Double surface plasmon polaritons (SPPs) for sensing purposes

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**DOUBLE SURFACE PLASMON POLARITONS (SPPs)
FOR SENSING PURPOSES**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING
2011

**DOUBLE SURFACE PLASMON POLARITONS (SPPs)
FOR SENSING PURPOSES**

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ABSTRACT

The thesis work describes the sensitivity enhancement of grating coupled surface plasmon resonance (GCSPR) using a novel approach - rotating the grating azimuthally to an angle where double surface plasmons polaritons (SPPs) can be excited and using an optimized polarization angle of incident light for the double SPPs excitation. This approach allows the sensitivity of GCSPR to be enhanced by fifteen times compared to non-rotated gratings and one order of magnitude higher than prism coupled surface plasmon resonance.

The thesis begins with the grating fabrication technique. The gratings were fabricated by interference lithography which is used to produce highly ordered and periodic structures with in large area. Many grating replica can be fabricated by imprinting the grating master (from interference lithography) to a UV-curable polymer substrate. Subsequently, the grating was thermally evaporated with 37 nm of Ag and 7 nm of Au. This makes the grating coupler an attractive approach for fabrication of low-cost SPR sensing structures.

The thesis continues with a study of surface plasmon excitation on an azimuthal rotatable grating. Once the grating is rotated azimuthally larger than a critical angle, two surface plasmons polaritons propagating in different directions with same frequency can be excited. By rotating the grating azimuthally, the propagation directions of the surface plasmons polaritons can be manipulated to cover a range of almost 2π . Other azimuthal orientations allow excitation of many SPP modes characterized by propagation over a large angular range. The large angular spread is

accompanied by an energy condensation of the SPP modes in correspondence to the energy threshold which increases as azimuthal angle of the grating increases. The kinematics of SPP propagation can be described by a model based on the wave-vector conservation law. Based on this, SPP dispersion relation, propagation direction, and normalized density of modes have been computed and shown to be in agreement with experimental measurements. The surface plasmons polaritons condensation modes are able to enhance the sensitivity of grating-coupled surface plasmon resonance.

This sensitivity enhancement is demonstrated on a Au grating surface using a dodecanethiol (C12) self-assembled monolayer (SAM). Using the approach, a shift in resonance angle as large as 2.2° can be observed, which is about $580^\circ/\text{RIU}$. The simulated sensitivity of this method shows that a sensitivity from $800^\circ/\text{RIU}$ to $1000^\circ/\text{RIU}$ is achievable, which is fifteen times larger than conventional fixed grating ($\varphi=0^\circ$) and one order of magnitude higher than prism coupled Kretschmann configuration. However, the simulated sensitivity is only achievable when the excited surface plasmon polaritons are in full strength.

The study continues to explain why the excited surface plasmon polaritons in azimuthal rotated grating using *p*-polarized incident light is no longer suitable. When light direction is perpendicular to the grating grooves, i.e. the scattering plane is parallel to the grating symmetry plane, reflectivity does not depend on polarization and only *p*-polarization is effective for SPP excitation. For a general azimuthal angle, not only *p*-polarized light but also *s*-polarized light can contribute to SPP excitation. Hence, the optimized polarization angle of the incident light that can fully couple the SPPs was investigated. Experimentally, the optimal polarization angle can be obtained

by rotating the polarization angle until the deepest dip in reflectivity spectrum can be observed. Experimental results and simulations show that only the incident electric field belonging to the grating symmetry plane is effective for SPR excitation, while the orthogonal one is irrelevant. In addition, the optimum polarization angle for corresponding azimuthal angle, incident wavelength and resonance angle can be determined analytically.

Exciting the double SPPs with the optimized polarization angle of incident light, sensitivity up to 950°/RIU was demonstrated experimentally which is within the calculated value. This is corresponding to a shift in resonance angle as large as 3.6° before and after C12 functionalization on the Au grating surface. Using the optimized polarization angle, well-defined, sharper spectra are obtainable and the positions of the minima are more obvious. The Figure of Merit (FOM) increases by 50%-100% compared to spectra collected using *p*-polarized light. In principle, we expect the refractive index resolution of this method to be on the order of 5×10^{-7} RIU.

In addition, the study investigated the most important factors that affect the double surface plasmon polaritons excitation on the metallic grating. The grating's pitch should fall within the subwavelength scale, such that the surface plasmon polaritons are excited from the $m = 1$ diffraction order. In addition, the amplitude of the grating must be within the aspect ratio (amplitude/pitch) of 0.1. Furthermore, the grating consists of a bilayer of 37 nm Ag and 7 nm Au. The reasons for coating a bimetallic layer on the grating is because Ag has a smaller extinction coefficient than gold and therefore suffers less loss during coupling (higher plasmonic coupling

efficiency). However a very thin gold coating is used to protect silver from oxidation and provides an inert surface for bio functionalization.

Lastly as a practical demonstration, we show that C10 and C12 SAMs, which differ by only two carbon atoms, can be detected with a shift in resonance angle as large as 2.1° . This amount of shift is measurable only using the suitable grating, rotating the grating to a specific angle and using the optimized polarization angle of incident light.

In summary, this thesis describes the pioneering development of a new approach for grating coupled surface plasmon resonance based on the excitation of double surface plasmon polaritons using an optimized polarization angle of incident light on an azimuthally rotatable grating and validates its sensing capabilities experimentally. The approach could replace the current prism coupled surface plasmon resonance based sensor with better sensitivity and additional ease in optical alignment. The advances accomplished in this work will have a direct impact on the global effort of building miniaturized, highly sensitive and real time diagnosis sensors.

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LIST OF COMMON ABBREVIATIONS AND SYMBOLS

AFM	Atomic Force Microscopy
EM	Electromagnetic
FOM	Figure of Merit
GCSPR	Grating Coupled Surface Plasmon Resonance
PCSPR	Prism Coupled Surface Plasmon Resonance
RIU	Refractive Index Unit
SAM	Self-Assembled Monolayer
SEM	Scanning Electron Microscopy
SPPs	Surface Plasmon Polaritons
SPR	Surface Plasmon Resonance
TE	Transverse Electric
TM	Transverse Magnetic
SYMBOLS	
φ	Azimuthal Angle of Grating Rotation
θ_{in}	Angle of Incidence
θ_r	Angle of Resonance
λ	Wavelength of Incidence
β	Surface Plasmon Polaritons Propagation Direction
α	Polarization Angle of Incident Wavelength
α_{min}	Optimized Polarization Angle
ε_m	Dielectric Constant of Metal
ε_d	Dielectric Constant of Dielectric Medium
n_m	Refractive Index of Metal
n_d	Refractive Index of Dielectric Medium
ω_p	Plasma Frequency
S	Refractive Index Sensitivity

CHAPTER 1 INTRODUCTION

1.1 Background Information

Surface Plasmon Polaritons (SPPs) are of interest to a wide range of scientists, ranging from physicists, chemists and materials scientists to biologists. Renewed interest in surface plasmons has come from the dramatic advances in nanofabrication and full-field electromagnetic (EM) simulation techniques have enabled the realization of a wide variety of plasmonic structures^{1,2}. For instance, surface plasmons have been used in a wide spectrum of studies, ranging from electrochemistry³, wetting⁴ and biosensing^{5,6,7}, to scanning tunneling microscopy⁸, the ejection of ions from surfaces⁹, nanoparticle growth¹⁰, surface-plasmon microscopy¹¹ and surface-plasmon technology^{12,13,14,15}.

Surface Plasmon Polaritons (SPPs) are electromagnetic (EM) excitations that, being coupled to surface collective oscillation of free electrons in a metal, are bound to and propagate along metal/dielectric interfaces. Hence, SPPs can be considered as propagating electron density waves occurring at the interface between metal and dielectric. A good example of SPPs is in the Lycurgus Cup, as shown in Fig. 1.1. This was made in Roman times and under normal lighting appears green. However, when illuminated from within, it becomes red in colour. This is because of the metal nanoparticles with size much smaller than the incident light wavelength embedded inside the glass. The free electrons moving around the particles can only oscillate at certain frequencies corresponding to the plasma frequency of the metal. The light at this frequency is highly absorbed and scattered, leading to a much-reduced

transmission but enhanced reflection, giving the cup its properties. By altering the size of the metal particle the scattered colours (and therefore transmitted colours) are altered.

Fig. 1.1 Lycurgus Cup. Reproduced from The British Museum.

In addition, topology of the metal surface and adjacent dielectric medium determines the characteristics of various propagating SPP modes being excited at flat, curved, single and multiple surfaces, including SPP modes of complex particle arrays and metal nanostructures. SPP modes are renowned for their ability to concentrate electromagnetic fields beyond the diffraction limit, while enhancing local field strengths by several orders of magnitude.

The field of plasmons is an exciting new area for the application of surface and interface plasmons, in which surface-plasmon based circuitry merge the fields of photonics and electronics into nanoscale. The intrinsically two-dimensional nature of SPPs provides significant flexibility in engineering SPP-based all-optical integrated circuits needed for optical communications and optical computing^{16,17}. The relative ease of controlling SPPs on a surface opens an opportunity for their application in photonics and optoelectronics for scaling down optical and electronic devices to

nanoscale. Most importantly, active photonic elements based on nonlinear SPPs optics, which allow manipulating optical properties with light, are much easier to realize with suitably patterned metal surfaces, due to the SPP-related electromagnetic field enhancement near a metal surface and have been reported elsewhere^{1,18,19,20,21}.

Other than the properties mentioned above, a number of specific properties are particularly relevant to sensor applications: (1) the field enhancement, (2) the phase change of the reflected field upon SPP excitation and (3) the SP coherence range. Because of its nature, SPPs have been widely used as biosensor which is also one of the objectives of this study. As mentioned earlier, an SPP propagates wave-like along the planar interface between a metal and a dielectric medium, often vacuum or air, and its amplitude decays exponentially with increasing distance into each medium from the interface^{22,23,24}. Since the wave is on the boundary of the metal and the external medium (air or water for example), these oscillations are very sensitive to any changes at this boundary, such as the adsorption of molecules to the metal surface. This sensitivity is extensively used for studying adsorbates on a surface, surface roughness, and related phenomena. SPP-based devices exploiting this sensitivity have been used in chemo- and bio-sensors²⁵.

1.2 Motivations

Surface Plasmon Resonance (SPR) based sensors using prism coupler with Kretschmann configuration²⁶ typically show refractive index sensitivity for typical angular interrogation architecture that ranges between 50-150°/RIU^{27,28}, with higher sensitivity at shorter wavelengths²⁹. In addition, a commercial prism-coupled surface plasmon resonance (PCSPR), such as the instrument from BIAcore company using

Kretschmann configuration is available, and a refractive index resolution better than 1×10^{-7} RIU with up to 4 sensing channels^{30,31} has been established. The sensitivity of the current research of the PCSPR can reach up to 2.5×10^{-8} RIU using the benefit of long-range SPR and has been demonstrated by Homola's group³². However, the optical maintenance and technical service becomes extremely cumbersome³³. In addition, PCSPR is very expensive (USD 300,000)³⁴ and not amenable to miniaturization and integration³⁵. Although PCSPR as a sensor can avoid the complexity of nanostructure fabrication, nowadays this can be solved easily by cheap and quick method of interference lithography or soft lithography.

Besides using the prism coupler to excite SPR, other groups have used metallic nanostructures for plasmon excitation. Van Duyne and his coworkers^{36,37} are working on localized surface plasmon resonance (LSPR) of metallic nanoparticles arrays; Perez-Juste³⁸ and Yu³⁹ are working on metallic nanowires for sensing purposes, but they have a lower sensitivity (5×10^{-3} - 1×10^{-6} RIU) than PCSPR.

Another common way for SPR excitation is to use a metallic grating. In the past, the grating coupler is not preferred because of the difficulty in fabrication. However nowadays, due to the advance of soft lithography, mass production of grating replica (replication into plastic using nano-imprinting technique) becomes possible and makes the grating coupler an attractive approach. Grating coupled SPR (GCSPR) sensors with either wavelength or angular interrogation have been demonstrated to have sensitivity 2-3 times lower than PCSPR^{40,41}. However, GCSPR has the intrinsic possibility to be used with different sensing architectures and interrogation systems. Homola's group demonstrated an SPR biosensor with a

refractive index sensitivity of 695 nm/RIU with wavelength interrogation, exploiting the advantages of both long-range and short-range surface plasmons excited simultaneously on a diffraction grating⁴². Most recently, Alleyne⁴³ has exploited the generation of an optical band gap in GCSPR by using prism-coupling to achieve sensitivity down to 680°/RIU by bandgap-assisted GCSPR. A miniaturized GCSPR sensor implemented with a CCD allowed detection sensitivity of 160°/RIU over 200 sensing parallel channels^{44,45,46}.

Based on our understanding, little work has been done to study the effects of rotating the grating substrate itself. Although many previous work has demonstrated, both experimentally and by simulation, the effect of *P-S* conversion^{47,48,49,50,51} (*p*-polarized light is converted into *s*-polarized light), the sensitivity in the conical mounting is neglected. By exciting the SPPs in the conical mounting, not only the SPPs propagation direction can be controlled, but may further enhance the sensitivity of the GCSPR.

1.3 Objective and Scopes

This thesis aims to enhance the sensitivity of GCSPR by azimuthal control. The research is organized in a sequence of milestones:

1. Fabrication of the plasmonic gratings

It is of primary importance to establish a process capability to produce large area and periodic gratings for SPPs excitation. In this study, the gratings are fabricated using Interference Lithography (IL) and soft lithography. The IL is used to generate the grating master for fabricating the subsequent grating replica using the nano-imprinting

technique. The fabricated grating is subsequently thermal evaporated with 37 nm of Ag and 7 nm of Au.

2. Realizing SPP excitation on the azimuthally rotated grating

Much of the research to date has focused on the P - S conversion efficiency on azimuthally rotated gratings. However, this work is focused on the sensing capabilities of the SPP(s) excited on the azimuthal rotated grating. The excitation of the SPP(s) on the grating was studied systematically by rotating the grating azimuthally. The excited SPP(s) at different azimuthal angle are expected to be different due to different requirements in momentum conservation.

3. The role of polarization angle of the incident light in azimuthally rotated gratings

When incident light direction is perpendicular to the grating grooves, i.e. the scattering plane is parallel to the grating symmetry plane, reflectivity does not depend on polarization and only p -polarization is effective for SPP excitation. For a general azimuthal angle, not only p -polarized light but also s -polarized light can contribute to SPP excitation. In a classical mounting (non-rotated case), a diffraction grating is illuminated with light propagating along a direction perpendicular to the grooves. In this study, we investigated the polarization angle that optimizes the excited SPPs on the azimuthal rotated grating, i.e. further enhancement of the excited SPPs strength on the azimuthal rotated grating only by changing the polarization angle without

changing the resonance condition. In addition, a simple analytical model that can easily describe and determine the optimized polarization angle is developed.

4. Demonstrating the sensitivity of the azimuthally rotatable GCSPR

This study continues, to demonstrate the sensitivity of the SPP(s) excited on the azimuthally rotated grating. The demonstration on this sensitivity is done by using a dodecanethiol (C12) self-assembled monolayer (SAM) on a Au grating surface, representing a thickness difference of 1.5 nm compared to the uncoated grating. C12-SAM are chosen because SAMs are molecules that have the ability to form a dense and ordered assembly spontaneously onto different kinds of surfaces⁵². Various advantages of using SAMs include the ease of preparation and manufacturing. SAMs also offer a unique combination of physical properties that allow fundamental studies of interfacial chemistry, solvent-molecule interactions and self-organization. Their well-ordered arrays and ease of functionalization make them ideal model systems in many fields. For example, SAMs are invaluable substrates in bioanalytical, organometallic, physical organic, bioorganic and electrochemistry⁵³. They are expected to have good coverage even in high aspect ratio features due to their hydrophilic head-group which adheres well to the substrate. This behaviour makes them ideal for passivation. Besides that, the ability to tailor the monolayer-air interface makes SAMs promising for applications in several different areas, including molecular recognition, corrosion inhibition, molecular crystal growth, pH-sensing, patterned surfaces on the μm scale, alignment of liquid crystals and photoresist⁵⁴.

Finally, an analytical model that calculates the refractive index resolution of this configuration is developed.

5. Determination of the grating parameters suitable for the reported SPPs excitation

Although the reported configuration may enhance the sensitivity of the current GCSPR, not all the gratings are suitable to excite the reported SPPs. The grating parameters, ranging from amplitude and pitch that suitable for double SPPs excitation are investigated.

1.4 Organization of the Report

This report is divided into eight chapters and each chapter is briefly discussed as follows:

Chapter 1 gives a brief introduction of background information related to this research and presents the motivation and objective.

Chapter 2 deals with a literature review covering various topics related to this research work, such as basic theory of SPPs and state-of-the-art sensing techniques.

The original work accomplished in this research is presented in Chapters 3 to 8.

Chapter 3 serves to establish the fabrication of the grating used in this study. In addition, characterizations of the grating were discussed.

Chapter 4 presents the results obtained from azimuthal grating coupled surface plasmon resonance. A full analysis of this configuration was discussed. While chapter 5 demonstrates the sensitivity of this configuration.

Chapter 6 reports the role of polarization angle of the incident light to the azimuthal rotated grating coupled surface plasmon resonance. Details on experimental and analytical model of the relationship between polarization angle and azimuthal angle are discussed briefly. While chapter 7 describes the sensitivity of the configuration using optimized polarization angle.

Chapter 8 discusses the grating parameters which are suitable for double SPPs excitation.

Chapter 9 reports the C10 and C12 SAM which differ by only two carbon atoms can be detected easily using the pioneer approach.

Chapter 10 summarizes the important conclusions and major findings of this research and proposes potential areas for future research.

CHAPTER 2 SURFACE PLASMON RESONANCE BASED SENSOR – A REVIEW

2.1 History

In 1957, R. H. Ritchie discovered that the fast moving electrons lost up its energy when it passing through a thin metal film and he predicted that it is due to the existence of self-sustained collective oscillations at the metal surfaces⁵⁵. It was later on proved experimentally by Powell and Swan⁵⁶. The quanta of such oscillations was called the surface plasmon. After this, there is an important progress in both experimental and theoretical investigation of surface plasmons.

In Pines and Bohm's previous work⁵⁷ in 1952, a term called plasmon frequency, ω_p was investigated to determine the quantum energy collective plasma oscillations in a free electron gas (volume plasmon) with density of equilibrium n ($\hbar\omega_p = \hbar(4\pi ne^2/m_e)^{1/2}$). The surface plasmon at the metal planar boundary has frequency equals to the non-retarded region (the light speed can be considered as infinitely fast), called Ritchie's frequency $\omega_s = \omega_p/\sqrt{2}$ at wave vector q within the range of ω_s/c and qF (qF is the magnitude of the Fermi wave vectors) and as the wave-vector increases, it exhibits some dispersion properties (Fig. 2.1). When the surface plasmon's phase velocity ω_s/q is approaching to the light's velocity in the retarded region, the electromagnetic wave is coupled to surface plasmons. These surface plasmons has frequency range from 0 (at $q = 0$) to asymptotic value $\omega_s = \omega_p/\sqrt{2}$ and propagate along the metal surface boundary. Since the dispersion relation $\omega(q)$ is beyond the light line therefore has a wavevector longer than the normal incident light wave without passing through dielectric medium of the similar energy. Thus, surface plasmon polaritons

(SPPs) are called “nonradiative” in an ideal semi-infinite medium, i.e. a light wave incident directly on a metal with smooth surface is impossible to satisfy the surface plasmon excitation condition. In addition, surface plasmon cannot be decayed by emitting a photon. Their electromagnetic fields have a maximum at the thin metallic surface and decay exponentially into the medium normal to the surface.

Fig. 2.1. Schematic represents the plasmon dispersion in a solid. (1) volume, (2) surface plasmons, (II) light line. Reproduced from reference 22, Springer-Verlag.

2.2 Maxwell's Equations and Electromagnetic Wave Propagation

Using Maxwell's equations, the dispersion relationship of Surface Plasmons (SPs) can be determined. The Maxwell's equations are given as:

$$\begin{aligned}
\nabla \cdot \vec{D} &= \rho \\
\nabla \cdot \vec{B} &= 0 \\
\nabla \times \vec{E} &= -\frac{\partial \vec{B}}{\partial t} \\
\nabla \times \vec{H} &= \frac{\partial \vec{D}}{\partial t} + \vec{J}
\end{aligned} \tag{2.1}$$

where $\vec{D}$ is the electric flux density, ρ the volume charge, $\vec{B}$ the magnetic flux density, $\vec{E}$ the electric field, $\vec{H}$ the magnetic field and $\vec{J}$ the current density. ρ needed to be assumed equal to zero and for a perfect conductor, $\vec{J} = 0$ ($\vec{J} = \sigma \vec{E}$, where $\sigma = 0$), Eq. 2.1 can be transformed to

$$\begin{aligned}
\nabla \cdot \vec{D} &= 0 \\
\nabla \cdot \vec{B} &= 0 \\
\nabla \times \vec{E} &= -\frac{\partial \vec{B}}{\partial t} \\
\nabla \times \vec{H} &= \frac{\partial \vec{D}}{\partial t}
\end{aligned} \tag{2.2}$$

and

$$\begin{aligned}
\vec{D} &= \epsilon \epsilon_0 \vec{E} \\
\vec{B} &= \mu \mu_0 \vec{H}
\end{aligned} \tag{2.3}$$

where ϵ and ϵ_0 are the dielectric constant and electric permittivity of free space respectively. μ and μ_0 are the magnetic permeability and magnetic permeability of free space respectively.

The solution of Maxwell's equations for the electric field $\vec{E}$ in the case of plane waves (monochromatic waves) is presented by the equation:

$$\vec{E} = \vec{E}_0 e^{i(\vec{k} \cdot \vec{r} - \omega t)} \quad (2.4)$$

where $\vec{E}_0$ is the electric field amplitude, $\vec{r}$ is the position vector, ω is the angular frequency, $2\pi f$ (f : frequency), t is the time and $\vec{k}$ is the wavevector which is in the wave propagation direction. The magnitude of $\vec{k}$ is given by:

$$|k| = \sqrt{\epsilon \epsilon_0 \mu \mu_0 \omega^2} \quad (2.5)$$

in vacuum (or air), $\epsilon = 1$, $\mu = 1$, and $\lambda = 2\pi c/\omega$, $k = 2\pi/\lambda = \omega/c$.

$$c = 1/\sqrt{\mu_0 \epsilon_0} \quad (2.6)$$

The coherent oscillation of the electron charges on a metal boundary are called surface plasmon polaritons (SPPs or SPs). The field can be localized in the z -direction which is normal to the surface, and consists of a mixed longitudinal and transversal electromagnetic field that propagates along the x -axis and vanishes at $|z| \rightarrow \infty$ on both sides of the metal/dielectric interface, and has its maximum at $z = 0$ (Fig. 2.2).

Fig. 2.2. (a) Schematic represents the electromagnetic wave of SPs propagating along the x -direction of a metal surface. (b) The SP decay exponentially on both $+z$ and $-z$ sides into the medium normal to the metal boundary.

The plasmon waves have p -characteristics (Transverse Magnetic, TM) because the surface charges induce the discontinuity of the electromagnetic field in the z -

direction, which does not apply for s -waves (no $\vec{E}_z$ component). In other words, only transverse magnetic waves (TM waves) can be used to excite plasmons. Considering the dielectric ($\epsilon_1 > 0$, medium 1)/metal ($\epsilon_2 = \epsilon_2' + i\epsilon_2''$, medium 2) interface, the electromagnetic fields on both sides are expressed as:

$$\begin{aligned}
 z > 0 \quad & H_1 = (0, H_{y1}, 0) e^{i(k_{x1}x + k_{z1}z - \omega t)} \\
 & E_1 = (E_{x1}, 0, E_{z1}) e^{i(k_{x1}x + k_{z1}z - \omega t)} \\
 z < 0 \quad & H_2 = (0, H_{y2}, 0) e^{i(k_{x2}x - k_{z2}z - \omega t)} \\
 & E_2 = (E_{x2}, 0, E_{z2}) e^{i(k_{x2}x - k_{z2}z - \omega t)}
 \end{aligned} \tag{2.7}$$

k_{x1} and k_{x2} are the wavevectors in x -directions and k_{z1} and k_{z2} the ones along the z -axis.

Considering the continuity relations of the in-plane components:

$$\begin{aligned}
 E_{x1} &= E_{x2} \\
 H_{y1} &= H_{y2}
 \end{aligned} \tag{2.8}$$

and inserting (2.8) into (2.7) yields:

$$k_{x1} = k_{x2} = k_x \tag{2.9}$$

inserting (2.7) into (2.2), together with (2.6) one obtains:

$$\begin{aligned}
 +k_{z1}H_{y1} &= -\frac{\omega}{c}\epsilon_1 E_{x1} \\
 +k_{z2}H_{y2} &= +\frac{\omega}{c}\epsilon_2 E_{x2}
 \end{aligned} \tag{2.10}$$

Together with the continuity relations (Eq. 2.8), one obtains the dispersion relation of SPs:

$$\frac{k_{z1}}{\varepsilon_1} + \frac{k_{z2}}{\varepsilon_2} = 0 \quad (2.11)$$

This reveals that SPs can only be supported at the interface between two materials that have opposite sign in dielectric constants, e.g., a metal/dielectric interface.

