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**1- AND 2-DIMENSIONAL PLASMONIC
NANOSTRUCTURES: DESIGN, FABRICATION
AND CHARACTERIZATION**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

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**1- AND 2-DIMENSIONAL
PLASMONIC NANOSTRUCTURES:
DESIGN, FABRICATION AND CHARACTERIZATION**

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Abstract

Surface plasmon polariton (SPP) has captured huge interest because of the ability to work in optical range as well as interaction with nanostructures [1]. Its potential applications include waveguides, plasmonic-electronic chips and sensors [2-42]. The ability to sense minute changes in effective refractive index remains the most prominent and is thus the focus of this thesis [35, 43-47]. SPP excitation can be done through prism coupling or a periodic structure (plasmonic crystal) [7, 13, 48-52]. Plasmonic crystals (PCL) are preferred since they provide more flexibility to control SPP propagation and possess richer structures [49, 53-64].

This thesis explores the behaviour of 1D and 2D PCL by refractive index engineering, followed by optical characterization to study SPP response due to azimuthal rotation (ϕ), where double SPPs and other crystal momentum can be excited with optimized polarization [65-72] thus change its propagation direction [16, 33, 72, 73]. These approaches are done to obtain electromagnetic (EM) field enhancement for sensing purposes.

One way to accomplish refractive index engineering is physically through the dimensional orders of PCL. The plasmonic response of 1D, 1D to 2D transitional and 2D PCLs are studied experimentally and reported. In 2D PCL, the presence of diagonal crystal momentum will benefit due to the ability to explore first and second Brillouin zones. It will act as a complementary vector probe to explore conditions which are otherwise impossible to be done by the main axis due to limitations in wavelength and incident angle. Besides physical means, controlling SPP can be accomplished by engineering dielectric medium. An active material - hybrid organic-inorganic material - is introduced on PCL. It induces porosity that moves plasmonic generation condition to negative first order Brillouin zone thus improves sensitivity and removes the need of surface functionalization or chemical adsorption.

The thesis also describes the revolutionary of an original approach for SPP excitation using azimuthally rotated 2D PCL for all crystal momenta available at optimized polarization angle. The kinematics of all crystal momentum and light vectors based on momentum conservation to define SPP propagation on 2D PCL are demonstrated. The SPP can be controlled and fully enhanced as optimal polarization state (α_{min}) of incoming photon is utilized for each crystal momentum. The full sensitivity enhancement is demonstrated on 2D sinusoidal square lattice PCL under α_{min} using a decanethiol (C_{10}) self-assembled monolayer (SAM). To further examine the sensitivity, 2D PCL was used to detect the difference of 2 carbon atoms (C_{10} and C_{12}). In 2D PCL, double dips can be generated at lower azimuthal

angle (less than 45°) by y -axis crystal momentum. These are the advantages of 2D PCL which does not exist in 1D PCL.

The extraordinary transmission (EOT) and plasmonic crystal ellipsometry (PCE) modes will serve as complements to the 2D SPR technique. In PCE, PSI is more sensitive to corrugation hence the presence of PCL and analyte will change this value dramatically. In contrast DELTA is more sensitive to layer thickness. The combination of these approaches will be able to replace the prism and 1D PCL coupled SPR based sensor with better sensitivity and eliminate the surface chemisorptions requirement.

Keywords: Engineering refractive index, surface plasmon polariton (SPP), nanofabrication, plasmonic crystal, field enhancement, sensing

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1 Introduction

1.1. Background

The huge interest in nano-optics and plasmonics research and development in last few decades has grown significantly due to the tremendous field enhancement as the result of resonant condition of electromagnetic wave interaction with metallic nanostructures/particles [7, 13, 50, 52]. Generally photons are faster than electrons [21]. This helps make surface plasmon become hot research theme for the last ten years. When electromagnetic wave incidents on metallic film, the photon will couple to metal free electrons and move at the metallic/dielectric layer. This wave is known as surface plasmon polaritons (SPP) which experiences exponential decay as it travels with distance. The SPP field confinement at the vicinity of metallic/dielectric interface will enhance the EM field and give result in an extraordinary sensitivity to the effective refractive index changes at interface [48, 49, 74, 75]. These light-matter interactions and sensitivity due to the field enhancement are widely utilized for sensing [8, 9, 11, 23-42].

The essential characteristic of surface plasmon is the ability to work in optical range as well as X-Ray region that causes in rapid interaction and possibility to be coupled with nanostructures [1, 5]. The attribute of SPP offers great possibility in tailoring the best nanostructure that can be utilized for different purposes i.e. sensing and optoelectronic chips, as well as make sure the development based on these potential applications [2-42, 76, 77].

In this project, plasmonic crystal is the chosen focus because it provides more flexibility to control the SPP propagation and enables us to explore the ‘richer’ structure:

- Different structures (1D or 2D) will give different optical responses of plasmonic effects.
 - At certain azimuthal (ϕ) angle, the excitation of two SPPs (1D – lines) or more (2D – arrays) with the same frequency but in different propagation direction are possible.
 - Polarization effect especially on 2D PC has a possibility to enhance sensing selectivity.
- The plasmon excitation by PC is possible by both polarization states.

Numerous efforts have been done to study the plasmonic effect of some metals; Au and Ag are found to be the best combination to be used in a plasmonic crystal [6, 11, 61, 78-84]. The

plasma frequency of metals determines the refractive index and is an significant parameter which drives the SPPs [35, 45, 46]. Ag is found to have small extinction coefficient (k) among other metals which makes the propagation last longer (less losses). Very thin layer of gold is often used to cover up the silver film in plasmonic crystal [11, 61, 80-82].

1.2. Motivations

Plasmonic crystals are able to detect changes in effective refractive index in both reflection and transmission modes [51, 85]. The sensitivity to detect its changes becomes a very important issue in this thesis and it is greatly affected by EM enhancement and SPP propagation which can be finely controlled by engineering refractive index [66, 71, 86]. The *motivation* is mainly to obtain the highest sensitivity of 2D PCL sensor to minimum alteration in complex effective permittivity at the vicinity of metal-dielectric interface and enhancement due to higher SPP modes that is able to serve at a low incident light intensity.

1.3. Objective and Implication

The main aim of this dissertation is to engineer effective refractive index of plasmonic crystals as a novel method to drive the propagation of surface plasmon for sensing purposes. The implication is to attain optimum sensitivity of 2D PCL sensor to minimum modification in effective permittivity function at the boundary of metallic/dielectric layers and EM field enhancement due to higher SPP excitation modes.

1.4. Scope

Since SPP is extremely responsive to the effective dielectric function of adjacent metal-dielectric interface, a full SPP driving on metalic nanostructure can be realized by:

1.4.1. Physical - Geometry Effects

Although the periodicity and grating amplitude in 1D structure have been studied by Sambles and others [57, 87-90], it is still lack on the experimental parts hence intensive experimental and some theoretical works for both reflection and transmission modes in 1D PCL will be discussed. For 2D PCLs, up to now there is very limited information available related to their optical resposes especially in reflection mode. Furthermore the azimuthal and polarization effects are still not considered for both cases. After the extensive theoretical

study of electromagnetic field on bi-grating by N. E. Glass [66-68, 91], no further study has been done for 2D periodic structures and since the discovery by Ebbesen in 1998, the majority studies of 2D structures were done only in transmission mode [15, 63, 83, 84, 86, 92-103].

Reflection mode in 2D structure has seemingly been ignored in previous research maybe because the importance of azimuthal effects has not been recognized [72]. Without azimuthal rotation, 2D periodic structure will just be the same as 1D. It is hypothesized that by tuning the azimuthal 2D PCL orientation, richer information could be attained as a result of multiple crystal momentum (grating vectors) contribution and the generation of multi SPPs (two or more) with the identical frequency/wavelength are expected, which will give result in sensitivity enhancement. The effect of polarization angle requires to be examined to optimize the plasmonic coupling efficiency (PCE) as azimuthal angle is introduced into the system. 2D corrugated structure needs to be examined to comprehend the plasmonic evolution behaviour from one to two dimensional with respect to the changes in crystal momentum [104].

The profile effects will only be focused on 1D PCL. Since the similar fabrication method being used for both 1D and 2D PCLs, the roughness, aspect ratio, profile quality as well as density of the metals are assumed to be almost identical and will not be covered in this thesis.

Nanostructure fabrication

The main metallic nanostructure fabrication methods, for instance focused ion beam (FIB) and electron beam lithography (EBL) have the drawbacks of slow speed and costly, which is unsuitable for future industrial applications. Therefore, in this thesis, a fast and maskless fabrication technique was used—interference lithography (IL) for large-area parallel surface patterning on the photoresist layer and then transferring the nano-patterns to the thin metallic film via lift-off approach or metal etching approach.

IL is a technique of writing periodic or quasi-periodic patterns using two coherent interference laser beams [105, 106]. By adjusting the incoming angle and sample holder, the

pitch can be easily controlled [106]. Furthermore, double exposure was adopted to achieve the 2D array. Such procedure also provides the flexibility in photoresist patterning to control the geometry of PCL via a flexible, simple and cheap method. This fabrication technique is also used to study some geometrical parameters exclusively in 1D PCL which covers periodicity, roughness, profiles and film thickness.

Controlling surface plasmon resonance

Controlling propagation of SPP on metal nano-structures has attracted huge interest in recent times. Up to now, huge effort has been done to finely tune control the SPP, as well as the choice of suitable metallic films and adjacent dielectric medium, the unevenness, geometry and size of plasmonic crystals. Gold and silver are preferred in generating SPP due to their unique, sharp and clear SPR dip characteristics. Their resonance condition is within opticals and near IR regime.

Therefore, the study will be focused mainly on the optical properties of Au and Ag nanostructures. The observation of multiple Au and Ag plasmonic dips is greatly attractive due to their possibilities in controlling the propagation and magnitude of SPP. Multiple plasmon modes are explored by fabricating unique nanostructures which cover 2D corrugated structures and 2D PCLs.

1.4.2. Chemical – Engineering Dielectric Medium

A novel approach to finely control the permittivity function by incorporating dielectric film on plasmonic crystal [4, 6, 51, 85] is proposed. Hybrid material synthesized from *connected poly-silsesquioxanes* is chosen. This material has capability to produce internal porosities with distinguished optical characteristics [107-109]. The presence of porous sol-gel on plasmonic crystal may move the SPP generation to negative diffraction (Brillouin) order, subsequently causes the system to be more sensitive and the surface functionalization/binding of the analytes are no longer needed. By engineering refractive index the SPP can be controlled.

In this thesis all relevant effects – geometry effect of 1D PCL, dimensionality, active dielectric medium, porosity control, unique structures, azimuthal effect and polarization

angles - will be combined in order to give the highest enhancement in plasmonic excitation. Fluidic cell can be incorporated [110, 111]. Modeling has also been done to match the effective permittivity function of the crystal.

Below is the flowchart of the plan:

Figure 1.1. The Flowchart of the proposed project

The characterization and analysis of bare and coated plasmonic crystals with azimuthal rotation (ϕ) can be done in reflection, transmission and ellipsometry mode [72]. However, this work will be focused more on the SPP excitation as well as sensing performance of azimuthal rotated 1D and 2D PCL in reflection mode (SPR). The excited SPP(s) at different azimuthal angle are expected to be different due to unique requirements in momentum conservation. When incident light direction is parallel to crystal momentum, i.e. scattering's plane is at right angles to main axis of PCL symmetry plane; only p -polarization is effective for SPP excitation. However when azimuthal angle is introduced, s -polarized light could also participate in excitation. In this study, the polarization angle that optimizes the excited SPPs on the azimuthally rotated PCL is investigated to optimize the PCE without changing the

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

1.4.3. Sensitivity Measurement

To examine the sensitivity of 2D PCL, decanethiol (C_{10}) self-assembled monolayer (SAM) is chosen to be the analyte because SAM is able to form self ordering molecules with very high packing density on various surface' profiles [112]. SAMs have hydrophilic head-groups which enable them to hold on the substrate very well and cover the entire surface even in very high aspect ratio. These characteristics make SAMs very ideal candidate for surface stabilization (protection) from contaminations. As SAMs have capability to form monolayer and air interface, they become very important for various applications such as passivation agent (surface protector), reducing metallic bonding temperature, molecular recognition, and etc. Generally decanethiol is relatively very thin $\approx 1.3\text{nm}$ with ten carbon atoms. The demonstration on the sensitivity is done by using 2D PCL with bi-layer of Au-Ag thin films. Simulations and modelings of SAMs on PCL need to be done to analytically calculate the changes in permittivity function and sensing resolution of the system.

Further study on transmission and ellipsometry modes both experimentally and analytically are done to complete the description of plasmonic characterization on 2D PLC. The sensitivity in transmission is much lower than the SPR mode; however there is a common focal point for different polarization in transmission that can be used for switching purposes, opening opportunity in combining the optical and electronic functions in a single device. The effect of polarization and incident angle are discussed in transmission mode. Simulations are done to examine to verify the experimental data.

One very interesting issue in ellipsometry mode is the phase difference measurement. By combining the 1D and 2D PCL in ellipsometry, the sensitivity could be enhanced by two to three orders of magnitudes. Other researchers have done the phase difference measurement using interferometer (Mach Zehnder) on prism coupled SPR [113]; however this system is very complicated and generally not stable. In a single measurement, both relative reflectivity spectra (Ψ) and phase difference measurement (Δ) can be obtained. The Ψ is simply a SPR measurement normalized by the reflectivity of s -polarized light and the Δ is the phase

difference between p-polarized light that is coupled into PCL and the reference s-polarized beam that does not contribute in SPP generation [114, 115]. As azimuthal rotation is introduced, there is a certain portion of s-polarized light that contributes to SPP due to s-p conversion [116]; hence polarization control needs to be done.

1.5. Thesis Overview

This thesis comprises ten chapters which discuss a comprehensive study of the engineering refractive index of plasmonic crystal. This chapter gives a brief introduction of background information related to this project, motivation, objectives, scopes and the impact. The following chapter gives the theoretical background and literature review of the research topic. It covers various topics related to this research work, such as basic theory of SPPs and state-of-the-art of SPR sensing techniques.

The original work accomplished in this research is presented in Chapters 3 to 9. Chapter 3 reports the experimental methods and all information about sample preparation are given in the third chapter. It contains a description of the basic fabrication of 1D and 2D plasmonic crystal, SAMs deposition preparation, synthesis of active materials, simulation and analytical modeling of SPP both in reflection and transmission mode. The optical characterization methods in reflectivity, transmission and ellipsometric will close this chapter.

Chapter 4 discusses about engineering refractive index of PCL using geometrical approach. The technique to optimize the geometrical parameter in 1D PCL is discussed. Some calculations and simulation are reported. Chapter 5 presents the characterization of 1D, 2D PCL and transitional structure PCL in SPR mode. The full analysis including the azimuthal angle effect is discussed. Chapter 6 presents the characterization of 1D and 2D PCL in transmission mode.

Chapter 7 discusses about alternative way in engineering refractive index of PCL. Chemical approach is utilized by introducing the engineering dielectric medium. The effective refractive index is able to be controlled by the film's porosity. This approach may move the SPP generation to negative diffraction order (Brillouin zone).

The sensing capability as one of the applications of 2D PCL is discussed Chapter 8. The role of polarization of the incoming beam to the azimuthally rotated plasmonic crystal is explored. Details on experimental and analytical model of the relationship between polarization angle and azimuthal angle are discussed briefly in the following chapter. The last section of this chapter describes the sensitivity of the configuration using optimized polarization angle and the system is examined by measuring the differential signal of two carbon atoms.

A differential technique of SPR which involves phase measurement is discussed in chapter 9. Plasmonic crystal ellipsometry is introduced as a novel way to to measure the refractive index changes. Finally the summary of the important conclusions and major findings of this research are made and the proposed potential area for future research is discussed.

2 Literature Review

2.1. Theory of Surface Plasmon

Robert Williams Wood (1868-1955), first described his observations of an anomalous diffraction in the reflectivity measurement of metal evaporated 1D periodic gratings illuminated by polarized light [53]. Further study attributing this to surface charge waves generation was done by Ugo Fano [117]. In 1957 R. H. Ritchie postulated the existence of surface plasmon oscillation in thin metal films penetrated by electrons [54]. The postulate was then successfully demonstrated in energy-loss experiment by Powell and Swan in 1960 [118, 119]. The wave oscillation on the facade longitudinally is currently identified as surface plasmon¹ resonance (SPR). This SPR is defined as charge density oscillations of the photon of the incident light coupled with free electrons of metal travelling along the boundary of metallic/dielectric. This magnitude of the SPP decays exponentially from the boundary [13, 48-52]. Fig 2.1 shows schematic of electric field lines associated with an SPP.

Figure 2.1. Schematic of plasmonic field propagation on a smooth interface. Surface plasmons are constituted of resonantly charge fluctuation at the boundary of two medium and form electromagnetic wave. Exponential dependence of the field is presented in both media (as shown); however the field in the dielectric is stronger than in metal. Magnetic field intensity (H_y) is at a 90° to electric one (E_z) coincided to y-axis [52, 120].

In order to transform photons into polaritons, there are two different mechanisms; i.e. first, it can be done by prism coupler, in which the photon passes through greater refractive index medium before reaching the metal/dielectric interface [13, 48-52]. The light will experience a slower velocity and therefore higher wave vector, $k=\omega/c$. Another coupling mechanism uses *periodic* nanostructures with periodicity comparable to the SPP wavelength. When the incoming beam wavelength is toward the plasma frequency of metallic layer, the electrons can be excited to surface plasmon at these frequencies. Such periodic structures exhibit the

¹ The term “plasmon” derives from the assumption of electrons behaving like a charged gas (plasma) in the Drude model of metals.

properties of “plasmonic crystal” that affect the plasmonic resonance condition and results in a strong enhancement of the plasmonic density of states [49, 54, 57, 58, 72, 121, 122]. SPP is non-radiative form that has a wave vector $\vec{k}_{spp}$ larger than wavevector of incoming light at the equal frequency in vacuum. For that reason, enhancement of incoming electromagnetic wave is required to generate the plasmonic propagation on the metal surface.

The plasmon oscillation identified by the charge fluctuation is a mixture of both longitudinal and transversal electro-magnetic (EM), and confined parallel to z-axis in the *Thomas-Fermi screening* about a micron in length and follows the exponential function which has the highest value at the interface, $|z|=0$ and disappears after reaching the penetration depth, typical for SPPs. This explains the plasmon’s surface sensitivity. In this system, the environment plays an important role where any alteration on the interface will strongly move the SPP excitation condition.

One main attraction of surface plasmon polariton is the ability to work at optical range and X-Ray region [1]. The optimum condition for plasmon excitation at metallic/dielectric interface is when the permittivity of the dielectric and the metallic layer have almost the same magnitude but opposite signs, i.e. positive for dielectric and negative for metal [48]. This condition will give rise to higher plasmon momentum as shown in:

$$k_{spp} = \frac{\omega}{c} \sqrt{\frac{\epsilon_m \epsilon_d}{\epsilon_m + \epsilon_d}} \quad (2.1)$$

Some potential applications of surface plasmon are single-molecular-resolution biological/chemical sensors, sub-wavelength waveguides, and entire new classes of lasers based on plasmonic amplification [2-42].

2.2. TM and TE Polarizations

The SPP coupling condition and its efficiency are strongly influenced by the interaction of electromagnetic (EM) field with the materials (nanostructures). Hence the understandings of the electric and magnetic vectors in EM field happen to be very important. There are two particularly important polarizations, TM (transverse magnetic) and TE (transverse electric) which is described bellow.

Figure 2.2. Schematic of polarization state where the short arrows (TM-wave) in (a) represent an electric field whose vector is at a 90° to the incoming beam but parallel to the plane of incident (POI). The dots (TE-wave) in (b) represent an electric field oscillating in and out, perpendicular to the POI and the beam direction.

TM and TE polarizations are defined relative to scattering plane or plane of incidence (POI) which is plane containing the normal to the interface and incoming light. *p*-polarized light or transverse-magnetic (TM) wave is defined by its electric field direction being parallel to POI (Fig. 2.2 (a)). For *s*-polarized light or transverse-electric (TE) wave, the magnetic field is parallel to POI (Fig. 2.2 (b)) [123]. The magnetic and electric fields are 90° each other.

2.3. Maxwell Equation: Light and Matter Interaction

The fundamental equations governing electromagnetic phenomena are Maxwell's equations. These equations are important to derive the EM equations in SPP. In macroscopic media and without source terms they take the following form: [51, 124-127]

Name	Differential form	Eq.
Gauss's law:	$\nabla \cdot E = \frac{\rho(t, x)}{\epsilon_0}$	(2.2)
Gauss' law in magnetic field (w/o the presence of magnetic monopole):	$\nabla \cdot B = 0$	(2.3)
Differential form Faraday's law:	$\nabla \times E = -\frac{\partial B}{\partial t}$	(2.4)
Differential form of Ampere's Law:	$\nabla \times B = \epsilon_0 \epsilon(\omega) \mu_0 \frac{\partial E}{\partial t} + \mu_0 j(t, x)$	(2.5)

The unit is in SI with constitutive relations:

$$D = \epsilon.E, (\epsilon \text{ is permittivity function of materials, dielectric constant})$$

$$B = \mu.H, (\mu \text{ is permeability function of materials})$$

The solution for Maxwell's equation for electric and magnetic field in plane waves:

$$\nabla^2 E = \frac{1}{v^2} \frac{\partial^2 E}{\partial t^2} = \frac{\varepsilon(\omega)}{c^2} \frac{\partial^2 E}{\partial t^2} \quad (2.6)$$

with $c = (\mu_0 \varepsilon_0)^{-1/2}$, hence:

$$\nabla^2 B - \mu_0 \left(\varepsilon_0 \varepsilon(\omega) \frac{\partial^2 B}{\partial t^2} + \sigma \frac{\partial B}{\partial t} \right) = 0 \quad (2.7)$$

The speed of EM wave in dielectric is given by:

$$v^2 = \frac{c^2}{\varepsilon(\omega)} \quad (2.8)$$

where in vacuum the $\varepsilon(\omega) = 1$, so $v^2 = c^2$. The index refraction of a material is the fraction between the light velocity in space divided by light velocity in that dielectric medium, $n = c/v = \sqrt{\varepsilon(\omega)}$. Combining both wave equations, the complete electromagnetic diagram can be drawn as follows:

Figure 2.3. Electromagnetic wave propagation.

2.4. Optical Response of Matter

Both relative permeability $\mu(\omega)$ and permittivity $\varepsilon(\omega)$ are materials' property and strongly related to the energy of EM wave. The permittivity function is originated from the interaction between the electrons and photons (external EM field). The interactions in both medium can be regarded as harmonic function (oscillation of electrons and dipoles) which could further be directly correlated to linear dielectric constant using Drude (for metal) and Lorentz (dielectric) models. Different from metal, the electrons in dielectric cannot freely move and always attached to the atom. By solving mathematically [128], complex permittivity function $\varepsilon_r(\omega) = \varepsilon'(\omega) + i\varepsilon''(\omega)$ of both medium can be obtained. This model will be used for the 1D plasmonic crystal simulation works in chapter 4.

The light-matter interaction from Lorentz model can be represented by a model with nucleus and the outermost electron connected by a spring. The electrons and nucleus are separated by a distance, d and will create dipole moment, $p = q \cdot d$. External field induces electrons displacement. Nucleus is heavier than electrons, thus the movement can be ignored. The motion of an electron with mass m can be written:

$$\frac{d^2 x(t)}{dt^2} + \gamma \frac{dx(t)}{dt} + \omega_0^2 x = -\frac{e}{m} E(t) \quad (2.9)$$

γ and ω_0 are properties of the material. γ is a damping constant per electron mass (m) due to energy loss. ω_0 refers to resonance frequency of electrons and equals to square root of spring constant per electron mass (m). e and m are electron charge and its mass respectively, while E is the EM field. EM field and electron displacement are harmonic which can be represented: $E = E_0 \exp(i\omega t)$ and $x = d \exp(i\omega t)$ respectively. The solution for the charge displacement: $d = \frac{e}{\omega_0^2 - \omega^2 - i\gamma\omega} \cdot \frac{E_0}{m}$, where ω_0^2 is the natural oscillation frequency. The polarization is defined as total dipole moment per unit volume and given by $\chi = n \cdot p$, where n is electron density. Using the constitutive relation $\varepsilon_0(\varepsilon_r - 1)E = \chi$, the relative permittivity ε_r is given by [128]:

$$\varepsilon_r = 1 + \frac{\omega_p^2}{\omega_0^2 - \omega^2 - i\gamma\omega} \quad (2.10)$$

Where $\omega_p^2 = ne^2/m\varepsilon_0$ is plasma frequency. $\varepsilon_0 = 8.8542\text{pF/m}$ is the permittivity constant in vacuum [128]. ε_r is complex permittivity, with real and imaginary parts are proportional to refractive index and absorption respectively. For dielectric [128]:

$$\varepsilon'(\omega) = 1 + \frac{\omega_p^2(\omega_0^2 - \omega^2)}{(\omega_0^2 - \omega^2)^2 - (\gamma\omega)^2} \text{ and } \varepsilon''(\omega) = \frac{\omega_p^2\gamma\omega}{(\omega_0^2 - \omega^2)^2 - (\gamma\omega)^2} \quad (2.11)$$

Dielectric permittivity function is shown in Fig. 2.4. For $\omega \ll \omega_0$, (bellow resonance), the absorption is negligible and the material is transparent, however n increases and light velocity decreases. When $\omega = \omega_0$, the imaginary component dominates (the absorption is significant) and the real part changes sign as the ω goes past ω_0 . This rapid change with frequency is referred to as resonance which width is related to γ . ω_0 has a clear physical

significance of the frequency at which the system “resonates”. As $\omega > \omega_0$, it is just like in vacuum, with $n = 1$ and the absorption becomes negligible.

Figure 2.4. Real and imaginary values for permittivity function $\varepsilon(\omega)$ and refractive index (n) of dielectric medium [135].

The optical properties of metals were first introduced by Drude. In metal since the electrons are freely move (not bound by spring), the restoring force term $m\omega_0^2 x$ can be eliminated and $\omega_0 = 0$. The damping factor γ can be neglected hence the permittivity function becomes

$$\varepsilon'(\omega) = 1 - \frac{\omega_p^2}{\omega^2} \quad \text{and} \quad \varepsilon''(\omega) = \frac{\omega_p^2 \gamma}{\omega(\omega^2 + \gamma^2)} \quad (2.12)$$

An example of Ag complex permittivity function is demonstrated in Fig. 2.4

Figure 2.5. (left) Real and (right) imaginary parts of $\varepsilon(\omega)$ for Ag.

ε is negative when $\omega < \omega_p$ which means the refractive index is negative and metal is highly reflecting. This is due to fast response of free electrons to EM field. As $\omega > \omega_p$, $\varepsilon > 0$, the metal is transmitting and behaves like a dielectric. The plasma frequency depends on the density of valence electrons. Most metals have the plasma frequency around ultraviolet,

except for Ag, Au, alkali metals, and other few materials, which is in visible or near-ultraviolet range. In doped semiconductor, the plasma frequency is in infrared region.

Insulators generally have a small positive ϵ' and very small ϵ'' from visible to infra-red region while most of metals have a huge negative ϵ' and a smaller, positive ϵ'' at visible and longer wavelengths. This property enables light to be focused into a nanostructure [48].

The plasmon is plasma oscillation and considered as a quantum of energy in the collective oscillation of electrons in a metal. Its energy is quantized by:

$$\hbar\omega_p = \hbar\sqrt{ne^2/m\epsilon_0} \quad (2.13)$$

In reality, Drude model cannot precisely represent the optical properties of certain metals including Au and Ag. The electron(s) in valence band (6s – for Au) will be in charge for conducting effect. However in some cases the electrons in intra-band level may be involved [129]. Electrons interaction at outer shell will cause some variation in the permittivity function $\lambda < 500\text{nm}$ for Au (350nm for Ag) [130, 131]. The value will follow dielectric model which requires Lorentz model [132]. However the measurement will be done above these critical values.

The complex permittivity could be represented using complex function $n(\omega) + ik(\omega)$, with the k being the absorption/extinction coefficient.

$$n + ik = \sqrt{\epsilon' + i\epsilon''} \quad (2.14)$$

where $\epsilon' = (n)^2 - (k)^2$ and $\epsilon'' = 2nk$.

2.5. SPP Dispersion Relation

The charge oscillations of SPP are localized in z -axis which move along x -axis, vanish at $|z| \rightarrow \infty$ on the two sides of the metal/dielectric interface and have their maximum at $z = 0$. The plasmon waves have p -polarized character since the SPPs create interruption of the EM field in z axis, which does not apply for s -polarization (no $\vec{E}_z$ component). In other words, only transverse magnetic plane wave (i.e. TM wave) is able to excite SPP [133].

2.5.1. s-polarization (TE-wave)

Using Maxwell's equation, TE wave is considered as the incident light [12, 49, 88]. From Fig. 2.1, for metallic layer (where $z < 0$), the fields are given by:

$$H_m = \left(\frac{iEk_{z(m)}}{\omega}, 0, \frac{Ek_{x(m)}}{\omega} \right) \exp i(k_{x(m)}x + k_{z(m)}z - \omega t) \quad (2.15)$$

$$E_m = (0, E_{y(m)}, 0) \exp i(k_{x(m)}x + k_{z(m)}z - \omega t) \quad (2.16)$$

For dielectric layer (where $z > 0$)

$$H_d = \left(\frac{-iEk_{z(d)}}{\omega}, 0, \frac{Ek_{x(d)}}{\omega} \right) \exp i(k_{x(d)}x + k_{z(d)}z - \omega t) \quad (2.17)$$

$$E_d = (0, E_{y(d)}, 0) \exp i(k_{x(d)}x + k_{z(d)}z - \omega t) \quad (2.18)$$

The continuity of the first derivative of the fields gives:

$$(k_{z(m)} + k_{z(d)}) E = 0 \quad (2.19)$$

The k_z need to be greater than 0 hence the solution is $E=0$, thus in this case TE-wave cannot generate SPP.

2.5.2. p-polarization (TM-wave)

Referring to Fig. 2.1, for metallic layer (where $z < 0$) [49, 88, 134]

$$H_m = (0, H_{y(m)}, 0) \exp i(k_{x(m)}x + k_{z(m)}z - \omega t) \quad (2.20)$$

$$E_m = (E_{x(m)}, 0, E_{z(m)}) \exp i(k_{x(m)}x + k_{z(m)}z - \omega t) \quad (2.21)$$

For dielectric layer (where $z > 0$)

$$H_d = (0, H_{y(d)}, 0) \exp i(k_{x(d)}x + k_{z(d)}z - \omega t) \quad (2.22)$$

$$E_d = (E_{x(d)}, 0, E_{z(d)}) \exp i(k_{x(d)}x + k_{z(d)}z - \omega t) \quad (2.23)$$

with t is time, E_0 the electric field and k the wavevector. Due to the transverse nature of light, E_0 is always orthogonal to propagation direction (k). The fields are correlated each other:

$$H = \frac{c}{\omega \mu_0 \mu(\omega)} k \times E \quad \text{or} \quad E = \frac{c}{\omega \epsilon_0 \epsilon(\omega)} k \times H \quad (2.24)$$

where $B = \mu_0 \mu(\omega) H$ and $\frac{E_i}{B_i} = c$ (2.25) & (2.26)

i is the index of medium: m for metallic layer and d for dielectric layer. k and ω are related in dispersion relation:

$$\frac{\omega^2}{|k|^2} = \frac{1}{\mu_0 \mu(\omega) \epsilon_0 \epsilon(\omega)} \quad (2.27)$$

For nonmagnetic media ($\mu(\omega) = 1$, in vacuum), the speed of EM wave equals:

$$c = (\mu_0 \epsilon_0)^{-1/2} \quad (2.28)$$

The magnitude of k can be expressed in:

$$|k| = \omega \sqrt{\mu(\omega) \epsilon_0 \epsilon(\omega)} = \frac{\omega}{c} \sqrt{\epsilon(\omega)} \quad (2.29)$$

$k_{x(m)}$ and $k_{x(d)}$ are wavevectors in x-directions and $k_{z(m)}$ and $k_{z(d)}$ coincides with the z-axis.

Taking into account, the field continuity at the metallic/dielectric interface:

$$\left(\frac{E_x}{H_y} \right)_m = \left(\frac{E_x}{H_y} \right)_d \quad (2.30)$$

Substituting Eq. 2.30 into 2.20 to 2.23 will give:

$$k_{(m)} \cdot \sin \theta = k_{(d)} \cdot \sin \theta = k \cdot \sin \theta \quad (2.31)$$

Substituting Eq. 2.20 – 2.23 into Maxwell's Eq. 2.2 – 2.5, with Eq. 2.28, it becomes:

$$\frac{H_{y(m)}}{E_{x(m)}} = -\frac{k \epsilon_m}{k_{z(m)}} \quad (2.32)$$

$$\frac{H_{y(d)}}{E_{x(d)}} = \frac{k \epsilon_d}{k_{z(d)}} \quad (2.33)$$

Together with the continuity relations Eq. 2.30, one obtains the dispersion relation of SPPs:

$$k_{z(m)}\varepsilon_d = -k_{z(d)}\varepsilon_m \quad (2.34)$$

This equation demonstrates that SPPs can only be generated at the interface of materials with reverse sign permittivity values.

From Eq. (2.34) the SPP dispersion relation of SPPs:

$$k_{spp} = k \left(\frac{\varepsilon_m \varepsilon_d}{\varepsilon_m + \varepsilon_d} \right)^{1/2} \quad (2.35)$$

Considering an ideal metal/dielectric interface, ε_d is a real number in case of dielectric and ε_m is complex for metal with a negative real value and smaller, positive imaginary value. Under the condition of $\varepsilon_m'' < |\varepsilon_m'|$, k_x also becomes a complex quantity. To satisfy Eq. 2.34, k_z is also required to be complex [48, 49, 88, 120].

In the case of a Drude model, as the $\gamma \sim 0$ (lossless) then:

$$\varepsilon'(\omega) = \frac{\omega^2 - \omega_p^2}{\omega^2} \quad (2.36)$$

substituting this value to Eq. 2.35 and will give SPP dispersion relation in Fig. 2.6:

$$k_{SPP} = k_{ph} \sqrt{\frac{\omega^2 - \omega_p^2}{2\omega^2 - \omega_p^2}} \quad (2.37)$$

Figure 2.6. Free photons dispersion law (Light line) compared to SPP dispersion law.

SPP is non-radiative wave and its momentum is higher than the incoming light hence it cannot be generated directly by incident light and no intersection between them. At positive high wavevector the frequency of SPP becomes:

$$\omega_{k \rightarrow \infty} = \frac{\omega_p}{\sqrt{1 + \epsilon_d}} \quad (2.38)$$

2.6. Spatial Extension of the SPP Field

SPPs are propagated waves and confined at dielectric-metal boundary. The field amplitude is given by $\exp(-|k_{iz}Z|)$. The penetration depth can be calculated by [135, 156]:

$$d_z = \frac{1}{|k_{zi}|} \quad (2.39)$$

The penetration depth for both dielectric and metallic can be calculated:

$$\text{In metal, (positive } z) \quad d_{z(m)} = \frac{c}{\epsilon_m \omega} \sqrt{\epsilon_m - \epsilon_d} ,$$

$$\text{and in dielectric, (negative } z) \quad d_{z(d)} = \frac{c}{\epsilon_d \omega} \sqrt{\epsilon_m - \epsilon_d} \quad (2.40)$$

Generally penetration depth of SPP in dielectric medium is much higher than in metal. The penetration field in Ag is smaller than in Au due to smaller real component of permittivity value; however it is compensated by higher field in the dielectric film above the metal film. Generally higher permittivity value of dielectric will lead to shallower penetration depth.

2.7. Excitation of SPPs by Light

Electromagnetic (photon) dispersion relation in any dielectric medium (ϵ_d) is governed by:

$$k_{ph} = \frac{\omega}{c} \sqrt{\epsilon_d} \quad (2.41)$$

This value is always lesser than the SPPs wavevector, k_{spp} . The dispersion relation can be presented graphically as wavelength or energy vs wavevector (Fig. 2.7 (b)). For flat metallic/dielectric interface, the k_{ph} will never intersect with k_{spp} [49]. In other word, the incoming photon is not able to couple directly into plasmon i.e. non-radiative wave. Another

consequence is that, the p -polarized light cannot be used to excite SPPs directly, due to its insufficient k_{ph} . Experimentally, there are two coupling techniques to enhance k_{ph} , namely, prism coupling and grating coupling, in order to match the optical momentum at the metallic/dielectric interface [48].

The dispersion relation of SPP is controlled by the difference between metallic and dielectric permittivity, which is given by [49]:

$$k_{spp} = \frac{\omega}{c} \left(\frac{\epsilon_m \epsilon_d}{\epsilon_m + \epsilon_d} \right)^{1/2} > k_{ph} = \frac{\omega}{c} \sqrt{\epsilon_d} \quad (2.42)$$

For complex dielectric functions, the dispersion relation becomes [49]:

$$\begin{aligned} k_{spp} &= k_{ph} \left(\frac{(\epsilon'_m + i\epsilon''_m)\epsilon_d}{(\epsilon'_m + i\epsilon''_m) + \epsilon_d} \right)^{1/2} \\ &\cong \frac{2\pi}{\lambda} \left(\frac{\epsilon'_m \epsilon_d}{\epsilon'_m + \epsilon_d} \right)^{1/2} + i \frac{2\pi}{\lambda} \left(\frac{\epsilon'_m \epsilon_d}{\epsilon'_m + \epsilon_d} \right)^{3/2} \cdot \frac{\epsilon''_m}{2\epsilon'^2_m} \end{aligned} \quad (2.43)$$

Thus the complex value SPPs momentum:

$$\begin{aligned} \Re k_{spp} &= k_{ph} \left(\frac{\epsilon'_m \epsilon_d}{\epsilon'_m + \epsilon_d} \right)^{1/2} \quad \text{and} \\ \Im k_{spp} &= \frac{[\Re k_{spp}]^3}{k_{ph}^2} \cdot \frac{\epsilon''_m}{2\epsilon'^2_m} \end{aligned} \quad (2.44)$$

The SPP field decreases exponentially and proportional to imaginary part of SPP momentum. Propagation length of SPP where its field decreases to e^{-1} is given by [136, 137]:

$$L_{SPP} = \frac{1}{2\Im k_{spp}} \quad (2.45)$$

At 632.8nm incident light, the SPP propagation length at gold/air interface is around 10μm while as silver is utilized; the propagation length can be improved four times larger. As the SPP is generated in denser mediums, i.e. water and prism, the propagation length will be reduced. The propagation length in Ag is longer than in Au due to lower extinction coefficient [130]. Generally higher permittivity value of dielectric (2) will lead to shorter propagation length.

2.7.1. Prism Coupling

The SPP excitation by prism coupling method needs to be done at *total internal reflection* (TIR) [138]. ATR schematic of Kretschmann-Raether configuration is demonstrated in Fig. 2.7 [139]. If we look again at the plasmonic dispersion relation and briefly neglect the small imaginary component of the metal ($\epsilon_m = \epsilon_m'$), the k_{SPP} will always exceed the wavevector of light in air (k_{ph}) unless ω approaches zero. The light travels through a half-cylindrical prism ($\epsilon_d = \epsilon_p$), with its k_{ph} being enhanced to $\frac{\omega}{c}\sqrt{\epsilon_p}$ by a factor of $\sqrt{\epsilon_p/\epsilon_m}$. The dispersion relation before and after the enhancement by the prism are shown as point (1) and (2) in Fig. 2.7 (b), with a slope of $c/\sqrt{\epsilon_m}$ and $c/\sqrt{\epsilon_p}$, respectively. The SPP occurs if the x-component of wavevector matches the k_{spp} :

$$\frac{\omega_{laser} \sin \theta}{c} \sqrt{\epsilon_p} = k_{SPP,x} \quad (2.46)$$

Figure 2.7. (a) ATR schematic of alternative Kretschmann-Raether configuration, (b) The dispersion relation of photons in dielectric film and prism with $\epsilon_p > \epsilon_d$, and SPP before ($K_{spp(1)}$) and after ($K_{spp(2)}$) adsorption. Higher dielectric function lowers the slope of the light line, (c) The dips are representing the resonant coupling. The alteration in dielectric value will change the SPP coupling condition thus result in shifted resonance angle.

The calculated Kretschmann-Raether configuration angular SPR curves of three-mediums (prism/Ag/air, prism/Ag/water, prism/Au/air, prism/Au/water) are represented in Fig. 2.8. All curves show a critical angle θ_c and a resonance angle θ_{SPR} . The θ_c , whose value is affected by the permittivity function of prism and the dielectric medium, indicates the onset of the ATR. At the resonance angle, almost all of the percentage of incoming radiation is transferred into SPP excitation. There will be field enhancement at the interface of metallic and dielectric medium, thus a substantial reduction of the reflectance can be observed [81].

Figure 2.8. Hemi-cylindrical prism coupler SPR and the calculated angular reflectivity for (a) Otto, (b) Kretschmann-Raether and modified Kretschmann-Raether configuration (c).

The Kretschmann-Raether configuration is more versatile due to its robustness [139] and it requires a finite thickness of metal film (Fig. 2.8 (b)) which will influence θ_{SPR} , as well as plasmonic crystal efficiency, i.e minimum reflectivity [48]. To further understand the effect of dielectric constants and thickness, a non-absorbing prism ($\epsilon_{prism}=3.4$), metal film (Au or Ag) and non-absorbing dielectric ($\epsilon_d=1.78$) are considered using $\lambda=633\text{nm}$ and $\epsilon_m=-12.1+1.3i$ for Au ($-17+0.7i$ for Ag) [130, 140].

Small loss in reflectivity is observed due to the absorption of metal [130, 131]. At resonance angle θ_{SPR} , a drastic loss is observed since photon is fully coupled into surface wave (plasmon) and confined at metallic/dielectric interface. Under ATR condition, evanescent fields are generated at the interface [138]. The EM fields in x -direction is continuous at the interface, while based on Maxwell's equations boundary conditions the z -component of E-field is discontinuous and shows a great enhancement at the interface [141]. The simulated reflectivity curves for Otto and Kretschmann-Raether can be observed in Fig. 2.9 and reflectivity simulations for different metallic thickness are illustrated in Fig. 2.10.

Figure 2.9. Reflectivity simulation for Otto and Kretschmann-Raether configuration.

Figure 2.10. Reflectivity curves for Au as a function of incoming angle ($\lambda=632\text{nm}$), for different metal thicknesses.

At the boundary of two different medium with zero loss (due to absorption), the incident light will be reflected and/or transmitted as demonstrated in Fig. 2.11. In such case the momentum at the interface will be conserved.

$$\frac{k_r}{k_i} = \frac{\sin \theta_t}{\sin \theta_r} \quad (2.47)$$

As light incidents at the interface of lower density medium, it may experience total reflection (zero transmission) at a critical angle:

$$\theta_c = \arcsin\left(\sqrt{\frac{\epsilon_m}{\epsilon_d}}\right) \quad (2.48)$$

Thus, the resonance angle may increase with increasing n_m .

Figure 2.11. Diagram of incident (*i*), reflected (*r*) and transmitted (*t*) wavevectors using *p*-polarized light (TM wave) at the interface of two different medium.

2.7.2. Grating Coupling

A grating is a periodically corrugated surface modulation. It can be characterized by its periodicity or grating constant Λ and by its groove depth or rather by the amplitude a , being half of the groove depth. If the in-plane component of incident wavevector of a given order matches the SPP wavevector, plasmons can be excited [49, 54, 55, 57, 61, 89, 122, 142]. For a grating constant Λ , the magnitude of grating vector g equals to:

$$g = \frac{2\pi}{\Lambda} \quad (2.49)$$

As described in Fig. 2.12 (a), the incoming light wavevector, $\left(k_{ph} = \sqrt{\epsilon_d} \frac{\omega}{c}\right)$ pass through the dielectric (ϵ_d) hits a metallic grating (ϵ_m) with a grating constant Λ at an incident angle θ and coupled into SPP. The resonance state of SPP momentum is specified by [143]:

$$k_{spp} = k_{ph} \pm mg = \begin{pmatrix} k_x \\ 0 \\ k_z \end{pmatrix} \pm m \begin{pmatrix} 2\pi/\Lambda \\ 0 \\ 0 \end{pmatrix} = \frac{\omega}{c} \sqrt{\frac{\epsilon_d \epsilon_m}{\epsilon_d + \epsilon_m}} \quad (2.50)$$

with m is the order of diffraction and $g = 2\pi/\Lambda$, the grating vector. The SPP propagation on PCL surface is demonstrated in Fig. 2.12 (b) with two modes at different energy level (the red mode needs to travel longer than the blue one) hence create SPP bandgap [135, 144] which is greatly influenced by materials and geometry of the surface profiles.

