals and tabulated data of various constants and Sellmeier coefficients.

Banshi D. Gupta
Sachin K. Srivastava
Roli Verma

Acknowledgements

I consider myself very fortunate to have worked with Dr. Chandra Deep Singh, Professor Sunil Khijwania and Dr. Navneet K. Sharma on fiber optic evanescent field absorption sensors. My continuous interaction with them has certainly made me wiser in the field of fiber optic sensors. It was this interaction that resulted in the publication of my first book entitled “Fiber optic sensors: Principles and applications (2006). In 2004, I took initiation to work on fiber optic sensors utilizing surface plasmon resonance technique. The research carried out on this topic resulted in 8 Ph.D. theses. I thank Drs. Anuj K. Sharma, Rajan Jha, Rajneesh K. Verma, Sarika Singh, Priya Bhatia, and Satyendra K. Mishra, in addition to Drs. Sachin K. Srivastava and Roli Verma (the other authors of this book), who have worked with me in this exciting field. I learnt a lot from these colleagues through interaction. Indeed, a part of the book has emerged from the work carried out with them. I also thank my present graduate students Rana Tabassum, Anand Mohan Shrivastav and Sruthi Prasood U, for helping me in the preparation of the book. Finally, my special thanks to my wife Uma Gupta for her patience and understanding.

Banshi D. Gupta

Contents

<i>Preface</i>	v
<i>Acknowledgements</i>	vii
1. Introduction	1
1.1 Surface Plasmons: Historical Perspective	1
1.2 Kretschmann and Otto Configurations	3
1.3 Fiber Optic SPR Sensor Developments	4
1.4 Overview of the Book	13
References	14
2. Physics of Plasmons	21
2.1 Introduction	21
2.2 SPs at Semi-Infinite Metal–Dielectric Interface	23
2.2.1 Non-existence of SPs for TE modes	25
2.2.2 Existence of SPs for TM modes	25
2.2.3 Field	28
2.2.4 Penetration depth	29
2.2.5 Propagation length	30
2.3 Excitation of SPs	31
2.3.1 Prism-based method	31
2.3.2 Waveguide-based method	37
2.3.3 Grating-based method	39

2.4	SP Modes of a Thin Metal Film	41
2.5	Long and Short Range Surface Plasmons	42
2.6	Nearly Guided Wave SPR (NGWSPR)	43
2.7	Interrogation Techniques	45
2.7.1	Angular interrogation	46
2.7.2	Spectral interrogation	47
2.7.3	Intensity interrogation	49
2.7.4	Phase interrogation	50
2.8	SPR Imaging (SPRI)	51
2.9	Summary	52
	References	53
3.	Characteristics and Components of Fiber Optic Sensor	55
3.1	Components of a Sensor and Their Functions	56
3.1.1	Analyte/sample	56
3.1.2	Receptors	60
3.1.2.1	Enzymatic receptors	61
3.1.2.2	Antibody-based receptors	64
3.1.2.2.1	Polyclonal antibody	64
3.1.2.2.2	Monoclonal antibody	65
3.1.2.3	Nucleic acid based receptors	66
3.1.2.4	Cell-based receptors	67
3.1.2.5	Tissue-based receptors	69
3.1.3	Transducers	70
3.1.3.1	Electrochemical	71
3.1.3.1.1	Amperometric	72
3.1.3.1.2	Conductometric	72
3.1.3.1.3	Potentiometric	73
3.1.3.2	Piezoelectric	73
3.1.3.3	Thermometric	74
3.1.3.4	Optical transducers	74
3.1.4	Detector	75
3.2	Optical Fiber	77
3.2.1	TIR	78
3.2.2	Light ray propagation in an optical fiber	79

3.2.3	Numerical aperture	79
3.2.4	Fiber modes	80
3.3	Optical Fiber Sensors	81
3.4	Performance Parameters	84
3.4.1	Sensitivity	84
3.4.2	Selectivity/specificity	84
3.4.3	Limit of detection	85
3.4.4	Accuracy	85
3.4.5	Resolution	85
3.4.6	Repeatability	85
3.4.7	Reproducibility	86
3.4.8	Noise	86
3.4.9	Range	86
3.4.10	Response time	87
3.4.11	Linearity	87
3.4.12	Drift	87
3.4.13	Figure of merit	87
3.5	Summary	88
	References	88
4.	Theory of SPR-based Optical Fiber Sensor	93
4.1	Introduction	93
4.2	N -Layer Model	96
4.3	Excitation by Meridional Rays: On Axis Excitation	102
4.4	Excitation by Skew Rays: Off Axis Excitation	108
4.5	Diffuse Source	112
4.6	Performance Parameters: Sensitivity, Detection Accuracy, and Figure of Merit (FOM)	114
4.7	Summary	117
	References	118
5.	Fabrication and Functionalization Methods	119
5.1	Sensing Elements	120
5.1.1	Sensor surface	120

5.1.1.1	Preparation of the fiber probe	120
5.1.1.2	Coating of the metal layer	121
5.1.1.3	Criterion for support selection	126
5.2	Immobilization Techniques	127
5.2.1	Covalent binding	128
5.2.1.1	Thiol bonding	129
5.2.1.2	Disulfide bonding	129
5.2.1.3	Metal binding	129
5.2.1.4	Silanization	130
5.2.2	Entrapment	132
5.2.3	Encapsulation	133
5.2.4	Cross linking	135
5.2.5	Adsorption	136
5.3	Molecular Imprinting	139
5.3.1	Covalent molecular imprinting	140
5.3.2	Non-covalent molecular imprinting	140
5.4	Advantages and Disadvantages of Molecular Imprinting	141
5.4.1	Covalent imprinting	141
5.4.2	Non-covalent imprinting	142
5.5	Graphene Functionalized Receptors	143
5.6	Summary	146
	References	147
6.	SPR based Sensing Applications	155
6.1	Introduction	155
6.2	Refractive Index Sensor	157
6.2.1	Effect of oxide layers	159
6.2.2	Multi-channel sensing	161
6.3	pH Sensor	163
6.3.1	Silver/silicon/hydrogel based pH sensor	167
6.3.2	Silver/indium tin oxide/aluminium/ hydrogel based pH sensor	169
6.4	Ethanol Sensor	171