The wavevector k_i can be decomposed into k_{xi} and k_{zi} , together with (2.9), one obtains:

$$k_{xi}^2 + k_{zi}^2 = \varepsilon_i \left(\frac{\omega}{c} \right)^2 \quad (2.12)$$

From (2.11) together with (2.12), one yields the dispersion relation of SPs in another format:

$$k_x = \frac{\omega}{c} \left(\frac{\varepsilon_1 \varepsilon_2}{\varepsilon_1 + \varepsilon_2} \right)^{1/2} \quad (2.13)$$

In the case of the dielectric ($\varepsilon_1 > 0$, medium 1)/metal ($\varepsilon_2 = \varepsilon_2' + i\varepsilon_2''$, medium 2) interface, and assuming $\varepsilon_2'' < |\varepsilon_2'|$, the complex k_x is expressed by:

$$k_x = k_x' + ik_x'' \quad (2.14)$$

with

$$k_x' = \frac{\omega}{c} \left(\frac{\varepsilon_1 \varepsilon_2'}{\varepsilon_1 + \varepsilon_2'} \right)^{1/2} \quad (2.15)$$

$$k_x'' = \frac{\omega}{c} \left(\frac{\varepsilon_1 \varepsilon_2'}{\varepsilon_1 + \varepsilon_2'} \right)^{3/2} \frac{\varepsilon_2''}{2\varepsilon_2'^2} \quad (2.16)$$

Wavevectors k_{z1} and k_{z2} are imaginary due to the relations $\omega/c < k_x$ and $\epsilon_2' < 0$ (Eq. 2.12), so that as mentioned above, the field of the SPs decreases exponentially as $\exp(-|k_{zi}||z|)$, normal to the surface. When the field falls to $1/e$, the value is named as skin depth,

$$\hat{z} = \frac{1}{|k_{zi}|} \quad \text{or} \quad (2.17)$$

in the dielectric medium with ϵ_1 : $\hat{z} = \frac{\lambda}{2\pi} \left(\frac{\epsilon_1 + \epsilon_2'}{\epsilon_1^2} \right)^{1/2}$

$$\text{in the metal with } \epsilon_2: \hat{z} = \frac{\lambda}{2\pi} \left(\frac{\epsilon_1 + \epsilon_2'}{\epsilon_2'^2} \right)^{1/2} \quad (2.18)$$

The intensity of SPs propagating along the metal/dielectric interface (x -axis) decreases as $\exp(-2|k_{xi}''||x|)$. Therefore, the propagation length L_x is

$$L_x = \frac{1}{2|k_x''|} \quad (2.19)$$

can be defined, which influences the lateral resolution for surface plasmon microscopy applications. The damping of the electromagnetic field creates heat which is dissipated into the metal and dielectric medium.

2.3 Optical Excitation of Surface Plasmons (SPs)

The dispersion relation of a free photon in a homogenous dielectric (ϵ_1) is

$$k_{ph} = \frac{\omega}{c} \sqrt{\epsilon_1} \quad (2.20)$$

which is always smaller than the wavevector of SPs at the dielectric/metal interface, k_{spp} . This is shown graphically as $\omega(k_x)$ plots in Fig. 2.3 (curve SP and curve (a)). The

$\omega(k_x)$ curve of SPs approaches asymptotically the dispersion curve of the free photon ($|\epsilon_2'| > \epsilon_l$ for $\omega > 0$) with no intersection of the curves. In another word, direct light incident on a smooth metal surface cannot excite surface plasmons. For a free photon to couple SP, an enhancement in light momentum is required either by attenuated total reflection (ATR) or diffraction using prism, grating or waveguide coupler.

Fig. 2.3. The dispersion relation of free photons incident at (a) and (b) angle = 90° , (c) and (d) at a particular angle, θ . While the photon is propagating (a) and (c) in a homogenous dielectric (ϵ_l); and (b) and (d) is in a coupling prism with $\epsilon_p > \epsilon_l$.

2.3.1 Prism Coupler

The light travels through a half-cylindrical prism (ϵ_p), with its k_{ph} being enhanced to

$\frac{\omega}{c}\sqrt{\epsilon_p}$ by a factor of $\sqrt{\epsilon_p/\epsilon_l}$. The dispersion curves before and after the

enhancement by the prism are shown as curve (a) and (b) in Fig. 2.3, with a slope of

$\frac{c}{\sqrt{\epsilon_l}}$ and $\frac{c}{\sqrt{\epsilon_p}}$, respectively. At a certain wavelength of the laser (ω_{laser}), the

dispersion curve (SP) determines an incidence angle θ for the excitation of SPs (curve (d)). This occurs if the projection of the wavevector $\frac{\omega}{c}\sqrt{\epsilon_p}$ on the x -axis matches the x -component of k_{spp} .

$$\frac{\omega_{laser}}{c} \sin \theta \sqrt{\epsilon_p} = k_{SPP,x} \quad (2.21)$$

As is shown in Fig. 2.3, the enhanced wavevector Δk_x from point 1 to 2 is the contribution when light passes through the prism. The excitation of SPs can be identified as a minimum in the reflectivity spectrum, which can be quantitatively described by Fresnel's equations of multi layers system, with the aid of the transfer matrix algorithm⁵⁸.

Two prism coupling geometries are available currently, which named as Otto configuration⁵⁹ and Kretschmann-Raether configuration⁶⁰ respectively. Various shapes of prisms have been used for SPs excitation, such as triangular, half cylinder, hemisphere prism, etc. For simplicity, the half cylinder is used in the following discussions because the angle of light incident is not changed by the refraction at the air/prism interface. For using the triangle prism, the corresponding angle conversion needs be considered.

For the Otto configuration (Fig. 2.4(a)), the metal surface is separated by a dielectric gap sub-micrometer away from the prism. The resonant excitation of SPPs is achieved on the metal surface through the gap where the evanescent fields from both sides of the gap overlap. With the experimental parameters listed below the schematic,

a Fresnel simulation yields a deep and sharp minimum in the angular-dependent reflectivity curve because of the occurring of the surface plasmon resonance (SPR).

Fig. 2.4. Prism coupling geometries and their corresponding angular-dependent reflectivity simulations for (a) Otto configuration, (b) Kretschmann-Raether configuration, (c) alternative Kretschmann-Raether configuration with a refractive index mismatch between the prism and the substrate.

The Kretschmann-Raether configuration is easier because it is easier to carry out experimentally. As shown in Fig. 2.4(b), it requires a finite thickness d_m of the metal layer, which is evaporated directly to the base of the prism. The thickness d_m influences not only the coupling angle θ , but also the coupling efficiency (the depth of the minimum in the reflectivity spectrum). This dependency can be simulated by Fresnel's equations using the transfer matrix methods. As a general understanding, it is a result of the destructive interference between the partially reflected light wave

from the prism/metal interface and the re-radiated light wave from the metal/dielectric interface. A Fresnel simulation of the usual experimental conditions is also shown.

For a convenient experimental handling, the metal layer is usually deposited on a glass substrate with refractive index same as the prism. A transparent index-matching oil with refractive index same as prism and glass substrate is used to stick the prism and the metal coated substrate together. For practical reasons, substrates with lower refractive indices are sometimes coupled to the high index prism for surface plasmon excitation. The refractive index mismatch between the prism and the substrate brings extra features in the angular reflectivity curve, as shown in Fig. 2.4(c). For example, the reflectivity curve is superimposed by an angular-dependent interference pattern, which is caused by the extra reflection beam at the prism/substrate interface interfering with the beam from the substrate/metal interface. Another point is that, at an angle slightly higher than the SPR minimum angle, a second total reflection occurs at the prism/substrate interface and the SPR phenomenon vanishes abruptly. However, the surface plasmon dip still appears at the same angle when the refractive index of the extra layer of the substrate is same as the prism (Fig. 2.4(b)). In order to elucidate these phenomenons, we refer to the reflection/transmission law at dielectric interfaces.

Fig. 2.5. Schematic shows an incident, a reflected and a transmitted transverse magnetic plane wave at interface between two different dielectric mediums. The subscripts stand for ‘incident’ (i), ‘reflected’ (r) and ‘transmitted’ (t). The plane of incidence is determined by the wavevector of the incident beam and the surface normal. Note that the in-plane components of the wavevectors are equal.

As shown in Fig. 2.5, at the two dielectric medium interface with no absorption ($n_1 = \epsilon_1^{1/2}$, $n_2 = \epsilon_2^{1/2}$), the incident wave (e.g. a TM mode) is subjected to reflection and transmission. An important characteristic is the conservation of the in-plane wavevector $k_{||}$, i.e., the wavevector parallel to the interface.

$$k_i \sin \theta_i = k_r \sin \theta_r = k_t \sin \theta_t \quad (2.22)$$

Although the magnitude of $\vec{k}_t$ for $n_1 > n_2$ is smaller, it still yields for the transmission beam the same projection $k_{||}$ on the x-axis due to the increased θ_t . Therefore, SPR resonance is possible at the same angle (Eq. 2.21).

Moreover, with Snell’s law

$$n_1 \sin \theta_i = n_2 \sin \theta_t \quad (2.23)$$

for $n_1 > n_2$, $\theta_t = 90^\circ$, total reflection (i.e. no transmission light) will occur at a critical angle θ_c , with

$$\theta_c = \sin^{-1} \frac{n_2}{n_1} \quad (2.24)$$

Thus, with the same n_1 , θ_c increases with increasing n_2 . Using this equation, those two total reflection angles can be precisely positioned.

2.3.2 Grating Coupler

As is indicated mathematically by a Rayleigh expansion⁶¹ (approximation for shallow grating), a surface periodic structure can also enhance the wavevector of the incident light for resonance coupling. As shown in Fig. 2.6, light with momentum $k_{ph} = \omega/c$ from the dielectric (ϵ_d) shined on a metallic grating (ϵ_m) with pitch Λ at an incident angle θ_{in} . Assuming the dispersion relationship of the SP wave is not disturbed by the corrugated surface, the momentum matching condition can be written as:

$$k_x = k_{ph,x} \pm mg = \frac{\omega}{c} \sqrt{\epsilon_d} \sin \theta \pm mg = \frac{\omega}{c} \sqrt{\frac{\epsilon_d \epsilon_m}{\epsilon_d + \epsilon_m}} = k_{sp,x} \quad (2.25)$$

where m is the diffraction order and the grating wavevector is defined as $g = 2\pi/\Lambda = k_g$.

Fig. 2.6. Schematic represents the SPR coupling via a sinusoidal diffraction grating.

A minimum in the reflectivity spectrum can be recognized as the occurrence of SPR either as a function of incident angle or wavelength. Note that the grating pitch Λ should be within the same order-of-magnitude as the incident wavelength, because SPR coupling via the first diffraction order is always significantly more efficient than higher orders. A shallow grating with amplitude of several tens of nanometers (the grating aspect ratio (amplitude/pitch) must be smaller than 0.1) is proven to be sufficient for efficient SPR coupling.

2.3.3. Waveguide Coupler

A light wave guided in a waveguide is able to excite SP too. Similarly to prism coupler, waveguide coupler also guides the incident light based on the total internal reflection (TIR). Therefore, the basic SPR theory in prism coupler can be easily adopted in the optical fiber. This approach is illustrated in Fig. 2.7. Light propagates as a guided mode along the waveguiding layer and couple to surface plasmon when the evanescent wave of the light in the low refractive index medium propagate into a region coated with a metal layer. The coupling condition is satisfied when both of the waves have same propagation constants.

$$\beta_{mode} = \text{Re}\{\beta_{SP}\} = \frac{\omega}{c} \sqrt{\frac{\epsilon_d \epsilon_m}{\epsilon_d + \epsilon_m}} \quad (2.26)$$

where the waveguide's propagation constant is defined as β_{mode} .

Fig. 2.7. Schematic represents the waveguide surface plasmon sensor.

2.4 Long-Range and Short-Range Surface Plasmons

Two independent surface plasmons modes (symmetric and antisymmetric) at opposite boundaries of thick metal surface can be excited in a special structure. The structure consists of a thick noble metal surface sandwiched between two semi-infinite and identical dielectric medium. These two independent surface plasmons can be coupled to each other when the metal film is thin enough. The properties of these two modes are identified from Maxwell's equations by setting suitable boundary conditions^{62,63,64}. Basically, these two modes exhibit different properties. Symmetric (antisymmetric) surface plasmon has both attenuation and propagation constant increase (decrease) with metal film thickness increase⁶⁵. Hence, symmetric surface plasmon is able to penetrate much deeper into the dielectric medium and termed as long-range, while, antisymmetric is usually termed as short-range^{62,63}.

Fig. 2.8 Magnetic intensity distribution curves of symmetric and antisymmetric plasmons modes propagating on a gold film with thickness of 20 nm ($\epsilon_m = -30.5 + i1.6$) sandwiched by the same dielectric medium of refractive index = 1.328) with excitation wavelength of 850 nm. Reproduced from J. Homola, *Chemical Review*, **108**, 462 (2008)

2.5 Localized Surface Plasmon Resonance (LSPR)

When the light incident on particles with size much smaller than the incident light wavelength, the plasmons will oscillate around the nanoparticle in a resonance frequency called LSPR^{66,67}. The differences between SPR and LSPR are as the following:

- (i) SPR are propagating surface plasmon polaritons (SPPs), while LSPRs are nonpropagating.
- (ii) The SPR propagates tens to hundreds of micrometers along the metal surface with an associated electric field that decays exponentially normal to the metal-dielectric interface; whereas the LSPR is a nonpropagating plasmon that can be excited on metal NPs and in a thin metal film consists of nanoholes or nanowells.

Same as SPR, LSPR is also sensitive to the change of refractive index surroundings the nanoparticles^{68,69,70}. In LSPR, the wavelength shift interrogation is commonly employed to detect the changes. Generally, the LSPR wavelength is determined by the nanoparticle's shape, size, composition as well as the dielectric medium surrounding it.

Let's consider a spherical sphere with radius a that is irradiated by z -polarized light of wavelength λ ($a \ll \lambda$). In this limit, the extinction spectrum of a noble metal sphere can be expressed as:

$$E(\lambda) = \frac{24\pi^2 N a^3 \epsilon_{out}^{3/2}}{\lambda \ln(10)} \left[\frac{\epsilon_i(\lambda)}{\epsilon_r(\lambda) + \chi \epsilon_{out}^2 + \epsilon_i(\lambda)^2} \right] \quad (2.27)$$

where ϵ_r and ϵ_i are the real and imaginary dielectric constant of the metal respectively, ϵ_{out} is the external dielectric constant. The factor χ is equal to 2 for sphere, but can be as large as 20 for high aspect ratios geometries⁷¹. The χ for sphere and spheroids can be easily solved analytically, but it is not straight forward for other geometries. Hence, the discrete dipole approximation (DDA) and the finite-difference time-domain (FDTD) methods have been developed. In these methods, the interested particle is meshed into N finite polarizable elements, and each of them can interact with the applied electric field independently. Both simulation results are in good agreement with experimental results.

As mentioned, the maximum LSPR extinction wavelength, λ_{max} is sensitive to the refractive index of the surrounding dielectric medium. A shift in λ_{max} can be observed when analytes were absorbed on the metal nanoparticles and can be expressed as:

$$\Delta\lambda_{\max} = m\Delta n[1 - \exp(-2d/l_d)] \quad (2.28)$$

where m is the bulk refractive index of the nanoparticles; Δn is the refractive index change due to the presence of the analyte, d is the effective analyte layer's thickness and l_d is the decay length of the electromagnetic field.

2.6 Surface Plasmon Resonance (SPR) Based Sensor

SPR sensor belongs to the refractometric sensing devices which include the integrated Young interferometer^{72, 73}, the integrated optical Mach-Zehnder interferometer^{74,75,76}, the grating coupler sensor^{77,78}, resonant mirror sensor^{79,80}, and the white light interferometer^{81,82}, which use the electromagnetic field to measure the refractive index.

After the SPR for gases sensing is demonstrated in early 1980s^{12, 83}, there is a huge advancement in both technology and applications. Nowadays, SPR sensors become an essential characterization and quantification tool not only for biological species but also for chemical species.

2.6.1 Fundamentals of SPR sensors

The evanescent field of a surface plasmon wave reaches a maximum at the metal-dielectric interface, and decays exponentially into the dielectric medium at a distance of several hundreds of nanometers. Therefore the surface plasmon resonance technique is extremely sensitive to the changes of the refractive index coated on the metal surface. This enables SPR techniques to detect weakly bound species at the sensor surface in the presence of excess solution species. Molecular absorption events near the SPR sensor typically result in an increment in the effective refractive index

which modifies the characteristics of the interacting light as incidence angle, wavelength, intensity and phase. A measurement of any one of these characteristics, in principle, yields information about the molecular adsorption events. A schematic represents the principle of operation of SPR based sensing platform as shown in Fig. 2.9.

Fig. 2.9. Principle of operation of SPR-based sensor platform

Depend on which parameters are measured, SPR sensors can be classified into angular, wavelength, intensity, or phase modulation⁶⁵.

For angular modulation, surface plasmon is excited using a monochromatic light wave. Once the plasmon excitation conditions are satisfied, a dip in the angular reflectivity spectrum can be recognized as the existence of the surface plasmon. The

incident angle which yields the deepest dip and hence the best coupling condition can be defined as a sensor output⁸⁴.

For wavelength modulated SPR sensors, a collimated polychromatic light is used for surface plasmon excitation. The excitation of surface plasmons is still can be recognized as a minimum in the reflectivity spectrum in wavelength function. The sensor output can be determined from the incident wavelength that has the deepest dip⁸⁵.

In intensity modulated SPR sensors, single incident angle and wavelength is used to measure the coupling strength between the light wave and the surface plasmon and the intensity of light wave can be used as a sensor output⁸³. Whereas, the phase modulated SPR sensors, the phase shift is measured at a single incident angle and wavelength and used as a sensor output⁸⁶.

2.6.2 Performance of SPR sensor

The main performance characteristic of SPR sensors are sensitivity, refractive index resolution, and limit of detection (LOD).

2.6.2.1 Sensitivity

The sensitivity of a sensor is defined as the change of the sensor output with respect to the change of the measured quantity (e.g. analyte concentration). In SPR affinity sensor, the sensitivity depends on the sensor output's sensitivity to the refractive index and how effective is the adsorbates induced a change in refractive index⁶⁵. The sensitivity of a SPR sensor to a refractive index S_{RI} can be expressed as:

$$S_{RI} = \frac{\delta Y}{\delta n_{ef}} \frac{\delta n_{ef}}{\delta n_d} \quad (2.29)$$

where Y is the sensor output. The 1st term expresses sensor output's sensitivity to the surface plasmon's effective refractive index and is dependent on the sensor modulations. Whereas, the 2nd term expresses the ratio the change of the surface plasmon's effective refractive index to refractive index and is independent to the sensor modulations⁶⁵.

2.6.2.2 Resolution

The smallest detectable bulk refractive index change in the sensor output is termed as resolution of the SPR sensor. The magnitude of detectable sensor output change depends on the sensor output noise. The resolution, r_{RI} , can be expressed as $r_{RI} = \sigma_{so}/S_{RI}$, where σ_{so} is the standard deviation of the sensor output noise, and S_{RI} is the bulk refractive index sensitivity.

The resolution of all the SPR sensors approaches is usually limited by the noise intensity in the detected light. The origins of this noise are (i) the instability of the light intensity from the light source, conversion the light intensity into electrical signal by the detector and shot noise⁶⁵. Averaging the light intensities by either (i) time averaging using same detector or (ii) spatial averaging using multiple detectors can reduce the noise level.

2.6.2.3 Limit of Detection

The term limit of detection (LOD) is expressed as the smallest change in molecular mass that sensor output can detect⁸⁷. The LOD is depended on the sensor output noise and the sensitivity of the sensor and can be defined as:

$$\sigma_{\Gamma} = \frac{\sigma_{SO}}{S_h} \frac{h}{\left(\frac{\partial n}{\partial c}\right)_{vol}} \quad (2.30)$$

where $(\partial n / \partial c)_{vol}$ is the change in the volume refractive index with respect to the concentration of the molecule, S_h denotes the sensor output's sensitivity within the thickness h , c in this section is represent as the concentration of the molecule. For thickness much smaller than the surface plasmon penetration depth, L_{pd} , Eq. 2.3 can be rewritten as:

$$\sigma_{\Gamma} = \sigma_{RI} \frac{L_{pd}}{2\left(\frac{\partial n}{\partial c}\right)_{vol}} \quad (2.31)$$

where σ_{RI} is the bulk refractive index resolution.

2.7 Type of SPR sensors

Although they are many types of SPR sensors, we only report the most common SPR based sensors. They are prism coupler, grating coupler and waveguide coupler SPR based sensors. In addition, the LSPR sensors based on nanoparticles and nanowire are compared.

2.7.1 SPR Sensors Based on Prism Coupler

When there is a refractive index change on the sensor surface, this means that a variation of the ϵ_I in Eq. 2.13 changes $k_{spp,x}$, and thus the surface plasmon resonance angle is also needed to change as predicted by Eq. 2.21. In the mean while, the addition of a thin (i.e. thickness d much smaller than the SP decay length along the z axis) and non-adsorbing layer with different dielectric constant ($\epsilon_f \neq \epsilon_I$) also induces a change in the overall dielectric constant integrated over the evanescent field, therefore

shifts the SPR angle (with angular modulation) or wavelength (with wavelength modulation). The effective refractive index within the evanescent field increases assuming $\epsilon_f > \epsilon_l$. Therefore, the dispersion relation of Eq. 2.13 shifts to larger wavevector, depicted as curve SP-II in Fig. 2.10. Consequently, a larger incident angle $\theta' > \theta$ (or lower wavelength) is required to fulfil the resonance condition. For a thin, non-adsorbing layer, the resonant angle displacement $\Delta\theta$ is linearly proportional to the optical layer thickness, nd .

Fig. 2.10. The dispersion SPP curves before (SP-I) and after (SP-II) the thin film adsorb on the metal surface. A change in resonance angle from θ to θ' is observed by using the prism-based coupling SPR.

The SPR spectrum of both with plain Au film and coated Au films is shown in Fig. 2.11. The SPR curves exhibit a shift in resonance angle or wavelength when molecules adsorb at the sensor surface.

Fig. 2.11. The SPR reflectivity spectrums show the resonance angles (minima) for plain Au film before and after molecular adsorption respectively.

There are various methods proposed, to separate the two distinct parameters (n and d) within the optical thickness value, e.g., by measuring the SPR in a series of bulk media with different refractive indices⁸⁸ or under multiple light wavelengths⁸⁹. However, for biomolecules detection, the $\Delta\theta$ is directly correlated with the molecular surface concentration. For example, using radioisotope labelled protein, it has been found that $\Delta\theta$ depends linearly on the protein concentration (mass per area) and the dependence is irrelevant to the type of proteins studied⁹⁰. Usually, a layer of biomolecules can be treated as non-adsorbing layer. However, if the biomolecules carries external labels (e.g. gold nanoparticles, fluorescent dye, etc.) the resulting thin layer becomes absorbing, which distorts the SPR properties.

Nowadays, many SPR sensors are available commercially, such as the Biacore systems³¹, Spreeta sensor from Sensata⁹¹, Multiskop system from Optrel⁹², Springle SPR systems and Autolab Esprit from Eco Chemie⁹³, BIOSUPLAR 6 from Analytical μ -Systems⁹⁴, SP 7000 platforms from Reichert Analytical Instruments⁹⁵, Sensia β -

SPR Research Platform⁹⁶, Plasmonic from Hofmann Sensorsysteme⁹⁷ and SPR-20 from DKK-TOA Corp⁹⁸.

One of the most common SPR systems having the highest market share is the Biacore system. The system is based on angular modulation, consisting of a light-emitting diode (LED), a glass prism and a detector array with imaging optics. A divergent LED light is collimated, focused and incident on a gold coated prism consists of multiple sensing channels. The angular spectrum from each sensor channel is projected on different rows of the array detector. This configuration offers a refractive index resolution of 1×10^{-7} RIU with up to 4 sensing channels.

Although commercial SPR sensor is available, some interesting and better performance SPR sensors are still in the research stage, which is discussed below.

Zybin *et. al.* is demonstrating the sensitivity of dual-wavelength SPR imaging system with resolution up to 2×10^{-6} RIU⁹⁹ as shown in Fig. 2.12(a). The configuration is based on two turned on laser in sequent and the different in intensity from the two wavelengths were measure as the sensor output as shown in Fig. 2.12(b).

Fig. 2.12. The dual-wavelength configuration proposed by Zybin *et. al.* (a) The schematic of the configuration, (b) the difference in signal is the sensor output. Reproduced from reference 99, Analytical Chemistry.

