



UNIVERSITI PUTRA MALAYSIA

**OPTICAL PROPERTIES AND KINETIC BEHAVIOUR OF SOME
CHEMICAL AND BIOLOGICAL SPECIES USING SURFACE PLASMON
RESONANCE OPTICAL SENSOR**

WAN YUSMA WATI BINTI WAN YUSOFF

FS 2005 42

**OPTICAL PROPERTIES AND KINETIC BEHAVIOUR OF SOME
CHEMICAL AND BIOLOGICAL SPECIES USING SURFACE PLASMON
RESONANCE OPTICAL SENSOR**

WAN YUSMAWATI BINTI WAN YUSOFF

**MASTER OF SCIENCE
UNIVERSITI PUTRA MALAYSIA
2005**



**OPTICAL PROPERTIES AND KINETIC BEHAVIOUR OF SOME
CHEMICAL AND BIOLOGICAL SPECIES USING SURFACE PLASMON
RESONANCE OPTICAL SENSOR**

By

WAN YUSMAWATI BINTI WAN YUSOFF

**Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia,
in Fulfilment of the Requirements for the Degree of Master of Science**

July 2005



Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirements for the degree of Master of Science

**OPTICAL PROPERTIES AND KINETIC BEHAVIOUR OF SOME
CHEMICAL AND BIOLOGICAL SPECIES USING SURFACE PLASMON
RESONANCE OPTICAL SENSOR**

By

WAN YUSMAWATI WAN YUSOFF

July 2005

Chairman : Professor W. Mahmood Mat Yunus, PhD

Faculty : Science

Surface plasmon resonance (SPR) spectroscopy is a surface-sensitive technique that has been used to characterize the thickness and index of refraction of dielectric medium at noble metal interface. Nowadays surface plasmon resonance technique has emerged as a powerful technique for a variety of chemical and biological sensor applications.

In this study, gold and silver with purity of 99.99% were used to fabricate thin metal films. The thin film was deposited onto a glass cover slip and attached onto the surface of a 60° prism using index matching oil. Liquid samples, such as chlorine, saccharide, swimming pool water, pesticide, virus and DNA were studied using Kretschmann Surface Plasmon Resonance technique. All the measurements were carried out at room temperature. The experiment was carried out by measuring the intensity of the optical reflectivity as a function of incident angle.

It found that the shift of resonance angle ($\Delta\theta$) increased linearly with the sample concentration. The detection limit of the sensor was estimated better than 0.01 pM for the sample of DNA (Oligo2-Bio). Larger sensor sensitivity of $9.42^\circ/(\text{mol/L})$ is obtained for the sucrose sample.

The kinetic behaviour of the system was also examined to monitor the self-assembling process on the metal surface in real time. The shift in resonance angle increased greatly with time during the increment of the molecules deposited on the gold surface. In contrast it was found decrease with time during self-assembling process.

This work also studied the molecule-dielectric interaction for a thin Fatty Hydroxamic Acid (FHA) film (extract from crude palm oil), which the FHA layer was coated using spin coating on the top of metal film. When the medium outside the surface of Au film was changed from air to FHA layer, the resonance angle shifted to the higher value. The shift of resonance angle increased linearly with the increasing concentration FHA layer. When the metal ion was attached to the FHA film, the resonance angle was changed to the maximum value.

The experimental results reveal that the technique that based on surface plasmon resonance phenomenon can be used to determine the optical properties and the kinetic behaviour. It also suitable to study the molecule-dielectric interaction for the polymer film. This technique can become an effective chemical optical sensor. Saccharide, pesticide and chlorine concentration in water can be detected using this sensor. Furthermore it also can be used to detect DNA and viruses solution.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

**SIFAT OPTIK DAN PERLAKUAN KINETIK TERHADAP BEBERAPA
SPESIS KIMIA DAN BIOLOGI MENGGUNAKAN SENSOR OPTIK
RESONANS PLASMON PERMUKAAN**

Oleh

WAN YUSMAWATI BINTI WAN YUSOFF

Julai 2005

Pengerusi : Profesor W. Mahmood Mat Yunus, PhD

Fakulti : Sains

Spektroskopi Resonans Plasmon Permukaan (SPR) ialah satu teknik sensitif-permukaan yang digunakan untuk mengenalpasti ketebalan dan indeks biasan medium dielektrik pada antaramuka logam. Kini, teknik resonans plasmon permukaan telah muncul sebagai teknik yang berguna dalam pelbagai penggunaan pengesanan kimia dan biologi.