Figure 2.12. (a) Schematic of SPR coupling via a grating. In this Ewald-like construction, multiples m of the grating vector g can be added to k_{photon} . (b) SPP propagation on grating. The figure is reproduced from [135]

For a given grating vector, m indicates the diffraction order. When $m > 0$, the SPP is in forward coupling and for $m < 0$ backward coupling takes place [145]. The only parameters allowed are those that conserve the magnitude of the wavevector $|k_{diffracted}| = |k_{photon}|$ (elastic

scattering) and thus lie on a circle in reciprocal space². Vector combinations that exceed the length of k_{ph} require an imaginary k_z because of the relation:

$$|k_{spp}|^2 - \left(k_x + m \frac{2\pi}{\Lambda}\right)^2 = k_z^2 < 0 \quad (2.51)$$

An increment in effective permittivity function of the grating material decreases all the branches of the dispersion relation as described in Fig. 2.13. Focusing on the right half of the Brillouin zone for simplicity (from 0 to $+\pi/\Lambda$); adsorption results in enhancement or decrement of the resonance angle, relying on whether a right (+) or left (-) branch direction.

Figure 2.13. The plasmonic dispersion relation for grating. To excite SPP, a light at resonant frequency (dotted horizontal line) need to intersect with one of dispersion lines. As the light line passes intersect the same point (arrow) at different incident angle, energy and momentum conservation are satisfied and SPP can be generated. This figure is reproduced from [319].

2.8. SPP Response to Effective Refractive Index Function

The SPP field will reach maximum at the boundary two mediums and exponentially decay in dielectric layer at a distance of several hundreds of nanometers. Therefore it is extremely sensitive to any changes in permittivity value of the adjacent mediums [35, 43, 46-49]. By

² This method is identical to the Ewald construction in reciprocal space used in physics to describe the elastic scattering of X-Rays by a three-dimensional atomic lattice. The concept is extremely pictorial and hence simple to understand, in the treatment of grating coupling this advantage is lost since imaginary components of the wavevector are present that can't be shown in real space drawings.

tuning refractive index, the SPP and light transmission through PCL can be effectively controlled. One can perform several methods to engineer the refractive index, such as:

- modifying the geometry/structure of the plasmonic crystal will change the plasma frequency of the metal and the permittivity ϵ_m (Eq. 2.39 and 2.41)
- modifying the dielectric layer on top the crystal - definitely will change the dielectric ϵ_d
- introducing active material which optical characteristics are able to be directed externally by tuning the applied electromagnetic field.

Different structures give unique optical responses. Recent studies have proven transmission enhancement due to periodic nano-holes on metallic film. The light interaction with metallic nanostructure also has an effect on the reflection and absorption [97, 141, 146, 147].

In addition, the presence of dielectric film will alter the effective permittivity and therefore shifts the SPR angle or wavelength [148]. For non-absorbing dielectric film, the shifting will be linearly proportional to the film thickness d and refractive index n :

$$\Delta\theta \propto n \cdot d \quad (2.52)$$

Furthermore, when the dielectric material is doped with optically active materials, the resulting thin layer become absorbing (introduce the extinction coefficient or imaginary part in refractive index) and will disturb the linearity changes in SPP [149-151].

A conventional Kretschmann configuration with 50nm of Au (or Ag) coated prism offers a sensitivity of 5000nm/RIU [25] with detection limit of 3×10^{-6} RIU, i.e. a 3nm thick adsorbate whose index of refraction is 0.1 RIU different than the surrounding medium [152]. However grating coupled configuration (GCSPR), in which the electromagnetic wave is incident on the grating plane [88] has the advantages of portability and affordability [153] though this method currently offers a much lower sensitivity factor of 440nm/RIU and a detection limit of 4.5×10^{-5} RIU [154]. Although the detection limit of the grating is lower than prism coupling method, there still plenty of grating parameters that have not yet been optimized to increase its sensitivity, i.e. the azimuthal angle, 2D structures and geometrical effect. The optimization of these factors may enhance the SPP field and hence increase the sensitivity [62]. The flowchart of engineering refractive index of PCL is shown in Fig. 2.14.

Figure 2.14. SPP response to the changes in effective refractive index.

2.9. Leakage Radiation in SPP

During SPP propagation, there is always certain amount of evanescent wave tunneling from metallic film into dielectric medium and decoupled into propagating light due to momentum conservation (Fig. 2.15). This phenomenon is known as leakage radiation which is greatly affected by the thicknesses of metal-films [135]. Dissipation becomes a major issue for thick metal films. However as the thickness is reduced, the leakage starts to appear which leads to radiation loss thus reduce the L_{SPP} . It is important to choose proper metal to reduce the SPP losses [155].

Figure 2.15. Schematics of (a) incident light being coupled into SPPs (Kretschmann configuration) and (b) outcoupling from SPPs which cause leakage radiation.

2.10. Field Enhancement

A periodic nanostructure on a metal film will exhibit the properties of 1D or 2D PCL if its periodicity is near the SPP's wavelength [49]. The most common form of PCL is metallic gratings. The electromagnetic field enhancement in PCL can reach up to several orders of magnitude. Such huge enhancements are not present in photonic crystals. Most importantly, the PCL allows for the control of optical properties with light [139].

For *p*-polarized radiation, the electric field has two components (*x*- and in *z*-direction) while the magnetic field has only one component (*y*-direction). Since both fields are correlated, the enhancement is calculated for the magnetic field only. The angular magnetic field intensities normalized to the incident intensity are plotted against the reflectivity value in Fig. 2.16 for different mediums. The field intensity reaches a maximum near the reflectivity minimum.

Figure 2.16. Angular reflectivity simulation and the enhancement factor of 3 layer systems (prism/Ag/air, prism/Ag/water, prism/Au/air and prism/Au/water). Prism ($\epsilon=3.4$), Ag ($\epsilon=-17+0.7i$), Au ($\epsilon=-12+1.3i$), HeNe laser (632.8 nm).

The significantly higher enhancement factor on Ag is attributed to its smaller imaginary dielectric constant ϵ'' which results in lower dissipation of optical field [82]. The SPP field is pushed more into the metal by optically denser dielectric (e.g. water) than air, and therefore is more dissipated. Consequently, the field enhancement is lower in metal/water than in metal/air [66]. The non-real part of metallic permittivity, ϵ'' is the lossy component. The fields' enhancement in the two metals was compared and shown in Fig. 2.17, it is noted that the enhancement in Ag is greater than in Au. For the same reason, width at half height of reflectivity and field's enhancement is smaller for Ag.

Figure 2.17. Magnetic (left) and Electric (right) field enhancement at metal-dielectric surface ($\lambda = 632.8$ nm, $\epsilon_{prism} = 3.4$, $\epsilon_d = 1.8$) for 50nm of gold and silver.

2.11. Plasmonic Sensors

As mentioned earlier, the propagation of SPP is very responsive to the alterations in permittivity values at the boundary of metal-dielectric layers; hence the responses could be utilized for sensing purposes [152]. Commonly it is referred to as SPR based sensor. Optical sensor is defined as a device that has sensing capability by optical means; convert the measured quantity (changes in refractive index) to another quantity (output). Alteration in permittivity function of SPR sensor will change the SPP momentum and coupling condition of incident photon to SPP. SPR based sensors have become the most advanced label-free biosensor which are mainly used for the study on the recognitions and interactions of chemical substances and bio-molecules [156, 157]. In more than twenty years, SPR based sensors have made great improvement and served in various applications [27].

2.11.1. Classifications

Generally SPR sensors can be grouped in two big classes, i.e. wavelength and angular modulations [27]. There are others classifications e.g. intensity, phase and polarization modulation; nevertheless they have not been frequently employed due to greater intricacy [30, 156]. In angular type measurement, SPP is excited by a monochromatic light at multiples angles while the wavelength is predetermined. The signal could be adjusted to the effective refractive index for each wavelength. In wavelength type measurement, SPP is excited by broad spectrum light (multiples wavelengths) the incident angle is fixed. The later method has additional disadvantages as a result of the refractive index variation over the wavelength. In order to simplify the analysis, angular modulation is used in most of our experiment.

2.11.2. Sensitivity Measurement

The signal from SPR sensors can be measured either directly or indirectly. In direct measurement, the inputs directly modulate plasmon characteristics (e.g. geometrical effect) [41]. In indirect measurement, the inputs modulate intermediate quantities which afterward change the wavelength characteristics (dielectric layer), e.g. biosensing application [23]. The summary of PCL engineering and the outcomes are demonstrated in Fig. 2.18.

For engineering dielectric layer, usually the molecules are bound to molecular recognition before having contact with PCL to increase the effective refractive index (Δn_b) [24]. This increment will change the SPP propagation, $\bar{k}_{SPP}$ indicated by the shifting in SPP reflectivity dip. Δn_b is controlled by the refractive index changes per unit volume $(\partial n / \partial c)_{vol}$ of analyte multiplied by the changes in concentration Δc_v (mass/volume) which given by [27, 156]:

$$\Delta n_b = \left(\frac{\partial n}{\partial c} \right)_{vol} \Delta c_v \quad (2.53)$$

Figure 2.18. (left) Engineering refractive index of plasmonic crystal (PCL) by controlling: geometry and dielectric layer with absorbing molecules on metal surface will alter the total refractive index of the sensor therefore modifying the SPP magnitude and propagation which is noted by: shifting in resonant angle and wavelength, polarization angle or phase intensity. (right) Angular (top) and wavelength (bottom) modulation SPR measurement for two different refractive indexes.

Where Δc_v equals to $\Delta c / d$, changes in concentration divided by dielectric film's thickness. The most important parameters in describing the performance of SPR sensors are sensitivity, resolution and limit of detection [24, 27, 158, 159]. The challenges are to improve these parameters which become the major discussion in this thesis. This could be accomplished by controlling PCL's geometry, utilizing azimuthal angle and polarization angle. However the first one will provide greater contribution relative to the rest.

Resolution has become one of the most vital factor in plasmonic sensors due to its ability to measure smallest refractive index changes and turn it into detectable signal [152]. The output signal is greatly affected by the level of uncertainty and noise. Both can be from equipment or environment. The reproducibility of signal needs to be maintained for identical the molecules (refractive index value) under the similar conditions for certain period [27]. The detection limit of sensor is another vital issue which refers to the smallest concentration that still can be sensed.

Generally the sensitivity measures the shift in output relative to the difference in the analyte concentration. It can be grouped into two contributions namely: the changes of output to refractive index and the changes in total refractive index due to the variation in analyte concentration [27, 30, 156, 157].

The changes of output to refractive index are affected by method of SPP excitation (instrumental contribution) as well as the effective refractive index changes. For angular modulation, the changes of output equals to angular shift.

2.11.3. Plasmonic Sensor Types

The plasmonic based sensor can utilize the property of short, long or localized surface plasmon. Short range plasmon based sensor can be classified into high refractive index coupling and periodic nanostructures [27, 30, 157]. Long range plasmon based sensor is done on waveguide mode and the localized SPR are realized on nanoparticles and nanowires. In addition, most PCL couplers provide unique optical responses in transmission mode and therefore can be classified as another group of sensors [32, 46, 153, 160, 161]. Currently, the resolution of SPR sensors are able to reach 10^{-7} refractive index units (RIU) [156, 157].

2.11.4. Prism Coupling Based Sensors

Additional analyte at the interface will change the effective dielectric function of the SPR system and bend k_{spp} curve to higher wavevector (Fig 2.19 (top)) and thus shift the excitation condition (resonant wavelength and angle) according to plasmonic momentum conservation equation as shown in Fig 2.19 (bottom) [162]. Consequently, a larger resonant angle (or lower wavelength) is required. Generally dielectric has very small extinction coefficient and can be considered as a non-absorbing medium thus the shifting in resonant angle $\Delta\theta$ is linearly proportional to the film thickness [27, 156]. However for bio-chemical molecule, $\Delta\theta$ is pretty much affected by the concentration. The presence of metallic nanoparticles in the dielectric medium will increase the absorption and distort the SPR characteristics [163].

Most of commercial SPR sensors are based on prism coupler, such as Biacore from GE Healthcare [164], XanTech bioanalytic [165], Autolab from Metrohm [166], BI series from Biosensing Instrument USA [167], Spreeta sensor from Texas Instrument [168], Multiskop system from Optrel [169], SPR LAB from Korea Materials and Analysis Corp. (K-MAC) [170], SPR* 100 from Thermo Scientific [171], SR 7000 platforms, double channel SPR from Reichert Analytical Instruments [172, 173], IBIS-MX96, an imaging SPR system from IBIS Technologies [174], Plasmonic from Hofmann Sensor systeme [175], SPRimager® II from GWC Technologies [176], Nanofilm SPR from Accurion GmbH [177], SPR-20 from DKK-TOA [178], BIOSUPLAR 6 from Analytical μ -Systems [179], SPRi-series from Genoptics [180], SPR-2 from Sierra Sensors GmbH [181] and Sensia β -SPR Research Platform [157].

Figure 2.19. The changes in SPP curves dispersion due to thin dielectric film and. A change in resonance angle from θ to θ' is observed by using the prism-based coupling SPR.

Biacore is one of the most common SPR systems and having the highest market share. The summary of commercialized SPR sensors is given in Table 2.2

Table 2.1. Commercialized SPR Sensors

Brand	Description	Claims	Ref
Biacore	Sensor is attached with imaging system that allows the projection of reflection from each channel on separate area of detector's array with 4 multiple sensing channels	$R \leq 1.0 \times 10^{-7}$ RIU	[164]
Xantec	Excellent baseline stability and a compact size 40×33cm	$R \leq 1.8 \times 10^{-7}$ RIU	[165]
Reichert Analytical Instrument	Dual channels, can be coupled with mass spectroscopy, liquid chromatography as well as fraction collectors for chemical analysis	$R \leq 3.5 \times 10^{-4}$ RIU	[173]
IBIS technologies	Imaging SPR with lateral resolution down to 25μm	$R \leq 2.0 \times 10^{-5}$ RIU	[174]

R is resolution (unit in RIU), S is sensitivity (unit in °RIU or nm/RIU)

Besides the commercialized one, there are lots of prism coupler SPR sensors that are still under development with many promising features and better performances that are reviewed and presented in Table 2.3.

Table 2.2. Prism coupler SPR sensors

Author (Name)	Description	Claims	Ref
Mastubara, et. Al.	Multi photodiode array enables the reconstruction of the angular reflected divergent spectrum with 0.01° accuracy.	$R \geq 5.0 \times 10^{-5}$ RIU, $S \leq 200$ °/RIU	[182]
Zhang, et. Al.	Self-referencing configuration with angular interrogation, with 2×2 photodetectors to replace photodiode array. The system is able to record four intensities at one time using 635nm red laser	$R \geq 1.0 \times 10^{-7}$ RIU, $S \leq 130$ °/RIU	[183]
Campbell, et. Al.	Imaging SPR with 120 channels. The images can be obtained simultaneously for different incident angles	$R \geq 5.0 \times 10^{-6}$ RIU	[184]
Piliarik, et. Al.	Polarization contrast to detect small oligonucleotides (23 mers) with 64 channels	$R \geq 2.0 \times 10^{-6}$ RIU, LOD ≤ 0.1 nm	[185]
Nenniger, et. Al.	Wavelength interrogation with halogen light source. Multimode optical fiber is used to produce collimated beams with 50nm Au film sensor chip attached on prism.	$R \geq 2.0 \times 10^{-7}$ RIU, $S \geq 7500$ nm/RIU, LOD $\leq 1.5 \times 10^{-3}$ nm	[186]
Homola, et. Al.	Dual-channels with original signal separation using dielectric overlayer to sense the surface and bulk background signal simultaneously.	Accurate signal with background reference	[187]
Guo, et. Al.	Dual modes: long range (L) and short range (S) SPR using one wavelength in angular interrogation. The S_{SR} is still comparable to typical single-mode method.	$S_L \leq 9.92$ °/RIU $S_S \leq 103.4$ °/RIU	[188]

Kawazumi, et. Al.	Miniaturization angular SPR with Kretschmann configuration with four micro channels. 2D images captured by CCD camera at resonance condition are analyzed. Trapezoid prism is used for compacting purpose and laser alignment. The detectability of the system is examined using salt at diverent molarities.	$R \geq 1.0 \times 10^{-6}$ RIU, Size 6.5×3.8×6cm S to ppb levels ≈ conventional SPR system	[189]
Spreeta 2000, Melendez, et. Al.	Miniaturized SPR prism coupler sensor with plastic prism, near infrared LED light source (830nm) and array of photodiode with resolution of 128 pixels. Noise $\leq 2 \times 10^{-7}$ RIU. The noise and signal quality were examined by Chinowsky et al. [190]	$R \geq 8.0 \times 10^{-5}$ RIU, Size 1.5×0.7×3cm	[191, 192]

R is resolution (unit in RIU), S is sensitivity (unit in %RIU or nm/RIU), LOD is limit of detection (unit in nm)

2.11.5. Plasmonic Crystal Based Sensors

The use of plasmonic crystal (PCL) based sensors was pioneered in 1983 by W. Lukosz and K. Tiefenthaler [193] in the form of grating couplers (GC) which makes use of the physics of a diffraction. The resonance angle is affected by on the thickness and refractive index molecules embeded on top of the grating. The grating's amplitude and period will control the resonance wavelength and need to be optimized.

The working principle for grating coupled surface plasmon resonance (GCSPR) sensor is similar to Prism Coupler (PC) with the difference of using grating for replacing the glass prism [49, 143, 194]. As the surface of metallic grating is modified (physically or chemically), the effective refractive index and the SPR excitation condition will be changed (Eq. 2.25), noted by a shifting either in resonance angle or wavelength [29, 195].

PCLs have received less attention compared to PC SPR sensors due to their lower sensitivity [196]. However, from mass production point of view, PCL offers an attractive approach for low cost fabrication sensing chips by means of imprinting method. In addition, it also offers the possibility of miniaturization and integration into a system. Furthermore, cumbersome optical alignment can be avoided. In recent times, efforts to enhance the limit of detection based on PCL systems are reported and some are recapped in Table 2.4.

Table 2.3. Plasmonic crystal based sensors

Author (Name)	Description	Claims	Ref
Thirstrup, et. Al.	Plasmonic grating is used to diffract the incident light which is focused, collimated into a small beam on SPR chips and captured by a 2D photodetector	$R \geq 5.0 \times 10^{-7}$ RIU, S $\leq 140^\circ$ /RIU	[195]

Hu C.	Au-Al bi-metallic grating SPR exhibit negative diffraction order. Al shows a very narrow SPR dips hence amplifies the signal and improves the detection limit	$S \leq 187.2^\circ/\text{RIU}$	[145]
Piliarik	Angular SPR imaging with 6×36 sensing channels ($0.5 \times 0.5\text{mm}$ each). A collimated monochromatic beam is focused onto a row - flow channel then reflected back to cylindrical lens, re-collimated and aligned onto a imaging lens and captured by 2D CCD array	$R \geq 5.0 \times 10^{-6} \text{ RIU}$	[197]
P. Adam	Simultaneous excitation of multiple SPP using a multi-periodic grating. Polychromatic light incident on grating with five harmonic components; hence multiple SPR dips can be obtained (one for each periodicity).	multiple SPR dips	[40]
J. Homola	Short-range (SR) and long-range (LR) SPP sensor similar to [188], however specially designed grating is employed. The grating's structure is $\text{AlF}_3/\text{Au}/\text{Water}$, AlF_3 is chosen because similar refractive index as water ≈ 1.33 -1.34.	$R \geq 3.5 \times 10^{-6} \text{ RIU}$	[157]
Telezhnikova, et. Al.	SPR coupler and disperser (SPRCD) with collimated polychromatic light incident on grating, 2 nd diffraction order will be coupled to SPP, while 1 st order is dispersed and directed to a different position detector	$R \geq 3.0 \times 10^{-7} \text{ RIU}$, $S \leq 695\text{nm}/\text{RIU}$	[198]
Piliarik, et. Al.	Development SPRCD with compact sensor consisting of optical bench, microfluidics and supporting electronics, size around $15 \times 15\text{cm}$ and noise $\leq 2 \times 10^{-4} \text{ nm}$	$R \geq 3.0 \times 10^{-7} \text{ RIU}$, $S \leq 620\text{nm}/\text{RIU}$	[199]
Y. H. Cho, et. Al.	Disposable multi-channel nanograting SPR sensor chip to sense the small concentration of antibiotic 2-50 nM.	$S = 321.78$ - $514.26\text{nm}/\text{RIU}$	[200]
Cai, et. Al.	Improve the sensitivity using Double-dips method by optimizing both 1 st and 2 nd diffraction order of SPR dips.	$S \leq 237\text{nm}/\text{RIU}$	[201]
Alleyne, et. Al.	SPR grating system with a prism is used to enhance light momentum in exploring the bandgap region.	$S \leq 680^\circ/\text{RIU}$	[62]
Kubo, et. Al.	2D concentric Au nanorings with tunable gap (33nm) in wavelength modulation (1350-1550nm) may enhance the SPP field and offer high refractive index sensitivity	$S \leq 1075\text{nm}/\text{RIU}$ $\text{FOM} \geq 18.1$	[202]
N. Liu, et. Al.	Highly controlled 2D Au nanodisk on glass, 200nm Au layer and 30nm of MgF_2 film to obtain the maximum coupling efficiency with $\Lambda=600\text{nm}$, diameter and thickness of 352nm and 20nm respectively.	$\text{FOM} \geq 87$ $S \geq 400\text{nm}/\text{RIU}$, higher than Au nanorod [203]	[204]
H. Gao, et. Al.	2D inverted pyramids Au PCL with microfluidic channel for real-time detection based sensor in wavelength modulation with $\Lambda=400\text{nm}$ and 150nm of Au thickness.	$\Delta\lambda=3.6 \times 10^{-4} \text{ nm}$, $R \geq 9.7 \times 10^{-7} \text{ RIU}$, $S \leq 375\text{nm}/\text{RIU}$	[205]

R is resolution (unit in RIU), S is sensitivity (unit in $^\circ/\text{RIU}$ or nm/RIU), FOM is figure of merit

Although the sensitivity of PCL SPR based sensors are generally lower than prism coupler SPR sensor, there are still plenty of room for PCL modifications to improve the field enhancement and sensitivity. This will be the challenges and main focus in this thesis

2.11.6. Transmission SPR Sensors

Similar to reflection mode, transmission can be used as another sensing method. The contribution of plasmonics in transmission has been studied by many groups and the property is used for sensing purpose [92-96, 98, 99, 101, 206, 207]. The summary of transmission SPR sensors is presented in Table 2.5

Table 2.4. Transmission SPR sensors

Author (Name)	Description	Claims	Ref
Miyamaru, et. Al.	Periodic holes are used to sense in the terahertz (THz) region. The sensitivity is measured near the resonant transmission for SPP. The frequency shifting is mainly caused by the variation in permittivity value.	detect very low concentration of molecule	[208]
Brolo, et. Al.	Au nanoholes to observe the functionalization process of organic and bio-molecules.	$S \leq 400\text{nm/RIU}$ $\approx$ grating sensor in reflection mode	[209]
Byun, et. Al.	Using plasmonic grating in transmission mode	$S \leq 70^\circ\text{/RIU}$	[210]
C. Hu, et. Al	SPP coupled to radiation modes on 1D dielectric grating with 40nm Ag evaporated on prism (Kretschmann). $\Lambda=0.6\ \mu\text{m}$ with ratio of width to spacing equals to 1:1. Reflectivity can also be measured as complimentary data.	$S \leq 51.2^\circ\text{/RIU}$ (TM wave)	[145]
Yanik, et. Al.	2D nanoholes on Si_3N_4 membrane to detect live viruses at very low concentration. $\Lambda=600\text{nm}$, holes diameter of 200nm on 5nm of Ti and 100nm of Au. Reference sensor is needed to compare the resonance condition.	$\text{FOM} \leq 40$	[211]
N. Liu	- shape array on 30nm Au film exhibits transparency at visible range. The thickness and width of the structure are 400nm and 670nm with $\Lambda=800\text{nm}$ in both directions. Dip splitting in reflectivity spectra is clearer as the horizontal stripe is moved further from centre of symmetry	$S \leq 588\text{nm/RIU}$, $\text{FOM} \leq 3.8$	[212]

R is resolution (unit in RIU), S is sensitivity (unit in $^\circ\text{/RIU}$ or nm/RIU), FOM is figure of merit

2.11.7. Differential SPR Phase Measurement

New classification of plasmonic sensor is based on phase difference measurement. Instead of only measuring the reflectivity and transmission spectra, this advanced system measures the changes in phase of incident beams with respect to reference beams. A brilliant idea to combine a prism coupled SPP and phase measurement is suggested for the first time by Abelès in 1976 [213]. The phase-based sensitivity measurement is proven to serve high sensitivity compared to ordinary SPR on metal thin film or refractive index of media on the sensor surface, and therefore becomes an attractive sensing technology [214]. The phase measurement is susceptible to alteration both in permittivity values and thicknesses. The

phase sensitivity measurement is predicted to reach sensitivity 2 to 3 orders larger than the conventional one [215, 216]. Differential SPR phase sensors are summarized in Table 2.6.

Table 2.5. Differential SPR Phase sensors

Author (Name)	Description	Claims	Ref
S.G. Nelson, et. Al.	Experimental and simulation of optical heterodyne phase detection SPR sensor. The modeling result shows a strong effect on films thicknesses.	$R \geq 5 \times 10^{-7}$ RIU	[159]
H. P. Chiang, et. Al.	Optical heterodyne phase detection SPR sensor with monitoring the change the temperature.	Able to monitor temperature change	[217]
Wu, et. Al.	Phase shifting mach-Zehnder-SPR using two beams in parallel, the probe (<i>p</i> -polarized) and the reference (<i>s</i> -polarized) beams in identical optical paths. The phase difference between two polarization states at resonant condition can be measured with minimizing the noise.	$R \geq 5.5 \times 10^{-8}$ RIU 0.01± phase change.	[216]
Markowicz, et. Al.	Polarization measurement in frequency modulation equipped by phase retarder, photoelastic modulator and polarizer to enhance the phase-sensitivity of SPR based sensors by employing <i>s</i> -polarized light as a reference.	Higher harmonic serves as sensitive tool to measure the phase responses.	[215]
I. R. Hooper, et. Al.	Differential SPR ellipsometry to detect changes in permittivity function where TE wave serve does not undergo phase changes (reference), while TM wave does. This measurement was done using prism coupled SPR	$R \geq 2.0 \times 10^{-7}$ RIU	[115]

R is resolution (unit in RIU)

2.11.8. SPR Waveguide Sensor

In general, waveguide coupler SPR sensor is fabricated by removing silicon cladding from a little part of the fiber optic, and evaporated with metallic film. The coupling of the SPPs in the waveguide is mainly controlled by frequency, geometrical parameters of optical fiber such as size, shape and metal coating. Most miniaturization efforts among the SPR sensors are done using plasmonic optical fiber based sensors. The first generation of plasmonic optical fiber sensors were reported two decades ago [218-220]. The transmission signal from coupling effect can be obtained at fixed frequency/wavelength (intensity-modulated sensor) or wavelength interrogation. Summary of SPR waveguide sensors is shown in Table 2.7.

Table 2.6. SPR waveguide sensors

Author (Name)	Description	Claims	Ref
R. Slavik, et. Al.	Power modulated single mode plasmonic optical fiber sensor. The working region of the bare gold SPR structure is 1.42–1.41 and 1.33–1.34 for PCL SPR	$R \geq 2.0 \times 10^{-5}$ RIU	[221]

C. Rashleigh, et. Al.	The main drawback of [221] is the fiber deformation due to bending and twisting will cause polarization losses and influences the resonance conditions and intensity mode.	high birefringent (HiBi) fiber is used protect polarization states in the fiber	[222]
R. Slavik, et. Al	Wavelength-modulated with unpolarized radiation is used to replace the expensive HiBi fibers. Sensitivity may decrease to 3×10^{-5} RIU during deformations	$R \geq 5.0 \times 10^{-7}$ RIU	[223]
M. Piliarik, et. Al.	Specially designed fiber to uphold the polarization	$R \geq 2.0 \times 10^{-6}$ RIU	[224]
M. H. Chiu, et. Al.	Single mode plasmonic fiber optic sensor using D-shape fiber and heterodyne interferometry	$R \geq 2.0 \times 10^{-6}$ RIU	[225]
H. Y. Lin, et. Al.	System with a side-polished multi-mode optical fiber	$R \geq 3.0 \times 10^{-6}$ RIU	[226]
J. Dostalek, et. Al.	advanced waveguide sensor in wavelength modulation	$R \geq 1.0 \times 10^{-6}$ RIU	[227]
J. Vörös, et. Al.	Integrated optical grating coupler biosensors to record the alteration of index of refraction. Motorized detector stage is finely controlled with resolution smaller than 0.0001° .	$R \geq 1.0 \times 10^{-6}$ RIU	[29]
Y. Lim, et. Al.	Tapered optical fiber SPR (wavelength and angular modulations) can detect alteration of permittivity function in both vapour and liquid phase independently hence two SPP dips can be observed simultaneously The sensitivity can be further enhanced (15 times) by Teflon dielectric layer sandwiched between metal and tapered fiber core.	$R \geq 1.0 \times 10^{-6}$ RIU	[228]

Besides propagating surface plasmon classes of sensors mentioned earlier i.e. short range SPP excited by prism and plasmonic crystal as well as long range SPP on waveguide mode, there is another class that has not been discussed i.e. localized surface plasmon (LSP) which is excited by metallic nanoparticles. The strength of plasmonic field in LSP is greatly affected by materials, sizes, shapes and concentrations. Most extensive study related to this LSP was done by Van Duyne' research group from Northwestern University [153, 161, 229], Hallas and Norlander's group from Rice University [230, 231]. However the LSP does not give superior effect in sensing capability. From direct comparison that has been done by Svedendahl, et. Al., it is demonstrated that the detectability and FOM of propagating SPR is twenty times greater than LSP [232]. The LSP was exhibited on Au nanodisk synthesized using mask colloidal lithography with 30nm of thickness and 120nm of diameter. The resonance condition of this localized SPR is happened at around 700nm with sensitivity as high as 178nm/RIU and FOM is about 2. The propagating SPR is measured using prism coupler method on 50nm Au film with sensitivity as high as 3300nm/RIU and FOM equals to 54 for refractive index = 1.33 [232]. Due to the low sensitivity and FOM value, plasmon excitation using nanoparticles will not be discussed.

3 Experimental

3.1. Nanofabrication of Plasmonic Crystal

To study the control of SPP in a plasmonic crystal, 1D and 2D plasmonic crystal models are proposed as a working platform. Most of these models can be made by interference lithography method [22, 106, 233].

3.1.1. The Lloyd's Configuration

Fabrication of periodic nanostructure can be realized using two beam (arms) interference system (Mach-Zehnder). The optical path length of these two arms ideally needs to be identical. A minor mismatch in length will reduce the contrast function and depart from constructive interference condition. The system is very sensitive to vibration and beam motion; however Lloyd's configuration is generally unaffected by these problems. In Lloyd's setup, only one arm is employed [234]. The vibration is not the issue in this configuration since the mirror is always fixed relative to the sample holder. This makes Lloyd's mirror more stable and phase locking setup is no longer required.

Due to two identical arms, in Lloyd's Mirror Interferometer, one arm can be simply replaced by 90° mirrors. Lloyd's mirror is rigidly fixed perpendicular to the surface and used to reflect back a portion of wavefront back to the other half (Fig. 3.1).

The periodicity of gratings could be controlled by changing the angle of mirror/substrate and incoming beam. The grating constant is given by $\Lambda = \lambda / (2 \sin \theta)$.

Figure 3.1. Basic Lloyd's mirror configuration.

The advantageous of this Lloyd's configuration are:

- (1) Relatively uncomplicated and only require few optical elements.
- (2) Short optical path length. Periodicity can be adjusted by changing incident angle.
- (3) Both exposure and development process can be done immediately using additional developer compartment. Refractive index of developer is around 1.34 can be used to squeeze the grating periodicity down to 120nm using a laser with $\lambda=325\text{nm}$.

(4) A lens can be incorporated to the system to pattern chirped shape and curved gratings.

In Mach-Zehnder system, there is no optical element after the spatial filter; hence all disturbances can be suppressed. Here Lloyd's mirror becomes another optical element after spatial filter, hence all imperfectness from mirror will reflect to the pattern directly. Hence the flatness and the cleanliness of the mirror are very critical; otherwise the grating produced can be easily distorted [105, 106]. However the intensity of two arms in Lloyd's mirror will never be equal, because of the non ideal reflectivity of the mirror, thus will decrease the fringes' contrast. The IL setup with Lloyd's configuration is demonstrated in Fig. 3.2

Figure 3.2. Diagram of a Lloyd's configuration in laser interference lithography. The sample holder and the metallic mirror are perpendicular each other, and covered by expanded incoming beam. The periodicity of the gratings can be adjusted by rotating the stage.

3.1.2. Plasmonic Crystal Fabrication

1D and 2D PCL with pitch and amplitude match for SPP generation is able to be fabricated via IL according to the steps illustrated in Fig. 3.3. Initially, the grating pattern is recorded in photoresist layer. The sample is subsequently etched fix the structure on certain substrate. Adding a metallic film of suitable thickness on top of the profile completes the PCL fabrication. Since the Au can easily be removed from the glass without substrate attrition, new evaporation of Au allows multiple usages of PCL. Nanoimprinting can be a complementary technique in order to create series batch of identical samples [235-239].

Figure 3.3. Several steps of grating fabrication: (a) cleaning of the substrate, (b) deposition of a photoresist film by spin coating, (c) record the grating pattern from beams interference, (d) transfer of the surface relief into the glass by reactive ion beam etching, (e) metals evaporation.

3.1.2.1. Substrate Preparation

The substrates can be varied from Si wafer, quartz or BK-7 substrates. The Si substrate is favored because of the availability, better flatness and opacity. The wafer was sliced into 1×1 inch and washed in piranha mixture for 15 minutes. The solution can be prepared from three part sulphuric acids mixed into one part of hydrogen peroxide. The exothermic reaction may remove organic contaminants from the samples and oxidize metallic layer. The samples were then rinsed several times using deionized water for 15 minutes. The substrates should now be hydrophilic then blown dry with the N₂. The samples are further dried (dehydration) in the oven at 120°C for 10 minutes. BK-7 and quartz substrate are often evaporated using thin chromium layer to improve the adhesion of the photoresist film to surface, so that this film does not detach during development and ion etching. The back surface of the BK-7 and quartz need to be coated with absorbing layer to reduce the back reflection.

3.1.2.2. Photoresist Deposition

Most of materials may oxidize rapidly and absorb extensive H-bonds with H₂O that cause very poor bonding. Most of substrate's surfaces are hydrophobic and a primer needs to be deposited to improve its adhesion with resist. Primers for Si, SiO₂, and other metal oxides are 3-hexamethyldisilazane (HMDS), Trichloro phenylsilane (TCPS), C₆H₅SiCl₃ or Bistrimethylsilacetamide (BSA), (CH₃)₃SiNCH₃CO-Si(CH₃)₃ [106]. For positive resist, HMDS was applied on Si wafer. For glass substrate; the surface was treated with silane (Microposit UN 2924, Shipley) and left exposed for 30s.

During spin coating, the substrate was put on the spinner using the alignment tool under vacuum. Positive-resist Shipley-1805 was mixed in EC-solvent (both from Microposit®, Shipley) with volume ratio: 2 to 3, to obtain desirable thickness.

Figure 3.4. The ellipsometry modeling shows a very good matching between the photoresist spectra and the modeled Cauchy layer using generation oscillation method (genocs). The thickness is found to be consistent (around 139-141nm) for average of 10 samples under same condition.

Figure 3.5. (left) Photoresist S1805 thickness vs spin speed (RPM), (right) S1805 thickness vs concentration.

The spinning rate was divided into few steps: 2000 RPM for 1s, 3000 RPM for 1s and 5000 RPM for 30s and the acquired film thickness is around 130-140 nm as measured using ellipsometer (Fig. 3.4). The film's thickness is greatly affected by rotation speed, viscosity, concentration (Fig. 3.5) and molecular weight of resist.

This photoresist film was soft baked at 90°C for 12 minutes before exposure. The purposes are to modify the resist characteristic, evaporate partially photo-resist solvents, improve bonding, thickness regularity and geometrical control (aspect ratio).

3.1.2.3. Exposures

40mW and 30cm coherence length of HeCd laser ($\lambda=325$ nm) and high flatness Al coated mirror ($\lambda/20$) © Pyrex were used. The grating constant is give by: $\Lambda = \lambda / (2 \sin \theta)$. θ is the angle between incoming beam and mirror. For example, $\theta=19^\circ$, $\Lambda=500$ nm; $\theta=24^\circ$, $\Lambda=400$ nm.

Figure 3.6. Schematic of Lloyd's mirror with incident light angle θ .

The Lloyd's mirror as shown in Fig. 3.8 needs to be precisely 90° in order to fulfill the angle relation from mirror reflection (θ' to be equal to θ), otherwise

$$\theta' = 180 - 2\alpha + \theta \quad (3.1)$$

α is the angle between sample plane and mirror. The grating period relation to incident angle for HeCd laser ($\lambda=325$ nm) is demonstrated in Fig. 3.7. The fringe area (area of beam reflected by mirror that reaches the substrate) is restricted by the mirror's size as well as

incident angle. The fraction of mirror to fringes area is given by $\tan \theta$ (where $0^\circ < \theta < 90^\circ$). For larger periodicity, the incident angle becomes smaller; consequently the fringe area formed by the interference is reduced.

$$\text{Width of fringes} = \text{length of mirror} \times \tan \theta \quad (3.2)$$

Figure 3.7. Grating period relative to incident angle exposed by HeCd laser ($\lambda=325$ nm).

The beam power after passing through $5\mu\text{m}$ pin hole ought to be larger than $1\text{mW}/\text{cm}^2$ as measured by power meter. The exposure period is controlled by resist's threshold (about $18\text{mW}/\text{cm}^2$), divided by the laser power measured at distance d from the pinhole, just around the centre of Lloyd's mirror. The larger d is chosen to get larger and homogeneous area of the expanded incoming beam with plane wavefront.

3.1.2.4. Single and Double Exposures

Single exposure will result in 1D pattern (grating), however 2D structure can be made by double exposure at particular angle (Fig. 3.8 and 3.9). Double exposure at 90° substrate rotation will produce array of holes (negative resist) or pillars (positive resist) with square lattices; where 30° substrate rotation will produce hexagonal lattice.

Figure 3.8. (a) and (b) Single exposure produces a grating. Double exposure can produce (c) and (d) periodic nanoholes when negative resist is used or (e) periodic of posts when positive resist is used.

In IL, the periodic structures are formed on positive/negative photoresist exposed by standing wave from superposition of two or more coherent beams with relatively similar intensities which will create periodic lines in the resist and the pitch equivalent to $\lambda/(2\sin \theta)$. After the first exposure, 2D structure can be produced by rotating the substrate

at any angle, and exposed for a subsequent time. For identical intensity and exposure period, the total incoming dose is given by [105, 106]:

$$I = A \sin^2\left(\frac{\pi}{p}x\right) + A \sin^2\left(\frac{\pi}{p}y\right) \quad (3.3)$$

Figure 3.9. (a) Single exposure can form a 1D PCL with $\Lambda=500\text{nm}$. (b) Double exposure can produce $250 \times 360\text{nm}$ periodicity of posts when positive resist is used.

Constructive interference will have higher intensity and shown as maxima and perpendicular to the profile. However the destructive interference will lead to minima and shown as the valley. There is another area in between peak and valley that is referring to saddle points. The maximum total energy at constructive interference (maxima) can reach up to $2A$, and for the opposite can be as low as 0 and at saddle point will be about A with certain assumption that the two beams are identical [105, 106].

A major goal of process control in IL is control of the linewidth [234]. This is important to control plasmonic crystal's geometry which influences the coupling efficiency. When imprinting is used, the templated processes are often strongly dependent on the linewidth as well. A further complication with many IL systems is that the exposure dosage may fluctuate across the exposure region, so the linewidth will vary as well [234]. Understanding the response of the photoresist to changes in image characteristics is important both to produce a desired pattern and to understand the limit of structural geometries.

3.1.2.5. Interference Lithography Simulations

ILSim is interference lithography simulator for high numerical aperture (NA) that shows the image calculation and optimization using Amphibian XIS platform [240]. ILSim can also be used to simulate the interference using fluid immersion, polarization change, multi films reflectivity/transmission and field coupling and it can be explored for imaging using two, three, four or five beams at very high NA [240]. The optimum imaging condition and optical

responses of multi thin films such as fluid media, photoresist, top-layers, and anti reflective (AR) coatings can be calculated. The input optical parameters may include the wavelength, incident angle, periodicity, polarization angle (from TE to TM or non-polarized), NA (from objective lens) and demodulation (for defocus correlation). ILSim can be used to plot two and three dimensional intensity of interfered beams. The result for two beams can be array of lines (gratings) and three to five beams may produce 2D and 3D structures.

The detail about mathematical calculation used in ILSim is described in ILSim paper [240]. The doses contrast is shown in the simulation result as 2D. This contrast will justify whether the film stacks are suitable to be exposed with control over the amplitude of the resist corrugation. This simulation also helps to decide the best resist thickness and control the unexposed resist that may form a residual layer upon development process. This layer may inhibit further process such as pattern transfer through RIE. Some simulations of 1D and 2D pattern on resist are shown in Fig. 3.10.

Figure 3.10. 1D and 2D images on positive resist, obtained from ILSim simulations of interference patterns: (a) gratings obtained using two beams; (b) corrugated lines, obtained by using three-beams with beam orthogonal to one another, however the doses are different.

Some experimental parameters:

- Wavelength (λ) = 325 nm, power (P)=30mW
- Si wafer: thickness = 0.7mm, $n=3.962+0.021i$
- ARC (SiO₂): thickness = ~2nm, $n=1.47$
- HMDS: thickness = 2nm, $n=1.408$
- Resist: S1805, 2:3 to the thinner; thickness = 139.16nm, $n=1.6277+0.004366i$
(Obtained using point by point and confirmed by genocs method [114] with error <0.5%)
- Environment = Air, $n=1$

- Numerical Aperture = 0.13

3.1.2.6. Development

The exposure to the laser light induces a photochemical reaction in the photoresist that promotes solubility in the developer solution (CD 30, Microposit®, Shipley European Limited, U.K.). The remaining un-illuminated material remains insoluble. Optimal illumination and development times depend strongly on the laser power. It is typically in the order of 30s, but it has to be determined precisely for each batch. For photoresist S1805, it is not necessary to do post baking.

3.1.3. Modified Lloyd's Mirror

2D PCLs previously were fabricated using double exposure of interference lithography (IL). Using Lloyd's mirror which contains two identical beams, a 1D PCL (line pattern) can be created by single exposure only. 2D PCLs require second exposure by rotating the sample at certain angle. However there are several crucial stages that may reduce the probability of producing the 2D structures, namely:

- Longer exposure timing and sample rotation due to second exposure will lead to higher disturbance such as beam scattering due to small particles in the air and low throughput
- Photoresist responses during second exposure will be different from the first one, hence need to have exposure dose adjustment
- Non-symmetrical shape (deformed structure) of array structure for non orthogonal double exposures ($\alpha \neq 90^\circ$). The shape tends to be sharper at smaller angle ($\alpha < 90^\circ$), e.g. hexagonal array [241]
- The repeated quality is poor due to too many parameters (exposure time, angle of rotation, vibration, etc.)

These can be solved by independently adjustable three and four lasers IL system. However the cost for the additional lasers is quite significant furthermore the alignment can be more complicated than a Lloyd's interferometer as well as in changing the periodicity. Another possibility to solve the problem is based on development of modified J. Boor's three -beam Lloyd's mirror interferometer setups [241] in which the additional mirrors (two or three) are introduced to the Lloyd's setup so that the incident beam and its reflections from the mirrors

generate a periodic-regular interference pattern on the photoresist. This setup is very flexible which allows fabricating 2D PCL structures at any lattice symmetry (square, hexagonal or arbitrary angles) as shown in Fig. 3.11 using only single exposure.

Besides cutting some complicated steps (alignment, etc) and the need of additional lasers, this three and four beam setups offer similar advantages as the Lloyd's mirror. These include the large fabrication area (as large as the mirrors size), simple setup, and ease to control the periodicity. The trade-off of using mirror is the reduced intensities due to the reflectivity coefficient of the mirrors that highly dependent on wavelength and incident angle [241]. Choosing high flatness mirror with appropriate coating will be very crucial to reduce the beam scattering, high absorption and transmission; hence a good resolvable pattern can be obtained. Nevertheless, the 2D periodic array can be produced by single exposures that shrink time and effort. The wavevectors equations as well as the periodicities for both three and four beams modified Lloyd's mirror configuration can be found in Appendix B.2.