A SPR imaging system with resolution up to 5×10^{-6} RIU and simultaneously acquired SPR images sequentially from 120 channels was reported by Campbell's group¹⁰⁰. Homola's group has used the polarization contrast to achieve a resolution up to 2×10^{-6} RIU and limit of detection (LOD) of 100 pM for short oligonucleotides (23-mers) with 64 independent measurements simultaneously^{101,102}. This configuration is based on placing a quarter waveplate and two crossed polarizers in between the prism and a SPR chip containing patterned multilayer structure as shown in Fig. 2.13. Since the SPR chip has a patterned area, those uncoated area is not influenced by the SPR and thus blocked the light by the polarizer (located between the waveplate and CCD). However in the case of SPR-active layer, the TM-polarized light component couples with a surface plasmon and induce a change in both amplitude and phase. Compared to the TE-polarized light, there is only a slight shift in both amplitude and phase which is able to give bright spots on a weak background.

Fig. 2.13. (a) SPR imaging with polarization contrast, (b) Schematic represents the SPR imaging sensor surface using two types of metal-dielectric multilayers. Reproduced from reference 102, *Sensors and Actuators B*.

Thirstrup et. al. replaced the conventional cylindrical focusing optics by a diffraction grating to diffract the incident light beam on the sensor's surface as shown

in Fig. 2.14. The reflected light follows the same path and collected by a two-dimensional photodetector. This configuration offers a sensitivity of $140^\circ/\text{RIU}$ and resolution of about $5 \times 10^{-7} \text{ RIU}^{103}$.

Fig. 2.14. Polymer SPR sensor chip employing integrated focusing grating elements for in- and out-coupling. Reproduced from reference 103, Optical Engineering.

Homola's group has demonstrated a wavelength modulated SPR sensor^{104,105}. As shown in Fig. 2.15, a collimated polychromatic light from halogen lamp was incident on the prism. The reflected light from the channels was collected and coupled into the optical fibers. The signals were transmitted and analyzed by the spectrograph. The configuration has a resolution of $2 \times 10^{-7} \text{ RIU}$.

Fig. 2.15. Experimental setup of dual-channel surface plasmon resonance sensor. Reproduced from reference 105, International Journal of Food Microbiology.

Homola's group has combined the dual-channel sensing architecture with the novel spectral discrimination of the sensing channels by means of a dielectric overlayer to sense the surface and bulk non-specific effects simultaneously¹⁰⁶. In this configuration, a wide parallel beam of polychromatic light is incident onto a sensing surface consisting of a thin gold film, and part of it is coated with a thin high refractive index dielectric overlayer (tantalum pentoxide, 15 nm) as shown in Fig. 2.16¹⁰⁷. As known, the appearance of the overlayer shifts the resonance wavelength, hence two dips in the reflectivity spectrum can be observed, corresponding to the area with and without the overlayer. The plasmon excited by the higher resonance wavelength is able to penetrate deeper into the sample and causing bulk refractive index changes more weighted than surface changes.

Fig. 2.16. (a) Dual-channel SPR sensor with a dielectric overlayer for spectral discrimination of sensing channels. (b) SPR sensor chip with a dielectric overlayer (top view). Reproduced from reference 107, *Sensors and Actuators B*.

Another configuration with the same mechanism described above is based on using a special prism coupler¹⁰⁸. The special prism is designed such that the polychromatic light is incident on a thin metal film in two distinct regions as shown in Fig. 2.17. Since the light is incident at different angles in the two regions (denotes as

A & B), different resonance wavelengths are detected. As shown in Fig. 2.17, the prism is designed such that α has a larger angle than β , hence the resonance wavelength of region A is at smaller wavelength than B. As described previously, the surface plasmon penetration depth increase with wavelength, hence region B which has higher resonance wavelength is more sensitive to the change of the bulk refractive index. Using this approach, a SPR sensor with eight channels has a resolution of 1×10^{-6} RIU.

Fig. 2.17. (a) Special prism coupler for sequential excitation of surface plasmon wave and wavelength division multiplexing of sensing channels. (b) Schematic of the eight-channel SPR sensor combining parallel architecture with the wavelength division multiplexing of serially ordered channels. Reproduced from reference 108, *Sensors and Actuators B*.

A NIR narrow band-pass filter and an incoherent light source is used to achieve the resolution up to 10^{-5} RIU which is equal to 18-base oligonucleotides at concentration of 10 nM ^{109, 110}. The resolution can be further improved from 20% to 40% by introducing a special multilayer structure (SF10 Prism/Cytop/Au/Water) which can support long-range SPR¹¹¹. The Cytop is chosen because it has a very close refractive index to the water. *Nenninger et. al.* has reported SPR sensor spectroscopy using the

long-range SPR supported on a multilayer structure (Au/AF/Glass) and demonstrated a resolution of 2×10^{-7} RIU¹¹². Recently, the resolution is further improved to 2.5×10^{-8} RIU by Homola³².

A phase modulated SPR sensor based on Mach-Zehnder configuration with resolution as low as 5.5×10^{-8} RIU was proposed by Wu *et. al.*¹¹³. In this configuration, the *p*- and *s*-polarized components of a reference beam and a signal beam from a prism are interfered and separated by Wollaston prism and collected by two detectors as shown in Fig. 2.18. A PZT actuator modulated the optical path of the reference beam and thus the intensity of *p*- and *s*- polarizations can be modulated periodically. As known, only the *p*-polarized is affected by SPR, the sensor output can be determined as the phase difference between the interference signals of *p*-polarization (prism) and *s*-polarization (reference). In addition, the unwanted disturbances (e.g. noise and instabilities of the setup) may be cancelled out through phase subtraction.

Fig. 2.18. Experimental setup for measurement of differential SPR phase shift. Reproduced from reference 113, Biosensors and Bioelectronics.

2.7.2 SPR Sensors Based on Grating Coupler

The working principle for Grating Coupled Surface Plasmon Resonance (GCSPR) sensor is the same as the Prism Coupled SPR (PCSPR) sensor with the difference of using grating for SPR excitation. When there is a change in refractive index on the metallic grating surface due to the modification of the sensor (grating) surface, the SPR excitation condition is changed (Eq. 2.25) and can be determined as either a shift in resonance angle for a fixed incident wavelength, or a shift in resonance wavelength for a fixed incident angle.

Grating couplers have received less attention compared to prism couplers in SPR sensors. Nowadays, the grating coupler becomes an attractive approach because of its mass production possibility, typically replication into plastic using nano-imprinting (and hence could be a low cost SPR sensing substrate). In addition, the grating coupler offers the possibility of miniaturization and integration into a system. Furthermore, cumbersome optical alignment (needed for prism couplers) can be avoided.

The first demonstration of a SPR imaging device is done by Brockman and Fernandez⁴⁴. In his approach, a monochromatic light was focused on a plastic substrate consists of gold grating and 400 sensing channels. The reflected light was collected by a two-dimensional charge-coupled detector (CCD) array. HTS Biosystems (Hopkinton, MA) further developed this idea⁴⁵. In March 10th, 2005, Biacore International AB has completed the acquisition of FLEXChip System and related assets from the U.S. company HTS Biosystems.

Alleyne⁴³ has demonstrated a higher sensitivity of 680°/RIU by bandgap-assisted GCSPR, but this requires a prism to enhance incident light momentum for exploring the grating's bandgap region as shown in Fig. 2.19.

Fig. 2.19. Combined Attenuated Total Reflection (ATR) and indirect grating coupled SPR (Bandgap-assisted GCSPR). Reproduced from reference 43, Optics Express.

Angular surface plasmon spectroscopy containing 216 sensing channels with resolution of 5×10^{-6} was reported by Homala's group⁴⁶. The 216 diffraction gratings were defined by evaporating the Au film through a mask and 6 flow channels are integrated to the array of diffraction grating with each flow-cell chamber interfaced with 36 channels on the sensor chip as shown in Fig. 2.20(a). A collimated monochromatic light was focused on a row of gold-coated diffraction grating by a cylindrical lens (inside the scanning optics) and reflected. The reflectivity spectra from different rows of grating were read sequentially in a two-dimensional CCD array as shown in Fig. 2.20(b).

Fig. 2.20. (a) Sensor chip with array of diffraction gratings and fluidic system for sample delivery to the array of diffraction gratings. (b) The optical setup of SPR sensor chip reader. Reproduced from reference 46, *Sensors and Actuators B*.

Homola's group reported an SPR sensor using a multi-diffractive grating with five harmonic components to simultaneously excite multiple surface plasmons¹¹⁴. This approach is based on polychromatic light incident on a grating with different periodicity. Hence, the multiple SPR dips can be observed in the reflectivity spectra, one for each grating profile. As mentioned, the plasmon penetration depth is affected by the resonance wavelength. Thus, this approach can probe the variation in the distribution of the refractive index within the dielectric medium¹¹⁴.

Recently, Homola's group has combined the advantages of both short-range and long-range surface plasmons to demonstrate a sensor with a resolution as small as 3.5×10^{-6} RIU⁴². Since the long-range SP has longer penetration depth than short-range SP, it is able to distinguish the changes of the sensor response due to bulk or surface refractive index. The structure of the grating is $\text{AlF}_3/\text{Au}/\text{Water}$, AlF_3 is chosen because it has a similar refractive index as water about 1.33 - 1.34.

Telezhnikova and Homola developed a new approach based on spectroscopy of surface plasmons on diffractive grating with refractive index resolution of 3×10^{-7} RIU¹¹⁵. This approach consists of a special diffractive grating structure (named as SPR coupler and disperser (SPRCD)) that performs two tasks simultaneously. One of them is for plasmons excitation and the second is for dispersing the incident light over a position-sensitive detector. As shown in Fig. 2.21(a), a collimated polychromatic light was incident on the grating. The light diffracted into second order of diffraction was used to excite SP at the interface of metal-dielectric medium. Meanwhile, the first diffraction order of light was dispersed into different wavelengths and then collected by a position sensitive detector in different as shown in Fig. 2.21. A narrow dip in the spectrum can be observed when the light was coupled to surface plasmon. Recently, the group has developed a compact standalone sensor unit consisting of optical bench, microfluidics and supporting electronics with the footprint around $15 \text{ cm} \times 15 \text{ cm}$ (Fig. 2.21(b))¹¹⁶. The developed SPRCD sensor has sensitivity of 620 nm/RIU . Since the standard deviation of the baseline noise is $2 \times 10^{-4} \text{ nm}$, this gives a resolution of $3 \times 10^{-7} \text{ RIU}$.

Fig. 2.21. (a) Schematic represents the SPR sensor based on simultaneous surface plasmon excitation using polychromatic light and the light dispersion by a special grating coupler. (b) Principle of SPRCD sensor and the subset figure is the developed SPRCD sensor. Reproduced from reference 116, *Biosensors and Bioelectronics*.

2.7.3 SPR Sensor Based on Waveguide Couplers

In general, the waveguide coupler SPR sensors were fabricated by removing the silicon cladding from a small portion of the fiber core, and coated with noble metal layer. The light wavelength, fiber geometry, fiber parameter and the metal properties strongly affects the coupling of the SPs in the waveguide. For instance, single-mode and multi-mode optical fiber has different coupling mechanism due to different transmission mode properties depending on the number of modes that a fiber supports¹¹⁷. Among the SPR sensors, waveguide SPR sensors have the best miniaturization capability. In early 1990s, the waveguide SPR sensors were demonstrated^{118,119,120,121}.

In 1999, an intensity modulated fiber optic SPR sensor was reported by Homola's group and it shows a resolution of 2×10^{-5} RIU as shown in Fig. 2.22¹²².

Since the propagation constant of a surface plasmon wave depends on the refractive index of the medium adjacent to the gold film, it affects the strength of the interaction between the SPR and the fiber mode and consequently the fiber mode attenuation. Variations in the refractive index of the medium may be determined by monitoring changes in the transmitted optical power. The working region of the bare gold SPR structure is 1.4193–1.4104 and 1.3302–1.3422 for SPR structure with an overlayer.

Fig. 2.22. Optical fiber SPR sensing structure. Reproduced from reference 122, *Sensors and Actuators B*.

The main drawback of this method is the fiber deformation because of bending and twisting. Since the SP excitation is strongly polarization-sensitive, the deformation of the fiber caused polarization fading¹²³ and consequently affects both the detected coupling wavelength and the fiber attenuation mode in spectral and amplitude interrogation. To solve this problem, the fiber that hold the fiber polarization state called highly birefringent (HiBi) fibers are used. However, the HiBi fiber is expensive and complicates the sensor fabrication processes. Hence, Homola's group reported a wavelength-modulated version with unpolarized radiation. The unpolarized light that has uniform intensity distribution in polarization space is transmitted to fiber

deformation. The sensor offers a refractive index resolution of 3×10^{-5} RIU (under moderate deformations) and 5×10^{-7} RIU (no deformations)¹²⁴.

The deformation problem is dramatically reduced by using the polarization maintaining fibers. Using the fibers, the resolution with 2×10^{-6} RIU was established¹²⁵.

A single mode waveguide SPR sensor with a resolution better than 2×10^{-6} RIU using D-shape optical fiber and heterodyne interferometry was investigated by *Chiu et. al*¹²⁶. Later in 2007, *Lin et. al.* reported a resolution at least 3×10^{-6} RIU with using the side-polished multi-mode optical fiber¹²⁷.

An intensity modulated SPR sensor with one reference and sensing channel was investigated by *Mouvet et. al.*¹²⁸ as shown in Fig. 2.23. The signal from the reference can be used to normalize the signal from signal channel to enhance the sensor stability and provide a resolution better than 5×10^{-5} RIU¹²⁹. A wavelength modulated waveguide was reported a resolution of 1×10^{-6} RIU¹³⁰.

Fig. 2.23. Schematic represents the waveguide SPR sensor. Sensing occurs on the modified gold film sensor surface and the analyte is isolated from the rest of the chip. Reproduced from reference 128, *Analytica Chimica Acta*.

The use of tapered fiber in SPR sensors is another important milestone¹³¹. With a modified geometry in the tapered-fiber, the SPR resonance wavelength-angle pair can be tuned. Two different SPR dips corresponding to the surface plasmons excited in the gas and liquid active regions can be observed in the spectrum. The changes in refractive index occurred in both vapor and liquid phases can be detected in-situ by examining the SPR resonance wavelength from two sensing surfaces. The taper ratio and tapered profile is studied in details to enhance the sensitivity and performance of the sensor¹³². A highly sensitive tapered fiber-optics SPR sensor can be fabricated if an exponential-profile with high taper ratio is used. The sensitivity can be further enhanced (around 15 times) by introducing a Teflon dielectric layer sandwiched between metal and tapered fiber core¹³³. Here, a sensitivity of 1×10^{-6} RIU was demonstrated.

2.7.4 Nanoparticles Sensors

Light incident on the noble nanoparticles with size much smaller than the wavelength of the incident light is able to induce the electrons in the conduction band to oscillate collectively in resonance frequency. The nanoparticles' size, shape and materials strongly affect the resonance frequency. At the frequency, the wavelength is absorbed and coupled, thus the single nanoparticles can be observed easily by eye using dark field microscopy^{37,134, 135, 136, 137}. Due to this nature, the noble metal nanoparticles are used as labels for immunoassays detection^{135,137,138}, biochemical sensors^{139, 140, 141, 142, 143, 144} and surface enhanced raman spectroscopies (SERS)^{145,146,147,148,149,150,151,152,153}. In

addition, plasmonic nanoparticles provide unlimited long time to observe molecular binding events because it does not blink or bleach.

LSPR shifts can be optimized by choosing the appropriate nanoparticle properties, m , ld , and Δn . This requires a careful selection not only the nanoparticle size, shape and materials but also the molecules and resonant labels. A summary of the nanoparticle used in LSPR, the effect on extinction spectrum of different nanoparticle shape, and its response when the external environment changes are shown in Fig. 2.24.

Fig. 2.24. (a) Atomic force micrograph of a LSPR substrate fabricated by Nanosphere Lithography (NSL) fabricated nanoparticle arrays. (b) LSPR extinction responds for different nanoparticles shape. (c) & (d) the LSPR responds after every step as shown in (c). Reproduced from reference 37, Annual Review of Physical Chemistry.

Currently, Van Duyne and his coworkers are working on LSPR of noble metal nanoparticles arrays and reported resolution of 5×10^{-3} RIU and wavelength sensitivity of 196 nm/RIU³⁷.

Dahlin and co-workers used plasmonic nanohole arrays and found out a detection limit of detection of 0.1 ng cm^{-2} by reducing the shot noise using photodiode array spectrometers with high saturation capacities, which can therefore further enhanced the LSPR resolution¹⁴¹.

Generally, increasing the nanoparticle's size and aspect ratio (width/height) caused a red-shift in λ_{max} , longer decay length in electromagnetic wave and higher m values¹⁵⁴. Recently, a simulation demonstrated that the sharp nanoparticle (usually appears at the tip region of the triangular nanoparticles) can be acted as hot-spots to enhance the sensitivity LSPR sensor¹⁵⁵ and strengthen the surface enhanced raman spectroscopies (SERS)^{145,146,149,150,153,156}.

A “film over nanowell” plasmonic nanostructure was reported and demonstrated refractive index sensitivity of 538 nm/RIU and figure of merit (FOM) of 14.5 which is 3 times better than nanoprism array¹⁵⁷.

Three complementary approaches can be used to further enhance the sensitivity. The approaches are to increase the effective refractive index change caused by every molecule binding. First, using a larger molecule^{155,158,159}. Second, chromophores that absorb visible light^{160, 161, 162}. Third, using the nanoparticles separated by less than 2.5 particle radii^{163,164}. The second and third methods are based on plasmon coupling.

Although LSPR has great sensitivity, it only senses the refractive index changes on the surrounding medium; in another words, it can't recognize what molecules are adsorbed on the surface. To identify the molecules, SERS^{165, 166, 167} and laser desorption ionization mass spectrometry^{168, 169, 170, 171} can be used in parallel with LSPR substrates.

2.7.5 Gold Nanorod Molecular Probes (GNRMPs)

Gold nanorods (GNR) possess unique optical properties that make them appropriate for sensing application. Their optical properties strongly depend on the aspect ratio and shape, refractive index of the environment. For nanorods, two distinct plasmon modes are observed, transverse (~520 nm) and longitudinal plasmon mode (> 600 nm). The longitudinal plasmon modes are extremely sensitive to the refractive index change in the surrounding dielectric medium³⁸, because of larger area for molecular attachment on the surface. As the nanorod's aspect ratio increase, the sensitivity of the GNR increase^{172,173,174}.

Recently, Yu³⁹ shows the possibility of multiplexed sensing using the gold nanorod based on the longitudinal plasmon modes on the gold nanorods's aspect ratio (Fig. 2.25). In this study, different aspect ratio of gold nanorods were functionalized with different recognition molecules and dispersed into a single solution. Targets that were complementary to the different recognition molecules on the gold nanorods were then added to the solution to initiate binding events, which caused a selective red shifts of one or more of the longitudinal peaks. For example, when target 1 (complementary to the receptors on GNR 1) was added to the solution, a red shift in

the longitudinal peak corresponding to GNR 1 was observed with smaller shifts in the peaks corresponding to GNR 2 and 3 (Figure 2.25b). When targets 1 and 2 (complementary to the receptors on GNR 1 and 2, respectively) were added to the solution, a shift in the peaks corresponding to GNR 1 and 2 was seen, while only a small shift in the LSPR maximum associated with GNR 3 occurred (Figure 2.25c). All three peaks red shifted when their corresponding targets were added to the solution (Figure 2.25d). This method offers a resolution of 400 nm/RIU based on the aspect ratio of 3.

Fig. 2.25. (a) Schematic of a GNR molecular probe. Multiplexing detection of various targets on different aspect ratio of gold nanorods. Due to different specific binding on different aspect ratio of gold nanorod, multiplexing detection is possible. (b) one target, (c) two target, (d) three targets. Reproduced from reference 39, Analytical Chemistry.

CHAPTER 3. FABRICATION AND CHARACTERIZATION OF THE GRATING

The gratings used in this study were fabricated by either Interference Lithography (IL) or soft lithography processes. The soft lithography is typically a replication of the grating master (generated from IL) to many grating replicas by imprinting process. For a grating directly generated from IL, Reactive Ion Etching (RIE) process is needed to transfer the pattern to the substrate. After the gratings were fabricated, characterizations of the gratings were carried out by atomic force microscopy (AFM), scanning electron microscopy (SEM) and ellipsometer.

3.1 Gratings Fabrication Process

IL offers one of the most economical and efficient way to provide 1D, 2D and 3D array of periodic nanostructure for plasmonic crystal. In addition, IL offers advantages over electron-beam lithography due to its ability to define grid patterns over large areas in a single, fast, maskless exposure. Moreover, since IL defines periodic patterns with well-controlled periodicity, it provides an absolute reference that may facilitate read/write head position tracking. The feature size possible even in mid-ultraviolet region is beyond what is possible with the most advanced stepper based technology.

The interference of coherent light forms a standing wave pattern, which can be recorded in photoresist as shown in Fig. 3.1. For interference of two beams, the standing wave will form a dark (minima) and bright (maxima) fringes that can be developed to form grating pattern. Euler's relation gives the mathematical expression

for this phenomenon. The period, Λ of standing wave, given in Eq. 3.1 is a function of wavelength of the incident light (λ) and the half angle at where two beams intersect (θ). However the smallest grating periodicity is limited by the wavelength of the light source and the resolution of the resist.

$$\Lambda = \frac{\lambda}{2\sin\theta} \quad (3.1)$$

Fig. 3.1. Two-beam interference forms a standing wave (fringes).

Ideally the two arms of the interferometer must be equal in length, which can be setup by Mach-Zehnder interference lithography system, but it is very sensitive to vibration and beam motion. These problems can be solved by Lloyd's mirror which is almost immune to these effects¹⁹⁶. Due to symmetry of the two identical arms in Lloyd's Mirror Interferometer, one arm can be simply replaced by 90° mirrors as shown in Fig. 3.2. Lloyd's mirror is rigidly fixed perpendicular to the surface and used to reflect back a portion of wavefront back to the other half. In Lloyd's mirror, only a

single beam is used. Because the mirror is fixed in relation to the substrate, vibration of assembly or wandering of the incoming beam do not affect the exposure. This make Lloyd's mirror more stable and negates the need of phase locking system. The angle of interference and the periodicity of gratings are set only by rotating the mirror/substrate assembly around the point of intersection of mirror and the substrate. The incident angle is not a problem since just simple trigonometry guarantees that the light reflected off the mirror is always incident at the same angle as the original beam. The Lloyd's mirror interferometer used in this work is shown in Fig. 3.3. The HeCd laser has a wavelength of 325 nm is chosen because it is suitable to fabricate the desired grating periodicity.

Fig. 3.2. Basic Lloyd's mirror configuration.

Fig. 3.3. Schematic of a Lloyds-mirror interferometer. The substrate and mirror are fixed at a 90° angle to one another, and centered in a single incident beam. Rotating the substrate/mirror assembly as indicated varies the spatial-period of the exposed grating.

The silicon wafer is preferred as substrate in this project due to higher flatness and opaqueness. The substrate was cut into 2.5×2.5 cm and cleaned using piranha

solution for 20-30 minutes. The samples were rinsed in deionized water for 15 minutes and then dried in the oven at 120°C for 10 minutes. Many of the metals on the surface oxidize very easily and forms long range hydrogen bonds with water adsorbed from the air, causing poor adhesion. Hence prior to spin coating the substrates with photoresist, adhesion promoter (primer) was applied.

Photoresist S1805 (Microposit®, Shipley European Limited, U.K.) was diluted in EC-solvent (Microposit®, Shipley European Limited, U.K.) in ratio of 2:3, in order to get an appropriate film thickness of 130nm. The spinning rate is 5000 RPM for 30 seconds to achieve 130 nm film thickness as measured using a profilometer and ellipsometer (using *genocs* method)¹⁷⁵. Soft bake was performed at 90°C for 12 minutes. An antireflective coating (ARC, either Brewer Science XHRI-16 or AZ Barli) was used to minimize the back reflection into resist layer. The samples were then put in Lloyd's bracket and exposed to an interference pattern. The grating amplitude can be controlled by adjusting the dose modulation, exposure time, the distance from pin hole and the power of the incident beam. Several set of exposure time and distance have been tried as shown in Fig. 3.4. It can be observed from the figure that varying the exposure distances provide more severe effect in amplitude compared to exposure time. However the exposure time is proportional to the grating amplitude for smaller amplitude for constant development time (60 sec). Finally the desired grating amplitude which is 25 nm can be obtained by exposure time of 27 sec and at a distance of 1.5 m with a constant development time of 60 sec, as shown in Fig. 3.4. In addition, long distances from pin hole is preferred in order to obtain larger uniform

area to reduce non planar effects of the incident beam with the plane wave front, high control and stability over the exposure condition.

Fig. 3.4. The red line (left scale) is beam intensity (dose per unit time) measurement using power meter in front of sample stage as a function of exposure distance and the blue lines (right scale) are the amplitude measurements for different exposure times (doses) as a function of exposure distance.