Dalam kajian ini, emas dan perak dengan ketulenan 99.99% digunakan untuk membuat filem tipis logam. Filem tipis logam tersebut telah disaputkan kepada slip kaca dan dilekatkan kepada satu permukaan prisma 60° dengan menggunakan minyak indeks sepadan. Sampel cecair seperti klorin, sakarida, air kolam renang, pestisid, virus dan DNA dikaji dengan menggunakan teknik Plasmon Resonans Permukaan Kretschmann. Semua pengukuran telah dilakukan pada suhu bilik. Eksperimen telah dilakukan dengan mengukur keamatan keterpantulan optik sebagai satu fungsi kepada sudut tuju.

Keputusan menunjukkan anjakan sudut resonans ($\Delta\theta$) meningkat secara linear dengan kepekatan larutan sampel. Had pengesanan bagi pengesanan dianggarkan lebih baik daripada 0.01 pM untuk sampel DNA (Oligo2-Bio) dan kepekaan pengesanan tertinggi ialah $9.42^\circ/(\text{mol/L})$ untuk sampel sukrosa.

Perlakuan kinetik sistem juga telah diperiksa untuk memerhati proses berkumpul-sendiri pada permukaan logam dalam masa nyata. Anjakan sudut resonans bertambah secara mendadak dengan masa ketika peningkatan endapan molekul pada permukaan emas. Anjakan ini didapati menurun dengan masa ketika proses perhimpunan-sendiri.

Kajian ini juga mengkaji interaksi antara molekul-dielektrik untuk filem tipis Fatty Hydroxamic Acid, FHA (ekstrak dari minyak kelapa sawit mentah), dengan lapisan FHA telah disaput menggunakan 'spin coating' atas filem logam. Apabila medium permukaan luar filem tipis logam ditukarkan daripada udara kepada filem polimer FHA, sudut resonans berganjak kepada nilai yang lebih tinggi. Anjakan sudut resonans telah meningkat secara linear dengan kepekatan lapisan FHA. Apabila ion logam dilekatkan pada lapisan FHA, sudut resonans telah berubah kepada nilai maksimum.

Keputusan eksperimen menunjukkan teknik yang berdasarkan fenomena resonans plasmon permukaan boleh digunakan untuk menentukan sifat-sifat optik dan kelakuan kinetik. Ia juga sesuai untuk mengkaji interaksi molekul-dielektrik bagi filem polimer. Teknik ini boleh menjadi pengesanan pengesanan optik kimia yang berkesan. Sakarida, pestisid dan kepekatan klorin dalam air boleh dikesan

menggunakan teknik ini. Malahan pengesan ini boleh juga digunakan untuk mengesan DNA dan virus dalam larutan.

ACKNOWLEDGEMENTS

In the name of Allah, Most Gracious, Most Merciful...

Alhamdulillah, I gratefully thank God, Almighty Allah S.W.T., for giving me health and strength for successfully completing my project and writing this thesis. I also extend greet to Prophet, Muhammad S.A.W.

I wish to express my sincere gratitude and thanks to my research supervisor, Prof. Dr. W. Mahmood Mat Yunus for his kind advice, proper guidance and support throughout the project. Without his interest and continuous support, this academic research project will not be possible to finish.

Deep from my heart, I would like to convey special thank to my co-supervisors Prof. Dr. Mohd Maarof Moxsin and Assoc. Prof. Dr. Zainal Abidin Talib and all the staff in Department of Physics, Faculty of Science, Universiti Putra Malaysia in assisting and helping me in order to accomplish this research project successfully.

Last but no least, I would like to thank my ever supportive parents who never fail to be there for their love, support and prayers and also I want to thanked for their understanding and encouragement through the duration of this research project. Also, I am really proud of all my friends for their never ending support.

Thank you very much.

May Allah Ta'ala bless you all.