Figure 3.11. The arrangement of the mirrors for a) standard 2 beams Lloyd's mirror interferometer, b) modified 3 beams interferometer using 2 mirrors and c) modified 4 beams interferometer using 3 mirrors and the formed patterns for $\alpha=\alpha_1=\alpha_2=120^\circ$. $k=|k|=2\pi/\lambda$ where λ is the laser wavelength. In b) configuration, there are three incident waves: incident beam and its reflections from the other mirrors. The mirrors are positioned at right angles to the sample with the angle connecting the mirrors equals to α . For $\alpha=120^\circ$ when the laser enters the interferometer, three folds symmetry will be formed and produce hole/disks in hexagonal array.

3.1.4. Grating transfer

The pattern was transferred to its substrate by flowing CF_4 gas in reactive ion etching (RIE). The pattern formed in photoresist can be directly evaporated with a noble metal for once but then the removal of the metallic film will destroy the grating's profile. The transfer of the structure into the glass substrate yields PCL in more durable form and reusable [242, 243].

3.1.5. Metal Evaporation and Removal

A thermal evaporation chamber equipped with a quartz crystal microbalance to monitor the film growth was used for evaporation. First a silver layer of 37nm was evaporated (0.1 nm/s evaporation rate, 1.5×10^{-6} mbar) on the corrugated glass surface, followed by 7nm of Au (both metals of 99.99% purity, Leybold Optics) at the same rate. Fresh samples were stored in sealed coloration vessels under dry nitrogen to protect them from contamination. At this thickness the Au film can be considered optically opaque.

As studied in the previous section, SPR characteristics such as resonance angle position and depth are greatly affected by the metal thickness and permittivity function [11, 27, 145]. The choice of the type of metal is crucial since the sensor resolution, which is mainly due to full-width-half-maximum (FWHM) of SPR dip, greatly influenced by extinction coefficient of dielectric function. It's discussed in literature review that Ag layer guarantees a better resolution and less loss; however Au has a higher chemical resistance to oxidation and to binding to the sampling layer [11, 82]. Thus the use of a bimetallic layer joins the high resolution of Ag with the chemical stability of Au [72]. The effect of using bi-metallic films has been simulated. The aim is looking for the configuration which optimizes the reflectivity minimum at the resonance angle.

By increasing Au thickness, the FWHM of the dip increases. Considering that about 5nm of Au is enough to properly cover the Ag layer, the resonance curve FWHM with 7nm of Au is about twice greater than the single Ag layer however it is three times narrower than what can be achieved with the single Au film design. Simulated angular SPR curve for bimetallic structure (40 nm Ag - 7 nm Au) compared with single metal layer devices (50nm Ag or 45nm Au) is demonstrated in Fig. 3.12. For recycle purpose, both metal layers can be stripped chemically and the sample can be coated again.

Figure 3.12. Angular SPR for bimetallic layer (40 nm Ag - 7 nm Au) compared with single metal layer devices (50 nm Ag or 45 nm Au).

3.1.6. Nano Imprinting

In order to produce consistent and identical plasmonic crystal, nanoimprinting method was used to duplicate the structures [235-238, 244]. The soft lithography technique is adopted from the originally proposed by Whitesides because it is simple technique capable of copying of surface details with dimensions smaller than 30nm. The procedure of replication is illustrated in Fig 3.13. It consists of two steps in which master diffraction grating is cast into an elastomer stamp which is after used for transferring the grating modulation into a UV curable polymer [244].

Figure 3.13. Replication of master grating (a) elastomer stamp casting and curing, (b) release from the master grating (c) copy into a UV curable polymer, (d) stamp release from the replica grating.

The grating master was mounted into a special mould and a thin self adhesive Mylar sheet (thickness 100 μ m) was attached over its edges. Then, the mould was filled with liquid silicone based elastomer (Sylgard 184 from Dow Corning Inc., USA) and cured at the temperature 60°C for 6 hours. After the curing, PDMS elastomer stamp with cast relief modulation was released from the master grating. The thin self-adhesive Mylar sheet along the master grating edges produced a depression of the stamp surface at the grating circumference which allowed suppressing the imperfection during further replication.

Preparation process of replica gratings in a UV curable polymer layer using PDMS elastomer stamp:

- 1) Glass substrate was cleaned in Piranha solution, washed in deionized. After, the surface of the glass substrate was cleaned in ozone cleaner for 20 and again washed in de-ionized water and ethanol and dried in nitrogen stream.
- 2) UV curable polymer Norland optical adhesive 72 (NOA-72) was spincoated in a glass slide, rotation speed 7000 RPM for 30s.
- 3) UV curable polymer was brought in contact with elastomer stamp and let mechanically and temperature stabilizes for 30 min.
- 4) UV curable polymer can be cured at 315-450nm (UV-Vis range) with energy 5 J/cm².
- 5) Release the mold from the duplication grating.
- 6) The replica was heated to 150°C for 30 min.

The glass slide and the stamp were mounted slightly unparallel to avoid trapping of air bubbles in between PDMS stamp and replica [235-238]. Another good candidate for imprinting polymer is Ormstamp© from Miroresist Technology [245].

3.1.7. Nanoslits Array Fabrication

The fabrication of extra ordinary transmission (EOT) membranes requires few steps of process: electron-beam lithography; electro-deposition, wet and dry etching as demonstrated in Fig. 3.14. A Si₃N₄ membrane has been prepared starting from a double-polished Si(100) wafer, where 0.1μm Si₃N₄ low-stress layer had been previously deposited on both sides. The optical window has been obtained by (dry) etching of on the back side Si₃N₄ film and wet etching (in hot KOH) of the silicon substrate down to the other side Si₃N₄ film. As plating base electrode for the electrolytic growth 10nm chromium and 50nm Au has been deposited on the nitride layer by e-beam evaporator.

Figure 3.14. Steps of the nanofabrication process.

The patterns were fabricated by electron beam lithography (EBL) at 30keV and 0.14nA. A PMMA based resist is coated on substrate to form 0.45 μ m thickness and baked at 180°C in oven for 15min. A dose of 390 μ C/cm² has been used during the exposure. After the exposure, one third of isopropylacetone (MIBK) in 2-propanol (IPA) was used to develop the pattern (1min) and then rinsed in pure IPA.

Prior to electrodeposition of Au, the sample needs to be cleaned. Any residual resist will cause deposition non-uniformity. High pH and electrolyte concentration may degrade the structure hence acid cyanide (pH $\approx$ 4) was preferred. Potassium dicyanoaurate (I), KAu(CN)₂ from Sigma Aldrich was used as electrolyte with initial density 3.45g/cm³. For an optimal film growth quality the density can be adjusted into 9.4g/l by adding citric acid (i.e. 9.4mg KAu(CN)₂ in 1l citric acid) and the pH can be adjusted into 4.35 by adding KOH (around 50g/l). Platinum mesh is chosen as the anode to prevent any contamination and preserve pH and concentration of electrolyte. The reduction of the gold cyanide complex is inhibited by the cobalt ion. The sample with Cr/Au plating electrode is connected to the cathode. The temperature was kept about 36°C and the current density was set at 1mA/cm² with deposition rate of 10nm/s. Upon deposition, the sample needs to be rinsed by hot water and dried immediately to prevent spots. Final part is to remove the base plating on Si₃N₄ (Cr/Au bilayer) by two steps etching process: firstly Au removal in argon plasma (RIE) followed by Cr removal by wet etching solution consisted of sodium hydroxide + K₃Fe(CN)₆ in water.

3.2. Micro Fluidic Cell

The grating based micro-fluidic cell is shown in Fig. 3.15-3.17. A thin film of poly(dimethylsiloxane) (PDMS) with a hole need to be placed on the sample with the hole being centered over the grating area. PDMS is cast into the desired shape with a bathtub shaped Teflon mould. The elliptic hole is chosen with its principal axes being 4mm and 8mm. Being under pressure from the binder clamps, the cell volume can be determined to be approximately 10 μ l, which is much smaller than being calculated from its geometry when relaxed. The PDMS slide can be used for several times.

A flow cell and a simple fluidic system have been used for the bio-sensing study. These fluidic systems are advantageous in:

- 1) Accelerating mass-transport limited interaction kinetics (low analyte concentration);
- 2) Minimizing sample consumption;
- 3) Enabling automatic sample mixing, delivery, etc. [110, 111]

The grating micro-fluidic cell dimension and PCL based microfluidic system are demonstrated in Fig. 3.16 and 3.17 correspondingly.

Figure 3.15. Plasmonic Crystal with micro-fluidic Cell. Some solutions with different refractive index are introduced by non-contact (top) or direct contact (bottom). Peristaltic pump is employed to control the flow rate. Some solution may be destructive; hence non-contact set up (top) is preferred during the measurement; nevertheless the thickness of the substrate requires to be well controlled.

Figure 3.16. Grating micro-fluidic cell. The clamps are attached at the dashed positions on the screen. The plane of rotation of the goniometer is normal to the image plane.

Figure 3.17. The PCL with micro-fluidic set-up. Tygon tube flow the solution from the syringe to the micro-fluidic cell (left). The PCL is attached to the high accuracy rotatable stage to allow the SPR data collection of different azimuthal angle. However the system is still not sophisticated for transmission measurement.

3.3. Active Materials

Bridged polysilsesquioxanes was used to produce molecular level-engineered hybrid organic-inorganic materials [148] which are able to demonstrate a fine porosity control. The porosity increases reactive surface area, hence enhances chemical sensitivity on sol-gel matrix. The films were characterized by vibrational spectroscopy (i.e. FTIR) as well as ellipsometry measurements. The effects of the experimental parameters on the porosity were also investigated. The SPP excited from film on 1D PCL was utilized as very sensitive design for SPR based sensor to determine refractive index variations [107-109].

3.3.1. Hybrid organic-inorganic materials

Thin film prepared from sol-gel matrix has been used more and more to confine both bio- and chemical molecules for sensing purposes and other applications [107]. The pores also increase the reactive surface area, which enhances chemical sensitivity of the thin film sol-gel matrix. This is also a well-known result for most of porous dielectric films where the diffusion rate of any gases or liquids is accelerated exponentially with the thickness. There is much interest in the synthesis of sol-gel that can be incorporated with some active materials to change the optical properties and whose porosity can be adjusted at lower temperature to have shorter time, eliminate unnecessary process and avoid molecular degradation [246].

3.3.2. Sol Gel Synthesis

The precursor of the sol-gel is Bis(triethoxysilyl) octane (C8) from ABCR GmbH & Co., a bridged polysilsequioxane group which contains two Si atoms connected to each other by 8 methyl groups and each of the Si atom is attached to three alkoxy groups [148]. The sol-gel precursor was performed at 25°C. The precursor was prepared under acidic condition. The procedure of the preparation of acidic bridged polysilsesquioxanes: sol-gel, ethyl alcohol, HCl and H₂O were mixed for 30min (with molar fraction H₂O and precursor equals to six while SiO₂ may reach 80g/l and 1M HCl was added until molar ratio HCl to precursor

= 500:1) [148]. The synthesis of sol-gel starts with hydrolysis reaction, silanol functionalization and condensation reaction that produces a silica network (Fig. 3.18) [107].

Figure 3.18. Sol gel synthesis scheme: the first reaction is the hydrolysis then the condensation. The figure is reproduced from [148].

3.4. Self Assembled Monolayer (SAMs) and Characterization

The alkanethiols self-assembled monolayer on metal film is very attractive because they are able to create well self-organized thin monolayer with clear arrangement and height [247-250]. This property can be used as potential flexible structure for complex materials advancement i.e. connecting substances to the molecularly grafted metallic substrate in order to modify the surface properties. Specifically, acid-terminated alkanethiol is very attractive because they are able to respond and interrelate with surrounding chemicals, resulting in chemisorption of different molecules. The top and side view of decanethiol on Au film is presented in Fig. 3.19.

Figure 3.19. Left: top view atomic arrangement of C_{10} SAMs on Au film with orientation $(\sqrt{3} \times \sqrt{3})\angle 30^\circ$. The smaller light pink spheres correspond to Au atoms; the darker spheres correspond to thiol groups. Dark red spheres is oriented at $c(4 \times 2)$ super lattice for $(\sqrt{3} \times \sqrt{3})\angle 30^\circ$ lattice. The sulfur will occupy the face centered cubic (FCC) 3-fold sites on the Au atoms. Right: side view of decanethiol; C_{10} SAMs is tilted by 30° . This figure is reproduced from [251].

3.4.1. SAMs Preparation on Au film

Solution of decanethiol was prepared in absolute ethanol to form 1mM concentrations. The precursors were put in ultrasonic bath for few minutes (<10min) just before the PCL was dipped into the solution. C₁₀-SAM [decanethiol (CH₃-(CH₂)₉-SH)] was self assembled on Au metallic film coated 2D PCL at 25°C in glove box (N₂ environment) for >20hrs to obtain good quality of SAMs with high coverage (packed). The PCLs were immersed in the C₁₀-SAM solution using very clean glass container inside the glovebox (in N₂ environment) and following completion the SAMs on PCL was cleaned by EtOH and high purity water to eliminate some residual chemicals. The SAMs on PCLs need to be dried in vacuum desiccators for few hours before being characterized. SAMs are able to form self assembled of highly oriented arrangement with high density on Au film [247-250].

C₁₀ monolayers was considered to be measured as the object of sensing because of numerous rationales for instance, flexibility in control measure (SAMs are able to self organized as single-layer above PCL's metallic film for an adequate specified pitch and length of molecules are set uniformly across whole substrate) as well as reasonably thin enough (about 13Å) thus appropriate for the object of sensing.

3.4.2. SAMs Characterization

The growth of C₁₀ SAM on PCL can be characterized using spectroscopic ellipsometer. The spectra were collected from 300–1000nm using VASE which will be discussed in section 3.7.3. The optical function of each layers (substrate, Au-Ag and SAMs) were modeled. The assessment utilizes the dielectric function for the Ag-Au film and thiol solution. After measurement, the spectra were modeled to find the optical parameters of complex refractive index for the best-fit value of bi-metallic film and C₁₀ SAM thickness. An effective medium approximation was used to obtain the optical function of C₁₀ where the thiol layer is considered as an effective medium layer with main constituent refractive index of 1.46 and small portion of air inclusions inside the main layer. The parameters were refined in iterative way to provide the best fitness value of the measured spectra and smallest error.

3.4.3. SAMs Optical Property

The ellipsometry characterization and modeling for 1mM C₁₀ formed on gold film was further analyzed to obtain the accurate thicknesses as well as the permittivity function of the

monolayer. The monolayer is around 1.34 ± 0.08 nm thick which is matched with previous qualitative analysis and thickness estimation using X-Ray photo spectroscopy (XPS) characterization *via* the Au 4*f* core level that show the thickness of 1.3 ± 0.1 nm [251]. The index of refraction for C₁₀ is around 1.33 [112]. Generally the thickness of 1mM C₁₀ on Au film varies with deposition time (0.45–1.38 nm). Any contaminant will interrupt the initial adsorption of SAMs molecules onto the substrate. Hence the growth of the SAMs needs to be done under very clean environment such as in glovebox. The chain length of the thiol is approximately about 1.5 Å per methylene molecule [251]. The thickness obtained is around 1.1 nm with similar refractive index value.

3.5. Surface Plasmon Polariton Simulation in Reflectivity Mode

This section describes the simulation of optical responses and characteristics of propagated surface plasmon on PCL in reflectivity mode. Transfer matrix method was used in this simulation to solve EM interaction with PCL in reflection mode [128, 252]. Unlike plane surface, more intricate analysis and calculation need to be done to solve periodic structure such as PCL. Chandezon's method and coordinate transformation were utilized to transform sinusoidal profile into single plane in new coordinate system and solve the Maxwell's equations [253-255].

The simulations were performed to examine the effect of additional dielectric layer and geometry effect on 1D PCL which will be discussed in detail in following chapters. The optimum thickness of Ag film on PCL was calculated and the coupling efficiency was improved by additional Au thin film to protect silver from oxidation. The thicknesses of this bimetallic structure were optimized and the effect of azimuthal angle was studied. Finally, the optical responses due to thin dielectric film on PCL were analyzed as well.

Chandezon's theory [254] which is summarized in Appendix A provides analytical solution for monochromatic light incident on a multilayer periodically patterned structure (Fig. 3.20). The SPP simulation in reflectivity mode is done by solving Maxwell's equations (Appendix A) based on Chandezon theory using Wolfram Mathematica®. The mathematical problem is described using covariant form of Maxwell's equation to form linear differential equations with fixed coefficients whose solution is attained from eigenvalues and eigenvectors in every

medium. The full derivation of Chandezon's theory on multicoated grating can be found in [254].

Figure 3.20. 1D Plasmonic crystal representation: M-layers multicoated grating.

Chandezon in his paper [254] described the system based on a dielectric or metallic substrate with complex value n_0 , deposited by M metallic films with refractive index n_i and thickness d_i . The monochromatic light is arriving on PCL at the θ angle and wavelength λ . The top surface is described in the orthogonal system by the sinusoidal function $z=s(x)$. In the new coordinate system [254]:

$$x' = x, y' = y \text{ and } z' = z - s(x) \quad (3.4)$$

$$\text{where } s(x) = A \sin(\bar{g}x + \varphi_1) \quad (3.5)$$

The $s(x)$ is assumed to be perfect 1D sinusoidal function where g is a crystal momentum parallel to x axis direction and equal to $2\pi/\Lambda$. Λ is period of PCL profile and φ_1 is phase of the function, in this case is 0. Here the profile is considered as a perfect sinusoidal; however this is not always the case. The profile can be an arbitrary periodic function; as long as it is continuous, single value and the Fourier series is converged [270, 320]. The detail about Chandezon model is summarized in Appendix A.2.

3.6. Extra Ordinary Transmission Simulation

In order to simulate the transmission spectra analytically, COMSOL Multiphysics and FDTD simulation [257, 258] were used to model the transmission mode in PCL. The results will be compared and described in chapter 6.

3.6.1. COMSOL Simulation on 1D Nanoslits PCL

A COMSOL multi-physics simulation was done to model the transmission in 1D slits PCL. COMSOL is a *Finite Element Method* (FEM) implementation, numerical solution of partial differential equation (PDE) problems with proper boundary conditions. Availability of simulation packages for each physics field and possibility of multiphysics environment. The Radio Frequency module is used to provide solutions to Maxwell's equations [259].

Figure 3.21. Geometry of nanoslit 1D PCL with periodicity of Λ , width, a and the thickness of the slits, h which was used for transmission simulation in COMSOL.

Typical simulation steps: designing the geometry, inputting the domain description such as materials (n and k), defining the boundary conditions, meshing and finally solving the FEM. In the following simulations, 1D structure consisting of an array of gold slits was considered (Fig. 3.21). The parameters that determine the structure are: the grating's period, Λ , the width, a and the thickness, h of the slits. First $\Lambda=500\text{nm}$, a thickness of 375nm and width of 250nm , for normal incidence and TM polarization ($\alpha=0^\circ$) is simulated.

3.6.2. FDTD Simulation on 1D Nanoslits PCL

Finite-difference-time-domain (FDTD) was utilized to simulate complex 3D structures and provide optical response of the structure per unit time. FDTD developed by Yee [260] is an extremely powerful simulation method to calculate Maxwell's equation by dividing the structure into very small unit entity called a mesh. In this thesis, FDTD solution from Lumerical [258] was used due to its robustness.

The parameters used in the lumerical are as follow:

- The structures were drawn in the the software as eight parallel rectangular boxes with length of $3.8\mu\text{m}$ in x -direction, width of 280nm in z -direction and thickness of 370nm in y -direction. Materials of the structures were defined as Au with permittivity function from Palik [140].

- Boundary conditions:
 - Symmetry boundary can be set along x and z directions that are parallel to EM fields symmetry's plane. The simulation volume and time can be reduced by factors of 4.
 - X-direction: periodic boundary condition can be used because it has zero k_x value. The line grating is parallel with x -direction
 - Y-direction: since there is no repeating structure and it is just exposed to the air, open boundary is used. k_y is a plane wave that perpendicular to sample plane (x - z plane)
 - Z-direction: periodic boundary condition can be used because it has repeating structure in z -direction and zero k_z value.
 - When the source is at normal incidence, both periodic and Bloch boundary condition may give identical result. The earlier one is preferred due to less memory and time.
- Mesh size is very important to provide high quality simulation result. Since the smallest structure size is 220nm (slit width), the mesh size is 10nm. Smaller mesh size will give more reliable result however there is a tradeoff with the memory and simulation time.
- The EM source is parallel to y -axis, $0.5\mu\text{m}$ above top surface of the structure.
- Frequency-domain power monitor is chosen and located about $0.5\mu\text{m}$ from the bottom surface of the structure. This monitor collects high-accuracy power flow information in the frequency domain from simulation results across some spatial region.
- For different incident angle measurements, a script can be written to control the angle (theta) of the electromagnetic source.

3.7. Optical Characterization of Plasmonic Crystal

Fig. 3.22 shows diagram of the optical arrangement to acquire the reflection, transmission and ellipsometry of plasmonic crystal.

Figure 3.22. The schematic of optical arrangement to record the reflection and ellipsometry data of plasmonic crystal. The setup consists of goniometer stage to move the sample holder and the detector within the scattering plane whereas the laser remains unmoved.

3.7.1. SPR Measurement

The incoming light arrives at θ degree to z-axis (normal line) and the x-component of light wave-vector is proportional to $\sin \theta$. The optical characteristic data have been collected in theta-two-theta arrangement between 400nm and 1 μ m radiated by 75 Watt Xenon monochromatized light source. The polarization angle can be adjusted, the plane of incidence is set at x - z plane in which the sample plane will be perpendicular with and can be azimuthally rotated. The φ is ranging from 0° to 60° with an accuracy of 0.01°. Spectroscopic ellipcometer from Woollam Co. was employed for optical characterization [72].

The optical setup built for this work was designed to meet the following requirements:

- Measure the reflectivity, transmission and ellipsometry at different azimuthal angles.
- Permit all planes of polarization for the excitation beam
- Have access to the surface for functionalization without removing the sample

There are two basic modes of operation that were used to perform measurements:

- $\theta/2\theta$ -mode: the $\theta/2\theta$ -mode was used to take reflectivity measurements vs incident angle.
- Fixed/ θ -mode: the transmission is measured in this mode.

Additionally, the set-up can determine the grating constant. The grating is studied in the Littrow configuration [125], described by:

$$m\lambda = \Lambda(\sin \theta_{inc} + \sin \theta_{dif}) \quad (3.6)$$

where m is the order of diffraction, θ_{inc} and θ_{dif} are the incoming and diffraction angles. The grating constant can conveniently be measured for $m=1$, where the diffraction is strongest.

3.7.2. Extra Ordinary Transmission

The optical measurements have been performed in transmission mode and will be discussed in chapter 6. Measurements were collected at -90° to 90° polarization. The schematic of optical characterization in transmission mode is demonstrated in Fig. 3.23 for 1D PCL and Fig. 3.24 for 2D PCL. All transmission data were recorded by VASE spectroscopy ellipsometer and further analyzed by commercialized software from Woolam Co. [261].

Figure 3.23. Schematic optical characterization of 1D Nano slits PCL and the dispersion curve by p -polarized light. The red-line SPP dispersion relation is repeated in $2\pi/\Lambda$ in k_x direction. The k_{SPP} line is shown by *solid orange curves* and it has a possibility to induce radiative losses in leaky modes. Schematic is adapted from [262]

Figure 3.24. Schematic optical characterization of 2D diamond array PCL and the dispersion curve by p -polarized light. The red-line SPP dispersion relation is repeated in $2\pi/\Lambda$ in k_x direction. The k_{SPP} line is shown by *solid orange curves* and it has a possibility to induce radiative losses in leaky modes. Several diffraction orders are possible to be excited by this 2D PCL. Schematic is adapted from [262]

3.7.3. Ellipsometry Measurement

Beside the reflection and transmission, the ellipsometry measurement will provide additional information on the sample. The schematic measurement is demonstrated in Fig. 3.25. Two states of linear polarization light are utilized in this measurement (p - and s -). The light will be incident on the sample surface, reflected and finally recorded by the detector. As the light interacts with the sample, it will experience some alteration in intensity as well as phase for both polarization states. The changes in both parameters are measured by this ellipsometry

technique. Ellipsometry is able to measure the thickness of thin film thickness, optical function of materials, including complex effective refractive index (n_{eff} and ϵ_{eff}) of multi-layer or nanostructure [114]. The measurement utilizes spectroscopic ellipsometer from J.A. Woollam which is able to measure both angular and wavelength interrogation for both flat and plasmonic crystal samples.

Figure 3.25. Schematic diagram of ellipsometry measurement. The changes from both p - and s - polarization before and after reflection are measured to obtain the ellipsometry characteristic data. The figure is reproduced from [114].

Ellipsometry also can be employed to measure negative refractive index materials - both the complex permittivity and permeability value using dielectric and magnetic function tensors.

Generally the characterization techniques that were used this thesis is summarized below:

Characterization Technique	Objectives	Acquisitions
Atomic force microscopy (AFM)	To measure and visualize the geometry of plasmonic crystals	Periodicity, amplitude, shapes/profiles analysis
Field emission scanning electron microscope (FESEM)	To measure and visualize the geometry of plasmonic crystals	Periodicity, uniformity area
Power meter	To measure the intensity of beam in interference system	Intensity
Spectroscopic Ellipsometer	To measure: <ul style="list-style-type: none"> Film thickness (resist & SAMS) Surface Plasmon resonance Extraordinary transmission Ellipsometry data 	<ul style="list-style-type: none"> Thickness Reflectivity, resonant angle and wavelength Transmission (wavelength) Psi, delta, permittivity and refractive index (wavelength)
Fourier transform infra red (FTIR)	To measure absorption due to vibrational of certain functional group	<ul style="list-style-type: none"> Absorption, wavenumber

4 Engineering the Geometry of a Plasmonic Crystal

4.1. Optimization of PCL Profiles

During the fabrication, some non-linear processes cannot be avoided and will affect the surface profile of plasmonic crystal produced by interference lithography that may introduce such degree of distortions on the sinusoidal perfect profile. These profile distortions may dramatically change the optical responses such as the reflectivity spectra and SPP coupling efficiencies from the plasmonic crystal. Hence it is very practical to have a nearer observation on the plasmonic effects of variations to these parameters on the reflectivity curve [125, 127, 263]. Here the effect of geometrical parameter will be studied and optimized to attain the sharp and deep reflection curve which is important to obtain highest plasmon coupling efficiency, hence enhance the sensitivity [264].

Theoretically, the comprehensive simulation of SPP coupling to silver/gold PCL was numerically elaborated from expansion of Raether's equations based on Chandezon's theory [254] using Mathematica® [265]. The simulation's detail is described in section 3.5. Surface roughness from both pattern and metal depositions will strongly affect the SPP. For the experimental part, samples of different periodicity i.e. 420-470 nm and amplitudes were prepared by IL. Ag/Au bi-metallic thin film has been orderly evaporated with thickness variations. The PCL profiles were then characterized using AFM and every Fourier components were extracted to calculate the electromagnetic responses of the structures.

The plasma frequency of metals determines the refractive index and is an essential parameter that tunes the characteristic of SPP. Silver is found to have smaller extinction coefficient (k) among the other metals which make the propagation last longer (less losses) [11, 61, 81, 82]. For the same reason, width at half height of reflectivity dip and field's enhancement peak are smaller for Ag, since the system behaves as a resonator driven by the incoming light and the resonance width is correlated to the effect of dissipation sources. Very thin layer of gold is often used to cover up the silver film in plasmonic crystal. 37nm/7nm of silver and gold films was evaporated in sequence on top corrugated Si substrate. The first section of this chapter has been published in *Microelectronic Engineering*: 2009 [321].

4.1.1. Experimental

The fabrication of PCL was done by interference lithography (IL) as discussed in previous chapter. The calibration of the incident angle vs. the PCL periodicity is presented in Fig. 4.1.

Figure 4.1. Experimental data vs. calculated periodicity as a function of incoming angle using Lloyds' mirror setup. The AFM image and section analysis of 1D PCL produced by the IL are shown in the inset.

The measurements have been taken from $\theta/2\theta$ symmetric reflectivity configuration as discussed in section 3.7.1 from 15° - 80° with 0.2° resolution using 500-800nm wavelength and 0.425 nm standard deviation. All data acquisitions were done by VASE spectroscopic ellipsometer and analysed by WVASE software from Woollam Co. [261].

4.1.2. Results and Discussions

In order to study the geometrical contribution in SPP, some set of 1D PCLs with periodicities and amplitudes ranging from 420-470nm and 15-90nm respectively were produced using IL. The samples were then deposited with various silver thicknesses and covered by 7nm of gold film. The PCL profile's control is very critical to give most favorable responses of plasmonic crystal hence the relationships between each process parameters and the effects on the shapes need to be well understood. The grating's amplitudes are able to be tuned by adjusting the exposure dosage which is a function of exposure time, sample's distance from pin hole as well as incoming beam's (laser) intensity.

The experimental result from several samples describing that increment in exposure time - which is reflected in total doses - will subsequently increase the sinusoidal amplitude in parabolic manner. These were obtained after development for average 60s. This PCL's amplitude is strongly influenced by the lowest intensity produced from superposition of two expanded beams which in most conditions is not zero. So as to get clear distinction among grating's lines, the high intensity fringes need to have sufficient period to go into the certain depth of the resist (130nm). The graph below shows the relation between the exposure

distances, intensity of expanded beam and the corresponding amplitude result for different exposure times while the developing time is fixed. It can also be noticed that for larger exposure distance, the amplitude can be finely changed and controlled (Fig 4.2). The exposure distances give greater influence than the periods on the amplitudes for fixed developing time. In this part, we have shown that by tuning the dosage through exposure distance, exposure period and incoming angle, the accurate profile control in fabricating the PCL can be done perfectly to provide the maximum coupling efficiency.

Figure 4.2. (Left scale) The intensity measurements of expanded beam vs. the distance between the pin-hole and sample is shown by the red line. (Right scale) The PCL's profile amplitude for several exposure periods vs sample holder's distance are measured and shown by black lines. This figure is reproduced from [321].

4.1.3. Theoretical and Experimental Data

A theoretical calculation (section 3.5) of plasmonic generation on bi-metallic PCL was done from expansion of Raether's equations by adjusting some crucial geometrical factors such as periodicity and amplitude of PCL's profile, materials and film thickness. The simulation is calculated as a preliminary work towards the fabrication (experimental work).

The following Fig. 4.3 is the reflectivity simulation result of different grating amplitude, where the minima corresponds to the optimum plasmonic coupling condition. For 416nm periodicity, the highest SPP coupling efficiency was demonstrated by 32-40nm amplitude (peak-valley) with reflectivity value smaller than 2% can be obtained for the 32nm amplitude and 37nm Ag - 7nm Au. For the optical characterization the term coupling efficiency is used which can be calculated from $\eta = 1 - R_{\min}$. This value becomes an indicator for the quality when the geometrical parameters of plasmonic crystal are varied [70, 79]. From the spectra, it is shown that there is an angular shift to longer value by increasing the amplitude. The geometrical optimization is very important to obtain the highest coupling efficiency that can be done by excellent control in fabrication process.

Figure 4.3. Simulation of 1D PCL SPR reflectivity at different profile's magnitudes with fixed $\Lambda=416\text{nm}$, evaporated with 37nm/7nm of silver and gold. The maximum coupling condition (minimum reflectivity dip) is demonstrated by PCL with 32-40nm of amplitude (peak-valley).

Departing from optimal geometry parameter obtained from simulation and high precision nanofabrication capability, several PCLs with $\lambda=416\text{ nm}$ and 31-33nm of amplitude are produced. The reflectivity spectra of PCL is optically measured by SPR system (shown in Fig. 4.4) and it was found that the reflectivity minimum is slightly higher than the simulation. The resonance angle and reflectivity intensity for both simulation and experimental were fit. However there is some discrepancy in FWHM of both dips. Experimental dip is almost three times larger than the simulated one. This will affect the coupling quality and reduce the sensitivity FOM. After a careful consideration and further profile analysis, it is suggested that another geometrical factor that affect the SPP efficiency is the roughness. The average profile variations considered in this chapter is around 3nm (up to 10% from the amplitude) and has not been counted into the simulation. The inset confirms that the optimum Ag thickness for this structure is about 37nm.

Figure 4.4. Reflectivity curve of theoretical and experimental measurement for 1D PCL with $\lambda=416\text{nm}$, amplitude of 32nm and deposited with 37 and 7nm of silver/gold bi-layers. The measured reflectivity curve is much broader than the theoretical one, which contains more information. The reflectivity measurement for different silver thickness and wavelength is shown in the inset. This figure is reproduced from [321].

The effects of geometrical contribution on 1D PCL have been investigated experimentally and theoretically. The optimizations of geometrical parameters have been done to obtain the finest SPP coupling condition. The discrepancy between the theoretical and experimental measurement could be affected by the unevenness of PCL's profile.

4.2. Surface roughness, Shape variations and Distortion

Both arbitrary and regular profile roughness on PCL may contribute to SPP generation. This surface corrugation has been exploited for sensing purposes, i.e. surface enhanced Raman scattering measurement (SERS) [266]. However arbitrary unevenness is very hard to be characterized. Some random surface can be represented as being statistically correlated, nevertheless it is complicated to predict and calculate the propagation of the SPP on that surface [267, 268].

These difficulties can be avoided for deterministic and periodic surface [269]; hence it can be characterized experimentally and theoretically. In this case, the corrugated surface can be represented mathematically for further analysis. This structure can be studied from the SPR dips related to SPP generation by the PCL. It finally leads to mathematical representation [270] that includes the geometrical variations on PCL responses. The optimum geometry can be presented in order to obtain maximum plasmonic field enhancement, hence improve the sensitivity.

Here, the effects of profile's roughness/distortion on SPR curves and coupling efficiency were studied theoretically using Chandezon's theory [270]. The FWHM and shape of SPP resonance was controlled by the PCL's surface profile and the effective permittivity value of the metal films. Thus by evaluating the reflectivity between the experiment and theory, the accurate plasmonic crystal's geometry can be parameterized.

4.2.1. Origin of Profile's Distortion and Variation

Plasmonic crystals (PCLs) are usually fabricated using IL on photoresist and exposed into developer to retain the periodic structures. PCLs fabricated through this method will demonstrate nearly sinusoidal contours; distortion from this profile may be caused by non-

uniformities of the resist's response during exposure and development process or after pattern transfer through RIE and imprinting process as demonstrated in Fig. 4.5.

Generally due to limitation in fabrication process, the PCLs profiles are distorted (non ideal case) and cannot be represented by single sine function. However the distorted PCL profiles are able to be represented by Fourier-expansion by introducing higher-harmonic terms [267]. In other words, the main harmonic function with additional second and third terms will alter SPP generation. These will contribute on SPR dip hence the profile distortions will not only change the coupling effectiveness but also introduce alteration in shape (depth) and resonance conditions (wavelength and angle) of SPR curves. The distortion will be enhanced for longer periodicity. This indicates that PCL is extremely responsive to the alterations in geometries that is able to be employed to characterize the Fourier component of PCL [269].

Figure 4.5. AFM images of 1D plasmonic grating's cross section with $\Lambda=500\text{nm}$ and 20-40nm amplitude. The perfect sinusoidal profile is demonstrated in (a), as the exposure is disturbed, non linear responses of photoresist, the tips are sharpened (b). The tips could also be rippled (c) and finally failing and forming digital wave structures (d).

4.2.2. Modeling Profile's Distortion and Variation

For understanding the contribution of the film roughness, it is vital to fully comprehend the mechanism of surface plasmon excitation in PCL. The wavevector of incoming light arrives on a PCL is smaller than SPP, hence it must be enhanced by $\Delta k = k_{spp} - k_{ph-x}$ additional momentum which can be contributed by sinusoidal harmonics of a periodic PCL parallel to interface to match the terms [72].

$$\vec{k}_{SPP}(\omega) = \vec{k}_{ph}(\omega) \pm \vec{g} = \frac{\omega}{c} \sin \theta_c \pm m \frac{2\pi}{\Lambda} \quad (4.1)$$

where k is the momentum wavevector, θ_c is incident angle, Λ is PCL's periodicity, and m is crystal momentum's diffraction order. As discussed in chapter 3, Chandezon method [270] is used to demonstrate the correlation of SPR dips and PCL profiles quality [253-255] by implementing perfectly matched EM border and resolve Maxwell's equations.

This method can be used to model PLC with high profile's amplitude relative to the periodicity (as shown in Fig. 4.3) and will not be limited by Rayleigh expansion where the ratio cannot be more than 0.07. This value will be reduced as higher harmonics terms are included to correlation function [267, 269]. As more terms are included, more time is needed to complete the computation. Thus some limitations are made for certain terms and magnitude of the profile.

4.2.2.1. Mathematical Approximation

The modeling correlates the crystal's geometry and SPP coupling condition hence maximum efficiency can be achieved. These complex profiles can generally be represented by statistical correlation function proposed earlier by Kretschmann [81] in general form:

$$s(x, y) = \frac{1}{T} \int_T z(x', y') z(x'-x, y'-y) dx' dy' \quad (4.2)$$

where z represent a point position beyond the mean surface (x, y) and T is total area bellow z values.

The optical response is unique for different geometries, hence various profile can be examined and represented mathematically, using sinusoidal function. Generally regular distorted PCL profile can be identified and characterized using additional combination of second and higher harmonic components. The profile can be defined as summation of several sine functions with different amplitudes, periodicities, and phases:

$$s(x) = \sum_{n=1}^p A_n \sin(n\bar{g}x + \varphi_n) \quad (4.3)$$

Where A_n is profile magnitude of the n^{th} harmonic term, $\bar{g}$ is grating vector equal to $2\pi/\Lambda_n$, Λ_n is the periodicity of the n^{th} sinusoidal (or harmonic) component and φ_n is the phase term. This series will be limited to several harmonics (p , usually first and second). For certain

small deviation of a sinusoidal profile, only few harmonic components are necessary to be included into the function. The phase term is taken into account since it contains elementary changes in SPR dips. When the truncation of the series is happened at $n=1$, then it will simply turn out to be a perfect single sinusoidal function (where $C=0$):

$$s(x) = A \sin(\bar{g}x + \varphi_1) \quad (4.4)$$

The variation of 1D PCL profiles due to minor distortion is discussed in Appendix B.1. 1D PCLs can be represented using single dimensional directional parameter, x since it only changes in one direction. 2D PCLs are more complicated due to the presence of another directional parameter, y .

The profile of a 2D PCL can generally be defined as summation of several functions:

$$s(x, y) = \sum_{n=1}^p A_{x(n)} \sin^2(n\bar{g}_x \cdot x + \varphi_{x(n)}) \cdot A_{y(n)} \sin^2(n\bar{g}_y \cdot y + \varphi_{y(n)}) \quad (4.5)$$

$A_{x(n)}$ and $A_{y(n)}$ are the amplitude of the n^{th} harmonic components, $\bar{g}_x$ and $\bar{g}_y$ are crystal momentum equal to $\frac{2\pi}{\Lambda_{x(n)}}$ and $\frac{2\pi}{\Lambda_{y(m)}}$ respectively, Λ_x and Λ_y are the periodicity of the n^{th} harmonic component and φ_x and φ_y are suitable phase for x and y . If n equals to unity, the profile will forms 2D sinusoidal function ($\varphi_{x(n)} = \varphi_{y(n)} = 0$):

$$s(x, y) = A_x \sin^2\left(\frac{\pi}{\Lambda_x} \cdot x\right) \cdot A_y \sin^2\left(\frac{\pi}{\Lambda_y} \cdot y\right) \quad (4.6)$$

The 2D PCL profiles (after RIE or heat treatment process) will be best represented by square sinusoidal function which eliminates the presence of saddle point as demonstrated in Fig. 4.6. The reflectivities' depth and efficiencies can be developed from different periodic profiles that are built by a variety of harmonic levels with certain degree of phase φ .

Figure 4.6. 2D PCL profile used in this thesis is best represented by square sinusoidal function (Eq. 4.6) and shows the absence of saddle point.

4.2.2.2. Parameters in SPR Dips

As mentioned previously, the SPR dips are greatly influenced by the alteration in geometry and the degree of roughness which can be easily identified by the changes in SPP dispersion curves. Besides simulation, analytical approaches can be done to calculate the reflectivity spectra. There are several essential parameters that define and form the SPR dips, such as the resonance angle (θ_c), reflectivity minimum and FWHM. These parameters are very important to analytically model the reflectivity dip of PCL.

The light can couple to SPP if the parallel component of light momentum equals the wavevector of the SPP. The resonance angle, θ_c is simply calculated using conservation of momentum in PCL [271]:

$$k_{spp}(\omega) = k_{ph} \sin \theta_c \pm mg \quad (4.7)$$

$$\frac{2\pi}{\lambda} \sqrt{\frac{\epsilon_m \epsilon_d}{\epsilon_m + \epsilon_d}} = \frac{2\pi}{\lambda} \sin \theta_c \pm m \frac{2\pi}{\Lambda} \quad (4.8)$$

$$\theta_c = \text{Arcsin} \left(\sqrt{\frac{\epsilon_m \epsilon_d}{\epsilon_m + \epsilon_d}} \mp m \frac{\lambda}{\Lambda} \right) \quad (4.9)$$

where m represents order of diffraction, λ is incoming wavelength, ϵ_m and ϵ_d are permittivity value for metal and dielectric respectively, and measured at certain wavelength. Λ is PCL's pitch. As the azimuthal angle is introduced, the equation becomes [72]:

$$k_{ph}(\omega) \cdot \sin \theta_c = mg \cos \varphi \pm \sqrt{k_{spp}^2(\omega) - (mg \sin \varphi)^2} \quad (4.10)$$

$$\theta_c = \text{Arcsin} \left(\frac{mg \cos \varphi \pm \sqrt{k_{spp}^2 - (mg \sin \varphi)^2}}{k_{ph}} \right) \quad (4.11)$$

where $\vec{g} = \left(\frac{2\pi}{|a|} \right) m\vec{x} + \left(\frac{2\pi}{|b|} \right) n\vec{y}$ for 2D PCL and for 1D PCL the $n=0$.

For example:

A monochromatic plane wave with $\lambda=600$ nm on Ag grating with $\Lambda=416$ nm, $n=1$ and $\varphi=0^\circ$. For silver $\epsilon_m=-17.0$. Using Eq. 4.9 for the flat configuration: $\theta_c=24.3^\circ$.

However analytical modeling by Chandezon's method provides the $\theta_c=24.28^\circ$ and FWHM of 0.29° with 2.6% reflectivity at resonant condition. The θ_c value is one decimal place more accurate than Eq. 4.9. The simulation is shown in Fig. 4.7.

Figure 4.7. Reflectivity curve for a plane wave ($\lambda=600$ nm) incident on Ag grating ($\Lambda=416$ nm).

The surface corrugation of sinusoidal grating confines the SPP propagation within the plane formed by normal (0, 0, 1) direction and crystal momentum. Based on prior hypothesis, the SPR intensity is proportional to the incident intensity (electric field component which is effective to SPP) on the PCL plane [116]:

$$R \propto |\hat{e} \cdot (\hat{g} \times \hat{n})|^2 \quad (4.12)$$

where $\hat{e}$ and $\hat{g}$ are the direction of electrical field and crystal momentum respectively. $\hat{n}$ is normal to sample surface. The electric field propagation direction in 3D system in which the scattering plane coincides with x - z plane is defined by:

$$\hat{e} = (\cos \theta, 0, \sin \theta) \quad (4.13)$$

In this case TM-wave is used and θ is the resonant angle.

While the crystal momentum direction is given by:

$$\hat{g}_x = (\cos \varphi, \sin \varphi, 0) \quad (4.14)$$

where φ is PCL azimuthal angle.

Substituting Eq. (4.13) and (4.14) into (4.12) will give:

$$R_{\min} = |\cos \theta \sin \varphi|^2 \quad (4.15)$$

where from Eq. 4.11:

$$\cos \theta = \left(1 + \frac{\epsilon_m \epsilon_d}{\epsilon_m + \epsilon_d} - \left(\frac{m\lambda}{\Lambda} \right)^2 \pm \frac{2m\lambda}{\Lambda} \cos \varphi \sqrt{\frac{\epsilon_m \epsilon_d}{\epsilon_m + \epsilon_d} - \left(\frac{m\lambda}{\Lambda} \sin \varphi \right)^2} \right)^{1/2} \quad (4.16)$$

FWHM of SPR dip is another important factor which is closely related to the SPP propagation length, L_{SPP} on the PCL. For sensing purposes, the FWHM required to be very small, to increase the figure of merit (FOM) value [156]. In other hand, for switching device, the width needs to be adjusted for specific requirement [45].

Generally FWHM of SPR dip will be affected by two damping parameters originated from materials selection (imaginary part of permittivity function, ϵ'') which has been explained previously in Eq. 2.12 and geometrical structure (profile's amplitude) [49, 272]. For bi-metallic layer, the effective permittivity function needs to be obtained from spectroscopic ellipsometry measurement. A high surface roughness may raise surface plasmon losses and reduce the SPP propagation length indicated by broadening the FWHM of SPR curves, due to scattering losses at the interface. For small grating amplitude ($A/\Lambda \leq 0.07$), comparable to the sample used in this thesis, the scattering effect will be minimized and the FWHM will be mostly determined by ϵ'' [57]. While as the corrugation's pitch is increased, the PCL becomes more conductive thus the effect of imaginary part will be less prominent however as the profile's amplitude increases, the scattering effect will need to be taken into account.