6.5	Enzyme based Sensors	174
6.5.1	Urea sensor	175
6.5.2	Naringin sensor	178
6.5.3	Organophosphate pesticide	178
6.5.4	Phenolic compounds	179
6.5.5	Glucose sensor	182
6.5.6	Low density lipoprotein sensor	185
6.6	Molecular Imprinting based Sensors	187
6.6.1	Vitamin B ₃ sensor	188
6.6.2	Tetracycline sensor	189
6.7	Multi-analyte Sensing	197
6.8	Gas Sensors	203
6.8.1	Ammonia gas sensor	204
6.8.2	Hydrogen sulphide gas sensor	207
6.9	Summary	213
	References	213
7.	SPR based Fiber Optic Sensors: Factors Affecting Performance	217
7.1	Introduction	217
7.2	Influence of Intrinsic Stimuli	217
7.2.1	Fiber parameters	217
7.2.1.1	Core diameter	218
7.2.1.2	Sensing length	219
7.2.1.3	Numerical aperture	221
7.2.2	Change of metal	223
7.2.3	Influence of dopants in fiber core	227
7.2.4	Role of high index dielectric layer	227
7.2.5	Probe design	234
7.2.5.1	Tapered probe	234
7.2.5.2	U-shaped probe	239
7.3	Influence of Extrinsic Stimuli	243
7.3.1	Influence of temperature	243
7.3.2	Influence of ions	245
7.4	Summary	248
	References	249

8. Future Scope of Research	251
Appendix A Dispersion Relations of Dielectric Materials and Metals	255
A.1 Optical Absorption	255
A.2 Dispersion Relations: Dielectrics and Metals	255
A.2.1 Dielectrics: Lorentz model of damped oscillators	256
A.2.2 Metals: Drude model	258
Appendix B List of Constants	261
B.1 Sellmeier Relation	261
B.2 Plasma and Collision Wavelengths for Plasmonic Metals	261
B.3 Dispersion Relations of Various Dielectric Materials and Metal Oxides	262
<i>Index</i>	265

Chapter 1

Introduction

1.1 Surface Plasmons: Historical Perspective

The first observation of the phenomenon of surface plasmon resonance (SPR) dates back to 1902, when Wood¹ reported the “*uneven distribution of light in a diffraction grating spectrum*” while he observed patterns of unusual dark and bright bands in the light reflected from a metal backed diffraction grating. Although, he speculated the possible interaction of the grating-metal arrangement with the incident light, no obvious and clear reason for the observed phenomenon was provided.

The first theoretical description of these anomalies was provided by Lord Rayleigh² in 1907, when he published the *dynamical theory of gratings*. He assumed that the scattered electromagnetic field can be expanded in terms of outgoing waves only and predicted singularities in the scattered field at several wavelengths. He could predict that these wavelengths (called Rayleigh wavelengths after his name) resemble the Wood’s anomalies and occurred only when the electric field was polarized perpendicular to the grating rulings. He called it *s-anomalies*. His theory predicted no singularities for *p-polarization*. However, the existence of *p-anomalies* was reported by Wood in his later observations and further confirmed by Palmer^{3,4} when he found the existence of *p-anomalies* in deeply ruled gratings.

Around the same time, in 1907, Zenneck theoretically formulated a special surface wave solution to the Maxwell's equation and demonstrated that the radio frequency surface electromagnetic waves occur at the boundary of two media when one medium is either lossy dielectric or a metal and the other is loss free.⁵ He also suggested that the lossy part of the dielectric constant is responsible for the binding of the electromagnetic waves to the interface. Sommerfeld, in 1909, formulated that the field amplitudes of the surface waves postulated by Zenneck, vary inversely as the square root of the distance from the source dipole.⁶ In 1941, Fano theoretically concluded that the anomalies reported by Wood¹ in the diffraction grating spectra were observed due to the excitation of surface waves on the interface.⁷ Ritchie, in 1957, for the first time coined the word 'surface plasmons' while explaining the characteristic losses of energy experienced by fast electrons when they travel through thin metal films and demonstrated theoretically that the surface plasmons could be excited on the surface of a thin metal film.⁸ In 1959, Turbadar reported that illumination of thin metal films on a substrate leads to a large drop in the reflectivity at certain conditions, but this observation was not linked to the excitation of surface plasmons.⁹ In 1960, the excitation of surface plasmons at the metal surface was observed by Powell and Swan.¹⁰ They used accelerated electrons for the excitation of surface plasmons. Soon after, in 1960, Stern and Ferrell showed that the electromagnetic waves at the metallic surface involved electromagnetic radiation coupled to the surface plasmons.¹¹ In 1968, Otto explained the results obtained by Turbadar⁹ and demonstrated that in attenuated total internal reflection, the drop in the reflectivity occurred due to the excitation of surface plasmons.¹² Although the first experimental observation of surface plasmons was observed in 1959 by Turbadar, a clear experimental understanding of the phenomenon was presented only in 1968 by Otto.¹² In Otto configuration (discussed briefly in the next section), a small gap of a few nanometers is to be maintained between a prism base and the metal layer, and the dielectric medium is sandwiched between the prism base and the metal layer. The metal layer is coated on a glass substrate. The Otto configuration