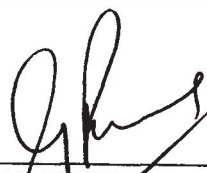
I certify that an Examination Committee met on 13th July 2005 to conduct the final examination of Wan Yusmawati Wan Yusoff on her Master of Science thesis entitled “Optical Properties and Kinetic Behaviour of Some Chemicals and Biological Species Using Surface Plasmon Resonance Optical Sensor” in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

Zaidan Abd. Wahab, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Abdul Halim Shaari, PhD
Professor
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

Azmi Zakaria, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

Noriah Bidin, PhD
Associate Professor
Faculty of Science
Universiti Teknologi Malaysia
(External Examiner)



GULAM RUSUL RAHMAT ALI, PhD
Professor/Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 22 AUG 2005

This thesis submitted to the Senate of Universiti Putra Malaysia has been accepted as fulfilment of the requirements for the degree of Master of Science. The members of the Supervisory Committee are as follows:

W. Mahmood Mat Yunus, PhD

Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

Mohd. Maarof Moxsin, PhD

Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

Zainal Abidin Talib, PhD

Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Member)



AINI IDERIS, PhD
Professor/Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 08 SEP 2005

DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any degree at UPM or other institutions.



WAN YUSMAWATI WAN YUSOFF

Date: 19 AGOS 2005

TABLE OF CONTENTS

| | Page |
|--|--|
| ABSTRACT | i |
| ABSTRAK | iii |
| ACKNOWLEDGEMENTS | vi |
| APPROVAL | vii |
| DECLARATION | ix |
| LIST OF TABLES | xii |
| LIST OF FIGURES | xiv |
| LIST OF ABBREVIATIONS/NOTATION/GLOSSARY OF TERM | xviii |
| | |
| CHAPTER | |
| 1 | INTRODUCTION |
| 1.1 | Surface Plasmon Resonance 1.1 |
| 1.1.1 | The architecture of the measurement setup - why using a prism? 1.4 |
| 1.1.2 | How the surface plasmon excited? 1.6 |
| 1.2 | Sample Background 1.7 |
| 1.2.1 | Saccharide 1.7 |
| 1.2.2 | Chlorine 1.8 |
| 1.2.3 | Pesticide 1.10 |
| 1.2.4 | DNA Solution 1.12 |
| 1.2.5 | Virus 1.12 |
| 1.2.6 | Heavy Metal 1.13 |
| 1.3 | Benefit From The Surface Plasmon Resonance Study 1.14 |
| 1.4 | The Objective of the Study 1.15 |
| 1.5 | Chapter Organization 1.15 |
| | |
| 2 | LITERATURE REVIEW |
| 2.1 | Review on Surface Plasmon Resonance 2.1 |
| 2.2 | Review on Metal Surface 2.2 |
| 2.3 | Literature Review on the Dielectric Constant 2.3 |
| | |
| 3 | THEORY |
| 3.1 | Surface Plasmon Resonance 3.1 |
| 3.1.1 | Surface Electromagnetic Waves at Two Media Interface 3.2 |
| 3.1.2 | Surface Plasmon Resonance Scattering 3.5 |
| 3.1.3 | Angle Dependence of the Reflectivity of Surface Plasmon Resonance 3.8 |
| 3.1.4 | Surface Plasmon Resonance Coupling 3.10 |
| 3.2 | Real Time Interaction Analysis 3.11 |
| | |
| 4 | METHODOLOGY |
| 4.1 | Sample Preparation 4.1 |
| 4.1.1 | Substrate Cleaning 4.1 |