For a direct use grating, a reactive ion etching process was required to transfer the photoresist pattern to the substrate. Subsequently the grating was thermally evaporated with 37 nm of Ag and 7 nm of Au as shown in Fig. 3.5.

Soft lithography process¹⁷⁶ was used for replication of master grating as it allows fabrication of grating replicas with high fidelity and without damage to the master. The elastomer stamp was cast from poly(dimethylsiloxane) (PDMS, Corning, USA), which was poured on the master grating, cured at the temperature of 80°C and gently released. The replica gratings were produced by copying the elastomer stamp into a UV-curable polymer NOA-72 (Norland, USA). This polymer was dissolved at the ratio of 1:10 with tetrahydrofuran (Sigma, USA) and spun onto a cleaned glass slide (rotation speed 3500 rpm). The elastomer stamp was accurately placed on top of

this polymer film producing the modulation on its outer surface. After the polymer was cured with UV light ($\lambda = 366$ nm), the elastomer stamp was peeled off leaving the finished polymer replica. It was possible to use the elastomer stamp repeatedly for more than 10 times without any observable degradation in the replica parameters. To form an SPR grating coupler, the polymer replica gratings were subsequently coated with 37 nm of Ag and 7 nm of Au by thermal evaporation in vacuum at room temperature. The summary of the whole fabrication process is shown in Fig. 3.5,

Fig. 3.5. A summary of the grating (direct use or replica) fabrication process.

3.2 Characterization of the Grating

Due to the high coherence length of interference lithography pattern, a high periodicity of grating uniformity over a large region (20×20 mm²) can be obtained

(Fig. 3.6(a)). AFM (Fig 3.6(b)) shows the well-defined shape grating with a grating constant of 468 nm and amplitude of 25 nm.

Fig. 3.6. Grating characterization using (a) FESEM and (b) AFM. AFM shows the grating periodicity and the subset figures in (b) represent the corresponding grating period through section analysis and Fourier transform of the grating.

Further characterization of the grating profile was done using Fourier transform. As shown in the subset of Fig. 3.6(b), the grating profile is almost sinusoidal and shows spectral components peaked at $2 \mu\text{m}^{-1}$ and with a bandwidth of 8%. The broadening of the Fourier transform peak is due to the finite scanned sample size. In addition, the width of the Fourier transform peak represent the non-sinusoidal components of the grating profile, i.e. the smaller curvatures of the valleys with respect the top hills. The bandwidth is therefore due to inharmonic components of the sinusoidal profile instead of variation of periodicity.

Another way to determine the grating pitch is using the diffraction properties of the grating itself as shown in Fig. 3.7. The collected experimental data from the ellipsometer is shown in Fig. 3.8. It is collected at incident wavelength from 300 nm to 450 nm at a fix incident angle of 45° , and the detector is swept from -35° to -60°

relative to 90° . When a peak is observed in the reflectivity spectrum, the diffraction of the grating in m^{th} order is diffracted as shown in Fig. 3.8.

Fig. 3.7 Schematic represents the different orders of diffraction of an incident light from a grating surface.

Fig. 3.8. Diffraction edge data collected from the grating.

From the grating equation,

$$\sin \theta_m = \sin \theta_{in} + m \lambda_{in} / \Lambda \quad (3.2)$$

where θ_m is the output angle where m^{th} diffracted light is collected, θ_{in} is the incident angle (which is 45° in our case) and λ_{in} is the incident wavelength (which is from 300

nm to 450 nm). Since the angle of detector (relative scatter angle) is always in minus sign which means only $m = -1$ is excited. Thus the Eq. 3.2 can be rearranged as:

$$\lambda / \Lambda = \sin \theta_{in} - \sin \theta_m$$

$$\Lambda = \frac{\lambda}{\sin 45^\circ - \sin(45^\circ + \theta_{detector})} \quad (3.3)$$

where $\theta_{detector}$ is the relative scatter angle.

Using Eq. 3.3, one can determine the pitch of the grating is around 468 nm.

3.3 Chapter Summary

In summary, the grating used in this study can be fabricated using IL and imprinting technique. The grating amplitude can be controlled by varying the exposure time and the exposure distance. Subsequently, Ag and Au with a thickness of 37 nm and 7 nm were evaporated in succession. The grating pitch can be determined not only by AFM but also by the diffraction edge method.

CHAPTER 4. AZIMUTHAL DISPERSION AND ENERGY MODE CONDENSATION OF GRATING-COUPLED SURFACE PLASMON POLARITONS

4.1 Introduction

In this chapter, the SPP(s) excitation on the grating replica fabricated from Chapter 3 is discussed. Before going into details, the motivation of the study is summarized.

Grating Coupled surface plasmon resonance (GCSPR) has been widely used for a variety of biomedical and chemical sensing applications^{25,51}. Current GCSPR sensors have sensitivity on the order of 3×10^{-7} RIU¹¹⁵, almost in the sensitivity range of prism-coupled SPR^{27,31,177}. The GCSPR approach is particularly interesting for those bio-sensing applications that require prismless detection in an array format combining simultaneous high throughput and sensitivity. Advantages as well as drawbacks of GCSPR based techniques have been widely discussed in chapter 2.

Although the excitation of SPP modes and their interaction with gratings have been extensively studied^{50,178, 179,180}, the SPP effect on rotatable grating is not fully explored yet.

In this chapter, the author will focus on a specific feature that is exclusive to grating coupling, i.e. controlling the plasmon propagating direction on the plane of the metallic grating. This possibility is provided by the well known conical configuration where the incident wavevector of the incident light is not required to be parallel to the grating Bragg vector. When the grating is rotated azimuthally, symmetry is broken with an additional component due to the grating momentum. As a result, the final SPP propagating direction is no longer perpendicular to the groove but rotated instead.

Breaking the collinear symmetry greatly enlarges the set of physical combinations that satisfy SPP coupling. In particular it has been demonstrated that a fraction of p -polarized light is converted to s -polarized light⁴⁷, an effect that has been fully explained using computational^{181,182} and recently, fully analytical approaches¹⁸³. Studies on conical mounting include characterization of metal gratings⁵⁰, narrow-ridged short-pitch metal gratings in the conical mount¹⁸⁴, sharp resonances¹⁸⁵, waveguiding¹⁸⁶ and outcoupling of SPPs to radiation modes in the grating-prism combined configuration¹⁸⁷.

However, notwithstanding the high interest for GCSPR, little attention has been paid to the direction and the number of different modes that can be excited with the conical configuration. In this chapter, the author specifically investigates the conditions for SPP excitation as a function of azimuthal rotation angle on the grating plane. The author shows a new way to use a single incident wavelength to excite two SPPs with different propagation directions. Particularly interesting are the conditions for the merging of the two SPPs that propagate perpendicularly to the incoming light. The wave-vector conservation provides a simple description of the kinematics of SPP grating coupling and also allows determination of the wave-vector direction of rotation and the related energy dispersion. Furthermore the angular spreading of SPP wave-vector directions can be described and related to the number of SPP modes that can be excited by a single wavelength. Azimuthal orientation allows the possibility to simultaneously excite a large number of SPP modes with the same energy but different orientations. This effect has been related to an energy density condensation

mode that occurs in correspondence to the energy threshold for SPP excitation. The implications of these findings in the context of sensing applications will be described.

4.2 Experimental

The grating replica used in this study was produced from the method described in Chapter 3.

The optical measurements have been performed in $\theta/2\theta$ symmetric reflectivity configuration, scanning angular position with a precision of 0.005° and using a 75W Xe lamp, monochromatized between 600 nm and 900 nm with a bandwidth of 2.7 nm. All measurements were collected by a p polarized incident light. The schematic of the configuration used in this study is shown in Fig. 4.1. Incoming light with a $\vec{k}_{ph}$ wave-vector after passing through the polarizer forms an angle θ with the normal z -axis. In our experimental setup the scattering plane (x - z plane) is fixed and the samples with gratings were mounted on a sample holder (x - y plane) that can be rotated azimuthally to define the φ angle. The grating's orientation was varied by rotating azimuthally from 0° (i.e. grating vector is parallel to the incident light or x -direction) to 60° with a precision of 0.01° . All measurements were acquired using a J.A. Woollam Co. VASE instrument.

Fig. 4.1. Schematic of the configuration used in this study

4.3 Results

The first evidence of the azimuthal rotation effect on the SPR excitation is shown by the reflectivity spectra collected at different azimuthal grating rotations (Fig. 4.2). The azimuthal rotation is accompanied by clear shift of the resonance angle position and by an increase in the width of resonance, i.e. an increase in the full width half maximum (FWHM) of the dip. However, this effect changes dramatically when azimuthal rotation exceeds a critical value, which in our case is $\varphi_c = 45.62^\circ$. The SPR reflectivity spectra in Fig. 4.3 were collected at $\varphi = 52.5^\circ$ with light of different wavelengths ranging from 602-625 nm. It is clearly shown that two minima can be excited using wavelengths up to 610 nm. The two minima approach each other as the excitation wavelength increases, and finally merge into a single broad dip at 612 nm with a full width at half minimum of $\Delta\theta_{\text{FWHM}} = 28^\circ$. Further increment in the wavelength results in shallower reflectivity dips, and the dips finally disappear at wavelengths larger than 625 nm.

Fig. 4.2. Reflectivity spectra collected for different φ angles at $\lambda=650$ nm. Shifting and broadening of resonance angle can be observed with different azimuthal grating rotation ($\varphi = 0^\circ, 18^\circ, 35^\circ, 44^\circ$).

Fig. 4.3. The grating reflectivity of different wavelengths was collected after azimuthal rotation, $\varphi = 52.5^\circ$. This graph shows the possibility to excite two plasmonic resonances with a single wavelength.

The described phenomena are confirmed by the full set of SPR data (λ, θ_r) in Fig. 4.4, where θ_r is the resonance angle and defined as the position of reflectivity minima. We have also reported the FWHM of reflectivity dips, $\Delta\theta_{\text{FWHM}}$, whose amplitude increases with the azimuthal angle. The guiding lines clearly show that by increasing the azimuthal rotation, the slope of wavelength vs. incidence angle decreases. For azimuthal angles greater than a critical value φ_c that in our case has been evaluated 45.62° , a single wavelength can excite two SPPs. Further increase in wavelength will merge the two SPPs into a single broad dip until a maximum wavelength above which SPP excitation is prevented.

Fig. 4.4. The data collected from different azimuthal rotation angles 0° , 18.1° , 35.4° , 43.7° , 49.7° , 52.5° and 55.7° are plotted. The error bar in each point corresponds to $\Delta\theta_{\text{FWHM}}$, the full width half maximum of the resonance reflectivity dips.

4.4 Data Analysis

The mechanism of the surface plasmon polaritons excitation in grating coupled SPR can be understood by considering that the periodic grating changes the wave-vector of the incident radiation by adding an integer multiple of the grating wave-vector, $\vec{g}$. The excitation of SPP on grating is achieved when the momentum conservation condition is satisfied:

$$\vec{k}_{sp} = \vec{k}_{ph} \pm m \vec{g} \quad (4.1)$$

where $\vec{k}_{sp}$ is the diffracted SPP wave-vector and m identifies the diffraction order. The scattering plane (x, z) is normal to the grating plane (x, y) and contains wave-vector of the incident light direction, which forms an angle θ with the surface normal z .

The light wavevector is represented by $\vec{k}_{ph} = \frac{2\pi}{\lambda}(-\sin\theta, 0, \cos\theta)$. In our frame of

reference, the grating momentum, $\vec{g} = \frac{2\pi}{\Lambda}(\cos\varphi, \sin\varphi, 0)$, lies in the (k_x, k_y) plane,

is inversely proportional to the grating pitch Λ , and is oriented perpendicular to the grooves of the gratings whose rotation is measured by the azimuthal angle φ . The

direction of the diffracted SPP wave-vector, $\vec{k}_{sp}$, is in the grating plane and is identified by the angle β (see Fig. 4.5(a) for frame of reference of the reciprocal space).

The SPP wave-vector magnitude is related to its wave frequency by the dispersion relation

$$k_{sp}(\omega) = \frac{\omega}{c} \sqrt{\frac{\epsilon_1 \epsilon_2}{\epsilon_1 + \epsilon_2}} \quad (4.2)$$

where ϵ_1 and ϵ_2 are the dielectric constants respectively of the dielectric and of the metal. In the case of light travelling in vacuum ($\epsilon_1=1$) and incident on a metallic medium with plasma frequency, ω_p and dielectric constant $\epsilon_2 = 1 - \frac{\omega_p^2}{\omega^2}$, the SPP dispersion relation becomes

$$k_{sp}(\omega) = \frac{\omega}{c} \sqrt{\frac{\omega^2 - \omega_p^2}{2\omega^2 - \omega_p^2}}. \quad (4.3)$$

The x-components of $\vec{k}_{sp}$, is given by the relation

$$k_{sp_x} = k_{sp}(\omega) \cos \beta = \pm \sqrt{k_{sp}(\omega)^2 - (mg \sin \varphi)^2} \quad (4.4)$$

where we used the conservation of wave-vector along the y-component, i.e.

$$k_{sp_y} = mg \sin \varphi \quad (4.5)$$

In Fig. 4.5(a) the large circle in k -space represents equi-magnitude $\vec{g}$ vectors at different azimuthal orientation. The dashed line represents the x -component of the incident light wave-vector. The smaller circle represents all possible $\vec{k}_{sp}$ vectors with equal magnitude. This is indeed the case in our experiment because the grating momentum $\vec{g}$ is always greater than the incident light momentum in the wavelength regime that we used for our experiments. A further consequence of our experimental setup is that only the first diffraction order is relevant ($m=1$).

Fig. 4.5(a) The scheme represents wave-vectors combination. The large (smaller) circle represents equi-magnitude $\vec{g}$ ($\vec{k}_{sp}$) vectors. The dotted lines represent a photon wave-vector. The capital letter represent possible position of the crystal wavevector $\vec{g}$. The corresponding letter with sp identifies as the SPP wavevector. (b) Dispersion curve of SPP (Eq. 4.4) in three dimensional (k_x, k_y, E) plot. On the $(k_x, k_y, 0)$ plane is represented configuration identified by point B in (a). The oblique and the vertical line represent the light dispersion curve in the case of surface parallel ($\theta=90^\circ$) and perpendicular ($\theta=0^\circ$) direction. The origin of light dispersion curve is posed at the tip of the circle of radius $\vec{g}$ to take into account the crystal momentum contribution. The horizontal line represents the range of the x-component of the incident light, k_{ph_x} for a selected energy (in the picture arbitrarily chosen at 2eV). The SPP excitation condition is satisfied when the horizontal line crosses the SPP dispersion curve. The intersection point determines the energy and the wave-vector of the SPP whose magnitude is represented by the smaller circle on the $(k_x, k_y, 0)$ plane. (c) Similar construct, representing in this case the SPP excitation identified by point C in (a) The SPP curve has been cut for clarity at $k_y = G \sin(\varphi)$. The horizontal line cuts the SPP curve in to two mark points, determining the condition for double SPP excitation.

Eq. 4.1 allows the transformation of the experimental (λ, θ_r) sets of reflectivity minima into a set of points of an *energy vs. wave-vector* plot. In particular, the experimental values of the x -component of SPPs have been obtained using the following relation

$$k_{sp_x} = g \cos \varphi - \frac{2\pi}{\lambda} \sin \theta_r. \quad (4.6)$$

The experimental data of the SPP excitation grouped for different φ angles have been compared with the relations provided by Eq. 4.4. The experimental data and model dispersion curves have been plotted in Fig. 4.6(a).

For each set of data points a single azimuthal φ angle has been used as a fitting parameter. The value of the pitch of the grating was initially determined from AFM and used as a constant in Eq. 4.4. Afterwards, we keep the φ angles values fixed testing the convergence on the lattice parameter finding a fitting value of $\Lambda = 468 \pm 2$ nm, comparable with the initial AFM determination. The independent fitting of both lattice parameter and azimuthal angle for each set of data converged at the same values previously obtained and the resulting values have been reported both in Fig. 4.4 and in Fig. 4.6(a). The good agreement of the model with the experimental data provides a high confidence level on the overall data analysis method.

The angle defining the $\vec{k}_{sp}$ direction can be determined by,

$$\beta = \tan^{-1} \left[\frac{k_{sp_y}}{k_{sp_x}} \right]. \quad (4.7)$$

The experimental values of the SPPs rotation can be obtained substituting in Eq. 4.7 the Cartesian component of $\vec{k}_{sp}$ provided by Eq. 4.5 and 4.6. Likewise,

substitution of Eqs. 4.4 and 4.5 into Eq. 4.7 yields the modelled analytical dependence. The energy dispersion of experimental data and the modelled relation for the SPP direction of propagation have been reported in Fig. 4.6(b). The φ angles used for the SPP direction are the same ones used for the determination of k_{sp_x} , reinforcing the confidence of the fitting method.

The error bars in Fig. 4.4 represent the FWHM angular width, $\Delta\theta_{FWHM}$, measured from the SPR reflectivity dips. Using Eqs. 4.4 and 4.5, $\Delta\theta_{FWHM}$ has been transformed into the spread of wave-vectors, Δk_{sp} , and of the SPP angle direction, $\Delta\beta$, and have been plotted as error bars respectively in Fig. 4.6(a) and 4.6(b).

It is clear that $\Delta\theta_{FWHM}$ is increasing with azimuthal angle rotation and this behaviour is reflected also in Δk_{sp} and $\Delta\beta$. It is worth noting that the agreement between the model curves and the experimental data is much better than the error bar spread. As a consequence, the SPR reflectivity width is providing meaningful physical information about the number of SPP modes that can be excited. The quantity that measures the number of SPP modes (per unit of illuminated area) that are excited in a specific experimental condition is given by the differential area in the k -space centered on $\vec{k}_{sp\eta}$ that can be computed in polar coordinates as

$$\delta \vec{k}_{sp}^2 = |k_{sp} \delta k_{sp} \delta \beta| \quad (4.8)$$

It is worthwhile to normalize this to the differential area of a circle of radius k_{sp} .

$$\delta(\pi k_{sp}^2) = |2\pi k_{sp} \delta k_{sp}| \quad (4.9)$$

i.e. area covered in the k -space by the circular band of $|\delta k_{sp}|$ width around the circumference of $|k_{sp}|$ radius. The normalized fraction of polariton modes that can be excited together with mode $\vec{k}_{sp}$ is therefore given by the ratio of the Eqs. 4.10 and 4.11.

$$f(\vec{k}_{sp}) = \frac{\delta \vec{k}_{sp}^2}{\delta(\pi k_{sp}^2)} = \frac{|\delta \beta|}{2\pi} \quad (4.10)$$

Eq. 4.10 states that the fraction f of excited SPP modes is proportional to the error bar reported in Fig. 4.6(b). In other words, the spread of SPP azimuthal direction gives an indication of how many modes that can be excited in a specific configuration.

To complete the computation, we substitute Eq. 4.7, in Eq. 4.10 and after differentiating we obtain

$$f = \frac{1}{2\pi} \frac{|k_{sp_x} \delta k_{sp_y} - k_{sp_y} \delta k_{sp_x}|}{k_{sp}^2} \quad (4.11)$$

The terms in Eq. 4.11 are given by:

$$(k_{sp_i} \delta k_{sp_j})^2 = \sum_{\eta} \left(k_{sp_i} \frac{\partial k_{sp_j}(\eta)}{\partial \eta} \delta \eta \right)^2 \quad (4.12)$$

where $i, j = x, y$, whereas η represents the set of independent variables of k_{sp} function.

f and its model analytical energy dependence has been computed substituting respectively Eq. 4.5 and 4.6 in Eq. 4.12. The full set of data for $(\theta_r, \Delta\theta_{FWHM})$ and the experimental values of $\delta\eta$, namely $\delta\lambda = 2.7$ nm, $\delta g/g = 5 \times 10^{-4}$, $\delta\varphi = 0.015^\circ$, have been used for the determination of the experimental values of f and the results for the

different set of azimuthal angles are reported in Fig. 4.6(c). In order to determine the analytical behaviour of f , a similar procedure has been applied to Eq. 4.4, using the same values of $\delta g/g$ and $\delta\varphi$ and the natural spread of the SPP, $|\delta k_{sp}| = 0.0015$ nm. This latter value has been obtained experimentally, using the $\Delta\theta_{FWHM}$ value for $\varphi=0^\circ$, where the SPP spreading is not affected by azimuthal effects. The analytical curves have also been reported for comparison in Fig. 4.6(c). For ease of comparison the dispersion curve of SPP wave-vector, SPP direction and SPP normalized mode density are reported in Fig. 4.6 on a common energy axis.

Fig. 4.6(a) Dispersion curve of the x-component of the SPP wavevector. (b) Dispersion curve of the azimuthal SPP direction. (c) Normalized plasmon mode density where are shown the energy SPP thresholds. Similar colours in all plots represent different azimuthal orientations φ . Error bar in plot (a) and (b) represent wavevector and angular SPP spread respectively. Experimental (points) and model curves (solid lines) are compared.

4.5 Discussion

We use the pictures shown in Fig. 4.5 to explain the double SPPs excitation. The scheme of Fig. 4.5(a) represents the projection on the (k_x, k_y) plane of the dispersion curve of SPP (Eq. 4) that is shown in Fig. 4.5(b) and 4.5(c), where it is represented in a three dimensional plot, (k_x, k_y, E) . Because of the plus and minus conditions

inherent in the wave-vector conservation requirement (Eq. 4.1), all quadrants of the circle can be explored for plasmon resonances as long as the conservation is satisfied. However for symmetry reason only the k_y positive half space is shown.

In Fig. 4.5(b) the large circle in k -space represents equi-magnitude $\vec{g}$ vectors at different azimuthal orientation as well as in Fig. 4.5(a). The origin of k_{ph_x} is positioned at the tip of the circle of radius $\vec{g}$ to take into account the crystal momentum contribution. The oblique and the vertical line represent respectively the light dispersion curve in the case of surface parallel ($\theta = 90^\circ$) and perpendicular ($\theta = 0^\circ$) direction. The horizontal line represents the range of the x-component of the incident light, k_{ph_x} for a selected energy (in the picture arbitrarily chosen at 2eV). This line is scaled linearly in $\sin \theta$ such that the full length of the line at the incident angle θ_{in} of 90° corresponds to the maximum value of k_{ph_x} . The projection of this line on the (k_x, k_y) plane is also reported. In this picture the point B shows the case for $\varphi = 18.7^\circ$ (one of the experimental conditions). A successful SPP excitation corresponds to the condition for which the wave-vector conservation (Eq. 4.1) is satisfied; that is graphically represented by the point of intersection between the horizontal line k_{ph_x} and the 3D plasmon dispersion curve. This intersection also allows identification of the energy and the wave-vector of the SPP as well as the plasmon propagation direction β . For example at point B , the photon wave-vector can intersect the SPP circle only at B_{sp}^+ , thus exciting only a single SPP. This is also true for $\varphi = 0^\circ$ (point A

in Fig. 4.5(a)), for the common non conical configuration, where the grating, photon and SPP wave-vectors are all parallel.

The condition of double SPP excitation is shown in Fig. 4.5(c) for $\varphi=55.7^\circ$ (the largest φ value in the experiment). In this case, starting from point C on the g circle the k_{ph_x} can intersect the SPP dispersion curve twice providing the excitation of two SPPs at two possible conditions: C_{sp}^+ and C_{sp}^- , with the propagation directions of β_{sp}^+ and β_{sp}^- , respectively. It is remarkable that the symmetry properties clearly show that propagation angles satisfy the relationship, $\beta^+ + \beta^- = 180^\circ$.

Within the double SPP range (points C_{sp}^+ and C_{sp}^-), a small increment in φ at the same wavelength or small increment in wavelength at same φ will cause the two $\vec{k}_{sp}$ to merge, corresponding to the situation where two reflectivity dips merge into a single broad dip, as reported in Fig. 4.3. This "*SPP merging*" is described by the condition, $\beta^+ = \beta^- = 90^\circ$, meaning that the resulting SPP propagate along the y direction which is perpendicular to the incident light.

There is another interpretation of the SPP merging that takes into account, instead of the excitation of the SPP, the exciting light condition. The *SPP merging* is equivalently described by the condition:

$$\cos \varphi = \frac{k_{ph_x}}{mg} \quad (4.13)$$

This represents the geometrical condition in which k_{ph_x} is tangential to the SPP dispersion curve (point D in Fig 4.5(a)). In this condition the incident light

wavevector can explore tangentially the natural width of the SPP circle δk_{sp} and therefore intersect a larger area. This explains the larger azimuthal spreading and number of excited SPP modes.

The smallest critical angle, φ_c for which SPP merging can be achieved is given by Eq. 4.13 using the largest value of k_{ph_x} , i.e. when incident light is ideally parallel to the grating surface at $\theta=90^\circ$. That depends on the magnitude of crystal vector; in our case the value of $\varphi_c=45.62^\circ$, as previously reported. Further increasing of the φ rotation or shrinking of k_{sp} circle, makes the y-component of the $\vec{g}$ vector larger than the SPP wave-vector, $mg \sin \varphi > k_{sp_y}$, and thus no intersection can occur (point E). This corresponds to a condition where plasmon excitation is not possible.