Derived from [125], the FWHM of angular SPR dips can be estimated by:

$$FWHM \approx \arcsin \left(\frac{4\Im k_{spp}}{k_{ph} \cos \theta} \right) \cdot C \quad (4.17)$$

$\Im k_{spp}$ is imaginary part of SPPs momentum which is related to absorption and re-radiative losses and inversely proportional to SPP propagation length, L_{SPP} .

Substituting $\Im k_{spp}$ from Eq. 2.44, it becomes:

$$FWHM \approx \arcsin \left(\frac{2\epsilon''_m}{\epsilon_m'^2 \cos \theta} \left(\frac{\epsilon'_m \epsilon_d}{\epsilon'_m + \epsilon_d} \right)^{3/2} \right) \cdot C \quad (4.18)$$

where $\cos \theta$ is given in Eq. 4.16 as a function of azimuthal angle, φ .

C is the constant which affected by the profile characteristic of PCL. In 1D PCL, an ideal grating surface should contain only the main harmonic component (i.e. the perfect sinusoidal) and C equals to 1. For non-ideal profile, it contains additional harmonic components (roughness) hence the SPP can be coupled at certain range of angles and causes broadening [271]. In non ideal case (sinusoidal profile), C can be larger than one. The SPP propagation length (L_{SPP}) and resonant angle (θ) are unique for each crystal momentum, hence respective FWHM can be calculated individually.

4.2.3. Discussions

As higher harmonic components are introduced into simulation, the FWHM of SPR dip in Fig. 4.4 becomes wider. In this case, at least third harmonic component needs to be used to have better curve fitting. However the contribution of higher harmonic components is difficult to be verified. Alternatively the roughness can also be taken into account by the effective permittivity of metal. As the solution, heat treatment process was introduced to improve the PCL profile quality. This process may reduce the roughness and higher harmonic components hence SPR dip demonstrates lower FWHM as shown in Fig. 4.8.

Figure 4.8. The experimental SPR curve after heat treatment process shows SPR dip with lower FWHM

Both modeling and experimental results are able to present the reflectivity curve in wavelength modulation; however angular modulation is preferred as the earlier needs a complete measurement of metallic and dielectric permittivity values to be included into the model to precisely fit the data. This complication can be removed in angular modulation as the permittivity of metal and dielectric are constant for a fixed wavelength. In 1D PCL

conventional mounting, SPP can only be generated using TM-mode, while TE-mode is restrained due to the absence of electric field component on the sample's plane.

When the PCL crystal momentum is smaller than incoming light momentum, i.e. $\Lambda \gg \lambda$; it is likely to generate SPPs at different angles of incidence (several diffraction orders). In this case, SPPs can be excited for ± 1 diffraction order, and the coupling at ± 2 and higher diffraction order will be much stronger than the first order.

5 Plasmonic Crystal Characterization and Analysis

This chapter will describe the physical and optical characterization of 1D, 1D to 2D and 2D PCL. The effect of azimuthal rotation will be explored and discussed. The results from AFM and SPR were combined for a full mathematical description of the reflection behavior of a PCL. The magnitude and direction of SPP can be easily determined with the respect to azimuthal angle. Although the main focus is on 1D to 2D and 2D PCL, the characterization of 1D PCL that has been published in [72] will still be elaborated in first part to gain better understanding and build the principles for analyzing the plasmonic responses in higher dimensional structures. Analysis and optical response of both structures will be covered here.

5.1 1D Plasmonic Crystal

5.1.1 Sample Characterization

The grating was characterized by atomic force microscopy (AFM) as demonstrated in Fig. 5.1. The grating's profile is examined by AFM to complement optical characterization. Since AFM is a locally probing technique, the uniformity limits of the etched structures are specified first. 1D PCL was fabricated on Si wafer using IL method and imprinted on PMMA substrate as described in section 3.1 [235, 236]. The grating was evaporated by 37nm/8nm of silver and gold. The 1D PCL's profile employed here is nearly sinusoidal with 500nm pitch and magnitude of 25-28nm. The grating profile was further characterized using Fourier transform to check the PCL profile as demonstrated in Fig. 5.1 (b).

Figure 5.1. a) 1D Plasmonic grating (master) produced by IL and b) grating (replica) produced by nanoimprinting was characterized by AFM including the section analysis and Fourier transform of the gratings.

The sample was optically characterized using variable angle SPR spectroscopy and ellipsometry in $\theta/2\theta$ arrangement as discussed in section 3.7.1 from 600 to 800nm and evaluated using a software from Woolam Co. The 1D PCL was azimuthally rotated from 0° to 60° with a precision of 0.01° [72].

5.1.2 Experimental Result

Generally, the presence of SPP propagation on 1D PCL can be proven by the present of minima in reflectivity measurement as demonstrated in Fig. 5.2 ($\varphi=0^\circ$). This data can theoretically be calculated using Eq. 4.9-4.11 for different incoming angle, wavelength, dielectric constant, and periodicity. In order to satisfy the SPP excitation, for first diffraction order ($m=+1$), the wavelength increases with the resonant angle.

Figure 5.2. SPR reflectivity spectrum of 1D plasmonic crystal for zero azimuthal angle; the dips at different incident angle are excited by various wavelength.

The SPR dip in Fig. 5.2 is higher than Fig. 4.4. This is mainly due to non-optimized amplitude and metallic thickness for specific periodicity hence reducing the coupling efficiency. However in this part, the focus is to observe the PCL characteristic in resonance angle. The sample was further azimuthally rotated (where $\varphi \neq 0^\circ$) and SPR measurement of various azimuthal angle at 670nm is demonstrated in Fig. 5.3. Broadening and angular shifting in SPR dips are noted as azimuthal angle involved in reflectivity measurement [72]. The presence of azimuthal angle will move the position of SPR dips and increase FWHM.

Figure 5.3. SPR reflectivity of 1D PCL for different azimuthal angle at 670nm. Shifting to larger angle and dips broadening can be noticed by moving the azimuthal angle to higher value. The merging of double dips from a single wavelength excitation can be noticed at $\varphi=50^\circ$.

However, the reflection spectrum alters significantly as azimuthal angle goes beyond a critical point, (in this sample $\varphi_c=45^\circ$). The SPR dips in Fig. 5.4 was collected for $\varphi=50^\circ$ and 55° from 655 to 680nm and 610 to 645nm respectively. The figure obviously shows the possibility to excite double SPP using single wavelength. By increasing the incident

wavelength, the dips will come closer to each other, and combine into single wide dip. At longer incident wavelength, the dips will be reduced and finally vanished.

Figure 5.4. SPR reflectivity spectrum of 1D grating for different wavelength where a) $\varphi=50^\circ$ and b) $\varphi=55^\circ$.

Generally by increasing azimuthal angle, the SPP wavelength range decreases and the double dips moves to lower incident angle (for $\varphi=50^\circ$, $\theta_c \approx 55^\circ$ and for $\varphi=55^\circ$, $\theta_c \approx 42^\circ$) as shown in Fig. 5.5. The separations between two dips become smaller by increasing the azimuthal angle as the first dip moves toward higher angle and second dip moves oppositely.

Figure 5.5. The resonant angle vs wavelength. (λ , $\theta_{\min}$) for different azimuthal angle. For the $\varphi > 40^\circ$, the graph shows a maxima which explains the possibility to generate double SPPs.

5.1.3 Data Analysis

The SPP generation using 1D PCL can be realized when the light at certain wavelength incident at resonant angle on the surface of grating and its momentum ($\vec{k}_{ph}$) together with the grating momentum ($m\vec{g}$) satisfy the SPP wavevector ($\vec{k}_{spp}$) [49, 72]:

$$\vec{k}_{spp} = \vec{k}_{ph} \pm m\vec{g} = \begin{pmatrix} k_x \\ 0 \\ k_z \end{pmatrix} \pm m \begin{pmatrix} 2\pi/\Lambda \\ 0 \\ 0 \end{pmatrix} = \frac{\omega}{c} \sqrt{\frac{\epsilon_d \epsilon_m}{\epsilon_d + \epsilon_m}} \quad (5.1)$$

where m is order of diffraction. The plane of incident is perpendicular to the sample with incoming beam momentum at θ angle relative to z -axis,

$$\vec{k}_{ph} = \frac{2\pi}{\lambda} (-\sin \theta, 0, \cos \theta) \quad (5.2)$$

However the equation above only works for $\varphi=0^\circ$. This configuration has been discussed previously in section 3.7.1. For the case where the grating is rotated azimuthally at certain angle ($\varphi \neq 0^\circ$), the crystal momentum $\vec{g}$ is no longer parallel to the $\vec{k}_{ph_x}$ direction, but lies in between $\vec{k}_{ph_x}$ and $\vec{k}_{ph_y}$ plane as demonstrated in Fig. 5.6. Hence the y component of the crystal momentum is not equal to zero, but proportional to $\sin \varphi$ and grating vector $\vec{g}$ is inversely proportional to periodicity, Λ and given by:

$$\vec{g} = \frac{2\pi}{\Lambda}(\cos\varphi, \sin\varphi, 0) \quad (5.3)$$

Figure 5.6. The schematic representation of 1D PCL for the non-zero azimuthal angle. The grating momentum coincides with x-axis, where the light is incident (scattering plane) at φ degree relative to y-axis. When the $\varphi \neq 0^\circ$, the $\vec{k}_{ph_x}$ is no longer parallel with $\vec{g}$.

The $\vec{k}_{spp}$ propagates on sample (x-y) plane and its direction is recognized by β . Recalling Eq. 2.35-2.37 from chapter 2: the SPP dispersion relation as a function of light frequency and permittivity values is given by Eq. 2.35. As the light is traveling in vacuum ($\epsilon_d=1$) and arrive on metal film with plasma frequency, ω_p and permittivity function (Eq. 2.36) thus the dispersion relation will be given by Eq. 2.37.

From SPP wave-vector schematic diagram (Fig. 5.8):

$$k_{spp_x} = \pm \sqrt{k_{spp}^2 - k_{spp_y}^2} \quad (5.4)$$

where:

$$\vec{k}_{spp_y} = \vec{g}_{(y)} \quad (5.5)$$

The propagation direction of SPP can be derived [72]:

$$\cot \beta = k_{spp_x} / k_{spp_y} \quad (5.6)$$

Taking Eq. 5.1 just in x direction and substituting Eq. 5.5 will solve the $\vec{k}_{ph_x}$ as a function of $\vec{g}$ and azimuthal angle φ :

$$k_{ph_x} = mg \cos \varphi \pm \sqrt{k_{spp}^2 - (mg \sin \varphi)^2} \quad (5.7)$$

This Eq. 5.7 allows the transformation of the experimental dips reflectivity data: resonant angle vs. wavelength. (λ , $\theta_{\min}$) as demonstrated in Fig. 5.5 into a set of energy vs. wavevector points (Fig. 5.7). Here, only positive first diffraction order ($m=+1$) is used as the grating vector $\bar{g}$ is larger than the incoming photon momentum ($\lambda < \lambda$).

Figure 5.7. The dispersion relation for various azimuthal angles (φ).

This experimental data were fitted with theoretical model using Eq. 5.7 and plotted in Fig. 5.7. The larger φ angle, the higher and the gentler the curves are. Single value of φ angle was used as a parameter to fit the experimental measurement. The periodicity of PCL was measured by AFM and taken as a fixed value in Eq. 5.7. While keeping the φ fix, the crystal pitch was fitted until reaching convergence. The self-determining fitting parameters for different azimuthal angle provide an excellent comparable value with the experiment result.

The light conservation momentum equation (Eq. 5.7) can be represented in Fig. 5.8. In 1D PCL only single crystal momentum is involved i.e. $\bar{g}_x$. The larger diameter circle corresponds to PCL grating momentum. The dashed line corresponds to x -axis component of incoming photon momentum, $\bar{k}_{ph_x}$ which is proportional to sine function of incoming angle while the z -axis component will only be the main contributor for the extraordinary transmission. The smaller diameter circle corresponds to SPP momentum. The dotted line that intersects at $\bar{g}$ circle corresponds to the crystal momentum at certain azimuthal angle. For $\varphi=0^\circ$, the crystal momentum, incoming light and surface plasmon momentum are all coincided.

The cutting point of $\bar{k}_{ph_x}$ line with $\bar{k}_{spp}$ circle determines k for conservation condition identified by the incoming angle θ and the $\bar{k}_{spp}$ propagation angle β [72]. The schematic in Fig. 5.8 may describe the phenomenon of double SPP in 1D PCL as well as 2D PCL; the sign and conventions will be identical.

Figure 5.8. Schematic representation of SPP wave-vector. The outer and inner hemi-circle represents equi-magnitude $\bar{g}$ and $(\bar{k}_{spp})$ vectors. The capital letter represents potential condition for SPP generation. The incoming photon line (horizontal) is able to cut the SPP curve twice (point A) for double plasmonic generation.

For 1D PCL, double SPP is possible to be generated once the critical azimuthal angle is reached as shown by point A (Fig. 5.8), i.e. $\varphi=55^\circ$. For this condition incoming light wave-vector line is able to intersect $\vec{k}_{spp}$ circle both at A^- and A^+ , indicating a possibility to generate double SPPs at β^- and β^+ [72] which are supplementary angles.

Within the range of allowable condition for double SPPs excitation, (between A^- and A^+), as the φ or λ is increased, double SPP dips will come closer and combine into a wide dip. Dips combination may take place when the SPP propagation direction is parallel to y -axis i.e. incoming photon line cut point $\mathbf{B}$. Here, the incident light may interact with larger plasmonic momentum bandwidth $\Delta\vec{k}_{spp}$ hence higher SPP modes can be generated.

For higher SPP modes, double SPP is the necessary condition therefore φ needs to be larger than φ_c . This value is dependent on the plasmonic crystal momentum. After dips combination, increasing φ angle or wavelength, will reduce the magnitude of $\vec{k}_{spp}$, hence the photon wave-vector could not cut $\vec{k}_{spp}$ circle and SPP generation is forbidden.

5.2 2D Plasmonic Crystal

One of the most significant physical contributions to be studied in SPP generation is the orders of the dimensions such as one, two and three-dimensional structures. In the reflection mode, 2D PCL has not been greatly explored and did not receive much attention compared to 1D grating. The possible reason is that without azimuthal effect, 2D PCLs will be similar to 1D grating and more complexities in fabrication could be another strong reason. Since the publication of non-periodic nano holes by Norwegian physicist and chemist: Prof. Thomas Ebbesen, periodic 2D PCLs were mostly explored to obtain extraordinary transmission [92] and recently they were developed for metamaterials, mainly negative refractive index materials for superlens and hyperlens [92, 273-276].

2D PCLs could be classified as:

- 1) Structured film
- 2) Nano-hole arrays

The first category is useful for reflection studies and the latter for transmission, where so-called “extraordinary transmission” [92]. The structured film and holes can vary in shape (i.e. sinusoidal, digital, and triangular), lattice symmetry (i.e. square, hexagonal) and geometry (i.e. amplitude, spacing and aspect ratio) [229, 277-279]. In other words, 2D PCLs has more affluent control parameters than 1D grating.

There are advantages in employing the 2D PCLs over the 1D conventional grating such as:

1. At azimuthal angle, greater EM field concentration caused by limited surface contour compared to 1D PCL; leading to better coupling efficiency and field enhancement.
2. The possibility of concurrent generation of no less than two or three sets of SPP at the 2D Brillouin zones, hence higher absorption (for solar harvesting, etc.).
3. Unlike 1D PCL, 2D PCLs can explore larger Brillouin zone (first, second and third) due to the diagonal array vector that can be smaller by half up to one third of 1D PCL vector.
4. Provide better sensitivity because more plasmon modes can be excited using single wavelength and the polarization optimization can be done uniquely for individual SPP.

These factors become great motivation to further explore 2D PCLs in transmission and especially in reflection mode for sensing purposes.

5.2.1 1D-2D Transitional Structure

The content of this 1D-2D transitional structure has been published in [104]. The periodic arrangement of wavy lines was fabricated and optically characterized to completely understand the intermediary structure of 1D to 2D PCL array. Modifications in surface morphology can then alter the effective permittivity function of PCL and SPP coupling conditions. The measurements were done on azimuthally rotated structure to analyze the magnitude of plasmonic wave-vector and its propagation direction. Comprehensive analytical modeling that simulates plasmonic excitation was done to improve efficiency and understand the effect of azimuthal rotation.

5.2.1.1 Experimental Procedure

Fabrication step involving double exposure IL method has been discussed in chapter 3. This method provides flexibility in adjusting the PCL's physical parameters to improve the field enhancement hence increase plasmonic coupling efficiency. The photoresist coated substrate was placed on Lloyd's sample holder and exposed at different time combinations to obtain the structures. Once developed, the patterned structures on photoresists were coated with 37nm/8nm of silver and gold. The profiles and optical characterizations were examined by AFM and Woollam's variable angle spectroscopic ellipsometer from 15°-80° at 600-900nm with step size of 0.5° and 2nm respectively, followed by analysis using WVASE software as elaborated in chapter 3. The azimuthal angle was explored between 0° and 60°.

5.2.1.2 Result and Discussions

5.2.1.2.1 Fabrication Process

Several PCLs with periodicity of 0.5 μ m and amplitude of about 30nm have been prepared by IL method and reported in Table 5.1. The ability to adjust of PCL's physical parameters is very critical to offer distinctive SPP responses. One dimensional PCL is able to be fabricated using single exposure; whereas periodic transitional structures and two dimensional sinusoidal gratings or nano-disks/holes can be patterned using double exposures with different time combinations. To form the structures, it is necessary to have much longer periods for first exposure. The FESEM image of the PCL is given in Fig. 5.9. The optical properties of the transitional crystal will then be measured to study the effects on coupling efficiency and investigate some distinctive responses to completely appreciate this intermediate structure.

Table 5.1. Different parameters to fabricate plasmonic crystals. This table is reproduced from [104]

	Samples			
	1	2	3	4
Exposure types	Single	Double	Double	Double
Lattice Angle	0°	90°	90°	90°
1 st Exposure	20s	18s	18s	18s
2 nd Exposure	0s	12s	15s	18s
Incoming Angle	26°	26°	26°	26°
Pitch (nm)	500	500	500	500
Surface Profile	1D Grating	Transitional	Transitional	Bigrating
Line Width (nm)	244	172	98	0
Vertical Height (nm)	30	34	35	38

Figure 5.9. FESEM image of transition structure with 500nm of periodicity and amplitude of 30-40nm. This figure is reproduced from [104].

5.2.1.2.2 Characterizations

The structure was optically measured for $\varphi=0^\circ$ - 60° and $\lambda=600$ - 900 nm. Reflectivity measurements for zero azimuthal angle is represented in Fig. 5.10 where the dips at different incident angle relate to the SPP generations. For visual purposes, only certain wavelengths were chosen to represent the full spectrum. For unbroken symmetry ($\varphi=0^\circ$) and $m=+1$, the reflectivity dips are similar to 1D plasmonic grating: the dip position moves to higher theta value as the wavelength increases, therefore giving general idea that the structure does not have any distinction compared to plasmonic grating. It can be hypothesized that for $\varphi=0^\circ$, the incoming photon only spots the array (in x axis) that is parallel to its momentum. The only differentiation is noted on the reduction of reflection curve which points out the increase in SPP effectiveness caused by focusing shape of structure thus enhance the plasmonic field [280, 281]. SPP efficiency is defined by the ratio of photon intensity coupled into SPP and incoming photon intensity which is shown by the reflectivity value at resonant angle at fixed wavelength. In the grating vector direction, 1D PCL has much smaller curvature (flat) than transitional structure and for identical periodicity, Au/Ag film thicknesses, resonance wavelength and angle; it can be shown that structure with larger curvature provides better SPP coupling efficiency.

Figure 5.10. Reflectivity measurement of 1D plasmonic grating (solid lines) and the transition structure (dashed lines) at zero azimuthal angle and $\lambda=700-800\text{nm}$. Inset is the graphic orientation of the structure, in which TM field parallel to the x . The crystal momentum g_x is collimated to x -direction ($\Lambda=a$) with diagonal momentum g_{dia} is 45° from x -axis ($\Lambda=a\sqrt{2}$). This figure is reproduced from [104].

Type of PCL	Curvature (1/r)	Reflectivity @720nm	Transitional PCL
1D PCL	$\approx 0 \text{ m}^{-1}$ (flat line)	$\approx 56\%$
Transitional PCL	$\approx 2.86 \times 10^6 \text{ m}^{-1}$	$\approx 40\%$	

For $\varphi=40^\circ$, two SPP dips are able to be identified in SPR measurement (Fig. 5.11). As the sample is azimuthally rotated, apparent angular shifting of SPR dips can be recognized, as reported previously [72]. For azimuthal angle larger than 50° , one of SPR dips demonstrates double SPP which at longer wavelength merges into single wide dip. Physical description and proposed theory of double dips combination have been elaborated in earlier section.

Figure 5.11. Reflectivity measurement for $\varphi=40^\circ$ and $\lambda=650-750\text{nm}$. Two SPP dips are able to be identified for different wavelength. This figure is reproduced from [104].

In transitional structure, two plasmons are able to be generated using single wavelength, demonstrated by two SPR dips. These dips do not correspond to double SPP where the dips may combine at longer wavelength. The dips are originated from two crystal momentum with periodicity of a and $a\sqrt{2}$ at 45° in x - z plane (inset Fig. 5.10). This hypothesis was confirmed by dispersion curve that points out the existence of two SPP generations as shown in Fig. 5.12. In transitional structure, the diagonal crystal momentum was taken into account.

Figure 5.12. (a) Dispersion curve of the structure for $\varphi=40^\circ$ from (Fig. 5.11). The theoretical curve can be constructed from Raether's equations and fitted the experimental data. (b) The schematic orientation of the structure. The primary and secondary dispersion lines are found to be originated from 40° CCW (black rings along x' axis) and 5° CW diagonal arrays respectively relative to x axis. This figure is reproduced from [104].

The reflectivity data from Fig. 5.11 (incident angle, wavelength and azimuthal angle) were extracted and represented in the dispersion relation (Fig. 5.12). The experimental data was fitted with simulated dispersion curve developed from Raether's to trace the origin of SPP dips. From Fig. 5.12 the first SPR dip is proven to be generated by azimuthally rotated x -axis arrays and secondary one is from series of pseudo-diagonal array (45°) with pitch. The dispersion relation and diagram of 40° CCW the structure are shown in Fig. 5.12. The significant distinction with 2D PCL is the absence of additional SPP due to y -axis array because no periodic structures are formed in that axis.

The mechanism of SPP generations in this intermediate structure is able to be explained using momentum conservation schematic illustrated in Fig. 5.13. The largest, medium and smallest hemi-circles respectively represent the wave-vector pitch, $\bar{g}_x$ with $\Lambda_x=a=500\text{nm}$, diagonal lattice, $\bar{g}_{dia}$ with $\Lambda_{dia}=a\sqrt{2}=707.1\text{nm}$ and SPP (k_{spp}) for $\lambda=650\text{nm}$. Since the periodicity in diagonal direction is larger than the wavelength, its momentum hemi-circle will be located inside the SPP momentum hemi-circle. Fundamentally the momentum diagram for the structure is similar to plasmonic grating (Fig. 5.8). The effects of diagonal wave-vector together with azimuthal rotation are included. When the structure is azimuthally rotated to larger angle (position 2, $\varphi=50^\circ$ for $\bar{g}_x$ or $\varphi_{dia}=95^\circ$ for $\bar{g}_{dia}$), both $\bar{g}_x$ and $\bar{g}_{dia}$ meet the SPP generation condition. The main crystal momentum intersects the SPP hemi-circle at two positions, i.e. 2_1 and 2_2 (correspond to double SPPs), and hence three plasmons are able to be generated (Fig 5.13).

Figure 5.13. Momentum diagram of the transition structure for $\varphi=50^\circ$. φ_{dia} is azimuthal rotation of diagonal vector relative to horizontal axis. Three plasmons (2_1 , 2_2 and $2'$) can be generated; 2_1 and 2_2 are double dips. This figure is reproduced from [104].

5.2.1.3 Expanding The Raether's Equation

Contrasting to bi-grating structure (section 5.2.2), the y -axis arrays in transitional structure are not perfectly separated hence its contribution in SPP generation will be abandoned. Nevertheless, at relatively high azimuthal angle, beside the x -axis array, the crystal momentum from diagonal arrays (in Fig. 5.13) needs to be taken into account. The additional SPP contribution from diagonal crystal momentum is given by [104]:

$$\vec{k}_{SPP-dia} = \vec{k}_{ph} + \vec{g}_{dia} \quad (5.8)$$

$$\text{where } \vec{g}_{dia} = \frac{2\pi}{\sqrt{\Lambda_x^2 + \Lambda_y^2}} \angle \left(\frac{\gamma}{2} + \varphi \right) \quad (5.9)$$

and for $|\Lambda_x| = |\Lambda_y|$, Eq. 5.9 becomes:

$$\vec{g}_{dia} = \frac{2\pi}{a\sqrt{2}} \angle (45^\circ + \varphi) \quad (5.10)$$

Hence the new SPP conservation momentum [104]:

$$\vec{k}_{SPP-TOTAL} = \vec{k}_{SPP} + \vec{k}_{SPP-dia} \quad (5.11)$$

At small φ rotation, this momentum addition could be ignored. Nevertheless for larger angle, this additional diagonal momentum ($\vec{k}_{SPP-dia}$) gives significant contribution to whole SPP momentum ($\vec{k}_{SPP-TOTAL}$) and consequently should be included.

5.2.1.4 Summary

The transition structure, intermediary structure between 1D and 2D array has been effectively produced by means of IL technique and optically measured by SPR spectrometer. Multiple SPPs were able to be selectively generated using single incoming wavelength by varying the azimuthal angle. Sharp curvature of the structure demonstrates enhancement in plasmonic coupling efficiency. The SPPs propagation on the transitional array can be theoretically calculated by Raether's equations, expanded to include the diagonal crystal momentum.

5.2.2 2D Square Lattice Plasmonic Crystal

In this section, the SPP(s) excitation on 2D PCL prepared by double exposures IL is discussed. For identical exposure periods, clear peak array from bi-sinusoidal grating can be observed however the depth of valley formed on the photoresist for both axes will be not equal, hence the second exposure needs to be slightly shorter. The sinusoidal profile's amplitude may directly influence the coupling efficiency. This problem can be eliminated as double mirrors are used in Lloyd's sample holder as mentioned in chapter 3. The longest exposure period will be limited by photoresist's dose to fully crosslink the polymer chains.

Unlike 1D grating, the application of 2D PCL has not been widely exploited. Some theoretical study of bi-grating optical properties has been done [66-69, 91, 282, 283], however they still lack of experimental data. Here 2D sinusoidal square lattice PCL shown in Fig. 5.14 will be discussed. The application of 2D PCL, besides nano holes array for extraordinary transmission (EOT), has not been greatly appreciated. Similar to 1D grating, 2D PCL employed in a variety bio-chemical molecular level detection [23, 29, 33, 145, 152, 195, 201, 284, 285]. The 2D PCL offers bio-sensing capability without using any higher index medium combining simultaneous high throughput and sensitivity.

The SPP excitation on 2D PCL has not really been experimentally studied and discussed elsewhere especially the effect of azimuthal rotation. In this section the SPP propagation on 2D PCL utilizing all of the crystal momentum will be discussed. The purpose is to have a full control on excited SPPs. The analysis will employ the conical configuration where the incoming photon wavevector is unnecessary to be coincided with the crystal momentum and

as the azimuthal angle is not zero, the diagonal and y -axis crystal momentum are taken into account. The mechanism of all wavevectors will be presented in the schematic including the direction of crystal momentum, light and SPP wavevector. For non-zero azimuthal angle it will significantly increase the possible conditions that satisfy SPP generation with certain degree of p -to s -polarization conversion which reduces plasmonic effectiveness [87, 96, 121, 123, 286].

Figure 5.14. (left) AFM images of 2D plasmonic crystals with the periodicity and height analysis (right) secondary electron images (SEI). The arrays have periodicity of 498nm and amplitude of 30-35nm.

A novel approach to employ a single incoming wavelength to generate at least three plasmons with unique propagation characteristics is demonstrated in this section. Some important findings include the contribution of diagonal crystal momentum and double SPPs combination. The SPPs conservation momentum offers very straightforward representation of plasmonic wave-vectors arrangement on rotated PCL including the incoming photon and energy dispersion. Azimuthal angle opens the possibility to concurrently generate a huge amount of plasmonic modes for identical frequency with unique directions.

5.2.2.1 Optical Characterization of 2D PCL

SPR reflectivity spectrum of 2D sinusoidal square lattice PLC was recorded for $\varphi=0-60^\circ$ and $\lambda=600-900\text{nm}$, nevertheless only several wavelengths were shown to represent the entire range. Similar to transitional structure, for zero azimuthal angle, the tendency of the SPR dips for the entire energy range are indistinguishable to the 1D plasmonic grating, hence providing the idea that 2D structure does not have any distinction compared to 1D plasmonic grating. Again the only differentiation is noted on the depth in reflectivity curve which points out the increase in SPP effectiveness caused by plasmonic focusing shape from the sharpening hills shape 2D and enhances the plasmonic intensity.

5.2.2.2 Azimuthal Effect in 2D PCL

The azimuthal contribution in SPP generation on sinusoidal square lattice 2D PCL is demonstrated by the SPR measurement at several plasmonic wave-vector orientations (Fig. 5.15). The measurement of 2D PCL for $\varphi=0^\circ-60^\circ$ was accompanied by the appearance of second SPP dips, SPR angular shifting, changes (broadening and sharpening) in FWHM of reflectivity dips and merging of double SPP dips.

In square lattice 2D PCL, for $\varphi \neq 0^\circ$ at least two SPPs can be generated using single incoming wavelength. Each SPP is demonstrated as individual dip in SPR measurement. The two SPPs are not related to double plasmon generations where the combination of the SPPs can be done as reducing the incoming light's frequency. However, the presence of two SPPs dips is originated from three wave-vector of 2D plasmonic crystal: the x -axis array $\bar{g}_x$, y -axis array $\bar{g}_y$ and diagonal array $\bar{g}_{dia}$ ($a=b$) differing by 45° in in-plane orientation.

5.2.2.3 Type of Plasmons in 2D PCL

In the reflectivity spectra shown in Fig. 5.15, two different types of plasmons are observed in 2D PCL, corresponding to propagating surface plasmon (SPP) originating from delocalized Bragg plasmon and localized surface plasmon (LSP). Both plasmons are surface plasmons (SP), however their behaviour is very different. The types of plasmons generated on periodic nanostructure are strongly dependent on its geometry and dimensions.

Figure 5.15. Reflectivity spectra of 2D PCL at several azimuthal angles, φ at $\lambda=680\text{nm}$. Angular shifting and dip broadening can be noticed as φ is rotated between 0° and 60° . The dips will be broadened and shifted to larger value as φ increases up to 45° and subsequent to that the dips will be thinned and shifted back to lower angle as $45^\circ < \varphi < 90^\circ$. The presence of localized surface plasmon (LSP) is detected at higher angle

Propagating surface plasmon (SPP) is excited from Bragg scattering off the PCL periodicity with continuous metallic film as demonstrated in Fig. 5.17 (a). Both 1D and 2D PCL may show evidence of this type of plasmon. SPP is recognized by a sharper dip, changes in the excitation wavelength and dependent on sample orientation. SPP shows a unique characteristic as the azimuthal angle is increased - the possibility to split in propagation direction, which is known as double SPP [72]. This SPP could be predicted from PCL pitch and influenced by the amplitude of surface profile and polarization state. Unlike a flat surface, as the orientation of the PCL is changed, the polarization will experience a certain degree of rotation. Hence there is a possibility of TE polarized light to be coupled onto the PCL at a certain azimuthal angle which will be described in following section.

However, as the amplitude of the profile increases, the effective refractive index increases and internal scattering will dominate due to high enclosed wall i.e. the valley; where the plasmon on either side of the walls will start to interfere and being ‘trapped’, which will lead to the presence of confined standing (localized) mode as shown in Fig. 5.16 [287, 288]. The localized mode may also be generated when the thermal evaporation excludes the vertical wall created on the structure during the RIE process and produces non-continuous metallic film as demonstrated in Fig. 5.17 (b). However the imprinting step (chapter 3) will eliminate this vertical wall issue. The localized mode will not be affected by the changes in azimuthal and incoming angle. Thus the position of localized mode will be independent of incoming angle and wavelength.

Figure 5.16. The green field on the peaks represents the propagation of surface Plasmon, while the localized surface Plasmons are trapped and may occur in the valley which is represented by dark red colour.

Figure 5.17. Side view of 2D PCL (a) sinusoidal structure (from developed photoresist or imprinting polymer) with continuous Au film and (b) digital structure with discrete Au film at the base and cap of the disk/pillar due to horizontal wall created during RIE process.

In this thesis, sinusoidal periodic nanostructure with optimum amplitude and continuous metallic film is desired and preferred to generate the best coupling condition for propagated surface plasmon (SPP) mode.

5.2.2.4 2D PCL Symmetry and Azimuthal Rotation

The SPP dips will be broadened and right shifted as the azimuthal angle increases up to 45° and subsequent to that, the dips will be thinned and left shifted back to lower angle as the azimuthal angle increases $\varphi > 45^\circ$ ($45^\circ < \varphi < 90^\circ$) in opposite way as judged against $0^\circ < \varphi < 45^\circ$. The phenomenon can be described using the symmetry of square array in the reciprocal lattice (Figure 5.18). Besides, the total symmetry cycle for square lattice 2D PCL is two times higher than 1D PCL. The square lattice 2D PCL has 4 folds symmetry so the cycle will be repeated every $2\pi/4$ (90°) and the central symmetry is at $2\pi/8$ (45°). As a result the optical trend from 0° to 45° (CCW) will be the same as 90° to 45° (CW). While 1D PCL gratings has 2 fold symmetry so the cycle will be repeated every π (180°) and the central symmetry is at $\pi/2$ (90°). As a result the optical trend from 0° to 90° (CCW) will be the same as 180° to 90° (CW). The changes in the distance is proportional to $|\sin \varphi|$ and it explains the shifting of the dips in the opposite direction for $\varphi > 45^\circ$.

Figure 5.18. Schematic of 2D disk square array rotated azimuthally from $\varphi=0^\circ$, 30° , 45° , 60° and 90° (CCW). The reciprocal lattice distance between two nearest disks located parallel to the k_{ph} line becomes larger as the azimuthal angle increases and reaches the maxima at 45° ; afterward it will reduce and finally form symmetry at smaller repeating angle (90°). It explains the shifting of the dips in the opposite direction for $\varphi > 45^\circ$.

The SPP generation in 2D PCL is proved by dips in the reflectivity measurement (λ , $\theta_{\min}$) as summarized in Fig. 5.19. The FWHM reflectivity dip, $\Delta\theta_{FWHM}$, is broaden as the azimuthal rotation move to higher value. As the azimuthal angle is getting larger, the gradient between the wavelength and incoming angles becomes gentler (Fig. 5.19). For $\varphi \neq 0^\circ$, the presence of second minima in reflectivity measurement could be detected. This dip is originated from the other lattice axis which is 90° away from origin axis. As a result, the curve for the 2nd dips

will be similar to 1st dip azimuthal angle of $90^\circ - \varphi$. This is proven by 2 pairs of curves which are close to one another: 1st dip of $\varphi=40^\circ$ with 2nd dip of $\varphi=50^\circ$ ($=\varphi'=40^\circ$) and 1st dip of $\varphi=50^\circ$ with second dip of $\varphi=40^\circ$ ($=\varphi'=50^\circ$). Another phenomenon is the combination of double dips which is shown by vertical trend line from the tail of the curves for $\varphi=40^\circ$ - 70° .

When $\varphi > \varphi_c$, single frequency of incoming photon may generate at least three sets of plasmon. Increment in wavelength may combine the double SPR dips into single wide dip up to certain limit beyond which the plasmon generation is prohibited. The error bars are shown for several points, correspond to $\Delta\theta_{FWHM}$. Without additional crystal momentum, the 2D PCL dispersion curve will just be similar to 1D PCL.

Figure 5.19. The data collected from square lattice 2D PCL for $\varphi=0^\circ$ - 60° are plotted. As azimuthal and resonance angle increase, the FWHM increase as well. There are additional curves that represented above: 2nd dips of azimuthal angle of 30° - 60° .

5.2.2.5 Data Analysis of 2D Square Lattice PCL at Different Azimuthal Angle

The dips' shifting and broadening will change significantly as the critical azimuthal angle is reached (e.g. here $\varphi_c > 40^\circ$). The measurements in Fig. 20 (a) were done for $\varphi=50^\circ$ and $\lambda=620$ - 770 nm. Three minima were generated for $620\text{nm} < \lambda < 680\text{nm}$. This indicates that 2D PCL gives more information than 1D PCL grating. From multiple SPPs being generated, one of them may demonstrate double SPPs. This double dips will come closer one another as the light moves to longer wavelength and at the end combine into a wide dip at $\lambda=682\text{nm}$ with $\Delta\theta_{FWHM}=38^\circ$. Further increase in the wavelength ($682\text{nm} < \lambda < 740\text{nm}$) consequences shallower SPR dips which at the end will vanish as $\lambda > 682\text{nm}$. The kinematic model and physical description behind the combination of double SPPs dip has been discussed earlier.

The plasmonic dispersion relation of square lattice 2D PCL at $\varphi=50^\circ$ (Fig. 5.20 (c)) is constructed from the three sets of reflectivity data (drawn in red, purple and green lines). Employing Raether's equation, simulated dispersion curves can fit the measured data very well and the origin of each curves can be easily traced i.e. the red curve is from red circles along x' direction with $\Lambda_x=a$, 50° CCW (from horizontal axis), while the purple curve is from purple circles along y' direction with $\Lambda_y=b$, 50° CCW (from vertical axis) and green curve is additional array originating from green circles along diagonal direction with $\Lambda_{dia}=a\sqrt{2}$, -5° CCW (from horizontal axis). In this case $\Lambda_x = a \approx b$ as demonstrated in Fig. 5.20 (c).

Figure 5.20. (a) SPR curve of 2D PCL for $\varphi=50^\circ$ at $\lambda=620\text{-}770\text{nm}$, (b) $\lambda=670\text{-}688\text{nm}$ and (c) dispersion curve with schematic orientation. At least three SPPs can be excited using single frequency: 50° CCW $\vec{g}_x$ in x' axis ($\Lambda_x=a$), $\vec{g}_y$ in y' axis ($\Lambda_y=b$) and $\vec{g}_{dia}$ is 5° CW from x axis ($\Lambda_{dia}=a\sqrt{2}$).

Schematic of rotated array 2D square lattice PCL relative to x - y axis for $\varphi=20^\circ$, 40° , 50° and 60° are demonstrated in Fig. 5.21.

Figure 5.21 Schematic representation of rotated array 2D PCL with the possibility of plasmon excitation for a certain direction: a) for $\varphi=20^\circ$, the red and purple circles array are rotated 20° CCW away from positive x - and y -axis respectively. Another possibility for plasmon excitation is the diagonal of square lattice (green circles); b) $\varphi=40^\circ$; c) 50° ; d) 60° .

5.2.2.6 Momentum Analysis in 2D Plasmonic Crystal

For SPPs generation in 2D PCL, lattice periodicity needs to be comparable with the incoming photon momentum. Similar to 1D PCL grating, the plasmonic generation in 2D PCL can be realized whenever wave-vector conservation condition is matched (Eq. 5.1). The plane of incident is perpendicular to sample's surface (Fig. 3.22) and consists of incoming photon momentum whose direction is at θ angle relative to normal line (Eq. 5.2). The $\vec{g}$ is a lattice vector momentum of PCL. The grating wave-vector (Eq. 5.3) sits on x - y momentum plane. 2D PCL has at least two periodicities for each lattice axis denoted by $\vec{a}$ and $\vec{b}$ with γ as the lattice angle. If $\vec{a} \perp \vec{b}$ ($\gamma=90^\circ$), as will always be the case here, then $\vec{g}$ is given as:

$$\vec{g}_{xy} = m\vec{g}_x + n\vec{g}_y \quad (5.12)$$

where m and n represent the diffraction order of x and y direction.

$$\vec{g}_x = 2\pi/|\vec{a}| \text{ and } \vec{g}_y = 2\pi/|\vec{b}| \quad (5.13)$$

where $\Lambda_x = |\vec{a}|$ and $\Lambda_y = |\vec{b}|$

5.2.2.6.1 Crystal Momentum Analysis

For 2D square lattice, the crystal momentum consists of: 1) $\vec{a}$ is on x -axis and $\varphi=0^\circ$ and 2) $\vec{b}$ on y -axis where the lattice angle equals to 90° and $|a|=|b|=\Lambda$. The reciprocal crystal momentum is similar to Eq. 5.12-5.13 and for non zero azimuthal angle, Eq. 5.13 becomes:

$$\vec{g}_x = \frac{2\pi}{|\Lambda_x|} \begin{pmatrix} \cos \varphi \\ \sin \varphi \\ 0 \end{pmatrix} \text{ and } \vec{g}_y = \frac{2\pi}{|\Lambda_y|} \begin{pmatrix} \sin \varphi \\ \cos \varphi \\ 0 \end{pmatrix} \quad (5.14)$$

For non-orthogonal lattices, further calculation need to be done relative to the angle between two axes in reciprocal space [40, 66, 69-71, 73]. Similar to transitional structure in section 5.2.1, for certain incident azimuthal angle, besides the two main axes, the diagonal crystal momentum will contribute in SPP excitation. The additional $\vec{k}_{SPP-dia}$ and $\vec{g}_{dia}$ for 2D PCL is identical to the one (Eq. 5.8-5.11) discussed in section 5.2.1.3.

To simplify the condition, all non 0° vector are split into x and y direction. The x -projected vector will contribute to the SPP, however y - will not contribute to the SPP (analogous to excitation of arrays in x -direction by s -polarized light).

5.2.2.6.2 Non Orthogonal Lattice Vector ($\gamma \neq 90^\circ$)

Figure 5.22. Lattice with arbitrary angle γ , real axis of a, b, and momentum vector $\bar{g}_a$ and $\bar{g}_b$.

Plasmon interactions in 2D PCL needs further study especially for non-orthogonal lattice. To represent the equation graphically, the model in Fig 5.22 can be considered. In the case of arbitrary angle (non orthogonal lattice, $\gamma \neq 90^\circ$), the $\bar{g}_a$ and $\bar{g}_b$ can be defined as:

$$\bar{g}_a = \frac{2\pi}{|\bar{a}|} \begin{pmatrix} \cos \varphi \\ \sin \varphi \\ 0 \end{pmatrix} \text{ and } \bar{g}_b = \frac{2\pi}{|\bar{b}|} \begin{pmatrix} \sin(\gamma + \varphi) \\ -\cos(\gamma + \varphi) \\ 0 \end{pmatrix}$$

They are momentum array vector for a and b respectively. γ is the lattice angle.