| | | |
|----------|---|------------|
| 4.1.2 | Thin Film Preparation | 4.2 |
| 4.1.3 | Preparation of Dielectric Medium | 4.3 |
| 4.2 | Experimental Setup | 4.7 |
| 4.2.1 | Modulated Beam Systems | 4.8 |
| 4.2.2 | Sample Cell | 4.9 |
| 4.2.3 | Data Acquisition | 4.9 |
| 4.3 | Experimental Procedure | 4.10 |
| 4.4 | Fitting Experimental Data to the Theoretical Data | 4.11 |
| 4.5 | X-Ray Diffraction Analysis | 4.11 |
| 4.6 | Spin Coating Technique | 4.13 |
| 5 | RESULTS AND DISCUSSION | |
| 5.1 | Introduction | 5.1 |
| 5.2 | Preliminary Study of Metal Surface | 5.1 |
| 5.2.1 | X-Ray Diffraction Analysis of Metal Surface | 5.2 |
| 5.2.2 | Environment Effect on the Metal Surface Stability | 5.4 |
| 5.3 | Optical Properties Measurement of Dielectric Medium | 5.12 |
| 5.3.1 | Preliminary Experiment | 5.12 |
| 5.3.2 | Saccharide | 5.14 |
| 5.3.3 | Chlorine | 5.18 |
| 5.3.4 | Swimming Pool | 5.20 |
| 5.3.5 | Pesticide | 5.22 |
| 5.3.6 | DNA Solution | 5.25 |
| 5.3.7 | Virus Solution | 5.28 |
| 5.4 | Surface Plasmon Optical Sensor | 5.31 |
| 5.4.1 | Saccharide | 5.31 |
| 5.4.2 | Chlorine | 5.34 |
| 5.4.3 | Pesticide | 5.36 |
| 5.4.4 | DNA Solution | 5.38 |
| 5.4.5 | Virus Solution | 5.41 |
| 5.5 | Kinetic Behaviour | 5.43 |
| 5.5.1 | Saccharide | 5.44 |
| 5.5.2 | Chlorine | 5.47 |
| 5.5.3 | Pesticide | 5.53 |
| 5.5.4 | DNA Solution | 5.55 |
| 5.6 | Polymer Film Study | 5.58 |
| 6 | CONCLUSION | |
| 6.1 | Conclusion | 6.1 |
| 6.2 | Suggestion | 6.4 |
| | REFERENCES | R.1 |
| | APPENDICES | A.1 |
| | BIODATA OF THE AUTHOR | B.1 |

LIST OF TABLES

| Table | Page |
|---|-------------|
| 3.1 List of real part, ε_r , and imaginary part, ε_i , of dielectric constant for common metal that has been used as thin film in surface plasmon studies | 3.8 |
| 5.1 List of optical properties ε_r and ε_i for three types of saccharide samples at concentration of 0.10 mol/L | 5.16 |
| 5.2 List of optical properties ε_r and ε_i for chlorine at concentration of 6 ppm | 5.19 |
| 5.3 List of optical properties ε_r and ε_i for pesticide at concentration of 0.1 %w/w | 5.24 |
| 5.4 List of optical properties ε_r and ε_i for DNA solution sample at concentration of 10 pM | 5.26 |
| 5.5 List of optical properties ε_r and ε_i for virus solution sample at concentration of 10 pM | 5.29 |
| 5.6 Kinetic behaviour parameter of saccharide sample at 0.1 mol/L | 5.47 |
| 5.7 Kinetic behaviour parameter of sucrose sample at different concentration | 5.47 |
| 5.8 List of kinetic constant and stretching coefficient for chlorine sample at concentration of 6 ppm | 5.49 |
| 5.9 Kinetic behaviour parameter of pesticide sample | 5.55 |
| 5.10 Kinetic behaviour parameter of DNA solution sample | 5.57 |
| 5.11 Kinetic behaviour parameter of DNA solution sample at two different concentrations | 5.57 |
| 6.1 List of detection limit and sensor sensitivity of samples | 6.2 |
| A.1 List of incidence angle, reflectance minimum, dielectric constant, and thickness for Gold film | A.2 |

| | | |
|-----|---|-----|
| A.2 | List of incidence angle, reflectance minimum, dielectric constant, and thickness for Silver film | A.2 |
| A.3 | List of incidence angle, reflectance minimum and dielectric constant for three type of saccharide | A.4 |
| A.4 | List of incidence angle, reflectance minimum and dielectric constant for two type of chlorine | A.4 |
| A.5 | List of incidence angle, reflectance minimum and dielectric constant for swimming pool water | A.5 |
| A.6 | List of incidence angle, reflectance minimum and dielectric constant for three type of pesticide | A.5 |
| A.7 | List of incidence angle, reflectance minimum and dielectric constant for DNA solution | A.6 |
| A.8 | List of incidence angle, reflectance minimum and dielectric constant for three type of virus | A.6 |