The x -component of the SPP curves for different azimuthal rotation angles is showed in Fig. 4.6(a). The curves represent sections of the 3D SPP dispersion curve obtained at different values of $k_y = g \cos \varphi$, as shown in example in Fig. 4.5(b) and 4.5(c). The higher the φ angle, the higher and smoother the SPP dispersion curve appears. For $\varphi > \varphi_c$ it is possible to achieve the SPP merging at the minimum of the SPP dispersion curve. This fact is better shown in Fig. 4.6(b), reporting the dispersion curve of the SPP azimuthal angle where the energy minima occurs at $\beta=90^\circ$. For each φ value the corresponding SPP direction varies over a large range of β angle. In particular, for the largest azimuthal rotation used in our experiment ($\varphi = 55.7^\circ$) we measured SPP azimuthal rotation well over 90° reaching a value up to $\beta=105^\circ$.

The error bar reported in Fig. 4.6(a) shows that the SPP mode spread increases when the φ angle is increased. This effect has a simple physical explanation that is based on Eq. 4.10 and by the interpretation of the corresponding error bar in Fig. 4.5(b). The number of SPP modes excited is proportional to their azimuthal direction distribution. In Fig. 4.6(c) we have reported as a function of energy both the experimental (points) and analytical (lines) values of the normalized SPP mode density, f , clearly showing a reasonable agreement. The analytical description shows a singularity corresponding to the minimum energy for double SPP excitation, where the agreement with experiment is expectedly less.

As is well known, a higher number of modes is expected for a flat energy band. The number of SPP modes is proportional to the inverse of the band curvature at the dispersion curve energy minima. Experimentally, this is clearly shown as error bars becoming larger for flatter energy dispersion curves, with a correspondingly increasing number of modes. For fixed φ value, the larger value of the error bar has been determined in correspondence of the energy minimum, namely in correspondence of the SPP merging condition. The largest error bar is achieved at SPP minimum of the largest φ value. These results clearly show that the possibility to excite several SPPs over a broad incidence angle is accompanied by a mode density condensation in correspondence of the energy threshold.

4.6 Chapter Summary

In summary, we have studied the kinematics of SPP propagation as a function of the azimuthal rotation, φ , of the metallic grating. Azimuthal rotation of grating also affects the dispersion curves of the SPP wave-vector in a way which is fundamentally different from that of classical prism coupling. The grating azimuthal rotation induces rotations of the SPP propagation direction that can cover the full 2π range. In particular conditions of incident wavelength and grating azimuthal orientation, distinct double SPPs can be excited and even multiple SPPs can propagate. The wave-vector dispersion is characterized by an energy threshold for the SPP excitation that increases as φ increases. For azimuthal rotation larger than a critical value, the SPP energy threshold corresponds to the excitation of SPPs directed perpendicularly to the incident light. Moreover, they correspond to a divergence of the wave-vector derivative and therefore to a maximum of the SPP density of states. We have shown that the possibility to excite several SPPs over a broad azimuthal angle is accompanied by a mode density condensation in correspondence of the energy threshold. We believe that this optimized coupling condition can be used as amplification leverage for enhancing sensitivity in GCSPR systems.

CHAPTER 5. SENSITIVITY ENHANCEMENT IN GRATING COUPLED SURFACE PLASMON RESONANCE BY AZIMUTHAL CONTROL

5.1 Introduction

As mentioned in chapter 2, Grating Coupled Surface Plasmon Resonance (GCSPR) sensors with either wavelength or angular interrogation have been demonstrated to have sensitivity 2-3 times lower than PCSPR. This is mainly because no study has been focused on GCSPR sensor based on the azimuthally rotatable grating substrate.

The work so far has demonstrated that the SPP propagation direction can be controlled by rotating the grating azimuthally and double SPP excitation by a single wavelength is possible when the grating azimuthal rotation is larger than a specific angle. The number of excited SPP modes in GCSPR is related to the azimuthal angle of the grating - the higher the azimuthal angle, the larger is the number of excited SPP modes, because of the bend curvature at the plasmon dispersion curve. Under this condition, a small change in refractive index should induce a much larger change in reflectivity, resulting in a higher sensitivity than that for the non-rotated case. In this chapter, the author shows that a self-assembled monolayer of dodecanethiol (C12-SAM) molecules, which is only 1.5 nm in optical thickness can be easily detected with an angular shift as large as 2.2° and an estimated sensitivity larger than $900^\circ/\text{RIU}$ is possible. The experimental data are accompanied by a model description that explains the principle of sensitivity enhancement.

5.2 Experimental

The grating used in this study is fabricated using method described in chapter 3 and its optical characterization technique is that same as that mentioned in chapter 4. In this study, two azimuthal angles were studied, 0° and 60° .

C12-SAM [dodecanethiol ($\text{CH}_3(\text{CH}_2)_{11}\text{SH}$, DDT)] was deposited on the gold coated grating surface at room temperature in a N_2 -purged glove box for 24hrs. The spontaneous assembly of the molecules is known to form a densely packed and highly oriented structure on the exposed gold surfaces. SAM is chosen because of the ease of preparation and better understanding of the molecules. In addition, they have good coverage even in high aspect ratio features due to their hydrophilic head-group which adheres well to the gold surface.

The measurements are collected before and after C12-SAM coating on Au grating in air environment. The sample is sitting on the center of rotation of the rotator, thus the location for data collection before and after coating with C12-SAM is not changed with azimuthal rotation.

Winspall simulation tool has been used to simulate the result from PCSPR between uncoated and C12-SAM coated Au film.

5.3 Results

In the Winspall simulation on PCSPR as shown in Fig. 5.1(a), the resonance angle difference between uncoated and C12 coated Au film is only 0.9° . The experimental evidence of the azimuthal rotation effect in enhancing the SPR sensitivity is shown in Fig. 5.1(c) where reflectivity spectra have been collected at different wavelengths. As

a reference, we first report the reflectivity spectra using GCSPR at conventional $\varphi = 0^\circ$ as shown in Fig. 5.1(b). In this configuration the difference in the reflectivity SPP minima before and after C12 functionalization, $\Delta\theta$, is typically less than 0.05° . On the contrary, when the grating is azimuthally rotated to an angle of about 60° ($\varphi = 61.58^\circ$ in our case), large angular differences, $\Delta\theta$, can be observed between reflectivity dips (Fig. 5.1(c)). The $\Delta\theta$ differences are of the order of 1.2° but can reach values up to 2.2° as for the case of $\lambda = 618$ nm. The occurrence of double SPP reflectivity dips for a single incident wavelength is due to double matching in the momentum conservation condition. By increasing the wavelength from 602 nm to 620 nm, the two resonance dips in the reflectivity spectra come closer together until they merge together into one broad dip at 622 nm. Further increase of wavelength reduces the resonance strength until SPR completely vanishes. The summary of the $\Delta\theta$ for both simulated PCSPR and experimental GCSPR is given in Table 1.

Fig. 5.1. Comparison of SPR spectrum between uncoated (solid line) and C12-coated (dashed line) Au grating. (a) Winspall simulation on prism coupler SPR, (b) Grating with $\phi = 0^\circ$ (conventional mounted grating), where different line colours correspond to different incident wavelengths; and (c) $\phi = 60^\circ$ (double SPPs by single wavelength excitation condition), different colours of line represent difference incident wavelength.

Table 5.1. Comparing the shift in resonance angle between uncoated & C12-coated in PCSPR, conventional GCSPR and double SPPs GCSPR.

SPR Approaches	PCSPR	GCSPR (conventional)	GCSPR (Double SPPs)			
Shift of Resonance Angle ($\theta_{PCSPR}/\theta_{GCSPR}$)	$\lambda = 632.8$ nm	700 nm		610nm	614nm	618nm
	0.9°	~0°	1 st dip	1.17°	1.7°	2.15°
			2 nd dip	1.27°	1.72°	2.2°

5.4 Analysis & Discussion

The analysis of the wave-vector components allows a description of double SPP excitation using the schematic shown in Fig. 5.2. The excitation of SPPs on a grating is achieved when the on-plane component of the incident light wave-vector and the diffracted SPP wave-vector $\vec{k}_{sp}$ match the momentum conservation condition:

$$\vec{k}_{sp} = \vec{k}_{ph_{\parallel}} \pm m\vec{g} \quad (5.1)$$

where $\vec{k}_{ph\parallel} = \frac{2\pi}{\lambda}(-\sin\theta_{in}, 0)$, θ_{in} is the angle of incidence, the crystal momentum is

$\vec{g} = \frac{2\pi}{\Lambda}(\cos\varphi, \sin\varphi)$ whose rotation is measured by φ , and Λ is the grating pitch. Only

the first diffraction order ($m=1$) is used because in our case, $\vec{g}$ is always greater than $k_{ph\parallel}$. All quadrants of the circle can be explored for SPP excitation as long as Eq.

5.1 is satisfied. For symmetry reason, only k_y positive half space is shown.

Fig. 5.2. Schematic represents wave-vector combination. The large circle represents equi-magnitude $\vec{g}$ vectors. The smaller black and green circles represent equi-magnitude vectors before, ($\vec{k}_{spp1}$), and after ($\vec{k}_{spp2}$) the surface functionalization with C12 SAM. The dashed lines represent a photon wave-vector and the dotted lines represent the SPP propagation direction, β . The letters A and B represent the $\vec{g}$ vector with azimuthal rotation $\varphi = 0^\circ$ and $\varphi = 60^\circ$ respectively. The capital letters with the primes represent the intersection of the photon wave-vector with the SPP semicircles.

The largest circle in k -space represents equi-magnitude $\vec{g}$ vectors at different azimuthal orientation. The two smaller circles represent all possible $\vec{k}_{sp}$ vectors with

equal magnitude respectively before and after C12 surface functionalization and whose modulus is given by

$$k_{SPP} = k_{ph} \sqrt{\frac{\epsilon_M \epsilon_D}{\epsilon_M + \epsilon_D}} = k_{ph} M \quad (5.2)$$

where ϵ_M and ϵ_D are the dielectric constants of the metal and the dielectric medium respectively. After the coating, the SPP modulus increases because of the small increase in ϵ_D due to the surface SAM functionalization with C12.

The dashed line at the tip of the circle of radius $\vec{g}$ represents the x component of the photon wave-vector $k_{ph_{\parallel}}$, the only component that participates in SPP excitation. The line is scaled linearly in $\sin \theta_{in}$ such that the full length of the line at the incident angle θ_{in} of 90° corresponds to the maximum value of $k_{ph_{\parallel}}$.

The intersections of the $k_{ph_{\parallel}}$ dashed horizontal line with the smaller k_{spp} circle determine the conditions for which Eq. 5.1 is satisfied and allows identification of both incident angle θ_{in} for SPP resonance excitation and SPP propagation direction, β . We consider first the case of the uncoated sample - the smallest of the semicircles. For example, point B on the $\vec{g}$ circle is identified by the azimuthal angle φ which allows the excitation of SPP at two possible conditions: B_1' and B_1'' , with β^+ and β^- , respectively. Within the double SPP range (point B), a small increment in wavelength makes the points B_1' and B_1'' merge, to form a very broad resonance as shown by wavelength dependence of the reflectivity spectra (Fig. 5.1(b)). On the contrary, at $\varphi = 0^\circ$ (point A) it is clear that the photon wave-vector can intersect the SPP circle only in

the first quadrant but not the second, thus exciting only a single SPP for each wavelength (Fig. 5.1).

The same understanding is applicable for light exciting SPP on the C12 coated sample. Due to larger k_{spp} , different excitation condition is expected. The intersection points change from B_1' and B_1'' to B_2' and B_2'' and from A_1 to A_2 . The sensitivity of the GCSPP is higher at high azimuthal angles because the condition for double SPP excitation around the circumference of the k_{spp} circle generates a shifts in k-space between points B_1' and B_2' , which is much larger than that between points A_1 and A_2 provided by a single SPP excitation condition for $\varphi = 0^\circ$.

The estimated refractive index sensitivity, S , of this configuration can be defined as:

$$S = \frac{\partial \theta}{\partial n} = \frac{\partial \theta}{\partial k_{ph_x}} \frac{\partial k_{ph_x}}{\partial k_{SPP}} \frac{\partial k_{SPP}}{\partial n} \quad (5.3)$$

In order to calculate S , we assume the rippling amplitude, δ , of the grating is so shallow ($\delta/\Lambda = 0.05$ in our case) that the dispersion curve of SPP travelling at the metal-dielectric interface of a grating can be approximated by the case of a flat sample as described by Eq. 5.2. The terms at the right hand side of the equation can be derived as the following:

$$\text{First term, since } k_{ph_x} = \frac{2\pi}{\lambda} \sin \theta = \frac{\omega}{c} \sin \theta \quad (5.4)$$

$$\text{Hence, } \frac{\partial \theta}{\partial k_{ph_x}} = \frac{c}{\omega} \frac{1}{\cos \theta} \quad (5.5)$$

Second term, with Fig. 5.2 as a reference, we know that,

$$\begin{aligned} k_{SPP} \sin \beta &= G \sin \varphi \\ k_{SPP} \cos \beta &= G \cos \varphi - k_{ph_x} \quad \text{and} \end{aligned} \quad (5.6)$$

$$k_{SPP} = \frac{G \sin \varphi}{\sin \beta} \quad (5.7)$$

By dividing the first and second equation in Eq. 5.6, we get

$$\tan \beta = \frac{G \sin \varphi}{G \cos \varphi - k_{ph_x}} \quad (5.8)$$

Substituting Eq 5.8 into Eq. 5.7, we get,

$$k_{SPP} = \frac{G \sin \varphi}{\sin(\tan^{-1} \frac{G \sin \varphi}{G \cos \varphi - k_{ph_x}})} \quad (5.9)$$

Hence,

$$\frac{\partial k_{SPP}}{\partial k_{ph_x}} = - \frac{\frac{\cos \varphi}{\Lambda} - \frac{\sin \theta}{\lambda}}{\sqrt{\frac{1}{\Lambda^2} + \frac{\sin^2 \theta}{\lambda^2} - \frac{2 \cos \varphi \sin \theta}{\Lambda \lambda}}} \quad (5.10)$$

Third term, the SPP wave-vector magnitude is related to its wave frequency by the dispersion relation described in Eq. 4.2. In the case of light travelling in a dielectric medium ($\epsilon_1 = n^2$) and incident on a metallic medium with plasma frequency,

ω_p and dielectric constant $\epsilon_2 = 1 - \frac{\omega_p^2}{\omega^2}$, the SPP dispersion relation becomes

$$k_{SPP} = n \frac{\omega}{c} \sqrt{\frac{\omega^2 - \omega_p^2}{(1 + n^2)\omega^2 - \omega_p^2}} \quad (5.11)$$

thus we get:

$$\left. \frac{\partial k_{SPP}}{\partial n} \right|_{n=n_0} = \left(\frac{c}{\omega} \right)^2 \left(\frac{k_{SPP,0}}{n_0} \right)^3 \quad (5.12)$$

where n_0 is the original refractive index.

Finally, the analytical expression for the sensitivity in angular interrogation can be found as:

$$S = -\frac{1}{\cos \theta_r} \left(\frac{M}{n_0} \right)^3 \frac{\sqrt{\frac{1}{\Lambda^2} + \frac{\sin^2 \theta}{\lambda^2} - \frac{2 \cos \varphi \sin \theta}{\Lambda \lambda}}}{\frac{\cos \varphi}{\Lambda} - \frac{\sin \theta}{\lambda}} \quad (5.13)$$

where M is defined in Eq. 5.2, n_0 is the refractive index of the surrounding dielectric medium, λ is the incident wavelength and θ_r is the resonance angle that is equal to

$$\theta_r = \sin^{-1} \left(\frac{\lambda}{\Lambda} \cos \varphi \mp \sqrt{M^2 - \left(\frac{\lambda}{\Lambda} \right)^2 \sin^2 \varphi} \right) \quad (5.14)$$

The functional behaviour of sensitivity for the first and second SPP dip is shown in Fig. 5.3 for a typical wavelength of $\lambda_{in} = 606$ nm. Both the sensitivities diverge when φ approaches its critical value φ_{MAX} , i.e. the maximum φ angle that supports SPP resonances. In this configuration, incident photon momentum is tangential to the k_{spp} circle and its length equals to the k_x -component of the grating momentum so that the denominator of the third term in Eq. 5.13 becomes null. Another condition for second dip sensitivity singularity is when the φ approaches critical azimuthal angle, φ_c , necessary to excite double SPP resonances, namely when the full length of the incident photon momentum is required to intersect the edge of the k_{spp} circle. Since the incident angle $\theta_{in} = 90^\circ$, $\cos \theta$ in the denominator of the first term Eq. 5.13 approaches 0 and S diverges.

Fig. 5.3. Sensitivity, S as a function of grating azimuthal angle, φ for the two dips for the SPR sensor with angular interrogation. The right y-scale refers to sensitivity values normalized to the first dip sensitivity at $\varphi = 0^\circ$ ($S_r = S/S_I(0)$). In the subset figure, more detail is shown. Blue colour is first dip and red colour is second dip.

Although φ close to the critical values provides a great enhancement in S (up to $2400^\circ/\text{RIU}$, 35 times higher than $\varphi = 0^\circ$), these configurations should be avoided because of experimental limits. For $\varphi \cong \varphi_c$, θ_r becomes large ($\theta > 70^\circ$) and broad, becoming impossible to resolve the SPP minimum. In addition, when $\varphi \cong \varphi_{MAX}$, the two resonance dips merge into a single broad dip which makes the two minima indistinguishable. Thus only limited parts of the azimuthal angular range are suitable for enhancing sensitivity significantly. The best conditions correspond to the middle of the “U-shape” of second dip functional behaviour (inset of Fig. 5.3) where the sensitivity ranges from 900 to $1100^\circ/\text{RIU}$, about 15 times higher than $\varphi = 0^\circ$ whose value is $67^\circ/\text{RIU}$. The sensitivity computed for the first SPP dip is smaller all over this range but it still provides values of the order of $500^\circ/\text{RIU}$.

The experimental determinations of the wavevector k_{ph} of the incoming light necessary for the SPP excitation have been successfully fitted with the help of Eq. 5.1, using as fitting parameters only the effective index of refraction and azimuthal angle. After surface functionalization we have determined a total increment in index of refraction equal to $\Delta n = 0.00357 \pm 0.00007$ RIU. This is a value that agrees with the estimation of $\Delta n = 0.0038$ RIU performed for effective refractive index change generated by a full surface coverage of close-packed self assembled C12 molecules, considering their length = 1.488 nm and dielectric constant $\epsilon_{C12} = 2.205$. Also the theoretical sensitivity determination is in good agreement with the experimental determination obtained as a ratio between $\Delta\theta$, the angular differences before and after C12 coating and the Δn determination as shown in Fig. 5.4. The average experimental sensitivity is of the order of $520^\circ/\text{RIU}$ for the first dip and reaches maximum values of $857^\circ/\text{RIU}$ for the second dip.

Fig. 5.4. Energy dispersion curve for the k_{ph} necessary for SPP excitation before (solid line) and after (dashed line) C12 SAM functionalization. The experimental data obtained by the reflectivity minima of Fig. 5.1 have been fitted using Eq. 5.1.

The final error of the refractive index determination has been estimated on the basis of chi-square minimization based on *a priori* determination of the SPP angular position. The reflectivity minima of this preliminary data set have been determined with a typical uncertainty of $\pm 0.07^\circ$ deg. However the *a posteriori* determination of the SPP angular average deviation with respect to the dispersion curve best fit is much smaller, on the order of 0.015° , as can be confirmed by a simple graphical inspection. Taking into account this more realistic value for the final evaluation of the uncertainty, the value of $\delta\Delta n$ is 7×10^{-5} RIU. However, because our experimental system has an instrumental resolution of 0.005° , we believe it will be possible to greatly decrease the present angular uncertainty by increasing the statistical signal-to-noise ratio (advanced detector) and using appropriate algorithms for data analysis (centroid method).

Although the simulated sensitivity of this configuration is ranging from $900^\circ/\text{RIU}$ – $1100^\circ/\text{RIU}$, it only can be achieved when the excited SPPs are fully coupled. As shown in Fig. 5.1(c), the reflectivity of the spectra becomes shallower and the FWHM of the dips becomes wider as compared with the non-rotated case Fig. 5.1(b). These actually decrease the sensitivity of the configuration. In order to reach the simulated value, fully coupled SPPs must be excited, i.e. the reflectivity spectra are the deepest and the FWHM of the dip is the narrowest. The approach to achieve these is discussed in detail in the next chapter.

5.5 Chapter Summary

In summary, we have shown that an enhancement in sensitivity can be obtained in GCSPR when double SPPs are excited after azimuthal rotation of the grating. The difference between uncoated and C12 SAMs coated metallic gratings is easily detectable in the vicinity of the double SPP condition. The shift in resonance angle detected is as large as 2.2° which is one order of magnitude higher than conventional prism-based SPR. In addition, the calculated sensitivity of this method is greater than $800^\circ/\text{RIU}$, one order of magnitude higher than conventional mounted grating ($\varphi = 0^\circ$).

CHAPTER 6. THE ROLE OF POLARIZATION ON SURFACE PLASMON POLARITON EXCITATION ON METALLIC GRATINGS IN THE CONICAL MOUNTING

6.1 Introduction

To excite the fully coupled double SPPs in the azimuthally rotated grating, the polarization angle of the incident light must be optimized. This is mainly because, in a classical mounting, a diffraction grating is illuminated with light propagating along a direction perpendicular to the grooves. In this mounting, the plasmon direction is aligned to the component of the incident light parallel to the surface. The p - (Transverse Magnetic, TM) and s - (Transverse Electric, TE) polarized incident fields conserve its polarization upon diffraction from the grating. It should be noted that in this configuration, it is normally only possible to excite plasmon with p -polarized (TM) light. However, plasmon excitation can also occur when symmetry is broken in the so called conical geometry, that is, when the grating is azimuthally rotated with respect to the scattering plane. This configuration has been investigated for the first time by *G. P. Bryan-Brown*⁴⁷, who observed that SPP excitation also induces a p to s polarization conversion^{48,49,180,184,186}. This striking result generated a list of other experimental papers enlarging the importance of the p - s conversion and deepening the effect of higher diffraction order or SPP excitation with s -polarized light.

Theoretical studies based on rigorous computational approach focused on the computation of the p - s conversion ratio^{181,182,188}, i.e. the fraction of the incident p -polarized radiation that has been converted to s -polarized radiation. Their results mediated by the complex computational algorithms confirmed the experimental data showing the effects of symmetry. Recently, *A. V. Kats* has demonstrated an analytical

theory of resonance diffraction in the conical mount^{183,189}. He concluded that the dependence of polarization, intensity, and phase of specular and resonance waves can be presented in explicit form and examined for arbitrary polarization of the incident wave as a function of the angle of incidence and the grating period, orientation and depth. However, to our knowledge it is still lacking a study that investigates the polarization angle that optimizes the excited SPPs on the azimuthally rotated grating, i.e. further enhancing the excited SPR strength on azimuthally rotated grating only by changing the polarization angle without changing the resonance condition.

In this chapter, we have experimentally investigated the polarization angle that optimizes SPP excitation in conical mount. By rotating the grating azimuthally and using only *p*-polarized incident light, the SPP coupling becomes less efficient (shallower dip in the reflectivity spectra) and a change of polarization angle is needed in order to recover the best SPP coupling (deeper dip). We report an analytical model based on a kinematical description of the SPP grating-coupling that provides a simple and precise description of the geometrical configuration for the optimized excitation. The analytical formula avoids complex numerical computation and will be useful for designing an experiment for sensing purposes.

6.2 Experimental

In this chapter, one more parameter, which is the polarization angle of the incident light, α , is input in the SPP excitation as shown in Fig. 6.1. Same grating was used and the measurements were collected at $\varphi = 0^\circ, 4.85^\circ, 20.3^\circ, 35.4^\circ, 47.8^\circ, 53.5^\circ$ for different incident wavelengths λ_{in} and polarization angles α from -90° to 90° ($\alpha = 0^\circ$

correspond to p -polarization). For every resonance condition at different φ , λ_{in} , θ_r , the corresponding optimal polarization α_{min} was obtained.

Fig. 6.1. Schematic of the configuration used in this study with including the polarization angle, α .