Another way to represent it is by the reciprocal lattice vector. The shape of the lattice is similar to the real lattice except that it is rotated 90° and the angle becomes $(180^\circ - \gamma)$; while the size is inversely proportional to the real lattice. For simplicity, it is assumed that one axis is parallel to x - or y -axis. If $\bar{g}_a$ is assumed to be coincided with positive x -axis, the total momentum array vector $\bar{g}$ is given as:

$$\bar{g}_{xy} = 2\pi p \left(\frac{\cos \varphi}{|\bar{a}|} + \frac{\sin(\gamma + \varphi)}{|\bar{b}|} \right) \hat{x} + 2\pi q \left(\frac{\sin \varphi}{|\bar{a}|} - \frac{\cos(\gamma + \varphi)}{|\bar{b}|} \right) \hat{y} \quad (5.15)$$

With the additional diagonal momentum lattice vector:

$$\bar{g}_{dia} = \frac{2\pi}{\sqrt{|\bar{a}|^2 + |\bar{b}|^2 - 2 \cdot |\bar{a}| |\bar{b}| \cos \gamma}} \left[\cos(\varphi + \gamma), \sin\left(\varphi + \frac{\gamma}{2}\right), 0 \right] \quad (5.16)$$

where p and q are diffraction order of x and y -direction. For square or rectangular arrays, $p=m$ and $q=n$ and $\bar{g}$ is given by Eq. 5.13. For a special lattice like hexagonal lattice ($\bar{a} = (1,0)$ and $\bar{b} = (1/2, \sqrt{3}/2)$ with $\gamma=60^\circ$ and $\varphi=0^\circ$), the reciprocal lattice vector is given as:

$$\bar{g}_a = \frac{2\pi}{|\bar{a}|} \hat{x} \text{ and } \bar{g}_b = \frac{2\pi}{|\bar{b}|} [(\cos 60^\circ) \hat{x} + (\sin 60^\circ) \hat{y}] \quad (5.17)$$

For $|a|=|b|$ and the $\bar{g}_a$ is assumed to be parallel with x -axis, Eq. 5.17 can be simplified:

$$\bar{g} = \bar{g}_a + \bar{g}_b = \frac{2\pi}{|a|} \left(\frac{2}{3}(m+n)\hat{x} + \frac{\sqrt{3}}{2}n\hat{y} \right) \quad (5.18)$$

5.2.2.7 SPP Propagation Direction

The direction of SPP momentum, $\vec{k}_{spp}$, is on PCL surface and can be noted by β angle (see Fig. 5.23 for frame of reference definition). 2D PCL has a possibility to excite multiple SPP (i.e. from $\vec{a}$, $\vec{b}$ and diagonal array). Each SPP has their unique $\vec{k}_{spp}$ and propagation direction, namely β_a , β_b and β_{dia} (or β_x , β_y and β_{dia} for square lattice) with this relationship:

$$\beta_b = \beta_a + \gamma, \text{ and } \beta_{dia} = \beta_a + \gamma/2 \quad (5.19)$$

The SPP momentum magnitude, $|\vec{k}_{spp}|$ as a function of incoming frequency can be represented by its dispersion relation (Eq. 2.35 and 2.37). Similar to Eq. 5.4-5.5, for any array directions, the x-components of $\vec{k}_{spp}$, is given:

$\vec{a}$	$k_{SPP(a)-x} = k_{SPP}(\omega) \cos \beta_a = \pm \sqrt{k_{SPP}^2(\omega) - (mg_a \sin \varphi)^2}$	(5.20)
$\vec{b}$	$k_{SPP(b)-x} = k_{SPP}(\omega) \sin \beta_b = \pm \sqrt{k_{SPP}^2(\omega) - (ng_b \sin(\varphi + \gamma))^2}$	(5.21)
Diagonal	$k_{SPP(dia)-x} = k_{SPP}(\omega) \cos \beta_{dia} = \pm \sqrt{k_{SPP}^2(\omega) - \left(pg_{dia} \sin\left(\varphi + \gamma/2\right) \right)^2}$	(5.22)

where the momentum conservation in y-axis direction:

$\vec{a}$	$k_{SPP(a)-y} = mg_a \sin \varphi$	(5.23)
$\vec{b}$	$k_{SPP(b)-y} = ng_b \sin(\varphi + \gamma)$	(5.24)
Diagonal	$k_{SPP(dia)-y} = pg_{dia} \sin\left(\varphi + \gamma/2\right)$	(5.25)

The schematic in Fig 5.23 is used to explain the crystal momentum vector in 2D PCL (5.20-5.22). The mechanism of single and double SPPs generation by 2D sinusoidal square lattice PCL is able to be well described by this momentum conservation diagram. For most SPR conditions only first diffractive order is collected ($m=1$), however in certain case when handling with lattice momentum in diagonal direction, the second diffraction order can also be detected ($m=2$). This because diagonal direction has smaller wavevector compared to the main lattice axis ($|\vec{g}_{dia}| \ll |\vec{g}_a|/a\sqrt{2}$ or $|\vec{g}_{dia}| \ll |\vec{g}_b|/a\sqrt{2}$).

Figure 5.23. Momentum conservation diagram of square lattice 2D PCL for $\varphi=30^\circ$ (top) and 50° (bottom). $\Lambda_x=\Lambda_y=a$, hence the $\bar{g}_x$ and $\bar{g}_y$ will share the same thick black line hemi-circle. As $\Lambda_{dia}>\lambda$, the $\bar{g}_{dia}$ will always be inside the plasmonic momentum hemi-circle. The angle between $\bar{g}_x$ and $\bar{g}_y$ is always 90° . The numbers (1, 2, 3 and 4) show several possible excitation conditions for different azimuthal angle. The β shows the propagation direction of surface plasmon for each crystal momentum.

The darker and lighter lines in Fig. 5.23 correspond respectively to the PCL wave-vector with periodicity of $0.5\mu\text{m}$ for $\bar{g}_x$; first and second order diagonal direction with periodicity of $0.707\mu\text{m}$ for $\bar{g}_{dia}$ and the red line represents $\bar{k}_{spp}$ for a unique incoming wavelength ($\lambda=670\text{nm}$). Since the periodicity in diagonal direction is larger than the incoming wavelength, the first order $\bar{g}_{dia}$ hemi-circle will be inside the red line. The $|g_x|$ equals to $|g_y|$ while $|g_{dia}| = \frac{m \cdot |g_y|}{\sqrt{2}}$. For first Brillouin zone, $|g_{dia}| = 0.7071 |g_x|$ while for second one $|g_{dia}| = 1.4142 |g_x|$.

As higher azimuthal angle is considered (Fig. 5.23, point **2**, $\varphi=30^\circ$ for g_x , point **2'** $\varphi_{dia}=75^\circ$ for g_{dia} , point **2₁''** and **2₂''** from g_y), several SPPs can be generated. For $\varphi=30^\circ$ the double dip from x -axis ($\bar{g}_x$) cannot be excited, however the array from y -axis ($\bar{g}_y$) is possible to excite double dips (proven in Fig 5.24-5.25). This is the uniqueness of 2D PCL thus four

SPPs (including points **2** and **2'**) can be excited. For $\varphi=50^\circ$ there are points **3₁**, **3₂** from $\bar{g}_x$, point **3'** from $g_{\text{dia}(1)}$, **3''** from $g_{\text{dia}(2)}$ and point **4** from $\bar{g}_y$. Here g_x cuts the k_{SPF} circle at **3₁** and **3₂** (double dips) thus five SPPs can be excited. Since the resonance conditions for plasmon excitation in **3₂**, **3'** and **4** are close to each others, they will appear as single broad SPP dip. As the wavelength increases the separation between **3₂**, **3'** and **4** could be clearer.

$\bar{k}_{\text{SPP}}$ conservation equation is applicable for all vector that have momentum larger than $\bar{k}_{\text{SPP}}$ with angle smaller than 90° such as points **2**, **3** in Fig. 5.23 and **3''** (second order diagonal array) or for vector array that has smaller momentum than $\bar{k}_{\text{SPP}}$ but with angle larger than 90° such as point **3'** (first order diagonal array). In this case, $\bar{k}_{\text{ph}_x}$ is in positive direction.

There are special cases where $\bar{k}_{\text{ph}_x}$ is in negative direction. It may happen for vector arrays that have smaller momentum than $\bar{k}_{\text{SPP}}$ with angle smaller than 90° such as point **2'** (first order diagonal array) or for vector array that has larger momentum than $\bar{k}_{\text{SPP}}$ but with angle larger than 90° such as point **4** (from g_y with angle $\varphi+90^\circ$). This adjustment (negative direction of $\bar{k}_{\text{ph}_x}$) is needed to compensate the different in vector directions, hence the plasmonic momentum will always be conserved.

Similar to 1D PLC [72], $\bar{k}_{\text{SPP}}$ direction for each array ($\bar{a}$, $\bar{b}$ and diagonal) can be determined:

$$\beta_{(a/b/dia)} = \text{ArcTan} \left(\frac{\bar{k}_{\text{SPP}(a/b/dia)-x}}{\bar{k}_{\text{SPP}(a/b/dia)-y}} \right) \quad (5.26)$$

The plasmonic propagation direction β could be calculated by putting Eq. 5.20-5.25 into Eq. 5.26 and it agrees well with the analytical model. The SPP dispersion curve for SPR measurement and theoretical result are demonstrated in Fig. 5.26 (left).

The example for double plasmonic generation condition is demonstrated in schematic of wave-vector (Fig. 5.23) for $\varphi=30^\circ$ ($\bar{g}_y$) and 50° ($\bar{g}_x$). $k_{\text{ph}-x}$ line may couple into $\bar{k}_{\text{SPP}}$ twice: noted by point **3₁** and **3₂** (for $\varphi=50^\circ$) and propagate at β_x^- and β_x^+ . As azimuthal angle is further adjusted to higher value (while wavelength is fixed) or vice versa, the two $\bar{k}_{\text{SPP}}$ may merge into single broad dip (as $\beta^- = \beta^+ = 90^\circ$, is at right angles to $k_{\text{ph}-x}$). Other properties on schematic of 2D PCL wavevector are identical to 1D PCL (section 5.1).

5.2.2.8 Combination of several SPPs with Similar Direction (β)

As shown in Fig. 5.23, for $\varphi=50^\circ$, there are five SPPs (point 3_1 , 3_2 from $\bar{g}_x$, point $3'$ from $g_{dia(1)}$, $3''$ from $g_{dia(2)}$ and point 4 from $\bar{g}_y$). Since the SPP propagation direction in 3_2 , $3'$ and 4 are close to each others, the individual dips cannot be clearly distinguished.

Figure 5.24. SPR reflectivity measurement of 2D PCL evaporated only with 37nm of Ag – 8nm of Au and has periodicity of $\Lambda=500\text{nm}$ – (a) at $\varphi=50^\circ$ generated by $\lambda=710\text{-}735\text{nm}$. (b) $\varphi=30^\circ$ generated by $\lambda=625\text{-}650\text{nm}$.

The double dips of $\bar{g}_x$ are getting closer at longer wavelength and combine into a wide dip. Before they merge (Fig 5.24 (left)); the third dip is already very broad due to combination of several nearest dips. Since the propagation directions of two SPP are close one another thus both SPPs may merge into single broad dip. The plasmonic propagation direction, β of the second dip from $\bar{g}_x$, first order $\bar{g}_{dia}$ and $\bar{g}_y$ - are relatively close to one another, hence have a possibility to merge into single broad dip. These show that the third dip has larger plasmon mode concentration and since then it may show better sensitivity. As the wavelength or azimuthal angle increases the separation will be clearer e.g. at $\varphi=60^\circ$ the dip from $\bar{g}_y$ and its combination with $\bar{g}_x$ can be clearly identified (Fig. 5.25). As wavelength increases, dip from $\bar{g}_y$ will go to higher angle while the second dip of $\bar{g}_x$ behaves oppositely.

Figure 5.25. SPR reflectivity spectrum of 2D PCL with at $\varphi=60^\circ$ and $\lambda=665\text{-}685\text{nm}$. the dip from $\bar{g}_y$ and its combination with $\bar{g}_x$ can be clearly identified.

The sample was also characterized at $\varphi=30^\circ$ to investigate the dip combination from $\bar{g}_y$ and it demonstrates a similar trend (Figure 5.24 (right)). For relatively low azimuthal angle like this, the y -axis component may excite double dips at 625-650nm. As x and y -axis are perpendicular each other, the excitation of double dips at 30° by y -axis is similar to 60° by x -axis. As the excitation wavelength is increased, the single plasmonic excitation dip from $\bar{g}_x$ can be demonstrated (680-900nm) as shown in Fig. 5.26.

Figure 5.26. SPR reflectivity spectrum of 2D square lattice PCL with $A=500\text{nm}$ at $\varphi=30^\circ$ and $\lambda=680\text{-}900\text{nm}$ shows the single SPP dip (fourth dip) from x -axis.

Correlating the reflectivity spectra with the schematic of wavevector at $\varphi=30^\circ$, four plasmonic dips are able to be identified for every frequency, namely:

- double dips (first and third) generated by y -axis ($\bar{g}_y$) at 625-650nm
- single dip (second) generated by first order diagonal crystal momentum ($\bar{g}_{dia}$)
- single dip (fourth) from x -axis ($\bar{g}_x$) at 680-900nm

From Figure 5.24 above, it can be observed clearly: before the double dips from y -axis merge (at $\lambda=645\text{nm}$), the middle dip ($m=+1$, $\bar{g}_{dia}$) and the third dip will combine first (at $\lambda=635\text{nm}$). The double dips are approaching each other as the frequency reduces ($625 < \lambda < 645\text{nm}$) and at last may combine into one broad dip at $\lambda=645\text{nm}$. All dips can be explained and included in the schematic momentum of 2D PCL (Fig. 5.23 top). The merging of some Plasmons which directions (β) are close one to another will benefit the 2D PCL sensor system due to high concentration of SPP modes density which may lead to better sensitivity [72]. At lower azimuthal angle the double dip from x -axis ($\bar{g}_x$) cannot be excited, however 2D square lattice PCL has y -axis ($\bar{g}_y$) that can excite double dips at lower azimuthal angle.

5.2.2.9 SPP Modes

Generally four sets of SPP dips were able to be identified in 2D sinusoidal square lattice PCL: single dip (first dip) from $\bar{g}_{dia}$ ($m=2$) the double SPPs from $\bar{g}_x$ and combined dips (fourth dip) from $\bar{g}_{dia}$ ($m=1$) and $\bar{g}_y$. Dispersion relation of x -component of all $\bar{k}_{SPP}$ momentum is demonstrated in Fig. 5.27, including the experimental and calculated SPP propagation directions. At higher azimuthal rotation, $\varphi=50^\circ$ and above, the double SPP dips (second and third dips) can be excited from x -axis. In particular, from schematic in Fig. 5.23, the x -component of $\bar{k}_{SPP}$ momentum for each crystal momentum can be calculated:

$$k_{SPP(a)-x} = mg_a \cos\varphi - \frac{2\pi}{\lambda} \sin\theta. \quad (5.27)$$

$$k_{SPP(b)-x} = ng_b \sin(\varphi + \gamma) - \frac{2\pi}{\lambda} \sin\theta \quad (5.28)$$

$$k_{SPP(dia)-x} = pg_{dia} \cos\left(\varphi + \frac{\gamma}{2}\right) - \frac{2\pi}{\lambda} \sin\theta \quad (5.29)$$

The plasmonic excitation conditions for certain azimuthal angles in 2D PCL were fitted to the theoretical prediction using equations above. The dispersion relation data for $\bar{g}_x$ and $\bar{g}_{dia}$ ($m=+2$) in Fig. 5.27 (a) and (b) were obtained experimentally from the SPR curve (markers) and matched against theoretical value (lines) by allowing two fitting parameters i.e. azimuthal angle and periodicity. For uniform grating periodicity, SPR dips are expected to be accurate and consistent with theoretical value. The fitting parameters will subsequently optimize the curve fitting of the experimental data hence good fitting between experimental and theoretical data can be obtained. For SPP propagation direction β , as both theoretical and experimental data use identical formula, they will also provide good fitting.

When the critical azimuthal angle is reached, the combination of double dips at minimum energy can be made possible. This condition can be well explained in Fig. 5.27 (right) where the plasmonic excitation using minimum energy may take place when $\beta=90^\circ$. The propagation of surface plasmon, β is able to be fully directed by adjusting azimuthal angle, φ . The sample was well characterized over 90° and the upper limit of azimuthal angle for which the double SPP dip still can be observed individually is $\varphi_{max}=65^\circ$ and the $\beta=115^\circ$.

Figure 5.27. Dispersion relation of $\vec{k}_{SPP}$ momentum for a) $\vec{g}_x$ and b) 2nd order of $\vec{g}_{dia}$ ($m=2$, $A=\sqrt{2}A_x$) at different azimuthal angle.

The $\Delta\theta_{FWHM}$ value could be obtained from the SPR dips and increases with azimuthal rotation. This parameter will intrinsically reflected through x and y -component of $\vec{k}_{SPP}$ also transformed into momentum divergence, $\Delta\vec{k}_{SPP}$ and propagation direction, $\Delta\beta$. Therefore, the width of SPR dip gives significant physical characteristic related to the quantity of generated SPP modes. The normalized SPP density mode is given by [72]:

$$f = \frac{|\Delta\beta|}{2\pi} \quad (5.30)$$

where from Eq 5.26, direction changes of SPP propagation can be approximated by:

$$\left| \Delta \beta_{(a/b/dia)} \right| = \frac{k_{SPP(a/b/dia)-x} \Delta k_{SPP(a/b/dia)-y} - k_{SPP(a/b/dia)-y} \Delta k_{SPP(a/b/dia)-x}}{k_{SPP(a/b/dia)}^2} \quad (5.31)$$

The experimental values of f can be calculated by putting Eq. 5.20-5.22 and Eq. 5.27-5.29 in Eq. 5.31 respectively. The width of resonant angle, $\Delta \theta_{FWHM}$ and the equipment characteristic includes $\Delta \lambda \approx 2.7 \text{ nm}$ and $\Delta \varphi \approx 0.01^\circ$, are used to calculate f value.

The SPP mode density is increasing with φ . This behavior has very simple physical meaning as described in Eq. 5.30. As the azimuthal angle increases, the slope of energy band becomes gentler and flatter therefore higher density can be generated thus increases the modes density [72]. Increased SPP modes may also take place both during double dips combination and at longer wavelength for $\bar{g}_{dia}$ crystal momentum. The largest mode can be obtained when $\beta \approx 90^\circ$ (during dips combination).

5.3 Chapter Summary

In summary, the model for propagated surface plasmon in azimuthally rotated 1D and 2D PCLs have been discussed. The presence of azimuthal angle in PCLs will dramatically change the plasmonic dispersion relation that is not exhibited by conventional grating neither the prism coupled. Multiple SPP can be generated simultaneously with control in propagation direction. For any azimuthal angle, 2D SPP shows greater EM field concentration caused by its surface controur compared to 1D PCL thus the coupling of incoming photon can be optimized and improve the over all SPR quality noted by deeper dips (lower reflectivity). 2D PCLs can explore larger Brillouin zones (first and second) due to the diagonal component that can be smaller by half which will be very useful in tuning SPP properties by single PCL.

In general resonance condition involving the incoming wavelength and azimuthal angle in 2D sinusoidal PCL, a unique double plasmonic dips can be generated and including several SPPs may appear as a single wide resonance. When the critical azimuthal angle is reached,

the SPP propagation direction is possible to be tuned perpendicular to incoming photon direction. Furthermore, it relates to the spreading of differential SPPs momentum and thus the number of plasmonic modes. The chance to generate multiple surface plasmons over a wide azimuthal range has been clearly shown. The full control of plasmonic propagation on 1D and 2D PCL enable to optimize the coupling efficiency and induce field enhancement which further improve the sensitivity.

6 Extraordinary Transmission of Plasmonic Crystal

6.1. Introduction

In past decade, the enhanced of transmitted light using metallic thin films have attracted much interest since Prof. Thomas Ebbesen's article on an extraordinary light transmission using perforated holes on thin metal layer [92]. Based on conventional diffraction theory, the transmission intensity of a nano-hole is very weak and in direct proportion to the ratio of the radius over the incident wavelength [98, 206, 207] ($d \ll \lambda$). Nevertheless, for metallic nanoholes array, the transmitted intensity for specific wavelength can be greatly improved [92, 94]. Generally the process of enhancement in transmission through sub-wavelength metallic holes array may be described as follow: coupling of incoming photon on PCL, followed by SPP propagation through the holes array, and finally SPP decoupling into light emission from back surface [63, 79, 86, 120, 289]. This enhancement is influenced by the geometry of array, wavelength, angle of incidence and materials [93, 97, 102, 290]. However the details of these assumptions need to be proven by both calculation and experiment.

Several following works [206, 291, 292] have clearly shown the crucial role the SPP play in extra-ordinary transmission (EOT). The transmission of TM wave through nano-slit was reported by Pang et al. [206]. It was demonstrated the EOT dependency on geometry (length, depth, period and number of slits) and SPP propagation the surface. Polarization is another main factor in SPP generation as reported by Crouse et al. [293] for TE-mode case. No SPP is able to be generated under this mode however the presence of cavity mode can still be identified. Several other studies have investigated and elucidated the microscopic mechanisms of the light propagation [294].

6.2. Transmission Enhancement

6.2.1. SPP Roles in EOT

Although the roles of propagating surface plasmons in EOT have been proposed, the comprehensive mechanisms of EOT are still under controversy [93, 94, 206, 295]. The SPPs role in this EOT is proposed, where high EM field is localized in close proximity to the metal's holes or slits that are smaller than the incoming wavelength and create an

extraordinary transmission. The periodic corrugated structures can provide the in-plane momentum to couple the incoming photon into propagated wave. During the propagation along the continuous metallic film, SPP may interfere with the localized field surrounding the surface discontinuities and thus stronger enhancement may be developed. For the other plane, assisted by crystal momentum, the light can be convined and transmitted although the opening size is smaller than the incoming wavelength [58, 63, 289].

At 90° incoming angle, only diffraction order $m=2n$ may participate in extraordinary transmission and interaction between tunneled photons that may result in enhancement [85, 295]. PCL provides additional energy to satisfy the plasmonic momentum conservation, which at that point, the resonance interaction with incident light will take place and produce very strong intensity in zero order transmission. The EOT mechanisms are greatly influenced by PCL, mainly the geometry as well as the metallic layer thickness [146, 290, 296].

6.2.2. Waveguide mode in Transmission

Basically two different mechanisms of EOT occur in nanoslits: surface plasmon (horizontal) [15, 86] and waveguide or cavity mode [297]. Unlike the waveguide mode, the earlier one is strongly influenced by the PCL pitch and incoming photon momentum, k_x . However the later one is strongly affected by thicknes h [85, 295, 298-301].

The waveguide mode with SPP contribution will modulate, tune the energy and transmitted photon intensity as well as utilizing the periodic nanostructure for plasmonic chips as promising candidate to interface electronic and photonic devices (optoelectronic). Plamonics chip is also able to control the temporal delay of the transmitted signal, which is very important and can be implemented for certain application in optical communications.

6.3. Transmission in 1D PCL

6.3.1. Nanoslit Array

The systematic investigation of subwavelength slits transmission spectra in Au metal film at the optical wavelength range was carried out. The 1D PCL was fabricated using e-beam lithography combined with electrolytic growth on Si_3N_4 membrane with periodicity of 500nm, slit width of 220nm and electroplated Au as elaborated earlier in section 3.1.7. The

electrolytic growth method is simple and economical that allows a careful control of the thickness and high fidelity pattern reproduction regardless of aspect ratio. The thickness was controlled to reach 370nm. The final structure is demonstrated in Fig 6.1 with area of $3 \times 3 \text{ mm}^2$. Another similar sample with 650nm periodicity was fabricated on Si_3N_4 using identical method, the slit width 300nm, thickness of 370nm and electroplated with 50nm of Au. The base plate of this second sample is fully eliminated using RIE; hence the transmission is expected to be much higher.

Figure 6.1. Field emission scanning electron micrograph of 1D nanoslit PCL, obtained at 15kV, at vacuum environment down to 1.14×10^{-5} mBar. The periodicity of nanoslit equals to 500nm, the thickness is 370nm with slit width of 220nm.

6.3.2. Characterizations

The optical characterization was done in transmission mode as discussed in section 3.7.2 from 300 to 1000nm by VASE spectroscopic ellipsometer and further analyzed using Wvase Software from Woollam. The sample was varied azimuthally from 0° - 60° with a precision of 0.01° and polarization from -90° to 90° .

6.3.3. Experimental Results

6.3.3.1. Wavelength interrogation

The transmission spectra of a 1D nanoslit PCL without base plate ($\Lambda=650\text{nm}$), collected from 400-800nm for p -, s - and 45° polarization angle, is demonstrated in Figure 6.2. For p -polarized light, the spectrum shows three resonance peaks at 546nm, 610nm and 649nm. Generally the spectra move to lower wavelength and the intensities are reduced as incoming angle rises. It is primarily affected by flux intensity reduction by factor of $\cos\theta$. For $\theta=0^\circ$, the last peak at 649nm is transformed into a dip when the polarization angle is moved from 0° to 45° and reaches minimum when it turns to s -polarization. This third peak corresponds to the SPP excitation, where the p -polarized light takes the maximum contribution.

Figure 6.2. Transmission measurement of 1D nanoslit PCL without base plate, $\Lambda=650\text{nm}$, collected from 400-800nm for different incident angle at p -, s - and 45° polarization angle.

6.3.3.2. p - to s - Polarization Conversion

As the incident angle is not perpendicular to sample's plane, the p - to s - polarization conversion is able to be detected (0.4%) and noted as a peak that is increased with the incident angle (Fig. 6.3). These peaks location corresponds to one of the dips in the transmission spectra (Fig. 6.2). An interesting phenomenon can be seen in s - to p - polarization conversion measurement (Fig. 6.3). A pair of transmission peaks (<0.01%) can be observed for each wavelength and the intensity is increased with the incident angle.

Figure 6.3. a) p - to s - and b) s - to p -polarization conversion transmission measurement using 1D nanoslit PCL without base plate, $\Lambda=650\text{nm}$. The conversion polarization peak location is corresponded to one of the dip in the transmission spectra.

6.3.3.3. Angular Interrogation

The transmission 1D nanoslit PCL without base plate ($\Lambda=650\text{nm}$) was measured in angular interrogation (Fig. 6.4) at $\lambda=600\text{-}650\text{nm}$ using p -polarized light. There are two pairs of peaks for each energy level and they are getting closer as the wavelength increases. The first pair of peaks are combined at 610nm (dark green line); and at higher wavelength, the second pair combined at 650nm (light blue line). The double peaks belong to second and third dips in wavelength interrogation for $\theta=0^\circ$ (Fig. 6.2). The peaks at the two ends should be at the same angle; however the grating vector may not be exactly parallel with normal line.

Figure 6.4. Transmission measurement of 1D nanoslit PCL without base plate, $\Lambda=650\text{nm}$ in angular interrogation measurement for $\lambda=600\text{-}650\text{nm}$ using p -polarized light shows a) first peaks (dark green line) and b) second peaks (light blue line) combination.

6.3.4. Effect of Polarization in Nanoslits with Base Plate

The experimental results show that transmission through the nano-slit is strongly correlated to polarization. The resonance wavelength is found to match transmission minima and the dip locations are sensitive to pitch of slits. The polarization effect on coupling effectiveness is proportional to $\cos(\varphi-\alpha)$, where α is angle between TM and crystal momentum. The transmission measurement for Au slit array with base plate ($\Lambda=500\text{nm}$) is shown in Fig. 6.5.

Figure 6.5. Transmission measurement of 1D nanoslit PCL with base plate, $\Lambda=500\text{nm}$, at 300-800nm for different polarization angle.

From figure above, the maximum intensity of the second peak at 512nm distinctly shows that EOT is generated by TM-wave, where SPP is involved. The intensity will subsequently decrease as polarization angle increases until the minimum at 90° polarization angle, after which the intensity will increase again in symmetry and reach maximum at 180°. A unique phenomenon can be observed where the appearance of intersection point general to all polarization states at $\lambda=560$ may indicate high symmetrical order of the system. This point is a turning condition in the spectra beyond which the highest (black line at p -polarization) become the lowest intensity and the lowest (purple line at 90° polarization) becomes the highest, while the rest are in between.

For TM-wave parallel to the crystal momentum, the transmitted intensity can be noted with maxima at 450-560nm and beyond that point it starts to reach minimum for the whole spectra ($\lambda=560-800\text{nm}$). At *s*-polarized state, the transmission spectra decrease (at 450-560nm) and finally reaching minimum. However beyond intersection point (560nm) increasing polarization angle will increase the transmission and finally reaching maximum for 90° polarization angle. This point is called a turning point where beyond this point the spectra will act in the opposite direction. The spectra of 40°-50° polarization angle will be the least affected by this point. The transmission vs. polarization angle for different wavelength before and after ‘turning point’ were examined and shown in Fig. 6.6

Figure 6.6. Polarization dependency in transmission measurement of 1D nanoslit PCL at particular wavelength 490, 512, 520 and 590nm. 490nm is just before the peak and 512nm is the maxima for *p*-polarized spectra. 520nm and 590nm are just before and after the turning point (at 560nm).

6.3.5. Effect of Polarization in Nanoslits without Base Plate

The transmission of second sample – 1D nanoslits without base plate ($\Lambda=650\text{nm}$), collected from 300-900nm using different polarization angle are demonstrated in Fig. 6.7. The base plate of this second sample was fully eliminated in RIE process; hence the transmission intensity for *p*-polarized light at resonance condition becomes 15 times larger than the first sample (with base plate). The intensity increment is more than the slit width (36%).

For *p*-polarized light, the spectra (Fig. 6.7) show three peaks at 546nm, 610nm and 649nm. The middle peak at 610nm is independent of polarization state. The first peak at 546nm is

decreasing as the polarization angle increases while the last peak at 649nm is transformed into a dip and reaches minimum when *s*-polarization is used. This third peak corresponds to the SPP excitation, where the *p*-polarized light takes the maximum contribution.

The intersection point common to all spectra appears two times at 670 and 840nm, in which within this region behave with an inversed polarization effect. The region is relatively large, over 170nm (wide window). The first point is considered as turning condition and after the second point, they return to initial arrangement. At these two points, there is no polarization effect on the structure. These points can be tuned by varying periodicity or incident angle.

Figure 6.7. Transmission measurement of 1D nanoslit PCL without base plate, $\Lambda=650\text{nm}$, at 300-900nm for different polarization angle.

One of interesting application for the nano-slits array based on the optical properties above is for switching device or new generation optoelectronic device such as photo-transistor. By controlling the azimuthal or polarization angle, the signal can be transmitted, blocked or finely adjusted for certain purposes (amplified or reduced).

6.3.6. Correlation of Experiment and Simulation of EOT

An example of complete correlation, both experimental and simulation, description, microscopic (at near field) and macroscopic of the EOT will be described. The 1D nanoslits with periodicity of 500nm, thickness of 370nm and slit width 220nm is compared in this section. The simulations were done by finite-difference time-domain (FDTD) provided by Lumerical [258]. This technique is able to solve 3D Maxwell's equation in plasmonic slits and measure its responses for broad range of EM source. The accuracy of the simulation highly depends on the meshing size which needs to be fine enough to resolve the minimum EM component as well as geometrical feature of plasmonic structure. The schematic model

and script written for the simulation are demonstrated in Fig 6.8. The simulation results on nano-slit structure are presented in Fig. 6.9.

Figure 6.8. Transmission calculation for 1D gold nano-slits using Lumerical FDTD simulation

Figure 6.9. Transmission measurement of 1D Au slits. Dashed line corresponds to FDTD result. Continuous line refers to experimental data by a) TM and b) TE-wave. Cut off mode exists at 500-550nm as shown in (b).

As can be easily observed in Fig. 6.9 (a), for TM a resonant peak is present around 512nm while, as illustrated in Fig. 6.9 (b) for TE, a positive trend in the transmittance spectra is evident starting from 520nm. These resonance peaks can be explained by two phenomenon [63, 98, 206, 297]. The first one arises from the coupling of incident EM field with a periodic structure and it leads to near field enhancements and strong transmission extinction. The second one is a cavity resonance which takes place within the slits and this becomes the source for transmission enhancement.

6.4. Transmission in 2D PCL

A transmission measurement of periodic diamond holes on Au film at the optical wavelength range was studied. The 2D PCL was fabricated using EBL on Si_3N_4 membrane with $\Lambda=500\text{nm}$ and $1\mu\text{m}$, the diamond width size of $280\times 280\text{ nm}^2$ and $560\times 560\text{ nm}^2$, both evaporated with 50nm of Au (Fig. 6.10). The thickness is controlled using reactive ion etching to reach 300nm of thickness. The final structure is shown in the figure with area of $3\times 3\text{mm}^2$ with base plate was left behind to support the structure.

Figure 6.10. FESEM images of 2D diamond arrays PCL, obtained at 2kV , $\text{WD}=5\text{--}6.2\text{mm}$, magnification $10,000\text{--}11,000\times$ at $1.5 \times 10^{-5}\text{ mBar}$. a) $\Lambda=500\text{nm}$ and b) $\Lambda=1\mu\text{m}$.

6.4.1. Results

6.4.1.1. Wavelength Interrogation

Both samples with periodicity of $1\mu\text{m}$ and 500nm were measured in transmission mode for different incident angle as demonstrated in Fig 6.11. As the periodicity is reduced by half, the position of resonance wavelength moves by 50nm (from the peak, 650 to 700nm) and the intensity curves representing different transmission orders look very similar to one another.

Figure 6.11. Transmission measurement of 2D diamond array PCL with base plate, a) $\Lambda=1\mu\text{m}$ and b) $\Lambda=500\text{nm}$, collected from $400\text{--}900\text{nm}$ for different incident angle at p -polarized light.

The spectra are compared individually for each incident angle. Surprisingly, the intensity for 2D PCL with smaller periodicity is larger by 60% which is most probably caused by the plasmonic enhancement (Fig. 6.12). For non-zero incident angle, the position of the minima is almost identical for both periodicities: 620nm for $\theta=10^\circ$ and 690nm for $\theta=20^\circ$.

Figure 6.12. Comparison transmission measurement of 2D diamond array PCL for periodicity of 500nm (solid line and 1μm (dashed line) for different incident angle: 0° (black), 10° (red) and 20° (blue).

However, we observed that the optical transmission spectra are identical to the multislit structures, with a distinction in transmission peak due to the bulk plasmon effect. The peaks can be calculated by [83, 262, 289, 302]:

$$(\lambda_{\max})_{m,n} = \frac{n_{SPP}\Lambda}{\sqrt{m^2 + n^2}} \quad (6.1)$$

$$\text{where } n_{SPP} = \frac{\lambda}{\lambda_{SPP}} = \Re \sqrt{\frac{\epsilon_m \epsilon_d}{\epsilon_m + \epsilon_d}} \quad (6.2)$$

For 1D PCL, the $n=0$, λ_{spp} is the SPP propagation wavelength; ϵ_m and ϵ_d are permittivity function of metallic and dielectric layer correspondingly. The measurement data of $\epsilon(\lambda)$ for the membrane deposited with Au was obtained using spectroscopic ellipsometry hence the effective permittivity function of the system $\epsilon_{spp}(\lambda)$ can be obtained (Fig. 6.13). The effective refractive index is assumed to be identical with SPP along the metallic/dielectric interface.

Figure 6.13. The real value of dielectric function of metallic layer and the calculated effective refractive index of 2D PCL.

6.4.1.2. Polarization Effect

Experimental results show that transmission through the 2D diamond array at normal incidence is almost not affected by polarization angle as shown in Fig. 6.14. Nevertheless,

for non-zero azimuthal angle, the symmetry is broken and transmission spectra will be dependant on polarization state, which may be very useful for promising applications of 2D periodic structures. The generated SPP wave-vectors on 2D PCL is given by [289]:

$$\vec{k}_{SPP} = \pm \left(\frac{2\pi}{|\Lambda|} \right) m \hat{x} + \left(\frac{2\pi}{|\Lambda|} \right) n \hat{y} \quad (6.3)$$

At 90° incident angle, surface plasmon can be generated when electric field is parallel to SPP propagation direction: $(\mathbf{E} \cdot \mathbf{k}_{spp}) \neq 0$ [74]. The polarization effect on the SPP coupling efficiency is influenced by $\frac{m \sin \alpha + n \cos \alpha}{\sqrt{m^2 + n^2}}$ factor, where α is angle of polarization. From

the analysis for four folds symmetry of 2D PCL, the polarization has a small effect on SPP generation however the transmission enhancement can still be obtained. However for low symmetry element (ellipses), polarization effect on transmission spectrum will be very important [96]. As the angle of polarization angle is moved nearer to TE, the main transmission peak will be reduced. This shows the contribution of *p*-polarized light to enhance the transmission.

Figure 6.14. Polarization effect in transmission measurement of 2D diamond array PCL with base plate, a) periodicity of 1 μm , $a=560$ nm and b) periodicity of 500 nm, $a=280$ nm, collected from 400-900 nm for $\theta=0^\circ$.

6.4.1.3. Sensitivity measurement

Sensitivity of 1 μm periodic diamond holes on Au film is measured in transmission mode. The structure is functionalized with 3-mercaptopropionic acid (MPA, $n=1.479$) [303] and its transmission behaviour is compared with the uncoated one (Fig. 6.15). The n_{eff} for bare square array equals to 1.119 and for coated the n_{eff} becomes 1.1206, hence $\Delta n=0.007\text{RIU}$. The enhancement for bare array can be seen from the transmitted intensity of normal

incident angle where the peaks generally increase for about 20% and minor shift of the peak can be observed from 650nm to 647.5nm. Similar phenomenon was also shown for 10° incident angle. MPA was used due to its thiol head that can be covalently bonded to Au [303].

The wavelength shift could be optimized by altering the polarization state, however the drop in transmission intensity was observed for coated sample. Both samples were re-measured under the optimized polarization, i.e. for bare: -1° and coated: +2° (Fig. 6.16). The wavelength shift of 4.6nm can be observed. The sensitivity of this system is approximately 657.15nm/RIU, which is comparable with other work done in similar system [304-306].

Figure 6.15. Transmission measurement of 2D diamond array PCL for periodicity of 1μm before (black solid line) and after (red solid line) coating with MPA for normal (left) and 10° (right) incident angle. Generally the transmission peaks are slightly shifted (≈ 2.5 nm) due to changes in refractive index.

Figure 6.16. Comparison main transmission peak of 2D diamond array PCL for periodicity of 1μm before (black) and after (red) coating with MPA for normal incident angle under optimized polarization angle: for bare: -1° and coated: +2°. The wavelength shift of 4.6nm can be observed.

6.5. COMSOL Simulation on 1D Nanoslits PCL

A COMSOL multi-physics simulation was also done to model the transmission in 1D slits PCL as discussed in chapter 3 (section 3.6.2). The simulation result is shown bellow.

Figure 6.17. Transmission spectra of nanoslit 1D PCL at normal incident with $a=250\text{nm}$, $\Lambda=500\text{nm}$ and $h=375\text{nm}$ collected at $\lambda=400\text{-}800\text{nm}$, normal incidence and TM wave.

From Fig. 6.17, an EOT peak appears at 550nm that is near the SPP excitation wavelength. The magnetic field intensity at the top and bottom slit surface is also calculated. The SPP on the upper surface of the slit was first excited at 520nm , and then followed by the other surface at 550nm (Fig. 6.18). The field enhancement of 12% is observed at $\lambda=550\text{nm}$ (blue line) at the bottom part of the slits which become a proof of EOT existence near λ_{SPP} as shown in Fig. 6.18. Another simulation shows that this phenomenon can only be done under p -polarized light and its intensity is greatly affected by grating pitch.

Figure 6.18. Magnetic field distribution for transmission spectra of Au nanoslits at normal incident with $a=250\text{nm}$, $\Lambda=500\text{nm}$ and $h=375\text{nm}$ collected at normal incidence and TM wave for $\lambda=440\text{-}800\text{nm}$

The effect of slit thickness was studied. The pitch and slit width were kept constant at 500nm and 250nm while the thickness is varied from 300nm to 500nm . The simulation result shows that the resonance peak is moving to higher wavelength as the thickness increases followed by the changes in intensity and FWHM (Fig. 6.19 (a)). However at around 500nm , the transmission is almost zero due to dielectric properties of Au which absorb most of the light. Furthermore the period and thickness were fixed at 500nm and 375nm while the slits width, a was varied. The simulation result is demonstrated in Fig. 6.19 (b) and show that the changes in slit width do not change the intensity, but only the resonance wavelength.

Figure 6.19. Transmission spectra of nanoslit 1D PCL at normal incident with (a) $a=250\text{nm}$, $A=500\text{nm}$ and thickness h is varied from 300-500nm and (b) $A=500\text{nm}$, $h=375\text{nm}$ and slit width is varied from 200-300nm collected using $\lambda=400\text{-}800\text{nm}$ at normal incidence and TM wave.

The peaks are located near the SPP resonance wavelength predicted by Eq. 6.1 which is applicable for both slits and diamond square array. This resonance wavelength is very sensitive. Polarization plays an important role in this 1D structure. As the polarization angle increases (from TM-wave), the peaks intensities decreases and almost vanishing at 90° (TE-wave). The simulation result is shown in Fig. 6.20. This confirms the plasmonic contribution in transmission peaks. Another peak will appear at higher spectral range ($1.2\mu\text{m}$) which is referred to as “cavity resonance” [94, 275], and not related to SPP. The simulation result is shown in Fig. 6.20.

Figure 6.20. Transmission spectra of nanoslit 1D PCL at normal incident with $a=250\text{nm}$, $A=500\text{nm}$ and thickness $h=375\text{nm}$ collected using $\lambda=500\text{-}1200\text{nm}$ at normal incidence.

6.6. Figure-of-Merit Simulation

The extraordinary transmission spectrum is also sensitive to gold surface functionalization. Adding an internal layer with $n=1.01$ ($\approx 1\text{nm}$ -thickness) to the previous structure, a shift in transmission conditions was realized (Fig. 6.21). The peak shifts $\Delta\lambda=4.8\text{nm}$ from 551.7 to 556.5nm, hence the sensitivity is around 480nm/RIU. However the transmission intensity is reduced 2% due to the absorption nature of dielectric medium.

Figure 6.21. Transmission spectra of nanoslit at normal incident with $a=250\text{nm}$, $A=500\text{nm}$ and thickness $h=375\text{nm}$ for bare (blue) and coated (green) 1nm dielectric ($n=1.01$) using TM wave.

6.7. Electric Metamaterials

It was reported that a medium with negative permittivity (ϵ) is able to recover the evanescent field using p -polarized light and may be used as a superlens to resolve the diffraction limit as the object is much smaller than the wavelength [307]. As periodic structure is introduced in the PCL, the magnitude and the range of negative permittivity can be tuned. The control of permittivity value over 1D and 2D PCLs are presented in Fig. 6.22 - 6.23. The magnitude and window of negative permittivity are able to be adjusted by changing the incoming angle of incoming photon. This property may open the possibility for 1D and 2D PCL to be used as electric metamaterials which exhibit superlens effect.

Figure 6.22. Real and imaginary permittivity (ϵ_1 and ϵ_2) value for nanoslit 1D PCL at different incident angle using TM-wave.

Figure 6.23. Real and imaginary permittivity (ϵ_1 and ϵ_2) value for 2D PCL at different incident angle using TM-wave. The magnitude for both real and imaginary are larger than 1D PCL which could be caused by field enhancement of 2D structures.

6.8. Chapter Summary

1D and 2D PCL for transmission measurement have been fabricated and grown by Au electroplating. Numerical simulations and optical characterization provide correlation of transmission spectra. Experimental data shows interesting results on TE-mode transmittance spectra. In fact, a resonance peak has been observed which is related to slit-cavity effects. There are two resonances phenomenons: the sharp one corresponds directly to propagated plasmon and the broader peak corresponds to the cavity modes.

Simulation by COMSOL multiphysics and FDTD were done to verify the 1D PCL experimental result. Sensitivity simulation for 1D nano slit has been done and may reach 480nm/RIU. A sensitivity enhancement in transmission is shown on 2D diamonds array experimentally and able to reach up to 657.15nm/RIU which is higher than simulated 1D nanoslits. However this value can be improved by tuning the geometry of PCL.

One interesting application based on 1D PCL EOT is switching device, which can be used for a novel optoelectronic devices e.g. photo-transistor. By controlling the azimuthal or polarization angle, the signal can be transmitted, blocked or finely adjusted for certain purposes (amplified or reduced). Key contributions in chapter 6 are summarized bellow.

No	Key Contributions	Remarks
1	Polarization conversion	This property can be used for optical transistor which responses are unique and can be controlled by incident and polarization angle at fixed azimuthal angle.
2	Single and double turning point effects	Beyond this point the spectra will have opposite transmission behavior. This point can be controlled by varying the incident angle and periodicity. One of interesting application is for switching or novel optoelectronic device such as photo-transistor. By controlling azimuthal or polarization angle, the signal can be transmitted, blocked or finely adjusted.
3	Simulations	FDTD and COMSOL simulations have been done to verify the experimental data
4	Polarization effect in 1D and 2D slit array	Polarization provides significant enhancement effect on 1D nanoslit array; however less effect is found for 2D structure.
5	Sensing capability	The sensitivity of 2D gold structure may reach 657.15nm/RIU
6	Electrical Metamaterial	1D and 2D PCL can be considered as electric metamaterials which may have possibility to exhibit superlens effect. The magnitude and window of negative permittivity can be adjusted by changing the incoming angle.

7 Engineering Dielectric Medium: Negative Diffraction Order

Since SPPs are very sensitive to the refractive index changes along the interface hence its excitation conditions can be effectively driven by modifying the geometry of PCL [146, 296] or by the dielectric layer on the PCL using an active material whose optical characteristics can be tuned externally by varying the EM-field [107, 308]. The physical approach can be done by modifying the geometries of the plasmonic crystal. This part includes the effect of higher dimensionalities which has been discussed in chapter 5. The latter method is a novel approach to control the plasmonic propagation and become the focus in this chapter. The optical characteristics of this dielectric medium could be adjusted by varying the experimental conditions, reaction steps, chemical composition and concentration.

7.1. Introduction

One way to modify the effective refractive index is by engineering the surface of dielectric layer. The resonance angle and evanescent field characteristics are sensitive to changes in dielectric function and this peculiar property makes surface plasmon resonance a powerful and sensitive technique to measure the changes of dielectric layer on metallic layer and characterize the coated dielectric film [27, 156]. The purpose of this part is to engineer the dielectric medium which controls the SPP excitation condition. By changing the refractive index and material density, the surface reactivity can be increased, thus enhancing the sensitivity. Optical characteristic of thin dielectric film could be controlled modifying the molarity, processing method and composition [107, 108, 246, 309, 310].