LIST OF FIGURES

| Figure | Page |
|--|-------------|
| 1.1 Schematic of surface plasmon waves at the interface between a metal and a dielectric. The plasmon propagates into the x-direction and it decays exponentially into z-direction | 1.3 |
| 1.2 Mechanism of the surface plasmon excitation | 1.6 |
| 1.3 The structure of glucose, maltose and sucrose by Haworth formula | 1.8 |
| 1.4 Chemical structure of the malathion, chlorpyrifos and glyphosate | 1.11 |
| 1.5 A) The structure of virion B) An example of virus | 1.13 |
| 3.1 Surface electromagnetic wave at the interface with complex dielectric function ϵ_1 and ϵ_2 | 3.3 |
| 3.2 Attenuated total reflection configuration for excitation surface plasmon resonance, dielectric constant and thickness | 3.9 |
| 3.3 Excitation of surface plasmon resonance in the Kretschmann geometry | 3.11 |
| 3.4 Excitation of surface plasmon resonance Otto geometry | 3.11 |
| 3.5 A sensorgram illustrating the binding of sample to the metal surface | 3.12 |
| 4.1 The principle of operation of the Sputter Coater | 4.3 |
| 4.2 Experimental Setup for Kretschmann Surface Plasmon Resonance Technique | 4.8 |
| 4.3 A structure of the cell for Surface Plasmon Resonance measurement | 4.9 |
| 4.4 The Programme Spinner Cycle Spin Coating Technique | 4.13 |
| 5.1 X-Ray Diffraction Pattern of Gold | 5.3 |
| 5.2 X-Ray Diffraction Pattern of Silver | 5.3 |
| 5.3 The variation of surface plasmon resonance curve for gold exposed only to air in one week from day 1 to day 8 | 5.5 |

| | | |
|------|---|------|
| 5.4 | The fitting graph from experimental (dot) as compare to the theoretical (line) | 5.6 |
| 5.5 | The dielectric constant as a function of time for gold sample | 5.6 |
| 5.6 | The gradual movement of a surface plasmon resonance curve for an Ag film expose to only air in one week from day 1 to day 8 | 5.9 |
| 5.7 | The incidence angle as a function of time | 5.9 |
| 5.8 | The reflectance minimum as a function of time | 5.10 |
| 5.9 | The dielectric constant as a function of time for Ag film | 5.10 |
| 5.10 | The graph of thickness for Ag film as a function of time | 5.11 |
| 5.11 | Fitting experimental data to the theoretical data for distilled water ($n=1.330$) | 5.13 |
| 5.12 | Reflectance curve for distilled water, glucose, maltose and sucrose at 0.10 mol/L | 5.15 |
| 5.13 | The real part of dielectric constant, ϵ_r as a function of saccharide concentration | 5.17 |
| 5.14 | The imaginary part of dielectric constant, ϵ_i as a function of saccharide concentration | 5.17 |
| 5.15 | The real part of dielectric constant, ϵ_r as a function of chlorine concentration | 5.19 |
| 5.16 | The imaginary part of dielectric constant, ϵ_i as a function of chlorine concentration | 5.20 |
| 5.17 | Optical reflectance as a function of incidence angle for swimming pool sample at different time collected | 5.21 |
| 5.18 | The real and imaginary part of dielectric constant, ϵ_r and ϵ_i as a function of time-collected sample | 5.22 |
| 5.19 | The real part of dielectric constant, ϵ_r as a function of pesticide concentration | 5.24 |
| 5.20 | The imaginary part of dielectric constant, ϵ_i as a function of pesticide concentration | 5.25 |
| 5.21 | The real part of dielectric constant, ϵ_r as a function of DNA solution concentration | 5.27 |