6.3 Results & Discussion

When light direction is perpendicular to the grating grooves, i.e. the scattering plane is parallel to the grating symmetry plane, reflectivity does not depend on polarization and only p -polarization is effective for SPP excitation. For a general azimuthal angle, not only p -polarized light but also s -polarized light can contribute to SPP excitation. The evidence of this effect is reported in Fig. 6.2, that shows a reflectivity spectrum scanned around θ_r with different α angles at fixed $\varphi = 41.2^\circ$ and $\lambda_{in} = 700$ nm. Reflectivity minimum strictly depends on the incident polarization, while θ_r is fixed. The lowest reflectivity has been observed at $\alpha_{min} = -35^\circ$. It is worthwhile to note that at

$\alpha = 55^\circ$, which is exactly 90° away from α_{min} , SPP excitation is completely suppressed

Fig. 6.2. Reflectivity spectrum shows SPP excitation in $\varphi = 41.2^\circ$ with $\lambda_{in} = 700$ nm and scanned α from -50° to 55° .

Fig. 6.3. Experimental reflectivity minima due to SPP excitation at fixed $\varphi = 41.2^\circ$ reported as a function of the polarization angle for different wavelengths. Data are fitted using Eq. 6.1.

The polarization dependence of reflectivity minima can be seen in Fig. 6.3, which clearly shows a sinusoidal dependence that is well fitted by the harmonic function:

$$R = f_1 - f_2 \cos(m \cdot \alpha + \gamma) \quad (6.1)$$

where f_1 , f_2 , m and γ are fitting parameters that depend on the incidence angles, wavelength and optical properties of the metallic grating. Typical values for f_1 and f_2 values collected for different wavelengths are, respectively, 0.61 and 0.34, whose sum (0.95) and difference (0.27) determine the maximum (SPP fully off) and the minimum (SPP fully on) of the reflectivity respectively. From data analysis of all the samples at different wavelengths we find the m has a mean value of $2.003 \pm 0.008 \text{ rad}^{-1}$, indicating the polarization oscillation has a π periodicity in accordance with the experimental results that SPP excitation can be suppressed at $\alpha_{min} \pm 90^\circ$.

The last fitting parameter is related to the phase γ of Eq. 6.1 and the determination of α_{min} . The functional dependence of γ on geometrical and physical factors can be obtained considering that, for a general incidence, only the electric field component that lies on the grating plane is effective for SPP. On the basis of previous assumptions, reflectivity at resonance is proportional to the incident intensity on the grating plane:

$$R \propto |\hat{e} \cdot (\hat{g} \times \hat{n})|^2 \quad (6.2)$$

where $\hat{e}$ and $\hat{g}$ are, respectively, the direction of the electrical field and of the crystal momentum, and $\hat{z}$ is the normal to the grating plane. If we assume an

orthogonal coordinate system xyz wherein the z -axis is one of the components and the scattering plane is parallel to the xz -plane, we can write the vector directions as

$$\hat{e} = (\cos\alpha \cos\theta, \sin\alpha, \cos\alpha \sin\theta) \quad (6.3)$$

$$\hat{g} = (\cos\varphi, \sin\varphi, 0)$$

$$\hat{k}_{spp} = (\cos\beta, \sin\beta, 0)$$

where $\hat{k}_{spp}$ is the SPP momentum direction and β is the angle formed by the SPP momentum direction with x -axis. Substituting expressions (6.3) into (6.2) and rearranging the terms, we have:

$$\begin{aligned} R &\propto |\hat{e} \cdot (\hat{g} \times \hat{n})|^2 = |\cos\alpha \cos\theta \sin\varphi - \sin\alpha \cos\varphi|^2 \\ &\propto \frac{\cos^2\theta \sin^2\varphi + \cos^2\varphi}{2} - \frac{\cos^2\theta \sin^2\varphi + \cos^2\varphi}{2} \cos(2\alpha + \alpha_0) \end{aligned} \quad (6.4)$$

which reproduces the harmonic dependence on polarization given by the fitting formula Eq. 6.1. By comparing the two expressions, we found $m=2$ which is consistent with the experimental estimation. The phase term γ of Eq. 6.1 is given by

$$\alpha_0 = \arcsin\left(-\frac{\cos\theta \sin 2\varphi}{\cos^2\theta \sin^2\varphi + \cos^2\varphi}\right) \quad (6.5)$$

In Eq. 6.4 the minimum of reflectivity takes place when the $\cos(2\alpha + \alpha_0)$ is equal to 1. Thus we find the relation $\alpha_{min} = -\alpha_0/2$ between the phase α_0 and the polarization angle α_{min} which optimizes the strength of the SPP coupling. The explicit expression for α_{min} can be obtained by calculating the polarization angle that minimizes the expression for reflectivity in Eq. 6.4:

$$\tan \alpha_{\min} = \cos \theta \tan \varphi \quad (6.6)$$

Eq. 6.6 gives the incident polarization value which optimizes the coupling with surface modes for a given incidence angle setup. For a fixed incident wavelength λ_{in} , at the azimuth angle φ , the resonance angle θ_r is given by:

$$\theta_r = \arcsin \left(\frac{\lambda_{in}}{\Lambda} \cos \varphi \mp \sqrt{S^2 - \left(\frac{\lambda_{in}}{\Lambda} \right)^2 \sin^2 \varphi} \right) \quad (6.7)$$

where Λ is the grating pitch and $S = \sqrt{\frac{\epsilon_M \epsilon_D}{\epsilon_M + \epsilon_D}}$. ϵ_D and ϵ_M are the dielectric functions of

the dielectric medium (air) and of the metallic layer on the substrate respectively.

Fig. 6.4 $\alpha_{\min}$ values from fitting experimental data (points) with Eq. 6.6 (lines) for different φ as a function of incident wavelength.

Experimental and theoretical data for the optimal polarization $\alpha_{\min}$ as a function of the incident wavelength for different azimuth angles are shown in Fig. 6.4. Experimental points are well reproduced by the analytical curves of the described

model. The sign of the polarization in our convention is contrary to the azimuthal angle rotation, but symmetry allows the inversion of both the sign of the φ and $\alpha_{\min}$. At fixed wavelength, $\alpha_{\min}$ increases with increasing azimuthal angle. It is worth noting that for azimuthal angles larger than a critical value, two SPPs can be excited at the same wavelength. In this configuration $\alpha_{\min}$ values greater than $\pm 55^\circ$ can be reached.

6.4 Chapter Summary

We explore polarization effects on the surface plasmon resonance (SPR) in the azimuthally rotated grating (conical mounting). By changing the polarization angle (α) of the incident light from p -polarized (TM) to other α angles, the strength of the excited SPR can be manipulated and the strength can be fully enhanced when $\alpha_{\min}$ is used. Experimental results and simulations show that only the incident electric field lying on the grating symmetry plane is effective to SPR excitation, while the orthogonal one is irrelevant. The optimal polarization angle $\alpha_{\min}$ can be obtained by rotating the polarization angle until the deepest dip in reflectivity spectrum can be observed: this angle can be determined analytically by using the assumption mentioned above.

CHAPTER 7. POLARIZATION OPTIMIZATION FOR A FULL SENSITIVITY IN AZIMUTHAL GRATING COUPLED SURFACE PLASMON RESONANCE

7.1 Introduction

In chapter 4, the author has demonstrated that the SPP propagation direction can be controlled by rotating the grating azimuthally and double SPP excitation by a single wavelength is possible when the grating azimuthal rotation is larger than a specific angle. Under this condition, a change in refractive index induces a large change in reflectivity, resulting in a higher sensitivity (more than 15 times) than that for the non-rotated case which has been discussed in chapter 5. However, using only *p*-polarized incident light, the sensitivity of this configuration is limited because the SPP strength is not fully realized, seen as a shallower dip in the reflectivity spectrum. The approach to fully couple the SPP is demonstrated and the analytical model to determine the optimized polarization angle is developed in chapter 6. Thus, optimally polarized incident light should be able to fully excite the SPP and hence the full sensitivity of this configuration is realizable. In this chapter, we demonstrate again the sensitivity that a self-assembled monolayer of dodecanethiol (C12-SAM) molecules, which is only 1.5 nm in optical thickness, can be easily detected with an angular shift as large as 3.6° and hence the resolution up to 5×10^{-7} RIU is possible.

7.2 Experimental

The grating used in this chapter is same as chapter 5. The optical characterization of the grating before and after C12-functionalization is collected only at $\varphi = 60^\circ$, where double SPPs can be excited. Under conditions which yield the broadest dip in the reflectivity spectrum (in our case, it appears at 622 nm) the polarization angle (α) is scanned from p-polarized to -60° with a step size of 0.5° . The optimized polarization angle ($\alpha_{min} = -50^\circ$ and -51° for before and after C12-functionalization) can be determined when the deepest dip is observed in the reflectivity spectrum as shown in Fig. 7.1.

Fig. 7.1. Reflectivity spectrum collected at $\varphi = 60^\circ$ and scanned the incident polarization angle from -50° to -51° for both uncoated and C12-coated grating to determine the α_{min} .

7.3 Results

The experimental evidence of the polarization angle effect in enhancing the SPR sensitivity is shown in Fig. 7.2 where reflectivity spectra have been collected at different wavelengths on azimuthally rotated grating where double SPPs can be excited using single wavelength. By increasing the wavelength from 602 nm to 620 nm, the two resonance dips in the reflectivity spectra come closer together until they merge together into one broad dip at 622 nm. Further increase of wavelength reduces the resonance strength until SPR completely vanishes. As a reference, we first report the reflectivity spectra collected at *p*-polarized light ($\alpha = 0^\circ$) as shown in Fig. 7.2(a). In this configuration, although the difference in the reflectivity SPP minima before and after C12 functionalization, $\Delta\theta$, is detectable, the amount of $\Delta\theta$ is not as clear as the spectra collected using the optimized polarization angle, especially for the incident wavelength of 620 nm. On the contrary, when the polarization angle of the incident light is changed to an optimized polarization angle ($\alpha_{min} = -50^\circ$ and -51° for before and after C12-functionalization respectively), the spectra is sharper with smaller FWHM and the position of the resonance angle is obvious. One should note that a clear $\Delta\theta$ of 3.6° at 620 nm is detectable only when the optimized polarization angle is used. It is very important for this configuration to detect the shift just before the 2 dips start to combine with each other into one broad dip, because this is where the largest $\Delta\theta$ can be found.

Fig. 7.2. Comparison of SPR spectrum between uncoated (solid line) and C12-coated (dashed line) Au grating. The spectrum is collected on the grating with azimuthal angle ($\phi = 61.38^\circ$) where 2 SPPs can be excited using single wavelength using (a) $\alpha = 0^\circ$ (p -polarized), and (b) $\alpha_{min} = -50^\circ$ and -51° for before and after C12-functionalization (optimized polarization angle in our case). Different colour lines represent different incident wavelength.

The shift in resonance angle $\Delta\theta$ at different wavelength for both p -polarized and optimized polarization angle is summarized in Fig. 7.3. As shown, $\Delta\theta$ is increased as the polarization angle of the incident light is changed from p -polarized to optimized polarization angle. In addition, the shift is also increased as the incident wavelength increase and the largest appears at 620 nm.

Fig. 7.3. Shift in resonance angle in 1st and 2nd dip in either p -polarized (black) or optimized polarization angle (red) as a function of incident wavelength.

Fig. 7.4 shows that the shift of resonance angle between region 1 and region 2 which are different locations in the C12-coated grating is almost 0° . Hence, the observed shift between uncoated and C12-coated is not random.

Fig. 7.4. The collected SPR spectra from different region of C12-coated grating at $\varphi = 60^\circ$.

7.4 Analysis and Discussion

The analysis of the wave-vector components allows a description of double SPP excitation using the schematic shown in Fig. 7.5. The excitation of SPP on a grating is achieved when the on-plane component of the incident light wave-vector and the diffracted SPP wave-vector $\vec{k}_{sp}$ satisfy the momentum conservation condition:

$$\vec{k}_{sp} = \vec{k}_{ph \parallel} \pm m \vec{g} \quad (7.1)$$

where $\vec{k}_{ph_{\parallel}} = \frac{2\pi}{\lambda}(-\sin \theta_{in}, 0)$, θ_{in} is the angle of incidence, the crystal momentum is $\vec{g} = \frac{2\pi}{\Lambda}(\cos \varphi, \sin \varphi)$ whose rotation is measured by φ and Λ is the grating pitch. Only the first diffraction order ($m = 1$) is used because in our case, $\vec{g}$ is always greater than $k_{ph_{\parallel}}$. All quadrants of the circle in Fig. 7.5 can be explored for SPP excitation as long as Eq. 7.1 is satisfied. For symmetry reasons, only k_y positive half space is shown.

Fig. 7.5. Schematic represents wave-vector combination. The large circle represents equi-magnitude $\vec{g}$ vectors. The smaller black and green circles represent equi-magnitude vectors before ($\vec{k}_{spp1}$) and after ($\vec{k}_{spp2}$) surface functionalization with C12 SAM. The dashed line represents a photon wave-vector and the dotted lines represent the SPP propagation direction, β . The letters A and B represent the same azimuthal rotation $\varphi = 60^\circ$ but with (a) smaller and (b) higher incident wavelength respectively. The capital letters with the primes represent the intersection of the photon wave-vector with the SPP semicircles.

The largest circle in k -space represents equi-magnitude $\vec{g}$ vectors at all possible azimuthal orientations within the positive half-space. The two smaller circles represent all possible $\vec{k}_{sp}$ vectors with equal magnitude, respectively before and after C12 surface functionalization, and whose modulus is given by

$$k_{SPP} = k_{ph} \sqrt{\frac{\epsilon_M \epsilon_D}{\epsilon_M + \epsilon_D}} = k_{ph} M \quad (7.2)$$

where ε_M and ε_D are the dielectric constants of the metal and the dielectric medium respectively. After the coating, the SPP modulus increases because of the small increase in ε_D due to the surface functionalization with C12-SAM.

The dashed line at the tip of the circle of radius $\vec{g}$ represents the x component of the photon wave-vector k_{ph_i} , the only component that participates in SPP excitation. The line is scaled linearly in $\sin \theta_{in}$ such that the full length of the line at the incident angle θ_{in} of 90° corresponds to the maximum value of k_{ph_i} .

The intersections of the k_{ph_i} dashed horizontal line with the smaller k_{spp} circle determine the conditions for which Eq. 7.1 is satisfied and allows identification of both incident angle θ_{in} for SPP resonance excitation and SPP propagation direction β . For example, point A on the $\vec{g}$ circle is identified by the azimuthal angle φ and allows the excitation of SPP at two possible conditions: A_1' and A_1'' , with β^+ and β^- , respectively in the uncoated case. However, it changes from A_1' and A_1'' to A_2' and A_2'' after C12 is functionalized on the surface. Within the double SPP range, a small increment in wavelength shrinks both the $\vec{k}_{spp1}$ and $\vec{k}_{spp2}$ circles, making the shift between B_1' and B_2' or B_1'' and B_2'' larger. With further increment in wavelength, points B_1' and B_1'' merge to form a very broad resonance as shown in Fig. 7.2 with incident wavelength equal to 622 nm.

We define the Figure of Merit (FOM) of this configuration as:

$$\text{FOM} = \frac{\text{Shift in Resonance Angle}}{\text{FWHM}} \quad (7.3)$$

Fig. 7.6 shows the FOM using the optimized polarization angle is always higher than the FOM with p -polarized incident light for both 1st and 2nd dips. With optimized polarization angle, the FOM is about 50% to 100% higher than that using only p -polarized light. In addition, the FOM of prism-coupled surface plasmon resonance (Fig. 5.1 (a)) is calculated and the value is 0.111 (632.8 nm) which is about 8.5 times lower than this method.

Fig. 7.6 shows the FOM of both p -polarized light (black) and the optimized polarization angle (red).

The value of Δn is 0.0038 RIU which is estimated based on the effective refractive index change generated by a full surface coverage of close-packed self assembled C12 molecules, considering their length = 1.488 nm and dielectric constant ϵ_{C12} = 2.205. The refractive index sensitivity of p -polarized and optimized polarization angle can be determined by dividing the maximum $\Delta\theta$ at p -polarized and optimized polarization angle with Δn . The corresponding value is 570°/RIU and 950°/RIU for p -

polarized and optimized polarization angle respectively and $950^\circ/\text{RIU}$ is within the simulated value ($800^\circ/\text{RIU}$ - $1100^\circ/\text{RIU}$). Hence by optimizing the polarization angle of the incident light, the refractive index sensitivity can be simply increased by $380^\circ/\text{RIU}$. This is mainly because the SPPs in the azimuthally rotated grating are fully excited which can be observed as a deeper dip in Fig. 7.2(b), resulting in a well-defined reflectivity spectra compared to those collected using *p*-polarized light only. These well-defined reflectivity spectra improve the signal to noise ratio and thus enhance the sensitivity of this configuration.

A simulation used to determine the conditions of the wavevector k_{ph} of the incoming light necessary for the SPP excitation for air and $\text{air} + 5 \times 10^{-7} \text{ RIU}$ with the help of Eq. 7.1 is shown in Fig. 7.7. Since our system has an angular resolution up to 0.005° , the refractive index resolution of this system is expected to reach $5 \times 10^{-7} \text{ RIU}$. However, this value may only be achievable if the present experimental angular uncertainty ($\pm 0.07^\circ$) is greatly reduced by using advanced detectors to improve the signal to noise ratio or using appropriate algorithm for data analysis (e.g. centroid method with dynamic baseline¹⁹⁰).

Fig. 7.7. Energy dispersion curve for the k_{ph} necessary for SPP excitation for air (solid line) and air + 5×10^{-7} RIU (dashed line).

7.5 Chapter Summary

In summary, we have shown that the sensitivity in the double SPPs GCSPR configuration is fully achievable when optimized polarization angle is used. The angular difference in reflectivity minima between uncoated and C12-SAM coated metallic gratings is easily detectable in the vicinity of the double SPPs condition only with the optimized polarization angle. The shift in resonance angle detected is as large as 3.6° which is one order of magnitude higher than conventional prism-based SPR. In addition, in the double SPPs configuration, the FOM obtained using optimized polarization is about 50% to 100% higher than that obtained using p -polarized incident light. The sensitivity of this new configuration can reach up to $950^\circ/\text{RIU}$ which is one order of magnitude higher than a conventional non-rotated grating ($\varphi=0^\circ$).

CHAPTER 8. SUITABLE GRATING FOR DOUBLE SURFACE PLASMONS POLARITONS EXCITATION

8.1 Introduction

In order to achieve the sensitivity of the GCSPR discussed from chapter 4-7, the grating which supports the double SPPs excitation with single wavelength becomes very important. However, not all gratings are able to excite double SPPs. In this chapter, the “suitable” grating for double SPPs excitation is investigated.

8.2 Results and Discussion.

Two sets of gratings were fabricated with different amplitude of 76 nm and 25 nm as shown in Fig. 8.1 (a) and (b) respectively. Although the grating profile is similar (sinusoidal wave like structure), the optical characterizations are different as shown in Fig. 8.2 (a), (b), (c) & (d).

Fig. 8.1 AFM shows the profile of fabricated gratings with amplitude (a) 76 nm and (b) 25 nm.

Fig.8.2. Optical Characterizations of gratings with amplitude 76 nm ((a) & (c)) and 25 nm ((b) & (d)). (a) & (b) is for unrotated grating ($\varphi = 0^\circ$); (c) & (d) is for grating rotated to an angle where double SPPs can be excited.

The grating with higher amplitude shows a deeper dip in reflectivity spectra (reaching almost zero in the reflectivity spectrum) than for shallower amplitude (only 0.6) which means it is able to excite SPP with higher strength as shown in Fig. 8.2(a) & (b). Although both gratings are able to excite double SPPs, the excited double SPPs in the higher amplitude grating do not approach each other when the incident wavelength increases, as shown in Fig. 8.2(c). This is not the same double SPPs as those mentioned previously. Since the excitation of the “correct” double SPPs is the most critical in this work, the grating with high amplitude is not suitable in our applications although it has shown a better SPP coupling efficiency (deeper dip) in $\varphi = 0^\circ$ than grating with smaller amplitude.

This is because for the SPP to be excited in grating to follow the surface plasmon dispersion, the grating aspect ratio (amplitude/pitch) must be smaller than 0.1^{183, 189}. Due to the resonance with surface electromagnetic wave, the amplitude of the corresponding diffracted order becomes less for a deep grating with aspect ratio ≥ 0.1 ^{183,189}. Hence, the grating with smaller amplitude (having an aspect ratio of 29/468 = 0.062) is able to excite double SPPs, whereas the grating with higher amplitude (ratio of 76/370 = 0.205 which is much higher than the critical value, 0.1) is unable to excite double SPPs.

Another grating with different pitch and amplitude was fabricated to confirm this phenomenon. This new fabricated grating has pitch and amplitude of 515 nm and 18 ± 3 nm respectively, hence the aspect ratio is 0.035 ± 0.058 which is within 0.1 as shown in Fig. 8.3. The optical characterization of the grating in both $\varphi = 0^\circ$ and φ for double SPP excitation are shown in Fig. 8.4. In the new fabricated grating, a better

coupling efficiency (in term of reflectivity) was observed at $\varphi = 0^\circ$, but the reflectivity of φ for double SPPs excitation is almost similar to the previous case as shown in Fig. 8.4(a) & (b). Although one would like to fabricate a grating with deepest reflectivity dip (reaching the zero in the reflectivity spectrum), it is only possible for $\varphi = 0^\circ$. For SPP excitation in a rotatable grating, the reflectivity dips are always shallower than $\varphi = 0^\circ$, because the *s*-polarization is less efficient than *p*-polarization for plasmon excitation. In addition, the double SPPs excitation can be fully coupled (deeper dips) by optimizing the polarization angle of the incident light.

Fig. 8.3. AFM shows the fabricated grating has pitch and amplitude of 515 nm and 18 nm respectively.

Fig. 8.4. The corresponding reflectivity spectra for grating shown in Fig. 3.8 at (a) $\varphi = 0^\circ$ and (b) φ for double SPPs excitation.

Although one can fabricate a grating with periodicity in micron range while the double SPPs still can be realized if the aspect ratio is smaller than 0.1, this gives a difficulty in analyzing the data because of too many reflectivity dips arising from different m . Fig. 8.5(a) shows the reflectivity spectra collected from a grating with periodicity of 4 μm and the corresponding dispersion curves from different m values are shown in Fig. 8.5 (b).

Fig. 8.5. (a) Reflectivity spectra collected from a grating with periodicity of 4 μm and (b) the simulated dispersion curve (lines) and experimental (points).

8.3 Determination of the suitable Ag and Au thickness

A simulation to determine the suitable Ag and Au thickness for SPP coupling on Ag/Au gratings is numerically done using an analytical model to solve Maxwell's equations in non-Cartesian system (Appendix I). The reasons for coating a bimetallic layer on the grating is because Ag has a smaller extinction coefficient than gold and therefore suffers less loss during coupling (higher plasmonic coupling efficiency). However a very thin gold coating is used to protect silver from oxidation and provides an inert surface for bio functionalization.

Fig. 8.6 shows the simulation (using Appendix 1) of SPPs coupling efficiencies as a function of Ag thickness for different Au thickness and grating amplitudes while the periodicity is fixed (468 nm). The optimum SPP coupling efficiency which can be represented by the deepest dips in the reflectivity spectra is shown when Ag thickness is ranging from 40 to 50nm and Au thickness is around 7 nm.

Fig.8.6 . Reflectance minima as a function of Ag thickness for different Au thicknesses (5, 7 and 9 nm) and grating amplitudes (28, 32 and 40 nm). The simulations show that the deepest reflectivity dips (perfect SPP coupling) is shown by plasmonic gratings with Ag and Au thickness range from 40 to 50 nm and around 7 nm respectively.

8.4 Chapter Summary

For “correct” double SPPs excitation in the azimuthally rotatable grating, one should obtain a grating with aspect ratio smaller than 0.1 and coated with 37 nm Ag and 7 nm of Au.

CHAPTER 9. DIFFERENTIATING BETWEEN SELF ASSEMBLED MONOLAYERS DIFFERING BY ONLY 2 CARBON ATOMS

9.1 Introduction

It is well known that ellipsometric measurement is a very useful method for determining both the optical constant and thickness of the thin film adsorbed on a substrate. However, this method cannot yield a unique optical constant and thickness for a thin film with thickness $< 200 \text{ \AA}$ ^{191, 192}. Recently, other researchers have combined both prism-coupled SPR and ellipsometric measurements to develop a higher sensitivity method^{193, 194}. Another technique which senses mass difference is the Quartz Crystal Monitor¹⁹⁵ which measures mass and viscosity in processes occurring at or near surfaces, or within thin films. It can measure mass ranging from micrograms to fraction of a nanogram, a detection limit corresponding to submonolayer of atoms. This technique will be useful in aiding the analysis obtained from our method.

The last work of the thesis is to demonstrate the difference between the decanethiol (C10) and the dodecanethiol (C12) SAM, which is only two carbon atoms apart from each other, can be distinguished easily using a grating coupled configuration by optimizing both the azimuthal angle of the grating and the polarization angle of the incident light.

9.2 Experimental

The grating used in this study is fabricated using method described in chapter 3 and has an aspect ratio smaller than 0.1 and coated with 37 nm Ag and 7 nm of Au which is suitable to excite double SPPs. In this study, the azimuthal angles of the grating, 0° , 20° , 25° , 50° and 60° were studied.