7.2. Types of Dielectric Films

Fig. 7.1 shows the effects of a non-absorbing and absorbing dielectric film on Ag film. The SPR excitation angle as well as reflectivity at the dip shows a strong correlation on dielectric's thicknesses. Dielectric layer with zero (negligible) extinction coefficients will only alter the excitation angle with no changes in the reflection intensity and they can be translated into nearly linear function between resonance angle and thicknesses.

Figure 7.1. Reflectivity curve in angular interrogation ($\lambda=632.8\text{nm}$) for different thickness of non-absorbing, $\epsilon_{\text{film}}=2.125$ (a) and absorbing film with additional $0.6i$ (b) on 50nm Ag thickness

As discussed in chapter 2, the angular shift is proportional to film thickness and permittivity function of the materials (Eq. 2.52). This fact will be very useful to characterize non-absorbing film, whose permittivity is proportional to the concentration. The angular shifting is primarily affected by changes in permittivity of the system as a result of the dielectric layer. ϵ_{eff} could be calculated approximately by exponential function of the skin depth, s :

$$\epsilon_{\text{eff}} = \frac{\epsilon_d}{s} \int_0^d \exp\left(-\frac{z}{s}\right) dz + \frac{\epsilon_D}{s} \int_d^\infty \exp\left(-\frac{z}{s}\right) dz = \epsilon_d + e^{-\frac{d}{s}} (\epsilon_D - \epsilon_d) \quad (7.1)$$

where $s = L/2$ and L is SPP penetration depth into dielectric film given by Eq. 2.40 as a function of ϵ_m and ϵ_D . However since ϵ_{eff} is affected by various parameters, the value will be best to be represented by ellipsometer measurement. Thus SPP dispersion relation will be:

$$\bar{k}_{\text{spp}}' = \frac{2\pi}{\lambda} \sqrt{\frac{\epsilon_m + \epsilon_{\text{eff}}}{\epsilon_m \cdot \epsilon_{\text{eff}}}} = \bar{k}_{\text{ph-x}} \pm m\bar{g} \quad (7.2)$$

Hence according to Eq. 4.9, the new resonance angle can be calculated. In absorbing film, the SPR dip intensity and resonance angle will increase with the thickness.

7.3. Active Materials

In this experiment, bridged polysilsesquioxanes was used to produce molecular-engineered hybrid organic-inorganic materials [148] which were able to demonstrate fine porosity control. The detail of experimental part and synthesis method was discussed in section 3.3.

7.3.1. Characterizations of Sol Gel Film on Si Substrate

The C8 sol-gel was deposited on Si wafer spun at 3000RPM for 60s and thermally treated at various temperatures up to 800°C for 30 minutes. The porosity of the film was characterized by TEM images captured by JEM-2100F TEM/STEM (JEOL) at 200 kV. The chemical analysis of the heat treated films were done using Fourier transform infrared spectroscopy (FTIR 620, JASCO) from 5000 to 400 cm^{-1} . The films thicknesses and refractive index changes were obtained by WASE spectroscopic ellipsometer and modeled by WVASE32 software. Several models and techniques were employed to fit the refractive index of the films i.e. Cauchy layer, point by point and genocs methods [114]. These dispersion relations are very useful for describing dielectric material indices over the spectral range 250-1000nm.

7.3.2. Results

Porosity evidence of C8 sol-gel thin film

The existence of porous layer is confirmed by cross-sectional analysis of 60°C thermally treated samples in TEM images (Fig. 7.2). The underneath structure was observed by adjusting the TEM focus plane to below the cross section surface. From the cross section images, the thickness of porous C8 layer is around 75-80nm.

Figure 7.2. (a) Low magnification cross-section sectional TEM image of heat treated sol-gel film. The TEM pictures were focused underneath the cross section to examine the inner structure in agreement to the presence of Fresnel fringes localized on the outer sample surface. The top layer of the film has been damaged during sample preparation. Beneath the ~30 nm thick damaged layer is a film portion containing randomly distributed darker small irregular areas recognized as ~5 nm width pores. (b) The enlarged image shows a particular section of porous layer. Selected area electron diffraction of porous layer (inset) indicates amorphous structure.

The first 10nm is characterized as poly-crystalline layer whose morphology is demonstrated in Fig. 7.2 (a). The pores are visible as randomly distributed darker dots with higher density down to ~ 20 nm from the top surface and shown as a highly packed good quality structure with 4-5 nm diameters of pores (b). At 5-7nm from surface, the pore shape changes severely from round holes into ellipses. The porous layer consists of nano crystals stretched out at right angles to the surface, generating a coarse surface. Selected area electron diffraction (SAED) of the porous layer indicates an amorphous structure (Fig. 7.2 (b)).

The correlation between FTIR analysis and ellipsometry measurement (refractive index and thickness) provides better information related to porosity formation. In Fig. 7.3 (a), residual of silanols (Si-OH) and trapped H_2O at $3200-3300\text{ cm}^{-1}$ can still be noticed in FTIR spectra. Methyl decomposition is noted from peak intensity reduction at 2930 and 2850 cm^{-1} . The formation of porous $Si-O_x$ networks can be identified by asymmetric, symmetric vibration and bending peaks at $1040-1070\text{ cm}^{-1}$, 820 cm^{-1} and 470 cm^{-1} respectively [311].

Figure 7.3. (a) FTIR spectra of thermally treated C8 film. The labels: (1) $3200-3300\text{ cm}^{-1}$ hydrolisis; (2) $2850-3000\text{ cm}^{-1}$ CH_3 decomposition; (3) $1040-1070\text{ cm}^{-1}$ assymmetric; (4) 820 cm^{-1} symmetric stretching (5) 470 cm^{-1} bending of Si-O-Si networks. (b) Refractive index and thinning of heat treated C8 sol-gel [311].

Fig. 7.3 (b) is obtained from ellipsometry modeling at 600nm, providing some information related to the optical properties and reduction in dielectric layer thickness as temperature is increased. Generally film densification will take place at higher temperature, noted by the thickness reduction. In most cases it will be accompanied by an increment in index of refraction. Nevertheless the opposite trend appears which is mainly caused by hydrolisis and organic decomposition as mentioned in FTIR analysis. This indicates the existence of pores

in the sol-gel medium – thus reducing the compactness. Above 500°C, the index of refraction of sol-gel layer increases again because of partially collapsed of Si-O-Si network [311].

7.4. Sol Gel on Plasmonic Crystal

Molecular-engineered dielectric materials synthesized from bridged polysilsesquioxanes demonstrates an excellent control in porosity allowing fine-control of PCL's dielectric function of a PCL [311]. The porosity increases reactive surface area thus enhances chemical sensitivity of sol-gel thin film. The SPP excited from sol-gel on 1D PCL is utilized as very sensitive design for SPR based sensor to determine refractive index variations of the system. It is found that SPP excitation is moved to a negative Brillouin zone ($m=-1$); therefore the rise in incident wavelength may shift the resonance angle to lower value. The sensitivity of this system may reach 667°/refractive index unit (RIU) with resolution down to 7.5×10^{-6} RIU. By further control and higher precision, the resolution could reach 10^{-7} RIU. The high sensitivity is attributed to replacement of the sign in order of diffraction from positive to negative, $m=-1$ by engineering refractive index of dielectric medium.

7.4.1. Bare Plasmonic Crystal

The 1D PCL employed in the experiment was produced by IL technique as described in section 3.1. The pattern transfer was done using reactive ion etching (RIE) followed by imprinting to PMMA slab and finally deposited with a 37nm of silver and 8nm of gold. The choice of the metal is crucial since the sensor resolution, which is mainly due to the FWHM of SPR dip, is correlated with the imaginary component of permittivity function (ϵ''). Having smaller ϵ'' value, Ag shows lower energy dissipation which is reflected in sharper curve (smaller FWHM). However, Au offers a higher chemical resistance to oxidation. Thus the use of a bimetallic layer combines the high resolution of Ag with the chemical stability of Au. The metal thicknesses were chosen to provide optimum SPP coupling efficiency, the details of which are discussed in Chapter 4. The final profile on PMMA slab was measured by AFM and has a period of 500nm.

The SPR characterization for bare as well as C8 deposited grating is similar to the one discussed in section 3.7.1 and 5.1. The SPR measurement of bare 1D Ag-Au PCL for $\varphi=0^\circ$ is shown in Fig. 7.4 where the reflection dips at different resonance angles and colors refer to different incident wavelength. In order to optimize plasmonic coupling efficiency, *TM-wave* ($\alpha=0^\circ$) is used. At $\varphi=0^\circ$, the resonant angle reduces with the frequency. At $\varphi>0^\circ$, the reflectivity minima will be increased due to reduced part of EM field that is coincided to crystal momentum.

Figure 7.4. SPR measurement of bare 1D PCL at $\varphi=0^\circ$ from 680-800nm and $\theta=15-45^\circ$, using TM-wave ($\alpha=0^\circ$). Inset is the AFM image of bare sinusoidal 1D PCL with $\Lambda=500\text{nm}$.

7.4.2. Characterization of C8 sol-gel on 1D Ag-Au PCL

The C8 film was coated on 1D Ag-Au plasmonic grating and heated at 60°C to form pores (to form porous SiO_x network) [311]. From Fig. 7.4 (right), it can be seen that coated PCL does not have significant changes. From the reflection spectra of C8 coated PCL in Fig. 7.5, some uncommon features can be observed. First, double SPR dips are present. In this analysis the presence of two SPR dips are originated from two different metal-dielectric interfaces; which will be discussed more in the following section. Secondly, unlike bare 1D grating, the resonant angle for both dips increases with excitation frequency.

For $m=1$ (positive first order), the resonant angle will increase together with the wavelength. Inversed trend can be observed for negative order m . To explain this phenomenon, $m=-1$ (negative first order) is used to fit the dispersion curve from SPR measurement since the

crystal momentum, $\bar{g}$ is smaller than the incoming photon momentum. The negative diffraction order ($m=-1$) of 1D PCL could be explored at this point because the effective permittivity function attributable to the addition of C8 sol-gel coating is high enough to bend the SPP curve at lower energy (higher wavelength). Consequently, in the same Brillouin zone, higher effective refractive index enables the excitation of negative first order of SPP at visible range. Using lower wavelength, dispersion for positive diffraction order ($m=1$) could be explored. However below 500nm, the optical properties of Au will change drastically from metallic to dielectric and inhibit SPP excitation.

Figure 7.5. SPR measurement (left) and dispersion curve (right) of sol-gel film coated on 1D PCL for $\varphi=0^\circ$; the SPR dips at different angles and colors refer to various excitation wavelength. While the wavelength increases, the SPR dips move to lower angle, opposite the behavior of bare PCL. The y-axis of dispersion curve refers to SPP excitation energy, between 1.5eV (827.5nm) and 3eV (413nm) while x-axis refers to wavevector of light coincided to grating. Inset is the AFM image of C8 coated sinusoidal 1D PCL with $\Lambda=500$ nm.

For metal ($\epsilon_m = \epsilon_m' + i\epsilon_m''$) interface or dielectric ($\epsilon_d > 0$), and assuming $\epsilon_m'' \ll |\epsilon_m'|$ [49], the plasmonic conservation momentum can be expressed in Eq. 5.1 while the index of refraction is given by Eq. 2.14. As the sol-gel film is introduced on the PCL, both effective refractive index and k_{SPP} will be increased thus the dispersion curve will become gentler (suppressed) and the SPP wavelength, λ_{SPP} turns out to be smaller. This can be a novel way to further squeeze the incident wavelength and enable it to interact with much smaller nanostructures.

7.4.3. Types of Surface Plasmon

The SPR measurement of C8 sol-gel coated on 1D PCL (Fig. 7.5 left) demonstrates an obvious double SPR dips; however these are not caused by the azimuthal rotation as

previously reported [72]. The dips at lower and higher incidence angle correspond to the fast and slow SPPs respectively. Their dissimilarity in energy and propagation length make them distinguishable [74]. A clear angular shift of the SPP dips can be observed.

The presence of double SPR dips are able to be explained, considering the insulator-metal-insulator (IMI) of metal film deposited between different polymeric layers which refractive index function are close to each other [3, 4]. The refractive index (n) of PMMA slab and the C8 film were measured (using spectroscopic ellipsometry) as follow: 1.489 and 1.49. These close values are possible to make the plasmonic frequencies at both interfaces to be close to each other and causes the k_{SPP} to split into higher and lower frequency mode, strongly depending on the incident light and metallic layer. The electric field of lower frequency mode is symmetric while the higher one is asymmetric to the plane $z=0$. At relatively low metallic thickness, the interference of EM fields at both interfaces (Fig. 7.6) cannot be ignored [3, 4, 6, 74] since it could alter the dispersion curves.

Figure 7.6. Schematic of insulator– metal – insulator (IMI) system represent PMMA slab with $\epsilon_{d(1)}$, Ag-Au bimetallic grating and porous C8 with $\epsilon_{d(2)}$.

The occurrence of multiple SPP generation can be described, considering two different dielectric layers (with similar permittivity value) with metal film in between (IMI structures) [2-4, 6, 12, 74]. For similar dielectric function, the SPP frequencies at both interfaces are comparable thus the electromagnetic fields interfere each other causing the SPP to split to upper $\omega+$ (asymmetric) and lower $\omega-$ (symmetric to plane $z=0$) frequency, depending on photon momentum and PCL geometry [49].

The EM wave interaction at two boundaries (Fig. 7.6) cannot be abandoned and the plasmonic dispersion relations will be affected due to the interferences [2-4, 6, 12, 74]. The fully symmetric case i.e. when the film is embedded in the same dielectric can be described analytically whereas for non symmetrical case, computational simulation needs to be done. At higher energy, SPPs confinement at the metallic interface will be diminished as plasmon converts into radiation whereas at lower energy the reverse behaviour may happen. The

penetration depth of SPP, δ_{SPP} in both medium is given by inverse of purely evanescent surface normal wave vector k_z which has been discussed previously in Eq. 2.39-2.40.

$$k_z = \sqrt{\epsilon_d k_{ph}^2 - k_{SPP}^2} \quad (7.3)$$

While as discussed previously, for propagation of SPP L_{SPP} is given by the non-real part of k_{SPP} in x -direction and can be calculated using Eq. 2.44-2.45 or Eq. 4.18.

7.4.4. Simulation

A modeling work based on the conditions above has been done to demonstrate the existence of two SPR dips that are related to faster plasmon at lower incoming angle as well as slower mode at lower angle (Fig. 7.7); taking into consideration the variation of coupling angle, energy/frequency as well as SPP path distance. The width in the SPR dips is greatly affected by extinction coefficient as well as the density of material especially dielectric layers which may cause variation in FWHM of the SPR dips.

Figure 7.7. The simulated SPR curve for fast and slow SPP at lower and higher incoming angle respectively.

7.5. Sensitivity due to negative diffraction order

Porous thin film sol-gel matrix with the addition of HCl is used here as a demonstration case study. The effective refractive index is changed as the porous C8 sol-gel is infused with HCl solution. For preliminary measurement, it is only focused on fast SPP located at smaller incidence angles to detect 10mM HCl solution due to its better coupling efficiency and higher sensitivity. Bare 1D PCL (without porous C8) are not sensitive to the presence of HCl due to the absence of surface binding (Fig. 7.8). However by depositing porous C8 film, the sensitivity is increased as shown in Fig. 7.9. The porous C8 film acts as nano-fluidic network

which able to trap the analyte due its surface tension. The sensitivity is then further improved as the azimuthal angle is utilized ($\varphi=50^\circ$) as shown in Fig. 7.9 (right). However, there is reduction in the reflection intensity due to HCl. Thus, in negative diffraction order mode, the azimuthal angle is also shown to improve SPR sensitivity system, similar to enhancement in the positive order as discussed by earlier [72]. In the absence of surface binding, microfluidic cell described in section 3.2 can be utilized.

Figure 7.8. SPR measurement of bare 1D PCL (without C8) before and after contact with HCl solution for $\varphi=0^\circ$ (left) and $\varphi=50^\circ$ (right).

Figure 7.9. SPR measurement of C8 coated PCL before and after contact with 10mM HCl at 560 and 610nm for $\varphi=0^\circ$ (left) and $\varphi=50^\circ$ (right).

As mentioned previously the effective refractive index is high enough to bend the SPP curve at lower energy (higher wavelength). Consequently, the SPP will be excited at negative first order and at lower wavelength compared to the positive order. As the permittivity function

of dielectric environment increases caused by the presence of HCl, the resonant angle θ_R will be shifted. Furthermore, the refractive index sensitivity using negative order of diffraction will be improved. This is also considering the angular shifting and the depth-width ratio of the resonance dips. Figure-of-merit (FOM) can be introduced to demonstrate the sensing quality of the system, defined as:

$$FOM = \frac{\Delta\theta}{\Delta n \cdot \theta_{FWHM}} \quad (7.4)$$

where FOM is to represent the general sensing quality of the system in subsequent part, $\Delta\theta$ is the angular shift caused by the increment in index of refraction Δn , and θ_{FWHM} is the FWHM of the SPR dip. Those values are summarized in Table 7.1. Generally, for negative order, both $\Delta\theta$ and FOM are larger for all instances, especially at non zero azimuthal angle due to the FWHM factor. The SPR dip at any wavelength for $m=-1$ will have much smaller FWHM than that for $m=1$, which experiences dip broadening at higher azimuthal angle.

Table 7.1. Sensitivity comparison and FOM value for positive and negative order SPR based sensor for the first (I) and second (II) dips.

	Positive SPP order (m = +1)				Negative SPP order (m = -1)							
	$\varphi = 0^\circ$		$\varphi = 50^\circ$		$\varphi = 0^\circ$				$\varphi = 50^\circ$			
	665nm	775nm	665nm		560nm		610nm		560nm		610nm	
			1 st	2 nd	1 st	2 nd	1 st	2 nd	1 st	2 nd	1 st	2 nd
$\Delta\theta$	0.1°	0.14°	0.14°	0.11°	1.2°	0.9°	1.3°	1.0	2.7°	NA	3.0°	3.0°
FOM	19.5	23.3	1.55	1.88	127	43.5	173	83.2	214.3	NA	300.6	185.7

Sensitivity enhancement is mainly because of the replacement of positive with negative order of diffraction. Similar sensitivity enhancement due to negative diffractive order has been shown previously by Hu [145] utilizing a bi-metallic Al-Au grating. However in this case, the $m=-1$ is explored by engineering refractive index of dielectric medium (C8). It can be shown from ellipsometry modeling, that after 10mM HCl filled the pores formed inside C8 layer, the index of refraction of the system is reduced by $\Delta n=0.0045$ RIU (1.460 down to 1.4555), also shown as a shift in Fig. 7.12. The sensitivity in this system is equal to $\Delta\theta/\Delta n=667^\circ/\text{RIU}$ and the angular resolution of the optical measurement system is down to 0.005° and makes the theoretical detectability of SPR sensor equals to 7.5×10^{-6} RIU. By

further control and higher precision, the system is expected to reach resolution down to 1×10^{-7} RIU. For accuracy measurement of angular resolution is obtained by high quality precision rotator low mechanical vibration environment. This value is purely properties of the optical system and theoretically only affected by the angular resolution of rotating stage. In practice, experimental constraints such as beam broadening (instability), refraction, mechanical vibration and thermal drift will reduce the resolution limit.

7.5.1. Analysis

When the sol-gel matrix is introduced on PCL, the dielectric film will bend the incident light with different factors, depending on its refractive index. The k_{SPP} dispersion relation relative to frequency can be calculated by Eq. 2.1. Previously the dielectric permittivity was considered to be one ($\epsilon_d = 1$), as the setup was directly exposed to air as dielectric medium. However when a sol-gel is coated on top of plasmonic crystal, it will act as another dielectric medium with permittivity ϵ_d . The light will travel through dielectric medium $\epsilon_d = n^2$ (where $\epsilon_d > 0$) and reach the non dispersive medium (metallic layer) with plasma frequency, ω_p and permittivity function (Eq. 2.36) thus k_{SPP} dispersion relation (Eq. 2.1) turns into Eq. 7.2.

Together with Eq. 5.2 and 5.7, the effect in optical properties due to sol gel matrix in k_{spp} can be represented. The new conditions (resonance angle, wavelength and propagation direction) for SPP excitation with refractive index n on the PCL can be calculated. Further, as the analyte HCl is introduced into the dielectric, the SPP recognize the addition complex-effective permittivity function ϵ_{eff} that could be estimated: $\epsilon_{eff} \approx \epsilon_d + \frac{2d}{L}(\epsilon_{HCl} - \epsilon_d) = 2.13$, where ϵ_{HCl} and ϵ_d are the permittivity values of analyte (HCl) and previous dielectric layer (C8) respectively. ϵ_{eff} is used to calculate the new resonance angle as shown bellow:

$$\theta_{eff} = \text{Arcsin} \left(\pm 1 - \frac{m\lambda}{\Lambda \sqrt{\epsilon_{eff}}} \right) \quad (7.5)$$

where θ_c is the resonance angle, ϵ_{eff} and ϵ_m are the permittivity function of system and metal respectively and $m=-1$. The limitation in the periodicity and wavelength to excite SPP for both positive and negative order [312] for specific applications which is governed by:

$$\frac{\Lambda}{\lambda} > \frac{m}{\sqrt{\epsilon_{eff}}} \quad m > 0 \quad (7.6)$$

$$\frac{|m|}{\sqrt{4\epsilon_{eff}}} < \frac{\Lambda}{\lambda} < \frac{|m|}{\sqrt{\epsilon_{eff}}} \quad m < 0 \quad (7.7)$$

Using Eq. 4.11 and 7.7, the angular shift for negative order can be estimated.

$$\Delta\theta = |\theta_{eff} - \theta_c| \quad (7.8)$$

7.6. Controlling the Tunability of the refractive index

Different concentration of solutions is able to be introduced to PCL through micro-fluidic channel system (section 3.2) and the corresponding SPR reflectivity is collected at different energy and azimuthal angle. The coverage of the solutions, C (in molecules/cm²) on metallic grating is also able to be calculated, provided the average thickness of analyte, d :

$$C = d \times M \quad (7.9)$$

M is the analyte's density ρ , in g/cm³ divided by the molecular weight and multiplied by Avogadro's number. While d can be measured using spectroscopic ellipsometer.

7.7. Chapter Summary

The SPP can be effectively controlled via engineering dielectric medium to finely tune the PCL's effective permittivity function. *Bridged polysilsesquioxanes* were used to form hybrid organic-inorganic material which is able to induce porosity that enhances the sensitivity of the system only by enlargement of the interface. Plasmonic generation on PCL will be altered to opposite diffractive order ($m=-1$) as a result of C8 porous film. The porous film acts as nano-fluidic network which able to trap the analyte due its surface tension hence no functionalization is needed for measurement. Using HCl as an analyte, it was demonstrated that porous C8 on a plasmonic crystal provides a significant sensitivity improvement. Furthermore, the azimuthal effect provides the amplification (1 order) of this sensitivity. The improved sensitivity is because of the replacement to negative diffractive order. Other family *Bridged polysilsesquioxanes* with different chain lengths could be utilized as a promising candidate to tune plasmonic responses by engineering the refractive index of PCL.

8 Polarization and Sensitivity Measurement

8.1. Polarization Effect in 2D PCL

In the conventional arrangement, the light is usually incident parallel to the grating's vector. For this geometry as well as prism coupling, SPPs are able to be generated by TM-wave (p -polarization); while TE-wave (s -polarization) is being completely suppressed [68, 70, 87, 123, 133, 286]. Identical to plasmonic grating, for non-azimuthally rotated ($\varphi=0^\circ$) 2D square lattice PCL, the SPP coupling effectiveness (η_{geo}) excited by TM-wave on $\vec{g}_x$ crystal momentum will be equal to one and without contribution from TE-wave. In this arrangement, the incoming photon only “sees” the $\vec{g}_x$ crystal momentum which is parallel to TM-wave ($\alpha=0^\circ$) and the $\vec{k}_{\text{SPP}}$ will also be lined up with incoming photon component that is parallel to sample plane. Both polarization states conserve polarization upon diffraction from the grating [87, 133]. In this arrangement, TM-wave can only generate surface plasmon from $\vec{g}_x$.

In 2D PCL, SPP can also be generated when $\varphi \neq 0$, as demonstrated in chapter 5, however polarization conversion will take place. As crystal momentum is not coincided with scattering's plane, SPR spectrum consist of the combination of both polarization states although only p -polarized light is used [87]. In this case the incoming photon cannot be fully coupled into SPP due to its reduced efficiency (this value will be decreased as increasing the azimuthal rotation) noted by shallower dip in SPR spectra. The angle of polarization needs to be corrected in order to recover the SPP's coupling efficiency similar to 1D PCL that has been studied previously [116]. The first section of this chapter has been published in [322].

8.1.1. p - to s - Polarization Conversion in PCL

The excitation condition for 2D sinusoidal square lattice PCL at $\varphi=0^\circ$ is shown in Fig. 8.1, generated by (a) p -polarized, while (b) p - to s - polarization conversion. The excitation by s -polarization is shown in (c) and (d) shows the s - to p - conversion from 700-1000nm. It can be seen from the graph that for $\varphi=0^\circ$, TM wave provides the highest efficiency to generate surface plasmon (a) as the conversion from p - to s - is forbidden (b). While TE wave will not participate in plasmon generation (c) and the conversion from s - to p - is prohibited (d).

Figure 8.1 SPR measurement of 2D sinusoidal square lattice PCL at $\varphi=0^\circ$ using (a) *p*-polarized light with (b) *p*- to *s*-polarization conversion, (c) *s*-polized light with (d) conversion from *s*- to *p*- state for $\lambda= 700$ -1000nm. This figure is reproduced from [322].

The SPR measurement for 2D PCL at $\varphi=50^\circ$ and $\lambda=700$ -740nm using different polarization states and conversions are demonstrated in Fig. 8.2. For azimuthally rotated PCL, the plasmonic efficiency generated from *p*-polarization state will be decreased (a) due to small portion (6%) of polarization conversion (b). The opposite conversion (d) will allow some contribution from *s*-polarization state in generating SPP; however the background noise caused by *s*-polarized light is much higher (c). It is very interesting that at $\varphi=50^\circ$ the amount of both polarization exchanges for the whole incident angle is similar, nevertheless the amount is pretty low (10%) judged against the drop in plasmonic efficiency.

Figure 8.2. SPR measurement of 2D sinusoidal square lattice at $\phi=50^\circ$ using (a) p -polarized light with (b) p - to s -polarization conversion, (c) s -polarized light with (d) conversion from s - to p - state for $\lambda= 700\text{-}740\text{ nm}$. This figure is reproduced from [322].

Prior publication on 1D grating [166], symmetry breaking permits the SPPs generation with combined p - and s - polarized waves, overcoming the constraints of a single polarization mode and polarization conversion which was studied by *Bryan-Brown* [55, 133]. This pioneer work has inspired and opened further research areas related to polarization effect on light-matter interactions, nanophotonics (near fields) as well as exploiting TE mode in plasmonic fields.

Several modeling and simulations works related to this polarization conversion have been reported such as developed model to calculate the ratio of the polarization states that contribute in SPP generation [286]. The polarization dependency can be represented

empirically relative to incoming angle, azimuthal angle and grating's pitch [104, 314]. Nevertheless, at present it is still lacking an experimental study for SPP polarization especially in 2D PCL. Here condition that optimizes plasmonic generation in 2D PCL is studied. Simple and robust mathematical representation that relates the optical configuration and plasmonic efficacy is presented. This model will be very valuable in designing experiments and devices exploiting any polarization for SPP excitation and propagation conditions.

8.1.2. Fabrication and Experimental Set-up

2D sinusoidal plasmonic crystal is prepared by multiple IL exposure as explained in section 3.1 with 500nm pitch, magnitude of 53nm and deposited with 37nm/8nm of silver and gold respectively. The SPR measurement is similar to characterization of 1D PCL and transitional structures discussed in section 3.7.1. The sample is characterized in $\theta/2\theta$ arrangement (Fig. 8.4), with resolution of 0.005° . In this chapter, the magnetic field orientation of incoming photon, α is taken into account. The SPR spectra were measured at $\varphi=0^\circ$ - 60° and polarization angles α (0° corresponds to TM-wave and $\pm 90^\circ$ for TE-wave), the corresponding optimal polarization α_{min} for each grating's vectors (at various $\varphi, \lambda_{in}, \theta_r$) was obtained. The schematic representation of the experiment is demonstrated in Fig 8.3. The PCL was optically measured by changing the azimuthal rotation, φ and polarization state, α .

Figure 8.3. SPR Measurement setup including the polarization angle, α , azimuthal angle, φ and lattice angle, γ . This figure is reproduced from [322].

8.1.3. Plasmonic Coupling Efficiency

The SPP efficiency (η_{geo}) for non-azimuthally rotated ($\varphi \neq 0^\circ$) 2D PCL generated by TM-wave ($\alpha = 0^\circ$) shall be reduced by increasing the φ . Additionally, η_{geo} will also be adjusted as p -polarized light is not parallel to plane of incidence (POI), $\alpha \neq 0^\circ$. α is defined as the

magnetic field orientation with respect to POI and ranges from -90° to 90° . As illustrated in Fig 8.4, the change of η_{geo} relative to EM orientation on 2D PCL for different grating vector which can be geometrically calculated as:

Vector	$\eta_{geo}, \varphi \neq 0^\circ$ (symmetry breaking)	
$\vec{g}_x$	$\eta_{geo-x} = \cos\theta \cdot \cos \varphi - \alpha $	(8.1)
$\vec{g}_y$	$\eta_{geo-y} = \cos\theta \cdot \sin \varphi - \alpha $	(8.2)
$\vec{g}_{dia}$	$\eta_{geo-dia} = \cos\theta \cdot \cos \varphi - \alpha + 45^\circ $	(8.3)

This efficiency will be directly correlated to the reflectivity of SPR dips for each crystal momentum for different azimuthal and polarization angles. For $m=+1$, the resonance angle will increase proportionally with the wavelength. The equation above point out that shorter wavelength always excites plasmons at higher efficiency due to $\cos\theta$. It can easily be identified that optimum SPP coupling efficiency can be reached as TM is parallel to crystal momentum. However for non-square lattice, another parameter is introduced, i.e. γ , lattice angle. For $\varphi=0^\circ$, g_a is parallel to x -axis and the coupling efficiency need to be adjusted:

Vector	$\eta_{geo}, \varphi \neq 0^\circ$ (symmetry breaking)	
$\vec{g}_x$	$\eta_{geo-x} = \cos\theta \cdot \cos \varphi - \alpha $	(8.4)
$\vec{g}_y$	$\eta_{geo-y} = \cos\theta \cdot \cos \varphi + \gamma - \alpha $	(8.5)
$\vec{g}_{dia}$	$\eta_{geo-dia} = \cos\theta \cdot \cos\left \varphi - \alpha + \frac{\gamma}{2}\right $	(8.6)

It is clear that the efficiency factor for TE-wave increases with decreasing lattice angle while TM-wave demonstrates oppositely. The efficiency of both polarizations states will reach one when the lattice angle equal to 45° .

In 2D PCL when the symmetry is broken ($\varphi \neq 0^\circ$), the polarization conversion is made possible, e.g. p - to s - polarization and vice versa. The polarization exchanges may occur due to optical energy exchange between SPP resonances at metal–dielectric interface. Unlike 1D grating, the loss caused by polarization conversion for azimuthally rotated condition ($\varphi \neq 0^\circ$) in 2D PCL is minimized therefore higher plasmonic coupling efficiency can be obtained. In 2D PCL, certain amount of converted p -polarized light (into s -polarized) can be fully coupled by another PCL's crystal momentum. For example when $\alpha=0^\circ$, the magnetic field

will be coupled to $\bar{g}_x$ with factor of $\cos \varphi$, some part of $\cos|\varphi + 45^\circ|$ will be coupled to $\bar{g}_{dia}$ and the other part of $\cos \theta \cdot \sin \varphi$ will be coupled to $\bar{g}_y$. This could provide an improvement in light harvesting area. However for both rotated and non-rotated 2D PCL, the polarization angle for each crystal momentum is necessary to be optimized.

8.1.4. Result and Discussion

When incoming photon is perpendicular to one of crystal momentum (scattering plane is parallel with symmetry plane's array vector), reflectivity does not depend on polarization and only p -polarization is effective for SPP excitation. For a general azimuthal angle in 2D PCL, both TM and TE-waves may contribute to plasmonic excitation. The evidence of this effect is reported in Fig. 8.4, that shows a reflectivity spectrum scanned around θ_r with different α angles at fixed $\varphi=50^\circ$ and $\lambda_{in}=700$ nm for three different grating vectors: (a) $m=2$, (c) $m=1$ from $\bar{g}_{dia}$ and (b) $\bar{g}_x$. Reflectivity minimum strictly depends on the incident polarization, while θ_r is fixed for three different PCL array vector. The lowest reflectivity for each vector at 700nm has been observed at α_{min} (a) = -3° , α_{min} (b) = -48° and α_{min} (c) = -3° . For $\alpha=90^\circ$ and 43° , which is exactly 90° away from α_{min} (diagonal crystal momentum) and $\alpha_{min}(\bar{g}_x)$ respectively, SPP excitation is completely suppressed.

Figure 8.4. Reflectivity measurement of two-dimensional crystal $\varphi=50^\circ$ and $\lambda_{in}=700$ nm with several α values for (a) $m=2$ of $\bar{g}_{dia}$, (b) $\bar{g}_x$ and (c) $m=1$ of $\bar{g}_{dia}$ from $-90^\circ < \alpha < 90^\circ$. This figure is reproduced from [322].

After knowing the optimum polarization angle, the reflectivity at $\varphi=50^\circ$ is recorded. The plasmonic generation of this structure at $\varphi=50^\circ$ and $\lambda_{in}=700$ -740nm for $\alpha=-3^\circ$ (lines) and -48° (dashes) are demonstrated in Fig. 8.5. The SPR dips for $\alpha=-3^\circ$ at 700nm (black solid line) are generated by $\bar{g}_{dia}$ appear at 23.5° and 77° while for $\bar{g}_x$ is at 33° . The SPR minima of $\bar{g}_y$ does not appear prominently since the efficiency of p - to s -polarization is relatively very small. The SPR dips of $\bar{g}_{dia}$ for $m=1$ and $m=2$ is optimized when $\alpha=-3^\circ$ and for $\bar{g}_x$ will be fully

coupled when $\alpha = -48^\circ$, while the previous $\bar{g}_{dia}$ dips are restrained to some extent and the $\bar{g}_y$ dip is fully restrained (absence of SPR dip at 52.25° , 700nm), since the $\bar{g}_y$ is at the right angle relative to $\bar{g}_x$ and $\alpha_{min}(\bar{g}_x) = \alpha_{MAX}(\bar{g}_y)$. At present α_{min} is assumed to be independent of wavelength.

Figure 8.5. 2D PCL SPR measurement at $\varphi = 50^\circ$ for $\alpha = -3^\circ$ (line) and $\alpha = -48^\circ$ (dashes). This figure is reproduced from [322].

However after cautious observation and data analysis, for a fixed azimuthal rotation, α_{min} varies with wavelength hence altering the reflectivity minimum value which is demonstrated in Fig. 8.6. Their relationship with other parameters during plasmonic generation can be mathematically modeled and studied in details.

Figure 8.6. Experimental reflectivity minima due to SPP excitation of: $\bar{g}_x$ (middle), $m=1$ (left) and $m=2$ (right) of $\bar{g}_{dia}$ at fixed $\varphi = 50^\circ$ with different polarization angle, α for $\lambda = 675, 700$ and 725 nm. The recorded data is matched with the theoretical result from Eq. 8.7. This figure is reproduced from [322].

Similar to 1D grating [116], the reflectivity *max/min* of this 2-dimensional structure relative to angle of polarization α will repeat its value in regular intervals and can be modeled using:

$$R_{MAX/min} = p + q \cdot \sin^2(\alpha_{MAX/min} + 0.5\phi) \quad (8.7)$$

where p , q and ϕ are tuning parameters which are influenced by the incoming angles and its frequency as well as effective permittivity of the crystal. The refinement values for tuning parameters for several wavelengths are reported in Table 8.1. The addition of p and q reflects the *max* reflectivity value while p indicates the *min* reflectivity value. The collected data in Fig. 8.7 demonstrates the interval of reflectivity oscillation relatives to α is equal to π . The ϕ (Eq. 8.7) is associated to phase term and determines the α_{min} . Eq. 8.7 is unfailing with plasmonic wave-vector equations for 1D and 2D PCL discussed in chapter 5.

Table 8.1. Refinement values for tuning parameters in the modeling for all grating's vectors in 2D PCL at $90^\circ < \alpha < 90^\circ$ with $\Lambda=500\text{nm}$ and $\varphi=50^\circ$. The α_{min} is perpendicular to α_{MAX} .

Crystal Momentum	λ (nm)	p	q	ϕ	R_{min}	R_{MAX}	α_{min}	α_{MAX}
2 nd order of $\vec{g}_{dia}$	675	0.4080	0.2910	272	0.3746	0.6744	-1.41°	88.59°
	700	0.3890	0.3010	277	0.3895	0.6903	-1.97°	88.03°
	725	0.3740	0.3010	282	0.4081	0.6991	-2.63°	87.37°
1 st order of $\vec{g}_x$	675	0.1274	0.5942	-12	0.1031	0.6724	-49.3°	40.70°
	700	0.1148	0.5806	2	0.1161	0.6996	-47.9°	43.10°
	725	0.1061	0.5634	13	0.1488	0.7172	-38.7°	51.30°
1 st order of $\vec{g}_{dia}$	675	0.4742	0.4262	-77	0.4744	0.9121	-1.41°	88.59°
	700	0.4576	0.4202	-82	0.4585	0.8769	-1.97°	88.03°
	725	0.4439	0.4266	-87	0.4744	0.8971	-2.63°	87.37°

The surface corrugation confines the plasmon propagation to the plane formed by normal (0, 0, 1) direction and crystal momentum. Recalling Eq. 4.12, based on the prior hypothesis, the SPR intensity is proportional to the incident intensity (electric field component which is effective to SPP) on the PCL plane [116] which is given by $R \propto |\vec{E} \cdot (\vec{g}_{x/y/dia} \times \hat{z})|^2$. $\vec{E}$ and $\vec{g}$ are electrical field and crystal momentum. Recalling Eq. 4.13, $\vec{E}$ is equal to $(\cos\alpha\cos\theta, \sin\alpha, \cos\alpha\sin\theta)$. For ortho-normal 3D cartersian system wherein the scattering plane coincides with x-z plane, then the crystal momentum are given by:

$$\vec{g}_x = (\cos\varphi, \sin\varphi, 0), \quad \vec{g}_y = (\sin\varphi, \cos\varphi, 0) \quad (8.8 - 8.9)$$

$$\vec{g}_{dia} = (\cos|\varphi + 45^\circ|, \sin|\varphi + 45^\circ|, 0) \quad (8.9)$$

$$\vec{k}_{spp-x/y/dia} = \begin{pmatrix} \cos\beta_{x/y/dia} \\ \sin\beta_{x/y/dia} \\ 0 \end{pmatrix} \quad (8.10)$$

where $\vec{k}_{spp}$ is the SPP momentum direction and β is the angle formed by the SPP momentum direction with x -axis. Substituting expressions above and rearranging the terms, the reflectivity of plasmonic crystal can be calculated as function of incident, polarization and azimuthal angles [116]:

$$R_x = |\cos \alpha \cos \theta \sin \varphi - \sin \alpha \cos \varphi|^2 \quad (8.11)$$

Using trigonometry identity: $\cos 2\alpha = 2\cos^2 \alpha - 1$, the above equation becomes:

$$R_x \approx (\cos^2 \theta \sin^2 \varphi + \cos^2 \varphi) \cdot \sin^2 \left(\alpha + \frac{\phi_x}{2} \right) \quad (8.12)$$

By similar derivation, the reflectivity for the other crystal momentum can be obtained:

$$\begin{aligned} R_y &\propto |\vec{E} \cdot (\vec{g}_{dia} \times \hat{z})|^2 = |\cos \alpha \cos \theta \cos \varphi - \sin \alpha \sin \varphi|^2 \\ &\approx (\cos^2 \theta \cos^2 \varphi + \sin^2 \varphi) \cdot \sin^2 \left(\alpha + \frac{\phi_y}{2} \right) \end{aligned} \quad (8.13)$$

$$\begin{aligned} R_{dia} &\propto |\vec{E} \cdot (\vec{g}_y \times \hat{z})|^2 = |\cos \alpha \cos \theta \sin(\varphi + 45^\circ) - \sin \alpha \sin(\varphi + 45^\circ)|^2 \\ &\approx (\cos^2 \theta \sin^2(\varphi + 45^\circ) + \cos^2(\varphi + 45^\circ)) \cdot \sin^2 \left(\alpha + \frac{\phi_{dia}}{2} \right) \end{aligned} \quad (8.14)$$

which reproduces the harmonic dependence on polarization given by the fitting formula Eq. 8.7. The ϕ of Eq. 8.7 for different grating's vectors can be calculated as follow:

$$\phi_x = \arcsin \left(-\frac{2 \cdot \cos \theta}{\cos^2 \theta \tan \varphi + \cot \varphi} \right) \quad (8.15)$$

$$\phi_y = \arcsin \left(-\frac{2 \cdot \cos \theta}{\cos^2 \theta \cot \varphi + \tan \varphi} \right) \quad (8.16)$$

$$\phi_{dia} = \arcsin \left(-\frac{2 \cdot \cos \theta}{\cos^2 \theta \tan(\varphi + 45^\circ) + \cot(\varphi + 45^\circ)} \right) \quad (8.17)$$

From Eq. 8.12-8.14 the minimum of reflectivity takes place when the sin term equals to zero. Thus the relation between the phase and the polarization angle become $\alpha_{min} = -0.5\phi_{x/y/dia}$ which optimizes the strength of the SPP coupling. The α_{min} could be acquired when the SPR intensity in Eq. 8.7 reaches minimum ($R \rightarrow 0$):

$$\vec{E} \cdot (\vec{g} \times \hat{z}) = 0 \quad (8.18)$$

$$\begin{aligned} \text{for } \vec{g}_x: \quad & \cos \alpha \cos \theta \sin \varphi - \sin \alpha \cos \varphi = 0 \\ & \tan \alpha_{\min-x} = \cos \theta \tan \varphi \end{aligned} \quad (8.19)$$

$$\begin{aligned} \text{for } \vec{g}_y: \quad & \cos \alpha \cos \theta \cos \varphi - \sin \alpha \sin \varphi = 0 \\ & \tan \alpha_{\min-y} = \cos \theta \cot \varphi \end{aligned} \quad (8.20)$$

$$\begin{aligned} \text{and for } \vec{g}_{dia}: \quad & \cos \alpha \cos \theta \sin(\varphi + 45^\circ) - \sin \alpha \cos(\varphi + 45^\circ) = 0 \\ & \tan \alpha_{\min-dia} = \cos \theta \tan(\varphi + 45^\circ) \end{aligned} \quad (8.21)$$

Here is the condition where the incoming EM field has no fraction being perpendicular to the symmetry plane, thus reflectivity has its minimum value.

This polarization angle refers to the maximum value in reflectivity. The $\alpha_{\min}$ and $\alpha_{\max}$ are related each other by exactly 90° , as expected. Eq. (8.19-8.21) gives the incident polarization value which optimizes the coupling with surface modes for certain incoming angle. The resonance angle could be calculated as follow:

$$\theta_{r-x} = \arcsin \left(\frac{\lambda_{in}}{\Lambda_x} \cos \varphi \mp \sqrt{M^2 - \left(\frac{\lambda_{in}}{\Lambda_x} \right)^2 \sin^2 \varphi} \right) \quad (8.22)$$

$$\theta_{r-y} = \arcsin \left(\frac{\lambda_{in}}{\Lambda_y} \sin \varphi \mp \sqrt{M^2 - \left(\frac{\lambda_{in}}{\Lambda_y} \right)^2 \cos^2 \varphi} \right) \quad (8.23)$$

$$\begin{aligned} \theta_{r-dia} (1^{st} \text{ order}) &= \arcsin \left(\frac{\sqrt{2} \lambda_{in}}{\Lambda_x} \cos(\varphi + 45^\circ) \mp \sqrt{M^2 - 2 \left(\frac{\lambda_{in}}{\Lambda_x} \right)^2 \sin^2(\varphi + 45^\circ)} \right) \\ \theta_{r-dia} (2^{nd} \text{ order}) &= \arcsin \left(\frac{\sqrt{2} \lambda_{in}}{2 \Lambda_x} \cos(\varphi + 45^\circ) \mp \sqrt{M^2 - \frac{1}{2} \left(\frac{\lambda_{in}}{\Lambda_x} \right)^2 \sin^2(\varphi + 45^\circ)} \right) \end{aligned} \quad (8.24 \text{ and } 8.25)$$

where Λ is the grating pitch and $M = \sqrt{\frac{\epsilon_M \epsilon_D}{\epsilon_M + \epsilon_D}}$. ϵ_M and ϵ_D are permittivity for both medium.