| | | |
|------|--|------|
| 5.22 | The imaginary part of dielectric constant, ε_i as a function of DNA solution concentration | 5.27 |
| 5.23 | The real part of dielectric constant, ε_r as a function of virus concentration | 5.29 |
| 5.24 | The imaginary part of dielectric constant, ε_i as a function of virus concentration | 5.30 |
| 5.25 | Optical reflectance as a function of incidence angle for maltose sample at different concentration | 5.33 |
| 5.26 | The shift of resonance angle versus glucose, maltose and sucrose concentration (mol/L) | 5.33 |
| 5.27 | Optical reflectance as a function of incidence angle for Calcium Hypochlorite at different concentration | 5.35 |
| 5.28 | The shift of resonance angle versus chlorine concentration (pM) | 5.35 |
| 5.29 | Optical reflectance as a function of incidence angle for malathion at different concentration | 5.37 |
| 5.30 | The shift of resonance angle as a function of %w/w concentration | 5.38 |
| 5.31 | Optical reflectance as a function of incident angle for DNA solution at different concentration | 5.40 |
| 5.32 | The shift of resonance angle versus Oligo1-Dig and Oligo2-Bio concentration (pM) | 5.40 |
| 5.33 | Optical reflectance as a function of incident angle for Viruses1-N solution at different concentration | 5.42 |
| 5.34 | The shift of resonance angle versus viruses concentration (pM) | 5.42 |
| 5.35 | The kinetic behaviour of distilled water | 5.43 |
| 5.36 | Shift of resonance angle versus time for glucose, maltose and sucrose at concentration of 0.1 mol/L | 5.44 |
| 5.37 | The shift of resonance angle versus time at different concentration (mol/L) of sucrose solution | 5.46 |
| 5.38 | The resonance angle shift versus time for two types of chlorine sample at 6 ppm | 5.48 |

| | | |
|------|--|------|
| 5.39 | The SPR shift of resonance angle as a function of time collected | 5.50 |
| 5.40 | The pH value as a function of time collected | 5.51 |
| 5.41 | The comparison of resonance angle versus time for samples | 5.52 |
| 5.42 | The resonance angle shift versus time for pesticide measurement at concentration of 0.1 %w/w | 5.54 |
| 5.43 | The time dependence of the shift in resonance angle for Oligo1-Dig and Oligo2-Bio interfaces at 10 pM solution | 5.56 |
| 5.44 | The kinetic behaviour for Oligo1-Dig and Oligo2-Bio interfaces at 10 and 5 pM solution | 5.57 |
| 5.45 | The typical reflectance of FHA at different concentration | 5.60 |
| 5.46 | The shift of resonance angle as a function of FHA layer concentration | 5.60 |
| 5.47 | The SPR curve measured for 1: a bare Au film; 2: Au film with an over layer of FHA; 3: Au/FHA/V (V); 4: Au/FHA/Cu (II) and 5: Au/ FHA/Fe (III) | 5.61 |
| A.1 | X-Ray Diffraction Pattern of Ag film for day 1 | A.3 |
| A.2 | X-Ray Diffraction Pattern of Ag film for day 8 | A.3 |

LIST OF ABBREVIATIONS/NOTATION/GLOSSARY OF TERM

| | |
|------------------|---|
| $\Delta\theta_0$ | The initial shift of resonance angle respect to distilled water |
| ε_r | Real part of dielectric constant |
| ε_i | Imaginary part of dielectric constant |
| ε_0 | Dielectric constant of medium prism |
| θ | Incidence angle |
| θ_r | Resonant angle of incidence |
| θ_i | External angle |
| θ_{SP} | Surface plasmon resonance angle |
| $\Delta\theta$ | The shift of resonance angle |
| α | Internal angle of prism |
| μ | Magnetic permeability |
| k_x | Wavevector component along surface electromagnetic wave propagation |
| k_{SP} | Wavevector of a plasmon |
| κ_1 | Wavevector media 1 |
| κ_2 | Wavevector media 2 |
| λ | Wavelength |
| n_p | Refractive index of prism |
| n_m | Refractive index of metal |
| n_o | Refractive index of dielectric |
| ε_1 | Dielectric constant of medium metal film |
| ε_2 | Dielectric constant of medium dielectric |
| DNA | Oligodeoxyribonucleic acid |
| RNA | Ribonucleid Acid |
| PC | Personal Computer |
| FHA | Fatty Hydroxamic Acid |
| HCl | Hydrochloric Acid |
| EDTA | Ethylene Diamine Tetra Aceticacid |
| UV | Ultra Violet |
| XRD | X-ray Diffractometer |
| MIP | Molecular Imprinted Polymer |