C10-SAM [decanethiol ($\text{CH}_3(\text{CH}_2)_9\text{SH}$, DDT)] and C12-SAM [dodecanethiol ($\text{CH}_3(\text{CH}_2)_{11}\text{SH}$, DDT)] was deposited on each half of the gold coated grating surface at room temperature in a N_2 -purged glove box for 24hrs respectively. The spontaneous assembly of the molecules is known to form a densely packed and highly oriented structure on the exposed gold surfaces. The reason for choosing C10 and C12 is because these two molecules have high stability in the environment, such that no distortions occur before we start the measurement.

For different azimuthal angles, different optimized polarization angles of the incident light were used for SPP excitation.

9.3 Results and Discussion

As shown in Fig. 9.1, the shift in resonance angle between C10 and C12-coated grating is not observable when the grating is rotated from $\varphi = 0^\circ$ to 50° where one plasmon is excited, Fig. 9.1 (a) – (d). However, a shift is detectable when φ is rotated to 60° , where double SPP can be excited 9.1(f). Although a shift in resonance angle for $\varphi = 60^\circ$ (at wavelengths 610 - 640 nm), which supports only single plasmon (one dip in the reflectivity spectrum for every incident wavelength) is detectable, the

amount of shift is much smaller compared to those wavelengths which support double SPP excitation.

Fig. 9.1. Comparison of SPR spectrum between C10-coated (solid line) and C12-coated (dashed line) Au grating. The spectrum is collected on the grating with azimuthal angle (a) $\varphi = 0^\circ$ with $\alpha_{min} = 0^\circ$ (p-polarized light), (b) $\varphi = 20^\circ$ with $\alpha_{min} = -18^\circ$, (c) $\varphi = 25^\circ$ with $\alpha_{min} = -19^\circ$, (d) $\varphi = 50^\circ$ with $\alpha_{min} = -31^\circ$, (e) & (f) $\varphi = 60^\circ$ with $\alpha_{min} = -37^\circ$. (e) is where only one plasmon is excited while (f) is where double SPPs are excited. Different colour lines represent different incident wavelength.

To avoid the experimental angular uncertainty, we have performed a fitting of the reflectivity spectra (the dips) using Gaussian function in ORIGIN software to find out the approximate resonance angle. All the fitting has a confidence level better than 98%. The resonance angle and the amount of shift in resonance angle between C10 and C12 for different φ angles and incident wavelengths are summarized in Table 9.1. Although a shift is still detectable from $\varphi = 0^\circ$ to 50° , the amount is too little to observe without software. Finally, optimizing both the grating azimuthal angle and polarization angle of incident light for double SPPs excitation, the shift in resonance angle between C10 and C12, which is only two carbon atoms apart, can be as large as 2.1° . The large angular shifts at the incident wavelength of 658 nm should be disregarded because they correspond to the case when the double dips in C12 have merged while those in C10 have not.

Table 9.1. The summary of resonance angles in C10 & C12 and their differences in differences φ angles.

φ	Incident Wavelength	Resonance Angle in C10	Resonance Angle in C12	Difference
0°	700	20.866°	20.74°	0.126°
	750	28.001°	27.993°	0.008°
	800	35.205°	35.149°	0.056°
20°	700	21.455°	21.053°	0.075°
	750	28.981°	29.03°	0.049°
	800	36.652°	36.633°	0.019°
25°	650	15.29°	15.35°	0.06°
	700	22.191°	22.297°	0.106°
	750	30.057°	30.122°	0.065°
	800	38.248°	38.304°	0.056°
50°	640	19.923°	20.113°	0.19°
	650	22.441°	22.731°	0.29°
	660	25.272°	25.424°	0.152°
	680	30.214°	30.51°	0.296°
	700	37.008°	37.252°	0.244°
	720	45.211°	45.486°	0.275°

60°	740	57.81°	58.232°	0.422°
	610	17.234°	17.625°	0.391°
	620	20.971°	21.467°	0.469°
	630	25.053°	25.727°	0.674°
	640	29.221°	29.768°	0.547°
	610	17.234°	17.625°	0.391°
	620	20.971°	21.467°	0.469°
	650	35.441°	36.656°	1.215°
		73.284°	72.080°	1.204°
	652	37.326°	38.402°	1.076°
		70.942°	69.282°	1.66°
	654	39.341°	40.827°	1.486°
		68.103°	66.077°	2.026°
	656	41.781°	43.593°	1.812°
		64.77°	62.627°	2.143°
	658	45.209°	52.89°	7.681°
		59.935°		7.045°

We have done a simulation (Eq. 5.1) to fit the experimental data points obtained from C10 and C12 at $\varphi = 60^\circ$ as shown in Fig. 9.2. The direction of shift is in agreement with the previous experimental data (uncoated and C12-coated, chapter 5 and 7).

Fig. 9.2. Energy dispersion curve for the k_{ph} necessary for SPP excitation on air, C10 and C12 SAM functionalization. The experimental data obtained by the reflectivity minima of Fig. 9.1(f) have been fitted using Eq. 5.1.

The shift in resonance angle between C10 and C12 at different φ angles with same incident wavelength of 650 nm is reported in Fig. 9.3. The amount of shift is proportional to the azimuthal angle and follows the trend as shown in Fig. 5.3.

Fig. 9.3. The shift of resonance angle between C10 & C12 with respect to different azimuthal angles of the grating under the same incident wavelength of 650 nm.

9.4 Conclusion

C10 & C12 SAM which is only two carbon atoms apart from each other can be distinguished easily and a shift in resonance angle as large as 2.1° is detectable if (i) the grating has an aspect ratio smaller than 0.1, (ii) the grating is rotated to an angle where double SPPs can be excited and (iii) the polarization angle of the incident light is optimized such that fully coupled double SPPs are excited.

CHAPTER 10. CONCLUSIONS & FUTURE WORK

This thesis made strides toward the development of highly sensitive surface plasmon resonance (SPR) based sensor through rotating the metallic grating azimuthally. In addition, fully coupled surface plasmons polaritons (SPPs) must be excited using the optimized polarization of the incident light. Combining these two important key findings, the sensitivity of the new configuration can reach at least $950^\circ/\text{RIU}$ and a refractive index resolution up to 5×10^{-7} RIU is achievable. The sensitivity is 15 times higher than the conventional non-rotated grating and 4 times higher than the prism-coupled SPR. The key findings and major contributions of this work are summarized as follows:

1. Demonstration of the double SPP excitation using a single wavelength on an azimuthally rotated metallic grating.

In this study, we have studied the kinematics of SPP propagation as a function of the azimuthal rotation, φ , of the metallic grating. Azimuthal rotation of grating also affects the dispersion curves of the SPP wave-vector in a way which is fundamentally different from that of classical prism coupling. The grating azimuthal rotation induces rotations of the SPP propagation direction that can cover the full 2π range. In particular conditions of incident wavelength and grating azimuthal orientation, distinct double SPPs can be excited and even multiple SPPs can propagate. The wave-vector dispersion is characterized by an energy threshold for the SPP excitation that increases as φ increases. For azimuthal rotation larger than a critical value, the SPP energy

threshold corresponds to the excitation of SPPs directed perpendicularly to the incident light. Moreover, they correspond to a divergence of the wavevector derivative and therefore to a maximum of the SPP density of states. We have shown that the possibility to excite several SPPs over a broad azimuthal angle is accompanied by a mode density condensation in correspondence of the energy threshold.

2. Demonstration of the sensitivity of the configuration.

We have demonstrated that an enhancement in sensitivity can be obtained in GCSPR when double SPPs are excited after azimuthal rotation of the grating. The difference between uncoated and C12-SAMs coated metallic gratings is easily detectable in the vicinity of the double SPP condition. The shift in resonance angle detected is as large as 2.2° , which is one order of magnitude higher than conventional prism-based SPR. In addition, the calculated sensitivity of this method is greater than $800^\circ/\text{RIU}$, 15 times higher than conventional mounted grating ($\varphi = 0^\circ$). However, the calculated sensitivity is only achievable when the excited double SPPs are fully coupled.

3. Contribution of the polarization angle of incident light to the strength of SPPs excitation.

When light direction is perpendicular to the grating grooves, i.e. the scattering plane is parallel to the grating symmetry plane, reflectivity does not depend on polarization and only p -polarization is effective for SPP excitation. However, for an azimuthally rotated grating, not only p -polarized light but also s -polarized light can contribute to

SPP excitation, hence the polarization angle of the incident light angle must be optimized in order to excited full strength of SPPs.

In this study, we have demonstrated the polarization effect on both $\varphi=0^\circ$ and $\varphi\neq0^\circ$. By changing the polarization angle of the incident light, the dip in the reflectivity spectrum is changed and an optimized polarization angle can be found when the deepest dip in the reflectivity spectra is observed. In addition, we have developed an analytical model to determine the optimized polarization angle, assuming that the reflection of electric field from the orthogonal to grating plane is zero. In addition, the SPPs excitation can be switched off when the polarization angle is changed to 90° off the optimized polarization angle.

4. Demonstration of the full sensitivity of the configuration.

In this study, we have demonstrated the full sensitivity of the configuration by both azimuthal control and using the optimized polarization angle. The angular difference in reflectivity minima between uncoated and C12-SAM coated metallic gratings is easily detectable and it is as large as 3.6° which is one order of magnitude higher than conventional prism based SPR. In addition, in the double SPP configuration, the FOM obtained using optimized polarization is about 50% to 100% higher than that obtained using *p*-polarized incident light. This is mainly because the dips are well-defined, shaper, narrower FWHM and the minima are more obvious when optimized polarization angle is used. The sensitivity of this new configuration can reach at least $950^\circ/\text{RIU}$ which is about 70% more than those double SPPs excited using the *p*-polarized light.

5. Fabrication a suitable grating for double SPPs excitation.

The grating which is suitable for double SPPs excitation was investigated in this study. To excite double SPP, the grating must have an aspect ratio (amplitude/pitch) smaller than 0.1. This is due to the resonance with surface electromagnetic wave, the amplitude of the corresponding diffracted order becoming less for a deep grating with aspect ratio ≥ 0.1 . Since the SPP excited on grating is only possible when the momentum of the diffracted light parallel to the surface equals to the propagation constant of the SPP, the grating with higher amplitude which gives less in diffraction will disturb the SPP dispersion law.

The suitable Ag-Au bimetallic thickness is also investigated. The suitable Ag and Au thickness that is required to be evaporated onto the grating is 37 nm and 7 nm respectively. Although both metals are suitable for plasmon excitation, Ag is easily corroded under air ambient and Au has higher extinction coefficient which results in a higher loss in coupling. Thus, combining the advantages of both metals (Ag having a smaller extinction and Au being more resistant in air), a better sensitivity and longer reliability sensor can be realized. In addition, the Au surface also provides an inert surface for bio-functionalization.

6. Differentiation between C10 & C12 SAM

Finally, using a grating with an aspect ratio smaller than 0.1, rotating the grating to an angle where satisfy the double SPP excitation conditions and using the optimized polarization angle of incident light. A shift in resonance angle between C10 & C12

which is only two carbon atoms apart from each other is detectable with an amount of shift as large as 2.1° .

7. Overall working algorithm

Fig. 10.1. Working algorithm of this configuration

The suggested working algorithm of this configuration is shown in Fig. 10.1.

Firstly, the grating with aspect ratio smaller than 0.1 was fabricated using IL and subsequently Ag and Au with thickness 37 nm and 7 nm was evaporated.

Secondly, the azimuthal angle for double SPPs excitation and their corresponding resonance angle can be calculated using the equations. Furthermore, the optimized polarization angle can also be calculated.

Thirdly, the reflectivity spectra were collected from the calculated azimuthal angle using the predicted optimized polarization angle and scanned the incident angle around the calculated resonance angle.

After the dips were observed, the grating was deposited with interested analytes.

After that, the optimized polarization angle was determined again using the deepest dip in the reflectivity spectra as a guideline. The optimized polarization angle needs to be determined again, because the resonance angle is shifted when analytes were coated on the grating surface.

Once the optimized polarization angle was found, the reflectivity spectra was collected again using the new optimized polarization angle at the same azimuthal angle and the incident angle was scanned around the previous resonance angle.

If the reflectivity minima have a shift before and after coating, we can confirm the presence of the analytes. If not, either no analytes was coated on the surface or the resolution of this sensor is not good enough. The possible solutions are:

- (i) Deposition of the binding species that can bind the interested analytes to the Au surface.

- (ii) Increasing the amount of analytes.
- (iii) Using other techniques, e.g. Surface Enhanced Raman Scattering (SERS).

Recommendations for future work include further study on the following areas:

1. Design and integration of a fluidic cell system on the configuration

A completed sensing device is achievable by designing a suitable fluidic cell and integrated together with the configuration as shown in Fig. 10.2.

Fig. 10.2. Schematic represents the microfluidic flow cell setting in GCSPR. (a) side view, (b) top view. 1. Au grating on BK7; 2. Studied analytes; 3. PDMS flow cell; 4. Inlet and outlet holes; 5. Microfluidic channel.

However, to compete with existing market, multi-sensing channels are required to develop as shown in Fig. 10.3. It is composed of a large area of grating (more than $40 \times 40\text{mm}^2$) on top of which some circular microfluidic channels have been patterned. The microfluidic channels are made of transparent material and sealed

on a covering glass. On the back of the glass is the grating. On top of it, an optical screen defines a rectangular window.

Fig. 10.3. Schematic shows the sensor chips. The chip consists of diffraction grating with sinusoidal profile fabricated using interference lithography on a silicon or glass substrate and evaporated with Ag and Au. On back of the diffraction grating, a microfluidic channels is patterned, and analytes can be flown through these channels. A small slit is located on top of the grating to control the active area (light that is incident on the diffraction grating).

The working principle is shown from Fig. 10.4 (a) - (d). A linear light beam source whose cross section is a small circle emits white beam from visible to near infrared. The optical system consists of a collimator lens and a polarizer. The collimator lens first collimates the light on the rectangular window, the polarizer controls the polarization angle of the incident wavelength. The optical system for the collection of the diffracted light is a linear CCD system. The system can detect light at different wavelengths.

Fig. 10.4. Schematics show the SPR sensor system in (a) & (b) side view with a-a cut and b-b cut respectively and (c) & (d) top view with un-rotated and rotated grating. The light is emitted from a light source, passing through a converging lens and focus on a slit which located on top of diffraction grating. The polarization of the incident light can be controlled using a polarizer. The diffracted beam from slit is collected by a CCD.

The fabrication of single- and multi-channel fluidic cell is shown in either Fig. 10.5(a) or (b). The first proposed approach is to fabricate the fluidic cell separately in a transparent substrate and attach the cell to the grating. Another method is to fabricate the fluidic cell and grating in a back-side opened silicon substrate.

Fig. 10.5. Schematic of the proposed approaches. (a) Integration of fluidic cell directly on the grating. (b) Integration of separated fluidic cell on the grating.

2. Portable Grating Coupled Surface Plasmon Resonance Based Sensor.

The proposed portable sensor is shown in Fig. 10.6. The portable sensor consists of grating integrated with fluidic channel(s), a light emitting diode (LED), polarizer, mirror and a charge-coupled device (CCD) to collect the reflectivity spectrum before and after surface functionalization.

Fig. 10.6. Proposed portable sensor.

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APPENDIX I: CHANDEZON'S METHOD

1. Introduction

When the grating period is under the subwavelength scale, rigorous method is required to solve Maxwell's equations. Two methods have been widely used, one is Chandezon's method (C-Method) introduced by Jean Chandezon in 1982ⁱ and another is rigorous coupled-wave analysis (RCWA)ⁱⁱ. Although both methods are completely a different approach for solving the grating problem, the solution for eigen-value problems is the most costly in computationally operation for both methods.

The simplest problem lies in the solution is the diffraction of a semi-infinite one-dimensional grating structure by an incoming plane wave. The grating is periodic with period Λ in the x -direction. The grating is assumed to be infinitely long, and the medium is assumed to be linear with respect to the electromagnetic fields, homogenous, isotropic, time-invariant, dispersion-free, source-free and non-magnetic. From the general grating theory, it is well-known that above and below the grating grooves, the Rayleigh expansion holds as a solution of the field:

$$A(x, y) = \sum_{m=-\infty}^{+\infty} A_m \exp(ik_{xm}x + ik_{ym}y)$$

where A is either the electric field E_z for TE polarized light or the magnetic field H_z for the TM case, A_m are the reflection coefficients in the upper half-space or the transmission coefficients in the lower half space. Rayleigh expansion doesn't hold inside the grooves since the complex permittivity is not a constant, but a function of spatial coordinates. The two different approaches to the problem are as follows:

- RCWA** By eliminating the y -dependency of the complex permittivity, it is possible to write the solution inside the grooves as a Fourier expansion, since only a dependency on the periodic coordinate x is present. This method realizes it by slicing up the grating domain such that inside each slice, the permittivity only depends on x . At the boundaries between the two slices, the tangential components of the electromagnetic fields are continuous, and these conditions make the unknown reflection and transmission coefficients of the upper and lower half space be connected to each other and determined. Introducing Fourier's expansion and truncation, the method gives an eigen-value problem of size $2N + 1$ in each slice, where N is the truncation order. In addition, the RCWA does not converge acceptably for sinusoidal metallic surfacesⁱⁱⁱ.
- C-Method** Its basic feature lies in the choice of a nonorthogonal coordinate system that maps the interfaces between different media into parallel planes. With the use of covariant form of Maxwell's equation in this new system leads to a linear system of differential equations with constant coefficients whose solution is obtained through the calculation of the eigen-value and eigenvector problem of a matrix in each medium. Since TE and TM polarization cannot be separated, the size of the problem is $4N + 2$.

Fig. 1: Schematic description of RCWA and Chandezon's method approach.

C-Method provides a more accurate analytical method for grating problem since it doesn't approximate the grating interface, and requires the solution of an eigen-value problem only in each medium. While in the RCWA method, we have to solve an eigen-value system for each slice. Since RCWA accuracy increases with the number of slices, it is evident that C-method results a great number of layers and hence a great number of eigen-value problems have to be solved. For example, to have the relative difference between the methods to below 1%, RCWA needs 15 to 20 layers, while for 0.1%, 50 to 80 layers are required. In RCWA method it is not the truncation order N that determines diffraction efficiencies mostly, but the number of layers.

In following sections C-Method is applied to sinusoidal grating analysis for an incident wave whose wavevector lies in the symmetry plane of the grating.

2. The new coordinate system - Maxwell's equations

The setup consists of a dielectric or metallic substrate with complex index n_0 , covered by M dielectric or metallic layers with indices n_i and thickness d_i (see Fig. 2). The grating is illuminated by a monochromatic plane wave with wavelength λ at an incidence angle θ in vacuum condition. The upper interface is described in the orthogonal O_{xyz} system by the periodic function $y = s(x)$, with period $\Lambda = 2\pi/K$. The upper limit in the i th medium is given by $y = s(x) - \sum_{j=i+1}^M d_j$. The new coordinate system is defined by the following transformation:

$$x' = x$$

$$y' = y - s(x)$$

$$z' = z$$

Fig. 2: Configuration of the diffraction problem: M-layers multicoated grating.

This choice simplifies the boundary condition of tangential components continuity in the solution of Maxwell's equations, since the interfaces are mapped into the parallel planes $y' = -\sum_{i=j+1}^M d_j$.

In this new system, a vector v can be described with its contravariant components $v^{j'}$ in the basis $e_{j'}$, or with its covariant components $v_{j'}$ in the basis $e^{j'}$. The relation between the new basis $e_{j'}$ and the orthonormal basis e_i is

$$e_{j'} = \Lambda_{j'}^i e_i$$

where Λ is the Jacobi's matrix of the coordinate transformation:

$$\Lambda_{j'}^i = \frac{\partial x^i}{\partial x^{j'}} = \begin{pmatrix} 1 & 0 & 0 \\ s' & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

According to Einstein's notation, repeated indices mean summation on those indices. Obviously the new basis system is a function of the position $(x'y'z')$. In fact

the Jacobi's matrix contains the element s' , the derivative of the grating form function, which depends on the coordinate x' .

The geometry in the new coordinate system is described by the metric tensor

$g_{i'j'}$:

$$g_{i'j'} = e_{i'} \cdot e_{j'} = \Lambda_{i'}^i \Lambda_{j'}^j \delta_j^i = \begin{pmatrix} 1+s'^2 & s' & 0 \\ s' & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

The metric tensor allows the passage from the contravariant to the covariant components:

$$v_{i'} = g^{i'j'} v^{j'}$$

while the inverse $g^{i'j'}$ is useful to pass from the covariant to the contravariant system:

$$v^{i'} = g^{i'j'} v_{j'}$$

$$\text{where } g^{i'j'} = \begin{pmatrix} 1 & -s' & 0 \\ -s' & 1+s'^2 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

To express Maxwell's equations in the new coordinate system, we have to use the covariant formulation of the curl and of the divergence of a vector^{iv}:

$$(\nabla \times v)^k = \frac{1}{\sqrt{g}} \varepsilon^{kji} \partial_j v_i = \frac{1}{\sqrt{g}} \left(\frac{\partial v_i}{\partial x^j} - \frac{\partial v_j}{\partial x^i} \right)$$

$$\nabla \cdot v = \frac{1}{\sqrt{g}} \sum \frac{\partial (\sqrt{g} v^i)}{\partial x^i}$$

where g is the metric tensor determinant, ε^{kji} is the completely antisymmetric Levi-Civita tensor. Maxwell's equations in the absence of free charges and current become:

$$\begin{aligned}\nabla \cdot D &= \frac{1}{\sqrt{g}} \sum_i \frac{\partial(\sqrt{g} D^i)}{\partial x^i} = 0 \\ (\nabla \times E)^k &= \frac{1}{\sqrt{g}} \left(\frac{\partial E_i}{\partial x^j} - \frac{\partial E_j}{\partial x^i} \right) = \frac{\partial B^k}{\partial t} \\ \nabla \cdot B &= \frac{1}{\sqrt{g}} \sum_i \frac{\partial(\sqrt{g} B^i)}{\partial x^i} = 0 \\ (\nabla \times H)^k &= \frac{1}{\sqrt{g}} \left(\frac{\partial H_i}{\partial x^j} - \frac{\partial H_j}{\partial x^i} \right) = \frac{\partial D^k}{\partial t}\end{aligned}$$

In our case $g = 1$ and considering a harmonic dependency on time, we obtain:

$$\begin{aligned}\sum_i \frac{\partial D^i}{\partial x^i} &= 0 \\ \frac{\partial E_i}{\partial x^j} - \frac{\partial E_j}{\partial x^i} &= i\omega B^k = i\omega g^{kt} B_t \\ \sum_i \frac{\partial B^i}{\partial x^i} &= 0 \\ \frac{\partial H_i}{\partial x^j} - \frac{\partial H_j}{\partial x^i} &= -i\omega D^k = -i\omega g^{kt} D_t\end{aligned}$$

3. Formulation of the problem

Since we are interested in the excitation of surface plasmon polaritons, we only consider TM-polarized incident plane waves. The normalized incident magnetic field in z -component is

$$H^i = \exp(ikx \sin \theta -iky \cos \theta)$$

where the time dependence $\exp(-i\omega t)$ is omitted. The problem is to determine the total field H in every point. The diffracted field is defined as $H^d = H - H^i$. Above the grooves, when $y > \max[s(x)]$, the diffracted field can be described by the Rayleigh's expansion:

$$H^d = \sum_n B_n \exp[i(\alpha_n x + \beta_n y)]$$

with $\alpha_n = k \sin \theta + nK$

$$\text{where } \begin{cases} \beta_n = \sqrt{k^2 - \alpha_n^2} & n \in U \\ \beta_n = i\sqrt{\alpha_n^2 - k^2} & n \notin U \end{cases}$$

U being the set of P integers such that $|\alpha_n| < k$. We note that the diffracted field H^d is the superposition of two parts: the asymptotic diffracted field F^{ad} and the evanescent diffracted field F^{ed} . The former part is equal to the sum of the finite number of terms in the Rayleigh's expansion corresponding to $n \in U$, the latter defines the evanescent waves and can be neglected when $y \rightarrow \infty$.

In general, the diffracted field expansion cannot describe the field inside the grooves. However, the asymptotic diffracted field was defined as a plane-wave expansion even inside the grooves when $s(x) < y < \text{Max}[s(x)]$:

$$F^{ad} = \sum_{n \in U} B_n \exp[i(\alpha_n x + \beta_n y)]$$

so the relation in the vacuum $F^d = F^{ad} + F^{ed}$ becomes for inside the groove.

The fundamental question is to know the efficiencies ε_n , defined for $n \in U$ as the energy of the n th order normalized to the incident energy. Since in the calculation, the incident field has unit amplitude:

$$\varepsilon_n = B_n B_n^* \cos \theta_n / \cos \theta$$

We now express the fields in the new coordinate system $x' = x$, $y' = u$, $z' = z$.