Since bi-metallic layer is used (37nm of silver and 8 nm of gold), the permittivity value of pure metal from text book or references cannot be used, therefore the optical properties need to be collected uniquely using variable angle ellipsometer. The data measurement and theoretical modelling for optimized polarization $\alpha_{\min}$ relative to wavelength and azimuthal

angles are shown in Fig. 8.7. For $\bar{g}_y$ crystal momentum, only theoretical modelling is presented in Fig 8.8. Experimental points are well reproduced by the analytical modelling.

Figure 8.7. Measurement and modelling at optimized polarization $\alpha_{\min}$ relative to incoming wavelength for (left) $\bar{g}_x$ and (right) $\bar{g}_{dia}$ at various azimuthal rotations. Data fitting is done using Eq. 8.20-8.22. This figure is reproduced from [322].

For $\bar{g}_x$ vector, $\alpha_{\min}$ will increase with azimuthal rotation. It is worth noting when the PCL is azimuthally rotated beyond the critical angle; double plasmonic dips are able to be generated by single frequency and the $\alpha_{\min}$ values could exceed $\pm 70^\circ$. For $\bar{g}_y$ vector the $\alpha_{\min}$ will behave in reversed trend relative to ϕ while for $\bar{g}_{dia}$, the $\alpha_{\min}$ curve will demonstrate reversed trends for $\phi < 45^\circ$ and $\phi > 45^\circ$ as shown in Fig. 8.7 (left). The centre of symmetry of $\bar{g}_{dia}$ crystal momentum is when $\phi = 45^\circ$ with $\alpha_{\min} = 0$. This indicates that the maximum coupling condition for this grating's vector is taking place when $\phi = 45^\circ$ noted by $\alpha_{\min} = 0$, a similar condition for SPP excitation using p -polarized light at zero azimuthal angle.

Figure 8.8. Theoretical modelling for the optimized polarization $\alpha_{\min}$ relative to incoming wavelength for $\bar{g}_y$ at various azimuthal rotations.

The relationship of $\alpha_{\min}$ for individual grating's vector will be another essential topic to be discussed. It could be noticed that the $\alpha_{\min}$ of $\bar{g}_x$ is about 45° away from $\alpha_{\min}$ of $\bar{g}_{dia}$ and 90°

away from $\alpha_{\min}$ of $\bar{g}_y$. This correlation indicates when the plasmonic generation of one grating's vector is maximized (g_x), the others are restricted (g_y as well as g_{dia}). The $\alpha_{\min}$ of g_x is $\alpha_{\max}$ of g_y and vice versa. Nevertheless, while the $\alpha_{\min}$ of g_{dia} is optimized, both g_x and g_y are partly restricted. Therefore the optimized polarization for every grating's vector has to be done individually (for linear polarization).

2D PCL shows advantages by having several plasmonic generations by different grating's vectors (x -, y - and diagonal axis). Nevertheless the plasmonic field in this structure could be further enhanced as most favorable conditions for plasmonic generation are utilized. Appreciating the correlation of $\alpha_{\min}$ for various pitches, azimuthal rotations and incoming wavelength could be a significant aspect to create an easier and vigorous approach to define the best possible coupling condition for every grating's vector; therefore the sensitivity of the structure will be extensively enhanced.

8.1.5. Section Summary

The influences of polarization state on the surface plasmon resonance for non-zero azimuthal rotation in 2D plasmonic crystal has been studied. By adjusting the polarization state (α) of incident photon, the plasmonic coupling power could be easily controlled and it could be fully optimized as correspond $\alpha_{\min}$ is employed for respective grating's vector. The optimal polarization angle, $\alpha_{\min}$ can be calculated using mathematical equations derived from optical configuration of SPR system elaborated earlier. Understanding $\alpha_{\min}$ correlation for various pitch, azimuthal rotation and frequency will be very useful to define the most favorable plasmonic generation condition for respective grating's vector in 2D PCL as well as SPP devices (e.g. sensor).

8.2. Polarization Enhanced SPR Sensitivity on 2D PCL

It has been explained in previous chapter that 2D PCL shows possibility of higher sensitivity enhancement than 1D lines grating, due to several reasons. First it has larger concentration of EM field because of limited surface profile (focusing effect) compared to GC-SPR structure, thus incoming photon can be coupled effectively leading to enhancement. Second, the

enhancement can also be attributed to simultaneous excitation of multiple SPPs (three sets and more) by various amplitude and gratings vectors (x -, y - and diagonal).

Nevertheless at non-zero azimuthal angle ($\varphi \neq 0^\circ$); when p -polarized light is used, the coupling efficiency will be reduced or partially suppressed thus the optimum coupling condition cannot be realized. It is noted by shallower dips in the reflectivity measurement [87, 96, 123, 286, 293]. The efficiency of SPP excitation can be optimized by controlling the polarization angle as discussed in previous section. Therefore, incoming photon with optimized polarization will improve the coupling efficiency thus enhance the sensitivity. Every grating's vector has to be optimized individually (for linear polarization).

In this section, the detection sensitivity of decanethiol, C_{10} - self-assembled monolayer (SAM) on 2D PCL under azimuthal control is examined. The sensitivity effect of optimizing the polarized light for each crystal momentum is studied. Earlier report demonstrated the performance of GCSPP to sense 15Å thick dodecanethiol (C_{12}), with a shifting about 2.2° with detectability about $857^\circ/\text{RIU}$ [315]. The work was done without optimizing the polarization angle. In this section, C_{10} that is $\sim 1.3\text{nm}$ thick [247-250] will be examined and as polarization of each crystal momentum is optimized, the sensitivity is expected to be improved. Both data measurement and theoretical model descriptions are compared to have better understanding on the mechanism of sensitivity enhancement.

8.2.1. Methodology

Another 2D sinusoidal square lattice PCL sample with $\Lambda=500\text{nm}$ was deposited by 37nm/8nm of silver and gold. The optical measurement for non-functionalized and C_{10} -functionalized 2D crystal is similar to lines grating and transitional structure characterization discussed in chapter 4-5. The measurement of 2D Au-Ag PCL uncoated and coated with C_{10} SAM were in air ambient. The point of measurement was at the center of rotation axis, hence the measurement spot before and after C_{10} deposition will remain the same although the sample is rotated at certain azimuthal rotation.

The measurements were collected at $\varphi=50^\circ$ where double SPPs can be excited, $-90^\circ < \alpha < 90^\circ$ ($\alpha=0^\circ$ represents TM-wave and $\alpha=\pm 90^\circ$ for TE-wave). For every resonance condition of

grating's vector at different φ , λ_{in} , θ_r , the optimal polarization α_{min} for both uncoated and C_{10} coated PCL were obtained. The measurement of polarization angle can be done in the presence of the largest dip from grating's vector of x- and diagonal array ($\lambda=730$ nm for $\bar{g}_x$ and 735nm for $\bar{g}_{dia}$). The most favorable polarization state with and without C_{10} -molecules could be verified by the lowest SPR dips as demonstrated in Fig. 8.9.

It is found that the optimized polarization for each crystal momentum is as follows:

Condition	Optimized Polarization, α_{min}	
	$\bar{g}_{dia}$ ($\lambda=730$ nm)	$\bar{g}_x$ ($\lambda=735$ nm)
Uncoated (bare)	-3°	-48°
C_{10} Coated	-4°	-49°

The functionalization of C_{10} will change the optimized polarization angle thus affect the optimum SPP excitation condition i.e. resonance angle and incident wavelength. These data will be used as controlled parameters in sensitivity measurement.

Figure 8.9. Reflectivity spectrum of 2D PCL collected at $\varphi=50^\circ$ for a) $\bar{g}_{dia}$ and b) $\bar{g}_x$ at specific wavelength with the broadest dip and optimized polarization angle for both C_{10} coated and uncoated with a) $\alpha=-3^\circ$ to -4° , $\lambda=735$ nm and b) $\alpha=-48^\circ$ to -49° , $\lambda=730$ nm to determine the α_{min} .

8.2.2. Experimental Results

To compare the result between PCL and prism coupler, C_{10} SAM coated on Ag-Au (37 and 8nm) PCL with thickness of 1.35 nm and refractive index $n_{C_{10}}=1.33$ was simulated using PCSPR Winspall[®] simulator [258] which is demonstrated in Fig. 8.10 (a). The resonance angle difference between uncoated and C_{10} coated ($\Delta\theta$) at 632.8nm (using HeNe laser) is about $\sim 0.4^\circ$. This is where the azimuthal and polarization cannot be utilized.

The SPR curve for non-rotated 2D crystal is demonstrated in Fig. 8.10 (b). At $\lambda=710\text{nm}$, $\Delta\theta=0.2^\circ$, which is 50% less sensitive than PCSPR at comparable wavelength. The angular shifting will rise with the wavelength, i.e. at $\lambda=1\mu\text{m}$ (near IR) $\Delta\theta=0.5^\circ$. Nevertheless this value is still very small weighed against other plasmonic systems, furthermore at low frequency, the noise is higher. The comparison of PCSPR, 1D and 2D PCL at $\varphi=0^\circ$ is presented in Table 8.2.

Table 8.2. Angular shifting between bare and SAMs coated plasmonic crystal.

PC-SPR	1D PCL ($\varphi=0^\circ$)	1D PCL ($\varphi=60^\circ$)	2D PCL ($\varphi=0^\circ$)
$\lambda=632.8\text{nm}$	$\lambda=700\text{nm}$	$\lambda=618\text{nm}$ (for C_{12}) [314]	$\lambda=700\text{nm}$
0.4° (Winspall simulation)	$\sim 0^\circ$ (for C_{12})	$1^{\text{st}} = 2.15^\circ$ $2^{\text{nd}} = 2.2^\circ$	0.2° (or 0.5° for $1\mu\text{m}$)

From $\varphi=0^\circ$ measurement of C_{10} -functionalized 2D profile, reasonable angular shifting was noticed. This reveals the benefit of utilizing 2D plasmonic crystal better sensing performance that is originated from the increase in coupling effectiveness because of plasmonic focusing and concentrating field caused by higher curvature of 2D profile.

Figure 8.10. (a) Winspall simulation for bare 37nm Ag – 8nm Au film (blue line) and coated C_{10} (red line) using prism coupler SPR, at $\lambda=632.8\text{nm}$. (b) SPR reflectivity measurement of bare (continuous line) and C_{10} -deposited (dashes) 2D Ag-Au square lattice PCL for $\varphi=0^\circ$ (conventional mounted grating).

From section 8.21, it is known that the optimum polarization for bare 2D crystal at $\varphi=50^\circ$ is -3° ($\bar{g}_{dia}$) and -48° ($\bar{g}_x$). The SPR measurement using these optimized polarization angles are shown in Fig. 8.11 and with enhancement more than 30% at 710nm.

Figure 8.11. Reflectivity measurement for two dimensional structure at $\varphi=50^\circ$ and $\lambda_{in}=710-730$ nm for $\alpha=-3^\circ$ (continuous line) along with $\alpha=-48^\circ$ (dashed line).

It is observed that the dip position is slightly shifted due to the change in polarization angle. At $\lambda=710-730$ nm, the third dip is very broad. As discussed in section 5.2.2.8, the dip is originated from the combination of 2nd dip of $\bar{g}_x$ and 4th dip (which is a combination of 1st order of $\bar{g}_{dia}$ and $\bar{g}_y$) due to similar SPP propagation direction (β). The double dips from $\bar{g}_x$ are getting closer as the wavelength increases ($710\text{nm} < \lambda < 732\text{nm}$) followed by dips combination at $\lambda=732\text{nm}$. The condition just before the merging (β almost near to 90°) became the interest in this experiment when dips' separation is still clear with the highest density of SPP modes, hence most desirable condition for the sensitivity measurement.

From SPR measurement above, the $\bar{g}_{dia}$ dips can only be optimized up to $\approx 3\%$ as α only moves from 0° to -3° ; however $\bar{g}_x$ can be optimized up to 30% at 710nm when $\alpha=-48^\circ$. Before the optimized polarization for $\bar{g}_x$ is introduced, the maximum wavelength for clear separation of the double dips is at 725nm. However after the optimization, they still can be distinguished individually up to $\lambda=730\text{nm}$. The combination of both crystal momentum optimizations will become a unique advantage of 2D PCL compared to other structures.

The bare and C_{10} coated SPR dips generated by TM-wave ($\alpha=0^\circ$) is demonstrated in Fig. 8.12. The optimized polarization angle will enhance the sensitivity in the presence of double SPPs. The spectra was then re-collected under optimized polarization for bare (line) and C_{10} -functionalized (dashed line) respectively. The measurements are summarized in Fig. 8.13.

Using p -polarized light, the double dips of C_{10} coated 2D PCL are getting close each other as the wavelength increases and the resolution limit for their clear separation is at 725nm, beyond which the dips will start to combine into single broad dip (Fig. 8.12). For $\alpha=-4^\circ$, the

separation of the double dip can still be observed up to 728nm (Fig. 8.13 (a)). This is primarily caused by the deeper fourth dip (i.e. optimization of first order of $\bar{g}_{dia}$ dip). Moreover as $\alpha=-49^\circ$, the separation can be resolved up to 730nm, where the the depth of second and third dips are increasing (i.e. optimization of $\bar{g}_x$) (Fig. 8.13 (b)). The largest angular shift is demonstrated at 735nm however the double dips have merged.

Figure 8.12. Reflectivity measurement of bare (continuous line) as well as C₁₀-functionalized (dash) 2D PCL at $\varphi=50^\circ$ using incident wavelength (715-735nm) and $\alpha=0^\circ$ (*p*-polarized) The Different colour lines represent different incident wavelength.

Figure 8.13. Reflectivity measurement of bare (continuous line) as well as C₁₀-functionalized (dash) 2D PCL at $\varphi=50^\circ$ under (a) $\alpha_{\min}=-3^\circ$ (bare) and -4° (C₁₀) and (b) $\alpha_{\min}=-48^\circ$ (bare) and -49° (C₁₀).

At optimized polarization, the reflectivity dips are getting sharper (smaller FWHM) and the angular shift, $\Delta\theta$ is improved from 2.86° at 725nm (Fig. 8.12) to 3.91° at 730nm (Fig. 8.13 (b)). The SPP field enhancement (largest SPP modes) under optimized polarization becomes the reason for sensitivity improvement which enables to resolve double dips at the moment before merging. The angular shift under different polarization states is presented in Table 8.3 and Fig.8.14. As shown, $\Delta\theta$ is getting larger with the increment of α as well as wavelength and will reach maximum at 735 nm for first dip ($\bar{g}_{dia}$) and 730nm for third dip ($\bar{g}_x$).

Table 8.3. Comparison of SPP angular shift excited under the optimized polarizations $\alpha_{\min}=-3^\circ$ and -4° for 1st and 3rd dips, $\alpha_{\min}=-48^\circ$ and -49° for 2nd dip with $\alpha=0^\circ$ (p-polarized).

2D Plasmonic Crystal at $\varphi=50^\circ$						
λ	$\alpha=0^\circ$			$\alpha=-4^\circ$	$\alpha=-49^\circ$	
	1 st Minima	2 nd Minima	3 rd Minima	1 st Minima	2 nd Minima	3 rd Minima
715nm	1.86°	1.63°	1.98°	1.93°	2.23°	2.61°
725nm	2.35°	2.24°	2.86°	2.58°	3.24°	3.39°
728nm	2.43°	(merged with 3 rd dip)	(merged with 2 nd dip)	2.71°	3.43°	3.71°
730nm	2.52°	(merged with 3 rd dip)	(merged with 2 nd dip)	2.83°	3.59°	3.91°
732nm	2.65°	(merged with 3 rd dip)	(merged with 2 nd dip)	2.96°	(merged with 3 rd dip)	(merged with 2 nd dip)
735nm	2.89°	(merged with 3 rd dip)	(merged with 2 nd dip)	3.14°	(merged with 3 rd dip)	(merged with 2 nd dip)

The measurement shows that the third dip is more sensitive than the rest at any polarization angle. This is because the third minima is extremely big attributable to merging with other two nearest dips thus it contains more SPP modes, f and provides better sensitivity [72] as described earlier in section 5.2.2.8. According to chapter 7, C_{10} can be considered as absorbing medium, since as thickness increases the reflectivity of SPR dips are increasing and resonance angle shifts towards greater values.

Figure 8.14. Resonance angle shifting for 1st (○), 2nd (□) and 3rd (●) SPR dips excited by different polarization state (black for TM-wave, red for $\alpha=-4^\circ$ and green for $\alpha=-49^\circ$) relative to incoming wavelength.

Similarly with the first dip, although not a double SPPs, it is positioned at high azimuthal rotation ($>45^\circ$), hence the plasmonic mode density f is higher than non rotated 2D crystal. f is proportional with azimuthal rotation until it reaches $\varphi_{\max}$. $\varphi_{\max}$ is the maximum azimuthal rotation to excite the double SPPs (in our case $\sim 60^\circ$). The first dip at $\varphi=50^\circ$ and $\lambda=735\text{nm}$ may reach sensitivity up to 3.14° and it still can be increased with the wavelength.

8.2.3. Analysis and Discussion

The plasmonic propagation on PCL can be generated when incoming photon momentum on sample plane match the $\bar{k}_{SPP}$ momentum as elaborated in section 5.2. The schematic of SPP wave-vector with C_{10} at 710nm under optimized polarization angles for each crystal momentum is demonstrated in Fig. 8.15 (a). The detectability of C_{10} ($\Delta\theta$) under p - and optimized polarization (α_{min}) are compared and the latter condition offers significant improvement. After the C_{10} functionalization, both k_{spp} circles' radius (before and after optimization of polarization angle) will grow bigger, consequently inducing an angular shift and improving the sensitivity of 2D PCL system.

Figure 8.15. Schematic momentum in square lattice sinusoidal 2D PCL for $\phi=50^\circ$ at different wavelength (a) 710nm and (b) 725nm under optimized polarization for $\bar{g}_x$ where $\alpha_{min}=-48^\circ$ and -49° - before and after C_{10} coating respectively. The purple and blue hemi-circles correspond to SPP momentum of bare ($\bar{k}_{SPP}$) and C_{10} coated ($\bar{k}_{SPP-C10}$) PCL. The black rings is the crossing point of the $\bar{k}_{ph}$ and $\bar{k}_{SPP}$ hemi-circles.

At $\varphi=50^\circ$, five SPPs can be excited (x_1, x_2 from $\bar{g}_x$; dia' from $g_{dia(1)}$; dia'' from $g_{dia(2)}$ and y from $\bar{g}_y$), where x_1 and x_2 are double dips. Since the resonance conditions for x_2 , dia' and y are close to each others, the individual dip cannot be clearly distinguished. By optimizing polarization angle, the SPP coupling efficiency will be brought into maximum (the α_{min} will optimize the magnitude of k_{spp}); however it will not change the propagation direction β .

The two outermost semi-circles in Fig. 8.16 correspond to $\bar{g}_{xy}$ and $\bar{g}_{dia}$ momentums at different azimuthal angle and the two inner semi-circles correspond to $\bar{k}_{spp}$ momentums for bare and C₁₀ coated PCL which magnitude can be calculated by:

$$k_{spp} = \frac{\omega}{c} \sqrt{\frac{\epsilon_m \epsilon_d}{\epsilon_m + \epsilon_d}} = \frac{2\pi}{\lambda} M \quad (8.26)$$

ϵ_m and ϵ_d are permittivity function of metallic and the dielectric layers. For functionalized PLC, the $\bar{k}_{spp}$ magnitude increases due to increment in ϵ_D . As C₁₀ coated $\bar{k}_{spp}$ semi-circle has a bigger magnitude, the resonance condition will be altered. The crossing points will move from x_1 and x_2 to x'_1 and x'_2 . A little increase in wavelength, the radius of k_{spp} circles (bare and C₁₀ coated) shifting the position of x_{1-2} and x'_{1-2} close one another hence move y' and dia' points away from x'_2 and clear separation between third and fourth dips is expected. With further increment in wavelength, x'_1 and x'_2 combine into single wide dip as demonstrated Fig. 8.16 for $\lambda=732\text{nm}$.

From the schematic, the k_{spp} magnitude (purple circle radius) and direction, β will be altered after C₁₀ functionalization. Using resonance angle θ for a fixed wavelength λ_{in} , at azimuth angle φ , as shown above, together with equation below, the changes in SPP propagation direction before and after functionalization can be determined. Since $k_{spp} \sin \beta = g \sin \varphi$ and $k_{spp} \cos \beta = g \cos \varphi - k_{ph} \sin \theta$ hence:

$$\tan \beta = \frac{\lambda \sin \varphi}{\lambda \cos \varphi - \Lambda \sin \theta} \quad (8.27)$$

Plasmonic propagation direction, β^+ and β^- , will be slightly moved to lower and higher angle respectively after C₁₀ functionalization. The effect of increasing the wavelength is similar to azimuthal angle; the double dips will get closer and at maximum condition, the

both $\bar{k}_{SPP}$ will combine into one direction shown by a single board dip. This is the condition where SPP mode density rises, thus enhance the sensitivity.

Unlike 1D PCL, the sensing capability of 2D PCL will be enhanced at both low ($\bar{g}_y$) and high ($\bar{g}_x$) azimuthal rotation as the circumstance for double plasmonic generation about the boundary of $\bar{k}_{SPP}$ semi-circle is able to shift in k -space. The shift is getting larger at higher wavelength, just before the double dips merge. The condition may work similarly for $\bar{g}_{dia}$ at $\varphi \neq 0^\circ$. Another origin sensitivity enhancement is the merging of some plasmon with very close propagation direction becomes single multi mode SPP as discussed in previous section.

The sensitivity, S for 2D PCL is defined by the angular shift per RIU [156, 315]:

$$S = \frac{\partial \theta}{\partial n} = \frac{\partial \theta}{\partial k_{ph-x}} \frac{\partial k_{ph-x}}{\partial k_{SPP}} \frac{\partial k_{SPP}}{\partial n} \quad (8.28)$$

With Fig. 8.15 as a reference the S can be calculated by differentiating the components in Eq. 8.28. Thus, the sensitivity for each dip in angular interrogation can be calculated:

$\bar{g}_x$ (where $A_x=a$)	$S = -\frac{1}{\cos \theta_r} \left(\frac{M}{n_0} \right)^3 \frac{\sqrt{\frac{1}{a^2} + \frac{\sin^2 \theta}{\lambda^2} - \frac{2 \cos \varphi \sin \theta}{a \lambda}}}{\frac{\cos \varphi}{a} - \frac{\sin \theta}{\lambda}} \quad [315]$	(8.29)
$\bar{g}_y$ (where $A_y=a$)	$S = -\frac{1}{\cos \theta_r} \left(\frac{M}{n_0} \right)^3 \frac{\sqrt{\frac{1}{a^2} + \frac{\sin^2 \theta}{\lambda^2} - \frac{2 \sin \varphi \sin \theta}{a \lambda}}}{\frac{\sin \varphi}{a} - \frac{\sin \theta}{\lambda}}$	(8.30)
$\bar{g}_{dia}$ ($m=1$, $A_{dia-1}=0.707a$)	$S = -\frac{1}{\cos \theta_r} \left(\frac{M}{n_0} \right)^3 \frac{\sqrt{\frac{2}{a^2} + \frac{\sin^2 \theta}{\lambda^2} - \frac{2(\cos \varphi \sin \theta - \sin \varphi \sin \theta)}{a \lambda}}}{\frac{\cos \varphi - \sin \varphi}{a} - \frac{\sin \theta}{\lambda}}$	(8.31)
$\bar{g}_{dia}$ ($m=2$, $A_{dia-2}=1.414a$)	$S = -\frac{1}{\cos \theta_r} \left(\frac{M}{n_0} \right)^3 \frac{\sqrt{\frac{1}{2a^2} + \frac{\sin^2 \theta}{\lambda^2} - \frac{(\cos \varphi \sin \theta + \sin \varphi \sin \theta)}{a \lambda}}}{\frac{\cos \varphi + \sin \varphi}{2a} - \frac{\sin \theta}{\lambda}}$	(8.32)

M has been described earlier in Eq. 8.26, n_0 is refractive index of environment, λ and θ are incoming wavelength and angle respectively which can be obtained from Eq. 8.22-8.25.

Even though for φ nearer to φ_c gives higher sensitivity, this range is not favourable due to greater probability of errors. As φ closes to φ_{MAX} , the resonance dip becomes wider and appears at higher angle ($\theta > 60^\circ$) hence it will be difficult to distinguish the two dips clearly.

For $\varphi > \varphi_{MAX}$ the double dips cannot be used for sensing purposes, however 2D PCL offers the first dip originated from second order of diagonal array (g_{dia}) which may provide good sensitivity at high azimuthal angle ($\varphi > \varphi_{MAX}$) with acceptable sensitivity. This is another advantage of 2D PCL – SPR based sensor which does not exist in 1D GC-SPR.

After surface functionalization, the refractive index of the system (measured by ellipsometer) increases to $\Delta n = 0.00327 \pm 0.00005$ RIU. This experimental result agrees the calculated one, $\Delta n = 0.0033$ RIU assuming the C_{10} length ≈ 1.335 nm and $\varepsilon_{Cl0} = 1.825$ [249]. The sensitivity measurement for double dip under non-optimized polarization may reach approximately: 750°/RIU for first, 825°/RIU for second minima and 930°/RIU for third minima. The sensitivity will further be improved up to 1070°/RIU for the third dip as optimized polarization is utilized for each crystal momentum.

There are *two conditions* where the double dips no longer can be used. *First* is when $\lambda > \lambda_{MAX}$ (~ 730 nm), although the sensitivity is high, the double dips cannot be clearly distinguished. *Second* is when $\varphi > \varphi_{MAX}$ being maximum azimuthal angle to excite the double SPPs ($\sim 60^\circ$). The solution to these issues is by using the first dip from diagonal crystal momentum (g_{dia}) which has comparable sensitivity for both conditions. Although not double SPPs, the first dip is positioned at high azimuthal rotation ($> 45^\circ$) hence the plasmonic modes density, f value is higher than single dip at $\varphi = 0^\circ$ and f value will increase with the azimuthal angle.

The system is able to detect changes $\Delta n = 10^{-4}$ RIU and with equipment's angular resolution, it is achievable to improve the signal-to-background ratio for better resolution ($\pm 10^{-7}$ RIU). As demonstrated in Fig. 8.14, the SPR dips are getting lower and the width are less sharp as contrasted against zero azimuthal angle. This condition eventually will reduce the sensing performance as well as the quality. To improve the performance, maximum plasmonic coupling condition needs to be generated with narrowest FWHM dip.

8.2.4. Figure of Merit (FOM)

The quality of 2D PCL sensing system is justified by its figure of merit (FOM), shown in Fig. 8.16. FOM is obtained from angular shift over FWHM of SPR dips at fixed wavelength.

$$FOM = \Delta\theta / \theta_{FWHM} \quad (8.33)$$

The FWHM value of reflectivity dips from each crystal momentum were obtained from Gaussian curve fitting [316] which is equal to $2\sqrt{2\ln 2} \cdot \sigma$, where σ is the standard deviation of each fitted Gaussian curve [317].

Figure 8.16. FOM of 2D PCL sensitivity excited by TM-wave (black) and optimized polarization (red) for each crystal momentum.

Generally the FOM for all dip generated using optimized polarization light is greater than TM-wave. The 3rd dip provides the highest FOM at 730nm, this is mainly because of the largest angular shift and lower FWHM at optimized polarization angle.

8.2.5. C₁₀ and C₁₂ Sensitivity Measurement

It has been demonstrated that 2D PCL is reliable to detect system with just ten carbon atoms. Under optimized polarization, the FOM of the system can be greatly improved with resolution down to 10^{-7} RIU. To determine the detection limit of 2D PCL, the decanethiol (C₁₀) and dodecanethiol (C₁₂-SAM) molecules were measured simultaneously using the same PCL under optimized SPP excitation conditions (resonance wavelength, incident, azimuthal and polarization angles).

8.2.6. Experimental Procedure

The C_{10} and C_{12} self-assembled monolayers were grown individually on 2D sinusoidal square lattice PCL side by side. This will prevent the misalignment and deviation due to geometrical variation. The PCL has been characterized previously using AFM and FESEM to have very uniform corrugated structure throughout the whole patterned area.

The samples are optically characterized similar to previous measurement in section 3.7.1. The measurements were collected at $\varphi=0^\circ$ - 60° . The optimum conditions for all crystal momentums were chosen to give highest sensitivity (largest shifting) upon functionalization of C_{10} and C_{12} . The α for each crystal momentum was individually optimized for both C_{10} and C_{12} . The optimized polarization can be predicted using Eq. 8.19-8.21.

8.2.7. Experimental Result

The SAMs functionalization was observed to change the optimized polarization angle which consequently will affect the optimum condition for SPP excitation i.e. resonance angle and incident wavelength in 2D PCL. The shift in double dips from main axis and single dip from diagonal crystal momentum were examined in different regions: $\varphi < 45^\circ$ and $\varphi > 45^\circ$.

a) The measurement for $\varphi=30^\circ$ is shown in Fig. 8.17.

Generally in 2D PCL for $\varphi > 0^\circ$, all crystal momentum may participate in SPP excitation. For $\varphi=30^\circ$, $\bar{g}_y$ is able to excite double SPP dips using single wavelength. The actual azimuthal angle for $\bar{g}_y$ is $90^\circ - \varphi = 60^\circ$ (a similar condition as for $\bar{g}_x$ at $\varphi=60^\circ$ to excite double SPPs).

Figure 8.17. Comparison of reflectivity spectra of C_{10} (solid lines) and C_{12} (dashed lines) at $\varphi=30^\circ$ for (a) $\bar{g}_y$ of 2D PCL with $\alpha_{\min}(C_{10})=+61^\circ$ and $\alpha_{\min}(C_{12})=+60.5^\circ$. The dip combination is at 646nm, while (b) $\bar{g}_x$ of 2D PCL with $\alpha_{\min}(C_{10})=-29^\circ$ and $\alpha_{\min}(C_{12})=-29.4^\circ$. The combination of double dips can be observed (b) at 630-635nm.

The difference in double SPP excitation using $\bar{g}_y$ is that as φ increases, the effective (actual) azimuthal angle will be smaller hence the centre of double dips will move to higher angle and the wavelength required to merge the double dips increases.

b) The measurement for $\varphi=50^\circ$ is shown in Fig. 8.18.

Figure 8.18. Comparison of reflectivity spectra of C_{10} (solid lines) and C_{12} (dashed lines) on 2D PCL at $\varphi=50^\circ$ for (a) $\bar{g}_{dia}$ at $\lambda=680\text{--}760\text{nm}$ with $\alpha_{\min}(C_{10})=-4^\circ$ and $\alpha_{\min}(C_{12})=-4.5^\circ$, (b) $\bar{g}_x$ at $\lambda=715\text{--}735\text{nm}$ with $\alpha_{\min}(C_{10})=-49^\circ$ and $\alpha_{\min}(C_{12})=-49.7^\circ$. The dip combination is at 732nm . The difference between optimized polarization for both axes is almost equal to 45° .

In 2D PCL for $\varphi>45^\circ$ the SPP dips will be dominated by $\bar{g}_x$ and. As discussed previously at $\varphi=50^\circ$, $\bar{g}_x$ is able to excite double SPP dips using single wavelength. Different from $\bar{g}_y$, as the φ increases, the double dips from $\bar{g}_x$ will move to lower angle and the wavelength required to merge the double dips decreases.

The angular shift due to C_{10} -and C_{12} -SAM on 2D PCL is summarized in Table 8.4. For the double dips both for $\bar{g}_x$ and $\bar{g}_y$, the condition just before the merging becomes the interest in this experiment since the separation of double dips are still clear with the highest density of SPP modes; hence most desirable condition for the sensitivity measurement.

Table 8.4. The angular shifting for all crystal momentum for 2D PCL

$\varphi=30^\circ (g_x)$		$\varphi=30^\circ (g_y)$			$\varphi=50^\circ (g_{dia})$		$\varphi=50^\circ (g_x)$		
$\alpha_{C-10}=-29^\circ$		$\alpha_{C-10}=+61^\circ$			$\alpha_{C-10}=-4^\circ$		$\alpha_{C-10}=-49^\circ$		
$\alpha_{C-12}=-29.4^\circ$		$\alpha_{C-12}=+60.5^\circ$			$\alpha_{C-12}=-4.5^\circ$		$\alpha_{C-12}=-49.7^\circ$		
λ (nm)	$\Delta\theta (g_x)$	λ (nm)	$\Delta\theta(1)$	$\Delta\theta(2)$	λ (nm)	$\Delta\theta (g_x)$	λ (nm)	$\Delta\theta(1)$	$\Delta\theta(2)$
710	0.23°	635	1.02°	1.16°	700	0.53°	725	1.32°	1.52°
770	0.52°	640	1.29°	1.42°	720	0.79°	728	1.55°	1.74°
830	0.83°	644	1.84°	1.95°	740	1.06°	730	1.79°	1.92°
890	1.03°	645	2.01°	2.13°	760	1.47°	732	2.03°	2.19°

At optimized polarization, the reflectivity dips of respective crystal momentum are getting sharper (smaller FWHM). With this condition an improved angular shift, $\Delta\theta=2.19^\circ$ in 2D PCL can be obtained at $\varphi=50^\circ$, $\lambda=732\text{nm}$ on double dips of $\bar{g}_x$ crystal momentum. Besides employing $\bar{g}_x$, the double dips from $\bar{g}_y$ provide a reasonable $\Delta\theta=2.13^\circ$ at low azimuthal angle $\varphi=30^\circ$, $\lambda=645\text{nm}$. In this case, for C_{10} and C_{12} measurement, PCL demonstrates superior performance (comparable/higher sensitivity at lower azimuthal angle) compared to 1D PCL reported previously ($\Delta\theta=2.14^\circ$, $\varphi=60^\circ$) [318].

The sensitivity measurement ($\Delta\theta$) will be increased with the incident wavelength until $\bar{k}_{SPP}$ reach the maximum wavelength for $\varphi=50^\circ$. The detectability of 2D PCL is greater at large azimuthal rotation for $\bar{g}_x$ (or low angle for $\bar{g}_y$) since the condition for double plasmonic generation at the k_{spp} semi-circle induces changes in the momentum that is greater than SPP generation at zero azimuthal angle. Similarly with $\bar{g}_{dia}$ for $\varphi \neq 0^\circ$. The 1st dip (from $\bar{g}_{dia}$) is oriented at large azimuthal angle ($>45^\circ$) thus the plasmonic modes density will be larger than the one in non-rotated case. In this experiment the single dip from second order diagonal crystal momentum has angular shifting of 1.47° at $\lambda=760\text{nm}$, $\varphi=50^\circ$.

The value of Δn is 0.0033RIU for C_{10} and 0.0036RIU for C_{12} that is obtained from the changes in effective permittivity function due to the presence of C_{10} and C_{12} SAM using spectroscopic ellipsometer, with thicknesses of 1.335nm and 1.503nm respectively and dielectric constant $\varepsilon_{C10}=1.825$ and $\varepsilon_{C12}=2.205$.

8.2.8. Summary

In summary, it has been demonstrated that the detectability in 2D sinusoidal square lattice PCL-SPR can be obtained when double dips (at low azimuthal angle for $\bar{g}_y$ or large angle for $\bar{g}_x$) as well as additional SPR minima from 2nd order of $\bar{g}_{dia}$ are generated in full range of azimuthal angle. It is also revealed that 2D plasmonic crystal shows better sensing performance than prism coupled and high azimuthal angle of 1D PCL-SPR. The distinction between non-coated and C_{10} functionalized crystal is simply visible in the surrounding of double plasmonic condition as well as the diagonal crystal momentum. Sensitivity from the diagonal vector is employed to complement the sensitivity of double dip which is limited by

azimuthal angle and wavelength. The SPR angular shifting of functionalized crystal equals to 2.86° with sensitivity of $929^\circ/\text{RIU}$. Further improvement can be achieved under optimized polarization. The SPR angular shifting in this condition may reach 3.91° , ten times larger than prism coupler SPR sensor. The calculated detectability of 2D PCL may reach $1070^\circ/\text{RIU}$, almost ten times larger than $\varphi=0^\circ$ 1D grating.

It has also been evidenced that 2D plasmonic crystal can detect the difference of 0.0003RIU between C_{10} and C_{12} which only $1.68\text{\AA}$ in thickness. The angular shift of 2.19° is observed in double SPP of $\bar{g}_x$ crystal momentum in 2D PCL-SPR at relatively high azimuthal angle ($\varphi=50^\circ$) under optimized polarization angle. The reasonably high angular shift about 2.13° is also observed in double SPPs of $\bar{g}_y$ at lower azimuthal angle ($\varphi=30^\circ$). The single dip from second order diagonal crystal momentum can be a solution when the maximum azimuthal angle and wavelength is reached. Although not double SPPs, the first dip is located at high azimuthal rotation ($>45^\circ$) hence plasmonic modes density is higher than zero azimuthal angle.

9 Plasmonic Crystal Ellipsometry

9.1. Introduction

2D PCL has been demonstrated to exhibit higher sensitivity than prism coupler and 1D PCL system; nevertheless there is always a challenge to improve its resolution (detection limit). A brilliant idea to combine a prism coupled SPR and ellipsometer is suggested for the first time by Abelès [213] in 1976. Hooper and Sambles demonstrated experimentally and theoretically the improved sensing capability using differential SPR ellipsometry to record the alteration in permittivity function, that can be employed for bio-chemical sensing purposes [102, 115]. This resolution in the order of 2×10^{-7} RIU, can be achieved using both TM and TE-waves [115]. The TE-wave in fact acts as reference beam and has no involvement in SPP generation hence will not undergo any phase change, whereas TM-wave (*p*-polarized light) does. This measurement was done using prism coupled SPR.

9.2. Theory

The idea of plasmonic crystal ellipsometry (PCE) is to measure not only the reflectivity or normalized reflectivity, but also the phase changes which cannot be done by conventional SPR system. Several experimental configurations have been proposed to measure the SPR phase variation, for example phase shifting interferometry using Mach-Zehnder configuration [113] however this set up is complicated, not stable and easily disturbed by environmental noise, like temperature and mechanical vibration, which inevitably degrades sensitivity. A derived acquisition method in Mach-Zehnder setup to enhance the SPR phase sensitivity was reported by Wu et al., 2003 [216]. The setup employs two beams in parallel, the probe (*p*-polarized) and the reference (*s*-polarized) beams in identical optical paths [113]. However this setup is much more complicated due to the possibility of interference of two beams and some additional equipment are needed such as lock-in amplifier, noise reducer, etc. Changes in sample geometry may also need optical re-alignment. In PCE, these complexities can be avoided simply by utilizing ellipsometry set-up.

Ellipsometry is very powerful method to characterize the optical property of various thin films by measuring the changes in polarization ratio of reflected or transmitted light. The alteration will be measured by the intensity fraction, Ψ as well as phase information, Δ . The changes will be mainly affected by optical characteristics and depth of each layer.

To obtain superior sensitivity both ellipsometry and SPR techniques are combined. Using ellipsometer to measure SPR, the resolution can be significantly enhanced and more information can be obtained for any measured analytes. In plasmonic ellipsometry, the Ψ and Δ can be measured. Furthermore the complex effective refractive index of the plasmonic crystal can also be calculated for different incident angle and wavelength.

The prism coupled SPR method is not favourable in this case. PCE is a novel technique which is very useful especially for sensitivity measurement. Basically the ellipsometry measurement is done on plasmonic crystal instead on flat surface and the ratio between Fresnel reflection coefficients is measured. Since the azimuthal angle is involved, the s -polarized component will partially participate in the SPP, as well as the p -polarized component. This ratio has both real and imaginary parts which includes phase information that enhances the sensitivity. The polarization angle can be optimized in similar way as discussed earlier in SPR technique. Ellipsometry is interested in the changes of p -polarization relative to the s -components hence a reference is needed. The change in polarization state from the ellipsometric measurement, commonly written as [114]:

$$\rho = \frac{r_p}{r_s} = \tan \Psi \exp(i\Delta) \quad (9.1)$$

$$r_p = \left(\frac{E_{0r}}{E_{0i}} \right)_p = \frac{n_t \cos \theta_i - n_i \cos \theta_t}{n_i \cos \theta_t + n_t \cos \theta_i} = \rho_p \exp(j\phi_p) \quad (9.2)$$

$$r_s = \left(\frac{E_{0r}}{E_{0i}} \right)_s = \frac{n_i \cos \theta_i - n_t \cos \theta_t}{n_i \cos \theta_i + n_t \cos \theta_t} = \rho_s \exp(j\phi_s) \quad (9.3)$$

r_p and r_s are Fresnell's reflectivity coefficients under p - and s -polarization states respectively. ρ is its reflectivity amplitude, where i is incident, t is transmitted and r is reflected beams. Ψ measures amplitude ratio between r_p and r_s . $\Psi = \arctan(\rho_p/\rho_s)$ and $\Delta = \phi_p - \phi_s$. The phase difference, Δ is the distinguishing factor between ellipsometry and SPR and provides very sensitive measurement. These equations are applicable to predict the optical responses of 1D and 2D PCLs however the n values will experience significant changes around resonance condition.

9.3. Plasmonic Crystal Ellipsometry

SPR of plasmonic crystal mainly measures the value of r_p . For non zero azimuthal angle, the r_p is reduced by the factor of $\sin(\varphi - \alpha)$ which converts into r_s due to symmetry breaking, while α is the angle between TM and crystal momentum on sample plane. Plasmonic Crystal Ellipsometry (PCE) is a differential measurement of SPR which combines the optical properties of PCL from SPR, signal amplification and phase difference measurement due to reference beam from ellipsometry. Generally Ψ is more sensitive to the surface roughness hence the presence of PCL and analyte will change this value dramatically. While Δ is generally more sensitive to layer thickness. These two properties will enhance the sensitivity measurement on PCL. The Ψ and Δ are both in degree. In SPR no phase difference can be detected since the reference beam is not in used. PCE setup is demonstrated in Fig. 9.1.

Figure 9.1. Typical plasmonic crystal ellipsometer (PCE) setup. At resonance condition, the corrugated profile will couple the p -polarized light while the s -polarized light will be unaffected; hence there will be a significant drop in Ψ and Δ value at resonance condition.

9.3.1. 1D Plasmonic Crystal Ellipsometry

The measurement of plasmonic crystal ellipsometry (PCE) has been done on 1D PCL with periodicity of 500nm and evaporated with 50nm Au. Initially the sample was measured in reflection mode to obtain the SPR curve both in angular and wavelength interrogation (Fig. 9.2-9.3), to be compared to the ellipsometry measurement. For angular interrogation, when the SPP occurs at particular angle, i.e. 21.3°, 28.3°, 35.3° and etc, there is a dramatic change in refractive index due the effective value introduced by PCL. This refractive index change will affect the phase of both p - and s - polarized light. The Δ curve will suddenly jump to maximum value when the light enters into different effective refractive index value. This can be seen from the SPR and Δ curve comparison where the curve suddenly moves in opposite direction just when the SPR curve starts to reduce in intensity and it will return to its previous trend as reflectivity curve recovers from the dip. The units for both are in degrees.

Figure 9.2. Angular interrogation of PCE measurement on 1D PCL at $\varphi=0^\circ$ for different wavelengths. The Ψ value (left) and Δ value (right) are compared to the SPR measurement and clear correlation can be observed. Phase information can be obtained from Δ value. At resonance condition, TM-wave will be coupled whereas TE-wave (s -pol) is unaffected hence there will be a significant drop in Ψ and Δ .

Figure 9.3. Wavelength interrogation of PCE measurement on 1D PCL at $\varphi=0^\circ$ for different resonance angles correspond to angular interrogation. The Ψ value (left) and Δ value (right) are compared to the SPR reflectivity curve and clear correlation can be observed.

The value for Ψ is from 0° up to 90° , and the common analyser in ellipsometer system can only measure Δ value from 0° to 180° ; in other word the system cannot differentiate left- or right- circularly polarized light. However using AutoretarderTM attached to the system, full 360° of Δ value can be measured [114]. In 1D PCL, for $\varphi=0^\circ$, only p -polarized light contributes in SPP excitation and experiences a phase change while s -polarized does not and acts as reference. To increase the SPP mode, the azimuthal angle is introduced to PCL, however it will reduce the coupling efficiency due to conversion from p - to s - and s - to p -. The s -polarized beam will no longer act as reference but participate in SPP excitation on PCL. This will depart from the initial purpose of PCE hence optimization in polarization angle needs to be made, to put the magnetic field back in line to crystal momentum.