| | |
|-----------|---|
| BaP | benzo[a]pyrene |
| DOP | dioctyl phthalate |
| ssDNA | single-stranded oligonucleotides |
| HDT | hexanedithiol |
| TM | Transverse Magnetic Field |
| TE | Transverse Electric Field |
| M | Concentration solution |
| V | Volume of concentration |
| MWR | Molecular weight relative |
| LFS | Low Square Fitting |
| SPR | Surface Plasmon Resonance |
| ATR | Attenuated total reflection |
| SP | Surface Plasmon |
| R | Reflection coefficient |
| R_{min} | Reflectance minimum |
| R_p | Reflectance as a function of incidence angle |
| R_T | Actual optical reflectance that loss factor has been considered |
| t^2 | Loss factor |
| A | Angle of prism |
| I_0 | Incidence light |
| I_r | Reflected light |
| d | Thickness |
| β | 'stretching coefficient' |
| τ | Time constant |
| c | Concentration |
| k | Adsorption constant |
| K | Kinetic constant |
| T | Absolute temperature |
| Au | Gold |
| Ag | Silver |
| G70 | Calcium Hypochlorite |
| G90 | Trichloroisocyanuric Acid |
| Cu (II) | Copper (II) |

| | |
|----------|-------------------|
| Fe (III) | Ferum (III) |
| V (V) | Vanadium (V) |
| wt/wt | Weight per weight |
| ppm | Part per million |
| pM | PicoMolar |
| rpm | Round per minutes |

CHAPTER 1

INTRODUCTION

1.1 Surface Plasmon Resonance

Surface plasmon resonance (SPR) is well known as a powerful and expensive optical method for the study of interface phenomena. SPR is an optical phenomenon arising in thin metal films under condition of total internal reflection. This phenomenon produces a sharp dip in the intensity of the reflected light at a specific angle (called the resonant angle). This resonant angle depends on several factors, including the refractive index of the medium (refractive index is directly correlated to the concentration of dissolved material in the medium) close to the non-illuminated side of the metal film. By keeping other factors constant, SPR is used to measure the change in the concentration of molecules in the surface layer of solution in contact with the sensor surface.

Surface plasmon resonance is a collective oscillation of the free electron charges, at a metal-dielectric boundary, which propagates along interface. These charge fluctuations are accompanied by an electromagnetic field having a maximum at the metal-dielectric interface and decaying exponentially with distance from either side of it [Sadowski et al., 1991; Kitajima et al., 1981]. The resonance excitation of the surface plasmon resonance occurs at a characteristic angle of incidence, which depends on the thickness as well as on the dielectric permittivity of the layers and of adjacent medium. Since the permittivity depend on the frequency of the exciting laser light, so does too the resonance angle. When the frequency is fixed, SPR

permits the measurement of changes in the refractive index in the medium adjacent to the metal film as well as changes in the absorption layer on the metal surface. The plasmon wave can be excited at the interface between a thin metal film and air or other non-metal medium with a positive dielectric sign. The wave can be thought of as having a section inside the thin film and a section outside of the film in the air / metal interface, much like an ocean wave has part of the wave unseen inside the ocean, while another part of the wave is seen in the ocean / horizon interface. Under normal circumstances, a laser light source incident upon a thin film is reflected or scattered, and there would be an insignificant surface plasmon wave, which would absorb very little of the incident energy [Kolomenskii et al., 1997].

Surface plasmon resonance occurs when the energy from incident light is of just the right frequency and angle of incidence to couple its energy with the surface plasmon, so that no light is reflected from a normally reflective surface. Thickness of a thin film can be determined through surface plasmon resonance due to the fact that as the thickness of the thin film increases, less of the surface plasmon is in the air / metal interface and more of it is contained within the metal itself. We can use the characteristic peak and shape of the resonance curve to characterize different thin film thickness of different materials.

Typically, SPR technique employs the principle of attenuated total reflection (ATR) using either Kretschmann or Otto geometries. Surface plasmon are collective oscillations of free charge of metal, which under appropriate conditions, may be coupled to by incident optical radiation resulting in the absorption of light. Coupling is accomplished in two ways either angular or spectral. In the former, the incident