The expression for the incident field for $u \geq 0$ is

$$H^i = \exp(-iku \cos \theta) \exp[-iks(x) \cos \theta] \exp(ikx \sin \theta)$$

that is developing the second exponential in a Fourier series:

$$H^i = \sum_m L_m(\beta_0) \exp[i(\alpha_m x - \beta_0 u)]$$

with

$$L_m(t) = \frac{1}{\Lambda} \int_0^\Lambda dx \exp\{-i[s(x)t + mKx]\}$$

In the same way the asymptotic diffracted field can be written as:

$$F^{ad} = \sum_{n \in U} \sum_m B_n L_{m-n}(-\beta_n) \exp[i(\alpha_m x + \beta_n u)]$$

Considering the magnetic and electric field curls in Maxwell's equations covariant formulation. For TM-waves with non-zero magnetic field z -component the magnetic curl gives in the i th medium:

$$\begin{aligned} \frac{\partial H_z}{\partial u} &= -i\omega\epsilon_i(E_x - s' E_u) \\ -\frac{\partial H_z}{\partial x} &= -i\omega\epsilon_i[-s' E_x + (1 + s'^2) E_u] \end{aligned}$$

Summing the two equations and substituting the expression for E_u :

$$E_u = \frac{1}{i\omega\epsilon_i(1 + S'^2)} \left(\frac{\partial H_z}{\partial x} - i\omega\epsilon_i s' E_x \right)$$

we obtain:

$$\frac{\partial H_z}{\partial u} = \frac{S}{1 + S'^2} \frac{\partial H_z}{\partial x} + \frac{i}{1 + S'^2} \omega\epsilon_i E_x$$

Substituting the same expression for E_u in the electric field curl:

$$\frac{\partial E_u}{\partial x} - \frac{\partial E_x}{\partial u} = i\omega\mu_0 H_z$$

we get the following differential equation:

$$-\frac{\partial E_x}{\partial u} = \frac{\partial}{\partial x} \left(\frac{i}{\omega \epsilon_i (1 + S'^2)} \frac{\partial H_z}{\partial x} \right) + i \omega \mu_0 H_z + \frac{\partial}{\partial x} \left(\frac{s'}{1 + S'^2} E_x \right)$$

We define the two covariant quantities F and G such that in the j th medium for TM-polarization

$$F = Z_0 H_z \quad G = -k \epsilon_i E_x$$

we have where $Z_0 = \sqrt{\mu_0 / \epsilon_0}$ is the vacuum impedance. With these notations, Eqs.20

and 21 become:

$$\begin{aligned} \frac{\partial F}{\partial u} &= \frac{s'}{1 + S'^2} \frac{\partial F}{\partial x} + \frac{i}{1 + S'^2} G \\ \frac{\partial G}{\partial u} &= \frac{\partial}{\partial x} \left(\frac{i}{1 + S'^2} \frac{\partial F}{\partial x} \right) + i \epsilon_j k^2 F + \frac{\partial}{\partial x} \left(\frac{s'}{1 + S'^2} G \right) \end{aligned}$$

These equations have to be solved in each medium with the boundary condition such that F and G/ϵ_j must be continuous at each interface.

4. Solution of the mathematical problem

In Eq. 22 the grating form function $s(x)$ appears only inside the two periodic functions

$$C(x) = \frac{1}{1 + s'^2} \quad D(x) = \frac{s'}{1 + s'^2}$$

which can be expanded in Fourier series:

$$\begin{aligned} C(x) &= \sum_p C_p \exp(ipKx) \\ D(x) &= \sum_p D_p \exp(ipKx) \end{aligned}$$

According to the Bloch-Floquet's theorem, we look for solutions of Eq. 22 in the form

$$F = \sum_m F_m(u) \exp(i\alpha_m x)$$

$$G = \sum_m G_m(u) \exp(i\alpha_m x)$$

Introducing these expansions into Eq. 22, we obtain an infinite system of linear differential equations of the first order in u with constant coefficients in each medium j . For the first equation we have:

$$\sum_m \exp(i\alpha_m x) \frac{\partial F_m}{\partial u} = \sum_p \sum_n D_p \exp(ipKx) i\alpha_n F_n \exp(i\alpha_n x) + \sum_p \sum_n iC_p \exp(ipKx) G_n \exp(i\alpha_n x)$$

$$\sum_m \exp(i\alpha_m x) \frac{\partial F_m}{\partial u} = \sum_p \sum_n D_p i\alpha_n F_n \exp(i\alpha_{n+p} x) + \sum_p \sum_n iC_p G_n \exp(i\alpha_{n+p} x)$$

and with the position $n + p = m$, we have:

$$\sum_m \exp(i\alpha_m x) \frac{\partial F_m}{\partial u} = \sum_m \sum_n D_{m-n} i\alpha_n F_n \exp(i\alpha_m x) + \sum_m \sum_n iC_{m-n} G_n \exp(i\alpha_m x)$$

$$\sum_m \exp(i\alpha_m x) \left[-i \frac{\partial F_m}{\partial u} - \sum_n (\alpha_n D_{m-n} F_n + C_{m-n} G_n) \right] = 0$$

which requires that for every n

$$-i \frac{\partial F_m}{\partial u} = \sum_n (\alpha_n D_{m-n} F_n + C_{m-n} G_n)$$

In the same way for the second equation, we have:

$$\sum_m \exp(i\alpha_m x) \frac{\partial G_m}{\partial u} = i \frac{\partial}{\partial x} \left[\sum_p \sum_n C_p \exp(ipKx) i\alpha_n F_n \exp(i\alpha_n x) \right] + ik^2 \varepsilon_i \sum_m \exp(i\alpha_m x) F_m + \frac{\partial}{\partial x} \left[\sum_p \sum_n D_p \exp(ipKx) G_n \exp(i\alpha_n x) \right]$$

$$\sum_m \exp(i\alpha_m x) \frac{\partial G_m}{\partial u} = -i \sum_p \sum_n C_p \alpha_n \alpha_{p+n} F_n \exp(i\alpha_{p+n} x) + ik^2 \varepsilon_i \sum_m \exp(i\alpha_m x) F_m + \sum_p \sum_n i\alpha_{p+n} D_p G_n \exp(i\alpha_{p+n} x)$$

and with the position $n + p = m$, we have:

$$\sum_m \exp(i\alpha_m x) \frac{\partial G_m}{\partial u} = -i \sum_m \sum_n C_{m-n} \alpha_n \alpha_m F_n \exp(i\alpha_m x) + ik^2 \varepsilon_i \sum_m \exp(i\alpha_m x) F_m + \sum_p \sum_n i\alpha_m D_{m-n} G_n \exp(i\alpha_m x)$$

$$\sum_m \exp(i\alpha_m x) \left[-i \frac{\partial G_m}{\partial u} - \sum_n (-\alpha_n \alpha_m C_{m-n} F_n + k^2 \varepsilon_i \delta_{mn} F_n + \alpha_m D_{m-n} G_n) \right] = 0$$

which requires that for every n

$$-i \frac{\partial G_m}{\partial u} = \sum_n [(-\alpha_n \alpha_m C_{m-n} + k^2 \varepsilon_i \delta_{mn}) F_n + \alpha_m D_{m-n} G_n]$$

Thus, the mathematical problem lies in the solution of the following system of linear equation in the unknown components F_m and G_m :

$$\begin{aligned} -i \frac{\partial F_m}{\partial u} &= \sum_n (\alpha_n D_{m-n} F_n + C_{m-n} G_n) \\ -i \frac{\partial G_m}{\partial u} &= \sum_n [(-\alpha_n \alpha_m C_{m-n} + k^2 \varepsilon_i \delta_{mn}) F_n + \alpha_m D_{m-n} G_n] \end{aligned}$$

In order to express the problem in a matrix form, it is useful to introduce a generalized vector $\zeta(u)$ having a double infinity of components which is the limit for $N \rightarrow \infty$ of the vector $\gamma N(u)$:

$$\gamma N(u) = [F_{-N}, \dots, F_N, G_{-N} / \varepsilon(u), \dots, G_N / \varepsilon(u)]$$

In this new notation, the problem lies in the solution of the following system in each medium:

$$-i \frac{d\xi}{du} = \{ |R(u)|^{-1} T(u) R(u) \} \xi$$

with the following definitions:

$$T = \begin{pmatrix} A & B \\ C & D \end{pmatrix} \quad R = \begin{pmatrix} R_1 & B \\ C & R_2 \end{pmatrix}$$

$A - D, R_1, R_2$ being four matrices of size $2N + 1$ given for m and $n \in (-N, +N)$ by:

$$\begin{aligned} A_{m,n} &= \alpha_n D_{m-n} \\ B_{m,n} &= C_{m-n} \\ C_{m,n} &= -\alpha_m \alpha_n C_{m-n} + k^2 \varepsilon_j(u) \delta_{mn} \\ D_{m,n} &= \alpha_m D_{m-n} \\ R_{1m,n} &= \delta_{mn} / \sqrt{\varepsilon(u)} \\ R_{2m,n} &= \delta_{mn} / \sqrt{\varepsilon(u)} \end{aligned}$$

R^{-1} is simply obtained by interchanging R_1 and R_2 in R .

The solution of Eq. 38 consists in solving the eigenvectors and eigen-values problem of the matrix $R^{-1}TR$ in each medium so that in the j th medium, we can expand $\xi(u)$ as a sum of exponentials:

$$\xi(u) = \sum_{q=1}^{\infty} b_q^j (R^{-1}V_q^j) \exp(i\lambda_q^j u)$$

where λ_q^j and V_q^j are the eigen-values and eigenvectors of the matrix T in the j th medium. The coefficient b_q^j represents the weights of the corresponding eigen-vectors in the expansion. Thus the form of $\xi(u)$ in the j th medium is given by

$$\xi(u) = M^j \phi^j(u) b^j$$

where b^j is a vector with components b_q^j , $\phi^j(u)$ is a diagonal matrix with elements $\phi_{mn}^j = \exp(i\lambda_m^j u) \delta_{mn}$, M is a matrix whose columns are the vectors $R^{-1}V_q^j$. Thus the problem lies in the determination of the coefficient b_q^j in each medium.

4.1 Imposing boundary conditions

The continuity of $\xi(u)$ at each interface u_j requires

$$M^j \phi^j(u_j) b^j = M^{j+1} \phi^{j+1}(u_j) b^{j+1}$$

From this relation and noting that

$$\phi^j(u_j) [\phi^j(u_{j-1})]^{-1} = \phi(u_j - u_{j-1}) = \phi^j(d_j) \quad \phi^{M+1}(u_M) = \phi^{M+1}(0) = 1$$

we finally deduce a relation between b^0 and b^{M+1} :

$$M^{M+1} b^{M+1} = [M^M \phi^M(d_M) (M^M)^{-1}] \dots [M^j \phi^j(d_j) (M^j)^{-1}] \dots [M^1 \phi^1(d_1) (M^1)^{-1}] M^0 \phi^0(-d) b^0$$

For a non coated grating ($M = 0$) the previous relation reduces to

$$M^0 \mathbf{b}^0 = M^1 \mathbf{b}^1$$

For a multicoated grating, it is worth noting that each medium is represented by the matrix $H^j = M^j \phi^j(d_j)(M_j)^{-1}$ and the equation can be written in the form:

$$H \mathbf{b}^0 = M^{M+1} \mathbf{b}^{M+1}$$

with

$$H = H^M H^{M-1} \dots H^1 M^0 \phi(-d)$$

Since we are interested in the asymptotic diffracted field determination, i.e. the efficiencies of the diffraction orders, the problem is to determine the coefficients $\mathbf{b}^{M+1}$.

4.2 Using outgoing-wave condition

The outgoing-wave condition imposes some restrictions for the solutions in the first and last medium. In the substrate, we must keep in $\mathbf{b}^0$ only the components b_q^j for which λ_q^j corresponds to a wave whose amplitude decreases for $y \rightarrow -\infty$ or is propagating downward. Since the u dependence of this wave is in $\exp(i\lambda_q^j u)$ we must keep only λ_q^j such that

$$\text{Im}(\lambda_q^0) < 0, \text{ or } \text{Im}(\lambda_q^0) = 0 \text{ and } \text{Re}(\lambda_q^0) < 0$$

In the vacuum, the situation is more complicated since we must distinguish between the incident field, the asymptotic diffracted field and the evanescent diffracted field. Thus for $j = M + 1$, we have

$$\xi^{M+1} = M^{M+1} \phi^{M+1}(u) \mathbf{b}^{M+1} + \exp(-i\beta_0 u) \mathbf{1} + M^1 \phi'(u) B$$

where 1 is a vector with a double infinity of components, the limit when $N \rightarrow \infty$ of the vector

$$\begin{pmatrix} 1' \\ 1'' \end{pmatrix}$$

with $m \in (-N, +N)$. From Eq. 16 follows that

$$1'_m = L_m(\beta_0)$$

Inserting the incident field expansion 16 into Eq. 20 and noting that $s' = \tan \theta = \alpha_0/\beta_0$, by solving G , one find:

$$1''_m = -(\beta_0 - mK \frac{\alpha_0}{\beta_0}) L_m(\beta_0)$$

B is a vector of components B_n ($n \in U$) and of size P , $\phi'(u)$ is a diagonal matrix size P and components $\exp(i\beta_n u) \delta_{mn}$, M' is a generalized matrix, the limit when $N \rightarrow \infty$ of a rectangular matrix

$$\begin{pmatrix} M'' \\ M''' \end{pmatrix}$$

M'' and M''' being two rectangular matrices of size $(2N+1) \times P$ given for $m \in (-N, +N)$ and $n \in u$ by

$$M''_{mn} = L_{m-n}(-\beta_n)$$

$$M'''_{mn} = [\beta_n - (m-n)K \frac{\alpha_n}{\beta_n}] L_{m-n}(-\beta_n)$$

where we used that for a given order $ns' = \alpha_n / \beta_n$. Eq. 40 becomes

$$Hb^0 = M^{M+1} b^{M+1} + 1 + M' B$$

Since the term $M^{M+1}b^{M+1}$ represents the evanescent field, the outgoing-wave condition in vacuum imposes that we must keep only the components of b^{M+1} corresponding to λ_q^{M+1} such that

$$\text{Im}(\lambda_q^{M+1}) > 0$$

4.3 Truncation

The numerical calculation requires the truncation of all the vectors and matrices appearing in Eq. 42. The infinite vector ζ is replaced by a finite vector of dimension $2(2N + 1)$. Under these conditions the matrix T has a size $4N + 2$ and we compute in each medium, its $4N + 2$ eigen-values and corresponding eigen-vectors V_q^j of size $4N + 2$. From the form of the T matrix it can be shown that the number of values λ_q^j satisfying condition Eq. 41 is equal to $2N + 1$. Thus the number of components of b^0 will be exactly $2N + 1$. In the same way the number of λ_q^{M+1} satisfying Eq. 43 is equal to $2N + 1$. In particular the number of λ_q^{M+1} such that $\text{Im}(\lambda_q^{M+1}) > 0$ is equal to $2N + 1 - P$, so the number of components of b^{M+1} is equal to $2N + 1 - P$. Since B has P components, Eq. 42 is nothing but a linear system of $4N + 2$ equations with $4N + 2$ unknowns. By using the classical theory of determinants of infinite order, it can be shown that the solutions of the eigen-value problems with truncated matrices tend to the exact solutions as the matrix order increases^v.

5 Application of the method to sinusoidal grating

The Chandezon's method was applied to a multilayer configuration where the shape function $s(x)$ is described by a harmonic function:

$$y = A \sin Kx$$

where A is the amplitude of the modulation and $K = 2\pi/\Lambda$, given a periodicity Λ .

Following the passages described in the previous paragraphs, we have to calculate Fourier's expansion of the function $C(x)$ and $D(x)$ which represents the shape contribution to the problem. In our case we have:

$$\begin{aligned} C(x) &= \frac{1}{1 + s'^2} \\ &= \frac{1}{1 + A^2 K^2 \cos^2 Kx} \\ &= \sum_{n=0}^{\infty} \frac{1}{n!} \left[\prod_{i=0}^{n-1} (-1-i) \right] (A^2 K^2 \cos^2 Kx)^n \\ &= \sum_{n=0}^{\infty} \frac{1}{n!} \left[\prod_{i=0}^{n-1} (-1-i) \right] \left(\frac{AK}{2} \right)^{2n} \sum_{p=0}^{2n} \frac{2n!}{p!(2n-p)!} e^{2iKx(p-n)} \\ &= \sum_{m=-\infty}^{+\infty} \sum_{n \geq |m|/2}^{+\infty} \frac{1}{n!} \left[\prod_{i=0}^{n-1} (-1-i) \right] \left(\frac{AK}{2} \right)^{2n} \frac{(2n)!}{(m/2+n)!(n-m/2)!} e^{imKx} \end{aligned}$$

with the position $p - n = m$ and m is even numbers. Thus we have the following expression for Fourier's terms of the expansion:

$$\begin{aligned} C_m &= \sum_{n \geq |m|/2}^{+\infty} \frac{1}{n!} \left[\prod_{i=0}^{n-1} (-1-i) \right] \left(\frac{AK}{2} \right)^{2n} \frac{(2n)!}{(m/2+n)!(n-m/2)!} \quad (\text{even } m) \\ c_m &= 0 \quad (\text{odd } m) \end{aligned}$$

$$\begin{aligned}
D(x) &= \frac{s'}{1+s'^2} \\
&= \frac{AK \cos Kx}{1+A^2 K^2 \cos^2 Kx} \\
&= \sum_{n=0}^{\infty} \frac{1}{n!} \left[\prod_{i=0}^{n-1} (-1-i) \right] (AK \cos Kx)^{2n+1} \\
&= \sum_{n=0}^{\infty} \frac{1}{n!} \left[\prod_{i=0}^{n-1} (-1-i) \right] \left(\frac{AK}{2} \right)^{2n+1} \sum_{p=0}^{2n+1} \frac{(2n+1)!}{p!(2n+1-p)!} e^{2iKx(p-n-\frac{1}{2})} \\
&= \sum_{m=-\infty}^{+\infty} \sum_{n \geq \frac{|m|+1}{2}} \frac{1}{n!} \left[\prod_{i=0}^{n-1} (-1-i) \right] \left(\frac{AK}{2} \right)^{2n+1} \frac{(2n+1)!}{(n+m/2+1/2)!(n-m/2-1/2)!} e^{imKx}
\end{aligned}$$

with the position $m=2p-2n-1$ and odd m values. Thus we obtain:

$$\begin{aligned}
D_m &= \sum_{n \geq \frac{|m|+1}{2}} \frac{1}{n!} \left[\prod_{i=0}^{n-1} (-1-i) \right] \left(\frac{AK}{2} \right)^{2n+1} \frac{(2n+1)!}{(m/2+n+1/2)!(n-m/2-1/2)!} \quad (\text{odd } m) \\
D_m &= 0 \quad (\text{even } m)
\end{aligned}$$

The following table shows Fourier's coefficients of the expansions till the fifth order in KA ($\sim A/\lambda$):

Order	C_n	D_n
0	$1 - 2\left(\frac{KA}{2}\right)^2 + 6\left(\frac{KA}{2}\right)^4$	0
± 1	0	$\left(\frac{KA}{2}\right) - 3\left(\frac{KA}{2}\right)^3 + 10\left(\frac{KA}{2}\right)^5$
± 2	$-\left(\frac{KA}{2}\right)^2 + 4\left(\frac{KA}{2}\right)^4$	0
± 3	0	$-\left(\frac{KA}{2}\right)^3 + 5\left(\frac{KA}{2}\right)^5$
± 4	$\left(\frac{KA}{2}\right)^4$	0

± 5	0	$(\frac{KA}{2})^5$
$ n > 5$	0	0

Since in the devices of interest $A/\lambda \sim 0.01 \div 0.1$, the approximation till the third or the fifth order reveals a good choice to simplify numerical calculation without losing too much in accuracy.

Next step is calculating Fourier's coefficients $L_m(t)$ that appear in the expansion of the incident plane wave in the new coordinate system (Eq. 16) and in the description of the asymptotic diffracted orders (Eq. 17). $L_m(t)$ is defined by the following equation:

$$L_m(t) = \frac{1}{\Lambda} \int_0^\Lambda dx \exp\{-i[s(x)t + mKx]\}$$

Using the sine Euler's definition and the binomial series we find the following results:

$$\begin{aligned}
 e^{its(x)} &= e^{-itA \sin Kx} \\
 &= e^{-itA \frac{e^{iKx} - e^{-iKx}}{2i}} = e^{-\frac{At}{2} e^{iKx}} e^{\frac{At}{2} e^{-iKx}} \\
 &= \left(\sum_{n=0}^{+\infty} \frac{1}{n!} \left(-\frac{At}{2} \right)^n e^{inKx} \right) \left(\sum_{p=0}^{+\infty} \frac{1}{p!} \left(\frac{At}{2} \right)^p e^{ipKx} \right) \\
 &= \sum_{n,p=0}^{+\infty} (-1)^n \frac{1}{n! p!} \left(\frac{At}{2} \right)^{n+p} e^{i(n-p)Kx} \\
 &= \sum_{m=-\infty}^{+\infty} \sum_{p=-m}^{+\infty} (-1)^{p+m} \frac{1}{(p+m)! p!} \left(\frac{At}{2} \right)^{2p+m} e^{imKx}
 \end{aligned}$$

when the substitution $n-p=m$ has been used. Then we obtain:

$$\begin{aligned} L_m(t) &= \sum_{p=-m}^{+\infty} (-1)^{p+m} \frac{1}{(p+m)!p!} \left(\frac{At}{2}\right)^{2p+m} \\ &= (-1)^m \left(\frac{At}{2}\right)^m \sum_{p=-m}^{+\infty} (-1)^p \frac{1}{(p+m)!p!} \left(\frac{At}{2}\right)^{2p} \end{aligned}$$

5.1 SPP resonance on sinusoidal grating

Using the mathematical instruments described in the previous section, the simulations of an incoming plane wave incident on a sinusoidal diffraction grating in air are shown. Grating configuration becomes more and more complicated by adding metal layer and dielectric films and analyzing response dependency on geometrical properties such as the grating amplitude.

Simulation algorithms have been written with the use of *Mathematica* software: applying Chandezon's method to sinusoidal gratings, the problem of diffraction of an incident plane wave is solved and the solution gives the reflectivity at the input incident angle. Analyzing numerical accuracy for varying truncation order, we find that at truncation order $N = 3$ precision in reflectivity output is about 10^{-6} , while at order $N = 4$, precision reaches 10^{-9} . Thus $N = 4$ guarantees a very good accuracy and is not a heavy computational work.

Considering a monochromatic plane wave with wavelength $\lambda = 633$ nm incident on a semi-infinite silver grating with amplitude $A = 25$ nm and period $\Lambda = 500$ nm. Diffracted light can couple to surface electrons excitation if the momentum of diffracted light parallel to the surface equals the propagation constant of the surface plasmon polariton:

$$k_{spp} = \frac{2\pi}{\lambda} \sin \theta_i + n \frac{2\pi}{\Lambda}$$

Using SPP dispersion law found for the flat configuration, the resonance angle θ_r can be found at:

$$\frac{2\pi}{\lambda} \sqrt{\frac{\epsilon_M \epsilon_d}{\epsilon_M + \epsilon_d}} = \frac{2\pi}{\lambda} \sin \theta_r + n \frac{2\pi}{\Lambda}$$

with $\lambda = 633$ nm, ϵ_M of silver = -17.0 . Assuming $n = -1$, $\theta_r = 13.60^\circ$. In order to solve the problem analytically, the Chandezon's method was applied and the $\theta_r = 13.56$ was found.

Fig. 3: Resonance curve for a plane wave ($\lambda = 633$ nm) incident on a semi-infinite silver grating ($\Lambda = 500$ nm, $A = 23$ nm).

5.2 Reflectivity dependency on amplitude

Reflectivity minimum at resonance shows an interesting dependency on the grating amplitude. We analyze the case of a semi-infinite silver grating in air. Grating period is 500 nm and the incoming wavelength is 633 nm. Fig. 4 shows several resonance

curves for different amplitude values. Fig. 5 shows the reflectance minima as a function of the amplitude and a minimum at $A = 23.2$ nm.

As shown in Fig. 4, resonance angle position varies with grating amplitude and gives an evidence of the dependence of SPPs dispersion law on the grating geometry (see Fig. 6). The approximation of considering the dispersion law of flat configuration:

$$k_{spp} = \frac{2\pi}{\lambda} \sqrt{\frac{\epsilon_M \epsilon_d}{\epsilon_M + \epsilon_d}}$$

gives a simple instrument to roughly localized resonance angle but if more accuracy is needed, Chandezon's method represents an essential choice to get the resonance position with higher precision.

Fig. 4. Resonance curves for different amplitude values.

Fig. 5. Reflectivity minima as a function of the grating amplitude.

Fig. 6. Optimal grating amplitude as a function of the grating period. Linear fitting curve: $A = m\Lambda + q$: $m = 0.0281 \pm 0.0003$, $q = -2.85 \pm 0.12$.

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APPENDIX II: LIST OF AUTHOR'S PUBLICATIONS

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