The optimum polarization angle for $\bar{g}_x$ is defined similarly to the SPR mode, given by:

$$\alpha_{\min-x} = \arctan(\cos \theta \tan \varphi) \quad (9.4)$$

The $\alpha_{\min}$ refers to condition where TM field is coincided with crystal momentum, thus reflectivity has its minimum value. The total intensity could be calculated by:

$$I_{\text{ellips}} = \frac{1}{4} \left(\frac{|r_p|^2 + |r_s|^2}{2} + |r_p||r_s| \cos(2\pi ft + \Delta) \right) \quad (9.5)$$

At optimized α , just TM-wave (p -pol) is permitted to generate surface plasmon therefore $|r_p|$ and phase difference of two polarization states, Δ are able to be calculated.

9.3.1.1. Azimuthal Effect in 1D PCL Ellipsometry

The effect of PCE in both angular ($\lambda=650\text{nm}$) and wavelength ($\theta=30^\circ$) modulations for various azimuthal angles is studied and presented in Fig 9.4-9.5 respectively.

Figure 9.4. Angular interrogation of PCE measurement on bare 1D PCL at $\lambda=650\text{nm}$ for different φ values.

Similar to SPR measurement, as azimuthal angle is increased, the PCE dips of angular interrogation will move to higher value (or blue shifting for wavelength interrogation) moreover the minima as well as the width of the dips will be increased gradually and finally forms a broad and deep minima at $\varphi=50^\circ$ due to double SPP phenomenon. However for wavelength interrogation, the minima will be decreased gradually and finally form a peak at $\varphi=50^\circ$. This phenomenon is caused by changes in the fraction of p - and s - polarization's

reflectivity coefficients. As discussed in chapter 8, the plasmonic coupling efficiency will be reduced when the azimuthal angle is increased due to only some portion of p -polarized light coupled into SPP, consequently the PCE dip will have shallower depth (higher Ψ value).

Figure 9.5. Wavelength interrogation of PCE measurement on bare 1D PCL at $\theta=30^\circ$ for different ϕ values.

9.3.1.2. Sensitivity in 1D PCL Ellipsometry

C_{10} -SAM [dodecanethiol ($CH_3(CH_2)_9SH$)] was self assembled on Au metallic film coated 2D PCL at $25^\circ C$ in glove box (N_2 environment) for >20 hours to obtain good quality of SAMs with high coverage (packed). The thickness of SAMs is known to be 1.335nm and Δn introduced to the PCL is 0.0033 RIU . The sample was measured in ellipsometry mode from 15° – 80° incident angle at different wavelength and shown in Fig. 9.6.

Figure 9.6. Angular interrogation of PCE measurement on 1D PCL at $\phi=0^\circ$ before (solid lines) and after C_{10} functionalization (dashed lines) using p -polarized light for different wavelengths. The Ψ value is shown on the left graph and Δ value is on the right.

The sensitivity from Ψ and Δ are compared and summarized in Table 9.1. The sensitivity is increasing with the wavelength and they are considered as angular sensitivity ($^{\circ}/\text{RIU}$). The angular shift in Δ function is clearer than Ψ . As predicted, the phase measurement will show greater sensitivity compared to conventional SPR. The theoretical prediction has shown that the phase measurement gives the sensitivity of about 2 to 3 orders of magnitude higher than the conventional SPR [26, 215-217]. Unlike conventional SPR, in Ψ measurement, the ratio between two polarization states is recorded; hence the effect of intensity fluctuations can be eliminated. Beside the angular and wavelength shift, the shifts in Ψ and Δ provide additional information. Some chemicals are able to rotate the polarization of the light (i.e. sugar water, chiral molecules, etc.) which directly affect the Ψ and Δ . Hence these two values can be used as additional source of sensitivity measurement.

Table 9.1. Sensitivity of angular shifting in Ψ and Δ function at $\varphi=0^{\circ}$ for different wavelengths.

Wave-length	$\Delta\theta$ at $\varphi=0^{\circ}$ (Ψ)	Sensitivity ($^{\circ}/\text{RIU}$)	$\Delta\theta$ at $\varphi=0^{\circ}$ (Δ)	Sensitivity ($^{\circ}/\text{RIU}$)	$\Delta(\Psi)$ at $\varphi=0^{\circ}$	Sensitivity ($^{\circ}/\text{RIU}$)	$\Delta(\Delta)$ at $\varphi=0^{\circ}$	Sensitivity ($^{\circ}/\text{RIU}$)
660nm	0.45 $^{\circ}$	136.36	0.6 $^{\circ}$	181.82	2.14 $^{\circ}$	648.49	8.36 $^{\circ}$	2533.33
700nm	0.35 $^{\circ}$	106.06	0.3 $^{\circ}$	90.91	2.76 $^{\circ}$	836.36	8.30 $^{\circ}$	2515.15
740nm	0.30 $^{\circ}$	90.91	0.4 $^{\circ}$	121.21	1.02 $^{\circ}$	309.09	14.28 $^{\circ}$	4318.18
780nm	0.25 $^{\circ}$	75.76	0.3 $^{\circ}$	90.91	1.71 $^{\circ}$	518.18	9.06 $^{\circ}$	2745.46
820nm	0.20 $^{\circ}$	60.61	0.4 $^{\circ}$	121.21	0.30 $^{\circ}$	90.91	16.80 $^{\circ}$	5090.91

The sensitivity measurement of 2 carbon atoms C_{10} and C_{12} in angular modulation 1D PCL for $\varphi=0^{\circ}$ are shown in Fig. 9.7 and summarized in Table 9.2.

Figure 9.7. Angular interrogation of PCE measurement on 1D PCL at $\varphi=0^{\circ}$ for C_{10} (solid lines) and C_{12} functionalization (dashed lines) for different wavelengths.

Table 9.2. Sensitivity of angular shifting in Ψ and Δ function to detect 2 carbon atoms at $\varphi=0^\circ$ for different incident angles.

Wave-length	$\Delta\theta$ at $\varphi=0^\circ$ (Ψ)	Sensitivity ($^\circ/\text{RIU}$)	$\Delta\theta$ at $\varphi=0^\circ$ (Δ)	Sensitivity ($^\circ/\text{RIU}$)	$\Delta(\Psi)$ at $\varphi=0^\circ$	Sensitivity ($^\circ/\text{RIU}$)	$\Delta(\Delta)$ at $\varphi=0^\circ$	Sensitivity ($^\circ/\text{RIU}$)
660nm	0.10 $^\circ$	30.30	0.4 $^\circ$	121.21	0.18 $^\circ$	54.55	16.01 $^\circ$	4851.52
700nm	0.11 $^\circ$	33.33	0.4 $^\circ$	121.21	1.49 $^\circ$	451.52	22.85 $^\circ$	6924.24
740nm	0.12 $^\circ$	36.36	0.6 $^\circ$	181.81	0.35 $^\circ$	106.06	25.95 $^\circ$	7863.64
780nm	0.13 $^\circ$	39.39	0.6 $^\circ$	181.81	0.70 $^\circ$	212.12	24.87 $^\circ$	7536.36
820nm	0.14 $^\circ$	42.42	0.4 $^\circ$	121.21	2.28 $^\circ$	690.91	33.66 $^\circ$	10200.00

9.3.1.3. Polarization Effect in Azimuthally Rotated 1D PCL Ellipsometry

As azimuthal angle is introduced in 1D PCL ellipsometry, the coupling efficiency will be reduced due to polarization conversions and s -polarized light will no longer act as reference but participate in SPP excitation on PCL hence optimized polarization angle needs to be made, to put the magnetic field back in line to crystal momentum to PCL. Normal spectroscopic ellipsometer measurement will be based on random polarization which value is near to Ψ (Ψ) [114]. However the sensitivity measurement based on this method is not reliable due to fluctuation in polarization. The sensitivity measurement to detect C_{10} at $\varphi=30^\circ$ 1D PCL ellipsometry using random and optimized polarization is presented in Fig. 9.8 and 9.9 while the data is summarized in Table 9.3 and 9.4.

Figure 9.8. Angular interrogation of PCE measurement on 1D PCL at $\varphi=30^\circ$ for bare (solid line) and C_{10} functionalization (dashed lines) using random polarization for different wavelengths.

Table 9.3. Sensitivity of angular shifting in Ψ and Δ function to detect C_{10} at $\varphi=30^\circ$ using random polarization for different incident angle.

Wave-length	$\Delta\theta$ at $\varphi=30^\circ$ (Ψ)	Sensitivity ($^\circ$ /RIU)	$\Delta\theta$ at $\varphi=30^\circ$ (Δ)	Sensitivity ($^\circ$ /RIU)	$\Delta(\Psi)$ at $\varphi=30^\circ$	Sensitivity ($^\circ$ /RIU)	$\Delta(\Delta)$ at $\varphi=30^\circ$	Sensitivity ($^\circ$ /RIU)
700nm	0.60°	181.82	1.0°	303.03	1.3°	403.03	0.24°	72.73
720nm	0.80°	242.42	1.0°	303.03	0.7°	221.21	3.30°	1000.00
740nm	1.00°	303.03	1.4°	424.24	1.5°	463.64	0.46°	139.40
760nm	1.60°	484.85	1.4°	424.24	3.1°	939.40	1.59°	481.82
780nm	2.20°	666.67	2.2°	666.67	0.1°	30.30	2.72°	824.24
800nm	2.40°	727.27	3.2°	969.70	4.1°	1242.42	3.68°	1115.15

Figure 9.9. Angular interrogation of PCE measurement on 1D PCL at $\varphi=30^\circ$ for bare (solid line) and C_{10} functionalization (dashed lines) under optimized polarization ($\alpha=30^\circ$) for different wavelengths.**Table 9.4.** Sensitivity of angular shifting in Ψ and Δ function to detect C_{10} at $\varphi=30^\circ$ using optimized polarization ($\alpha=30^\circ$) for different incident angles.

Wave-length	$\Delta\theta$ at $\varphi=30^\circ$ (Ψ)	Sensitivity ($^\circ$ /RIU)	$\Delta\theta$ at $\varphi=30^\circ$ (Δ)	Sensitivity ($^\circ$ /RIU)	$\Delta(\Psi)$ at $\varphi=30^\circ$	Sensitivity ($^\circ$ /RIU)	$\Delta(\Delta)$ at $\varphi=30^\circ$	Sensitivity ($^\circ$ /RIU)
700nm	0.80°	242.42	1.2°	363.64	1.8°	545.45	8.11°	2457.58
720nm	0.80°	242.42	1.4°	424.24	1.2°	363.64	6.81°	2063.64
740nm	1.00°	303.03	1.6°	484.85	1.9°	575.76	5.36°	1624.24
760nm	1.40°	424.24	2.0°	606.06	1.5°	454.55	8.53°	2584.85
780nm	1.80°	545.45	2.6°	787.88	1.2°	363.64	9.94°	3012.12
800nm	2.00°	606.06	3.4°	1030.30	0.9°	272.73	11.96°	3624.24

The sensitivity measurement to detect C_{10} at $\varphi=30^\circ$ 1D PCL ellipsometry using random and optimized polarization is compared in following Fig. 9.10.

Figure 9.10. Sensitivity measurement to detect C_{10} at $\varphi=30^\circ$ 1D PCL ellipsometry in angular modulation using random (black) and optimized polarization (red). The shifting in resonant angle, PSI and DELTA are shown by left axis and their respective sensitivity by right axis ($^\circ/\text{RIU}$)

It can be seen that the sensitivity of 1D PCL in wavelength interrogation mode may reach $1030^\circ/\text{RIU}$ and $3624^\circ/\text{RIU}$ for Ψ and Δ respectively at $\varphi=30^\circ$. These values are much higher than the one performed by 2D PCL in previous chapter. However as the azimuthal angle is increased, the setup has a possibility to cover higher sensitivity.

9.3.2. 2D Plasmonic Crystal Ellipsometry

The measurement of plasmonic crystal ellipsometry (PCE) has been done on ellipse array of 2D PCL with periodicity of 500nm and evaporated with 50nm Au. The sample was measured in ellipsometry mode. The result shown in Fig. 9.11 and 9.12 for $\varphi=0^\circ$ and 20° respectively, besides having normal dips as in 1D PCL, higher dimensionalities structure offers additional peaks that move oppositely with the other dips as incidence angle increases.

Figure 9.11. Wavelength interrogation of PCE measurement on ellipses array 2D PCL at $\varphi=0^\circ$ for different resonance angle. The Ψ value is shown on the left and Δ value is on the right. There is absorption spectra at 320nm, mainly due to Au property that becomes dielectric at lower wavelength ($<500\text{nm}$). This can act as a reference point to measure the shifting in other range of spectra due to any changes in surface of the PCL.

Figure 9.12. Wavelength interrogation of PCE measurement on ellipses array 2D PCL at $\phi=20^\circ$ for different resonance angle. The Ψ value is shown on the left and Δ value is on the right. By changing the azimuthal angle $\phi=20^\circ$, beside the absorption spectra at 320nm, there is another fixed point (peaks) at 570nm (both Ψ and Δ) which can act as a reference point.

9.3.2.1. Sensitivity in 2D PCL Ellipsometry

C_{10} -SAM was deposited on the square lattice 2D PCL surface. The thickness of SAMs is known to be 1.335nm and Δn introduced to the PCL is 0.0033 RIU. The sample was measured in ellipsometry mode from 15° - 80° incident angle at different wavelengths in angular interrogation to measure the sensitivity. The sensitivity measurement for $\phi=50^\circ$ is presented in Fig. 9.13 and summarized in Table 9.5.

Figure 9.13. Angular interrogation of PCE measurement on 2D PCL at $\phi=50^\circ$ for bare (solid line) and C_{10} functionalization (dashed lines) for different wavelengths.

Table 9.5. Sensitivity comparison of wavelength shift in Ψ and Δ function at $\varphi=50^\circ$ in 2D PCL. The changes in Ψ and Δ are shown in last four columns.

Wave-length	$\Delta\theta$ at $\varphi=30^\circ$ (Ψ)	Sensitivity ($^\circ$ /RIU)	$\Delta\theta$ at $\varphi=30^\circ$ (Δ)	Sensitivity ($^\circ$ /RIU)	$\Delta(\Psi)$ at $\varphi=30^\circ$	Sensitivity ($^\circ$ /RIU)	$\Delta(\Delta)$ at $\varphi=30^\circ$	Sensitivity ($^\circ$ /RIU)
580nm	6.40°	1939.39	8.14°	2466.67	5.07°	1536.36	12.70°	3848.48
600nm	6.69°	2027.27	7.65°	2318.18	3.50°	1060.61	16.21°	4912.12
620nm	7.66°	2321.21	8.10°	2454.55	2.70°	818.18	20.06°	6078.79
640nm	10.52°	3187.88	10.46°	3169.70	3.04°	921.21	27.05°	8196.97

The PEC of 2D PCL at high azimuthal angle shows better sensitivity compared to 1D PCL or to zero azimuthal angle. The best sensitivity performed by PEC is about 8196.97°/RIU when the angular shift measured in Δ at $\varphi=50^\circ$.

9.4. Chapter Summary

The idea of plasmonic crystal ellipsometry is to measure not only the reflectivity or normalized reflectivity, but also the phase changes which cannot be accomplished using conventional SPR system. Plasmonic crystal ellipsometry (PCE) measures 1D or 2D PCL under ellipsometry mode. Generally the Ψ measurement is similar to reflectivity measurement both in wavelength and angular interrogation. However the presence of reference beam will induce signal stability (normalization) and amplification over the whole measurement. Generally Ψ is more sensitive to the surface roughness and grading hence the presence of plasmonic crystal and analyte will change this value dramatically. While Δ is generally more sensitive to layer thickness. These two properties will enhance the sensitivity measurement on PCL. The PCE is proven to serve better sensitivity, especially for phase measurement. The best sensitivity performed by 2D PEC is about 3187.88°/RIU at $\varphi=50^\circ$. The phase measurement shows extreme sensitivity up to 8196.97°/RIU.

10 Summary

In order to increase the plasmonic field enhancement and sensitivity, several steps have been performed by engineering the effective refractive index of the plasmonic crystal:

- Physical approach: modifying the geometries/structural of the plasmonic crystal (PCL)
- Chemical approach: modifying the dielectric layer on top of the crystal

By engineering refractive index and plasmonic phenomenon, electromagnetic wave can be coupled, guided and controlled.

The thesis is focused on the behaviour of plasmonic nanostructures (1D and 2D PCLs). The PCLs were then optically characterized in reflection, transmission and ellipsometry mode to study the attributes of SPP employing the azimuthal rotation, where double SPPs and other crystal momentum can be excited under optimized polarization. These approaches were done to obtain a high sensitivity of SPP resonance conditions and the EM field enhancement. 2D PCL in reflection mode (SPR) provides the highest sensitivity. The sensitivity may reach at least $1000^\circ/\text{RIU}$ and resolution down to 1×10^{-7} RIU. The sensitivity is higher than 1D PCL and around an order magnitude larger than prism-coupled system. The key findings and major contributions of this work are summarized as follows:

1. Optimization and Fabrication of Plasmonic crystal

Engineering refractive index of the plasmonic crystal can be done using physical approach by modifying the geometries/structure of the plasmonic crystal. This part includes the effect of higher dimensionalities, related to 1D to 2D PCL transitional structure and 2D PCL. Both structures have been successfully produced by two beam interference lithography (IL).

The geometrical parameters of PCL need to be controlled to obtain the optimized surface profile of PCL. It is suggested that the amplitude of the optimized PCL is in the order of 9-12% from the periodicity in order to maximize the propagating plasmon on PCL. Larger than this value, the plasmon will be trapped inside the valley and becomes a localized surface plasmon (SP). Silver is a good candidate of metallic film on PCL due to its low extinction coefficient, hence less losses. Thin layer of gold will help to stabilize the silver from oxidation and it is inert to most of bio and chemical analytes. From simulation, it is proposed that the thickness of the silver to be 37-42nm and covered with 7-8nm of gold.

The effect of roughness and distortion in 1D PCL were studied. Higher harmonic components contribute to these distortions and increase the FWHM of SPP dips. This is not favorable in sensitivity measurement due to lowering the FOM. High quality, sinusoidal profile is desirable to allow only main harmonic component in SPP excitation. Heat treatment process may improve the roughness and reduce the contribution of higher harmonic component

To create 2D structure using conventional Lloyd's mirror, two times exposures are needed. This will increase the possibility of distorted structure due to vibrations and particle scattering. The modification of Lloyd's mirror can be used to produce different lattice angle in single exposure which is simpler and reduces the possibility of distorted profiles.

2. SPR Characterization of 1D and 2D PCL

One way to accomplish refractive index engineering physically is through improving the dimensional orders of PCL. 2D PCL is chosen over 1D grating mainly because it provides greater concentration of EM field as a result of highly focused structures – thus the coupling of photons could be optimized at any azimuthal angle leading to field enhancement.

The SPR characterization was done and the effect of azimuthal rotation was studied on 1D, 1D to 2D and 2D PCL for each crystal momentum. The analysis employed the conical configuration where the incident light wavevector must not necessarily be parallel to crystal momentum i.e. when the azimuthal angle is not zero, such that the symmetry is broken with an additional diagonal and y-axis crystal momentum (for square lattice 2D PCL). Wavevectors were presented in a schematic including the direction of crystal momentum, light and SPP wavevector and directions.

2D PCL has more grating vectors i.e. from x , y and diagonal axis that will provide better enhancement since more plasmon modes (at least three SPPs) can be generated simultaneously by single wavelength. Diagonal crystal momentum will be a benefit of 2D PCL since it can explore both first and second Brillouin zone with both larger and smaller momentum respectively. This momentum will act as a complement to explore the condition that is impossible to be done by the main axis due to limitations in wavelength and incident

angle. In low azimuthal angle, the double SPP dips can be excited by employing the y-axis crystal momentum. These additional crystal momentum vectors will be very useful in tuning the SPP properties as well as enrich the 2D PCL especially for sensing purposes.

The propagation of surface plasmon is greatly influenced by azimuthal angle, φ . This angle may also change the plasmonic dispersion relation uniquely from conventional prism coupled SPR. This angle controls propagation of surface plasmon which may include entire 2π range. For any azimuthal angle, 2D SPP shows greater concentration of EM field as a result of highly limited surface compared to 1D PCL structure; hence thus the coupling of photons will be optimized, leading to improvement noted by deeper dips (lower reflectivity).

3. Demonstration of engineering dielectric medium

This can be done by chemical approach: modifying the dielectric layer on top the crystal with active material. An active material, hybrid organic-inorganic material was introduced on PCL surface and heat treated. It induces the presence of porosity that alters the SPP propagation on PCL. The porous C8 film acts as nano-fluidic network which able to trap the analyte due its surface tension hence no functionalization (chemisorptions) of analyte is needed during measurement. The sample was characterized and it was found that this active material is able to move excitation window from first order Brillouin zone to the first negative order which induces higher sensitivity, proven by the detectability of very low HCl concentration. The sensitivity of this negative order is equal to $666^\circ/\text{RIU}$.

4. Extra ordinary transmission

1D and 2D PCLs allowing extraordinary transmission were fabricated on silicone nitride membranes followed by gold electroplating process. Numerical simulations and optical characterization techniques allow to measure transmittance spectra and validate the fabrication results. Experimental data shows interesting results on TE polarization transmittance spectra. In fact, a resonance peak has been observed which is related to slit-cavity resonance. This gives an experimental confirmation of numerical predictions reported in literature [293]. Modeling by COMSOL Multiphysics was done to verify the experimental results, especially for 1D nano slits. Sensitivity simulation for 1D nano slit has been done and may reach $480\text{nm}/\text{RIU}$. A sensitivity enhancement in transmission is shown on 2D

diamonds array experimentally, reaching up to 657.15nm/RIU which is higher than simulated 1D nanoslits. This value can be improved by tuning the geometry of PCL.

Novel application for the 1D nano slits and 2D diamonds array based on the optical properties in this thesis is optical switching. By controlling the azimuthal or polarization angle, the signal can be transmitted, blocked or finely adjusted for certain purposes (amplified or reduced).

5. Polarization effects in 2D PCL

The influences of polarization state on the surface plasmon resonance for non-zero azimuthal rotation in 2D PCL have been studied. By adjusting the polarization state (α) of incident photon, the plasmonic coupling intensity could be easily controlled and fully optimized as α_{min} is employed for respective grating's vector. Experimental results and simulations showed that only the incident electric field lying on the PCL symmetry plane is effective for SPR excitation, while the orthogonal one is irrelevant. The optimal polarization angle is able to be attained by rotating the α until the SPR dip reach the lowest possible value. α_{min} can also be obtained analytically using the assumptions mentioned above. Understanding α_{min} correlation for various pitch, azimuthal rotation and frequency will be very useful to define the most favorable plasmonic generation condition for respective grating's vector in 2D PCL as well as SPP devices (e.g. sensor).

6. Demonstration of sensitivity enhancement due to polarization optimization

The sensitivity enhancement is demonstrated on 2D square lattice PCL using a decanethiol (C_{10}) self-assembled monolayer (SAM). The presence of C_{10} SAMs functionalized on 2D PCL can be simply detected due to the presence of double dips and additional SPP from diagonal vector. The SPR angular shifting of C_{10} functionalized 2D plasmonic crystal equals to 2.86° with sensitivity of 929°/RIU. Further enhancement in sensitivity can be obtained as optimized polarization angle is utilized. The SPR angular shifting in this condition may reach 3.91° , ten times larger than prism coupler SPR sensor. The calculated detectability of 2D PCL may reach 1070°/RIU.

There are two conditions where the double dips no longer can be used. First, when the wavelength is longer than 730nm, although the sensitivity is much higher (3.98°), double SPPs are no longer be obviously separated; hence this is a poor condition for the sensitivity measurement. Second, when $\varphi > \varphi_{MAX}$. φ_{max} is the maximum azimuthal rotation to excite the double SPPs (in this case $\sim 60^\circ$). The solution to these issues is to make use of the first dip offered by 2D PCL, originated from diagonal crystal momentum. Although the sensitivity of the first dip at 730nm is lower ($860^\circ/\text{RIU}$) than the second and third dips, the angular shift is clearly observed with sharp dip (small FWHM), hence the FOM of first dip is reliable. This condition amplifies the signal over the noise therefore enhances the sensing capability. Moreover at 735nm where the double dips cannot be employed, the first dip demonstrates higher sensitivity up to $981^\circ/\text{RIU}$ and keeps increasing with wavelength and azimuthal angle. This is one of the advantages of 2D PCL – SPR sensor which does not exist in 1D GC-SPR.

To further examine the sensitivity, 2D PCL was used to measure the difference of two carbon atoms by comparing C_{10} and C_{12} self-assembled monolayer (SAM). Under optimized polarization angle, the two measurements can be distinguished up to 2.19° for around one quarter of nanometer height difference. This indicates that 2D PCL is more responsive to the thickness variation and index of refraction than 1D PCL.

8. Plasmonic crystal ellipsometry (PCE)

Another class of optical measurement namely plasmonic crystal ellipsometry (PCE) was introduced. PCE is a differential measurement of SPR which combines the optical properties of PCL from SPR, signal amplification and phase difference measurement due to reference beam from ellipsometry. In PCE, Ψ measures the amplitude ratio between r_p and r_s and $\Delta = \Delta_p - \Delta_s$. This phase difference, Δ becomes a distinguishing factor between ellipsometry and SPR. Generally Ψ is more sensitive to the surface profiles; while Δ is generally more sensitive to layer thickness. These two properties will enhance the sensitivity measurement on PCL. Sensitivity measurement was done on both 1D and 2D PCL using SAMs. This method is very promising. No analyte functionalization is needed for the measurement as long as the physical adsorption (physisorption) takes place. Due to limitation in the duration of project, this PCE was not fully explored, however it is recommended to investigate this technique in more detail.

In summary, this thesis describes the pioneering development of a new approach for SPP excitation using azimuthally rotated 2D PCL for all crystal momentum vectors available under optimized polarization angle and demonstrates the sensing capabilities experimentally. Below maximum azimuthal angle and merging condition, double dips serve as the most sensitive tool, however beyond those conditions; first dip from diagonal crystal momentum offers the solution. Although the sensitivity is lower than double dips, the angular shift is clearly observed with small FWHM. This is one of the advantages of 2D PCL – SPR sensor which does not exist in 1D GC-SPR. The engineering dielectric medium will provide additional features to explore both positive and negative Brillouin zone based on specific requirement. The EOT and PCE modes will serve as complements to the 2D SPR technique.

For conventional SPR in both 1D and 2D PCL, the analyte need to be functionalized or chemically adsorbed (chemisorptions) on the Au or Ag film. However in this thesis, two novel alternative methods are offered. Porous C8 film acts as nano-fluidic network which is able to trap the analyte due its surface tension hence no chemisorptions is needed. In other hand, PCE only requires the analyte to have good physical adsorption to the metal film during measurement. The combination of these approaches could replace the current prism and 1D PCL coupled SPR based sensor with better sensitivity. In addition, miniaturization of 2D PCL based sensor is proposed to offer high sensitivity with fast and accurate responses.

Some recommendations for future work include further study on the following areas:

1. Design and integration of a multichanneled fluidic cell system using principles uncovered in this thesis
2. Miniaturization of the 2D PCL sensor system to serve transmission, reflection and PCE modes as shown in Fig. 10.1.

Figure 10.1. Miniaturization of the 2D PCL sensor system

The algorithm of the working system is described by the following flowcharts:

Figure 10.2. The algorithm of the miniaturized 2D PCL sensor working system

Fabricating miniaturized 2D PCL based Sensor

The master mold of 2D PCL can be fabricated using interference lithography (IL) or e-beam lithography (EBL) at desired periodicity (recommended $\Lambda=400\text{-}500\text{nm}$) on negative photoresist coated on top of hard metal substrates followed by pattern transfer by reactive ion etching (RIE) with thickness of 50nm. The effective patterned areas should be at least $1\times 1\text{cm}^2$. It will form array of cylinder nanoholes as demonstrated in Fig. 10.3 (left).

The replication of PCL can be done on the cover of microfluidic chip which is made from PMMA or polycarbonate using hot embossing method at temperature slightly higher than glass transition temperature, T_g (PMMA $\approx 105^\circ\text{C}$ and PC $\approx 145^\circ\text{C}$). The mould needs to be coated with anti sticking agent (silane based) for easy release after embossing process. This embossing step is important to transform the cylinder nanoholes structure into 2D grating. Further heat treatment at T_g may need to be done to re-flow and smoothen the pattern.

Figure 10.3. (left) Secondary electron image (SEI) of 2D PCL master mold fabricated by IL or EBL and (right) AFM image of its replica on cover microfluidic chip by nanoimprinting/embossing.

The process is followed by metal deposition on patterned polymers (PMMA/PC) using thermal or e-beam evaporator to produce highly flat films with uniform thickness. Deposition of bi-metallic 37nm/8nm Ag/Au films are recommended to demonstrate the best plasmonic coupling efficiency.

Microfluidic Chip Fabrication

The microfluidic chip can be design using any CAD software and for small quantity, the chip can be fabricated directly on polymer sheets using laser micro-machining and milling. For

intricate shape and high aspect ratio, soft lithography may be needed. An example of microfluidic with 32 channels with dimension of $3\text{cm} \times 3.6\text{cm}$ is shown in Fig. 10.4 which is produced by laser machining. For nanofluidic chip, the structure can be made using EBL on metal film. While for large quantity production, the mould needs to be made and the chips can be easily replicated by injection molding, hot embossing or PDMS casting systems. The chip needs to be flat and thin to reduce scattering and absorption.

Figure 10.4. Schematic of 32 channels of microfluidic chip can be written by laser machining with dimension of $3\text{cm} \times 3.6\text{cm}$.

Plasma treatment may need to be done to control the hydrophobicity of polymer's surface as well as immobilization of bio/chemical receptors.

Bonding

The patterned cover is then bonded to the microfluidic chip using several methods such as thermal bonding, adhesive or laser welding. For strong thermal bonding, the material for cover and chip substrate need to be identical and clean. The laser welding offers very good quality of bonding for intricate and small structure. Adhesive or laser welding is preferred to prevent thermal degradation of microfluidic structure on polymer.

Figure 10.5. Thermal bonding cross section of microfluidic chip and its cover

Measurement System

Unlike 1D PCL, for 2D PCL sensor the stage can be designed with incident and azimuthal angle less than $\pi/5$ radian to exhibit high sensitivity due to double SPP generation using 632.8nm laser. Polarization at optimum angle is inserted in front of the laser head to maximize the coupling efficiency thus increase the sensitivity and FOM value. Focusing probes are needed to reduce the beam spot and fully cover the fluidic chip. For simultaneous multi-channel measurement, beam expander and 6×6 array photo detector need to be used. The four extra detectors may serve as reference signal.

Scientific contributions of this thesis include:

- Azimuthal and polarization effect on 2D PCL
- Generation of double SPP at low azimuthal angle in 2D PCL
- Multiple SPP excitations on 2D PCL by multiple crystal momentum
- Schematic of conservation momentum in 2D PCL
- Expanding Raether's Equation for transitional and 2D PCL
- High density of SPP mode due to combination of SPP with similar directions
- Single and double turning point effects in EOT of Au nanoslit array
- Engineering dielectric medium of PCL by introducing porous sol-gel
- Sensitivity enhancement due to negative Brillouin zone
- Plasmonic crystal ellipsometry (PCE)

Engineering contributions of this thesis include:

- Higher sensitivity refractive index sensor using 2D PCL due to: azimuthal effect, polarization effect, and diagonal crystal momentum
- Novel optical switching and optoelectronic devices based on EOT of nanoslit array
- Higher sensitivity refractive index sensor using negative Brillouin zone
- Free chemical adsorption SPR sensor by porous sol-gel coated PCL
- Higher sensitivity refractive index sensor of plasmonic crystal ellipsometry (PCE)
- Free chemical adsorption SPR sensor by PCE

Publications

Journal Papers:

1. F. Romanato, K. H. Lee, **H. K. Kang**, C. C. Wong, N. Zhang, Y. Zong and W. Knoll, "Azimuthal dispersion and energy mode condensation of grating-coupled surface plasmon polaritons", *Phys. Rev. B.*, 77, 245435 (2008).
2. F. Romanato, **H. K. Kang**, K. H. Lee, G. Ruffato, M. Prasciolu, C. C. Wong, "Interferential lithography of 1D thin metallic sinusoidal gratings", *Micro. Elec. Eng.* 86, 573 (2009).
3. F. Romanato, K. H. Lee, **H. K. Kang**, G. Ruffato, C. C. Wong, "Sensitivity Enhancement in Grating-Coupled Surface Plasmon Resonance by Azimuthal Control", *Opt. Exp.* 17, 12145 (2009).
4. **H. K. Kang**, A. Pistore, G. Brusatin, F. Romanato, C.C. Wong, M. Guglielmi, "Sensitivity of Plasmonic Crystal with Active Sol Gel Thin Film", *Int. J. Nanosci.* 8, 131 (2009).
5. **H. K. Kang**, K. H. Lee, C. C. Wong, F. Romanato, "1D to 2D Transitional Structure of Plasmonic Crystal: fabrication and characterization" *App. Phys. B.*, 97, 671-677 (2009)
6. K. H. Lee, **H. K. Kang**, F. Romanato, C. C. Wong, "Polarization optimization for a full sensitivity in azimuthal grating coupled surface plasmon resonance", *Sens. Act. B* 148, 181 (2010)
7. A. Pistore, **H. K. Kang**, C. Ferraris, F. Romanato, G. Brusatin and M. Guglielmi, "Active sol gel thin film on nanostructured plasmonic surface", *Solid State Sci.* 12, 1898 (2010)
8. Q. Zhao, **H. K. Kang**, C. H. Yip, C. C. Wong, "Real Time Visualization of Template Directed Colloidal Self Assembly", *Int. J. Nanosci.* 9, 363 (2010)
9. **H. K. Kang**, K. H. Lee, C. C. Wong, F. Romanato, "Profiles variations and characterization in 1D and 2D Plasmonics Crystal", *Int. J. Nanosci.* 9, 363 (2010)
10. **H. K. Kang**, K. H. Lee, Y. L. Wu and C. C. Wong, "The role of Polarization on 2D Plasmonic Crystal", *Plasmonics* 6, 373 (2011)
11. R. Deng, J. Li, **H. K. Kang**, H. Zhang and C.C. Wong, "Low Power Laser Directed Deposition of Silver Thin Films", *Thin Solid Film* 15, 5183(2011)
12. W. Zhao, J. Li, **H. K. Kang**, B. Zhou and C. C. Wong, "Direct laser interference writing on grating", *Nanosci. Nanotech. Lett.* 3, 246 (2011)
13. **H. K. Kang**, Y. L. Wu, A. Pistore, F. Romanato and C. C. Wong, "Exploring the negative diffraction order in plasmonic crystal by refractive index engineering", *IEEEExplore*, DOI: 10.1109/PGC.2010.5705945 (2011)
14. **H. K. Kang**, K. H. Lee, Y. L. Wu, F. Romanato and C. C. Wong, "Sensitivity enhancement in 2D Plasmonic crystal", *IEEEExplore*, DOI: 10.1109/PGC.2010.5705944 (2011)

Conferences

1. K. H. Lee, Q. F. Yan, **H. K. Kang**, C. C. Wong and F. Romanato, "Colloidal crystal nanoimprint method for the fabrication of 2D plasmonic crystals", 5th ISNM, Singapore (2008).
2. **H. K. Kang**, C. C. Wong, A. Pistore, G. Brusatin, M. Guglielmi, F. Romanato, "Active sol gel thin film on Plasmonic Crystal", The 7th International Conference on MP3, Singapore (2008)
3. **H. K. Kang**, C.C. Wong, A. Pistore, G. Brusatin, M. Guglielmi, F. Romanato, "Sensitivity of Plasmonic Crystal with Active Sol-Gel Thin Film", 1st Asia NANO, Singapore (2008)
4. **H. K. Kang**, K. H. Lee, C. C. Wong, F. Romanato, "1D to 2D Transitional Structure of Plasmonic Crystal", 1st AsiaNANO, Singapore (2008)
5. A. Pistore, **H. K. Kang**, C. Ferraris, F. Romanato, G. Brusatin and M. Guglielmi, "Active sol gel thin film on nanostructured plasmonic surface", E-MRS Spring meeting, France (2008)
6. **H. K. Kang**, C. C. Wong, G. Ruffato, T. Ongarello, F. Romanato, "Extraordinary Transmission and Surface Plasmon on 1D-2D Plasmonic Crystal", SPP4, Amsterdam (2009)
7. **H. K. Kang**, C. C. Wong, F. Romanato, "Field Enhancement in Plasmonic Corrugated Grating", SPP4 – Amsterdam (2009)
8. **H. K. Kang**, K. H. Lee, C. C. Wong, F. Romanato, "Geometrical effects in the Plasmonic Crystals", SPP4 – Amsterdam (2009)
9. F. Romanato, **H. K. Kang**, K. H. Lee, C. C. Wong, "Azimuthal dispersion and energy mode condensation of grating-coupled surface plasmon polaritons", SPP4 – Amsterdam (2009)
10. **H. K. Kang**, X. R. Chua, F. Romanato, C.C. Wong, "Optimization of Plasmonic Crystal Profiles in Fabrication by Interference Lithography", ICMAT & IUMRS-ICA, Singapore (2009)
11. Q. Zhao, M. R. Hartono, **H. K. Kang**, C.H. Yip, C.C. Wong, "Real Time Visualization of Template Directed Colloidal Self Assembly", ICMAT & IUMRS-ICA, Singapore (2009)
12. A. Pistore, **H. K. Kang**, G. Brusatin, M. Guglielmi and F. Romanato "Porous Films and Plasmonic Nano architecture", International Conference Sol-Gel, Pernambuco, Brazil (2009)
13. J. Li, W. Zhao, **H. K. Kang**, C.C. Wong, "Photoreduced Silver Gratings by Optical Interference", ThinFilm Conference, Harbin PRC (2010)
14. R. Deng, J. Li, **H. K. Kang**, H. Zhang, C.C. Wong, "Low Power Laser Directed Deposition of Silver Thin Films", ThinFilm Conference, Harbin PRC (2010)
15. G. Zacco, T. Ongarello, **H. K. Kang**, G. Ruffato, D. Garoli, M. Prasciolu, M. Natali and F. Romanato, "Fabrication of membranes for extraordinary optical transmission", META'10, International Conference on Metamaterials, Photonic crystals and Plasmonics, Cairo, Egypt (2010)
16. **H. K. Kang**, Y. L. Wu, A. Pistore, F. Romanato and C. C. Wong, "Exploring the negative diffraction order in plasmonic crystal by refractive index engineering", IEEE Photonic Global Conference, Singapore (2010)
17. **H. K. Kang**, K. H. Lee, Y. L. Wu, F. Romanato and C. C. Wong, "Sensitivity enhancement in 2D Plasmonic crystal", IEEE Photonic Global Conference, Singapore (2010)
18. **H. K. Kang**, Z. Qin, M. Leolukman, Y. L. Wu, C. C. Wong, "Optical Properties of Double Sided Plasmonic Nanostructures", ICMAT (MRS Singapore 2011)
19. **H. K. Kang**, K. H. Lee, Y. L. Wu and C. C. Wong, "Polarization Dependency in Periodic Nanostructures", ICMAT (MRS Singapore 2011)
20. Z. Qin, **H. K. Kang**, C. C. Wong, "Thermodynamically Study on Colloidal Assembly at Water/Oil Interface", ICMAT (MRS Singapore 2011)

Patent:

Sensitivity enhancement in grating coupled surface plasmon resonance by azimuthal control, US Provisional Patent Application No. 61/158, 940 (2009)

Appendix A

A.1. Maxwell's equations in curve coordinates

Recall the Maxwell's equations [141] from chapter 2 in the following, with the absence of free charges and currents:

Gauss's law	$\nabla \cdot E = 0$	(A.1.1)
Gauss' law for magnetism	$\nabla \cdot B = 0$	(A.1.2)
Faraday's law	$\nabla \times E = -\frac{\partial B}{\partial t}$	(A.1.3)
Maxwell–Ampère equation	$\nabla \times B = \varepsilon_0 \varepsilon(\omega) \mu_0 \frac{\partial E}{\partial t}$	(A.1.4)

These equations are valid in a 3D space where the scalar product between two vectors $\mathbf{v}_1$ and $\mathbf{v}_2$ is the usual one (euclidean space)

$$\mathbf{v}_1 \cdot \mathbf{v}_2 = \sum_{i,j=1}^3 v_1^i \cdot v_2^j g_{ij} \quad (\text{A.1.5})$$

with $G_{ij} = \delta_{ij}$

In a general curve coordinate basis, the matrix G_{ij} (metric tensor determinant) appears in the scalar product is different from the unity matrix and is in coordinates system. Components of a $\mathbf{v}$ may be expressed in the covariant $\mathbf{v}_i$ or in the contra-variant $\mathbf{v}^i$ form and the link between the two ones is given by the metric tensor:

$$v_i = \sum_{j=1}^3 v^j G_{ij} \quad (\text{A.1.6})$$

$$v^i = \sum_{j=1}^3 v_j G^{ij} \quad (\text{A.1.7})$$

where G^{ij} is the contra-variant form of the covariant G_{ij} which is simply the inverse matrix. The other Maxwell's equations that has the privilege of keeping the same form for any changes in coordinates (Einstein's principle of general relativity) in the absence of free charges and current:

$$\nabla \cdot \mathbf{D} = \frac{1}{\sqrt{G}} \sum_i \frac{\partial(\sqrt{G} D^i)}{\partial x^i} = 0 \quad (\text{A.1.8})$$

$$(\nabla \times \mathbf{E})^k = \frac{1}{\sqrt{G}} \left(\frac{\partial E_i}{\partial x^j} - \frac{\partial E_j}{\partial x^i} \right) = -\frac{\partial B^k}{\partial t} \quad (\text{A.1.9})$$

$$\nabla \cdot \mathbf{B} = \frac{1}{\sqrt{G}} \sum_i \frac{\partial(\sqrt{G} B^i)}{\partial x^i} = 0 \quad (\text{A.1.10})$$

$$(\nabla \times \mathbf{H})^k = \frac{1}{\sqrt{G}} \left(\frac{\partial H_i}{\partial x^j} - \frac{\partial H_j}{\partial x^i} \right) = \frac{\partial D^k}{\partial t} \quad (\text{A.1.11})$$

G is assumed to be 1 and considering a harmonic dependency of time:

$$\sum_i \frac{\partial D^i}{\partial x^i} = 0 \quad (\text{A.1.12})$$

$$\frac{\partial E_i}{\partial x^j} - \frac{\partial E_j}{\partial x^i} = i\omega B^k = i\omega G^{kt} B_t \quad (\text{A.1.13})$$

$$\sum_i \frac{\partial B^i}{\partial x^i} = 0 \quad (\text{A.1.14})$$

$$\frac{\partial H_i}{\partial x^j} - \frac{\partial H_j}{\partial x^i} = -i\omega D^k = -i\omega G^{kt} D_t \quad (\text{A.1.15})$$

A.2. Chandezon's Method for SPR Simulation

The detail of Chandezon's theory on multicoated grating can be found in ref. [254]. However a summary of this method is discussed bellow.

As the periodicity of 1D PCL is comparable to the wavelength of the light, accurate technique needs to be utilized for solving Maxwell's equations. The simplest scenario is the solution of plane wave diffraction on 1D grating structure. The grating is a periodic structure, with pitch Λ in the x-axis and constant in y-direction. From general grating theory it is known that above and below the grating grooves, the Rayleigh expansion can be the solution of the field:

$$F(x, z) = \sum_{-\infty}^{+\infty} A \exp[i(k_x x + k_z z)] \quad (\text{A.2.1})$$

F can be electric field E_y for TE-mode or magnetic field H_z for TM-mode. A is reflection and transmission coefficients for the upper and lower half space respectively. Rayleigh expansion cannot solve Maxwell's equation inside the grooves where the complex permittivity is not a constant, but a function of spatial coordinates. Hence Chandezon's method is used to obtain the Eigenvalue. Chandezon's method uses non-orthogonal coordinate system to map the medium interfaces into parallel planes. Using covariant of Maxwell's equation in new coordinate system leads to linear differential equations with constant coefficients whose solution can be calculated from eigenvalues and eigenvectors of the matrix in each medium. Since TE and TM modes cannot be separated at this point, the size of the problem is $4N + 1$.

Chandezon [254] described the system based on a dielectric with complex value n_0 , deposited by M metallic films with indices n_i and thickness d_i (Fig. 3.20). The monochromatic light is arriving on PCL at the θ angle and wavelength λ . The upper interface is described in the orthogonal O_{xyz} system by the periodic function $z = s(x) = A \sin(kx + \varphi_1)$, with period $\Lambda = 2\pi/k$. The upper limit in the i^{th} medium is given by $z = s(x) - \sum_{j=i+1}^M d_j$. $s(x)$ is assumed to be perfect 1D sinusoidal function (however this is not always the case) where k is a crystal momentum parallel to x axis direction and φ_1 is phase, in this case is 0.

The incident plane wave may be described as the superposition of a TM and TE-mode. The incident field y -component is $F_y^i = \exp(ikx \sin \theta \cos \theta)$ independent to phase component. The main issue is to solve the field in interface. The diffracted field, F^d can be calculated by the difference between total and normalized incident field.

Over the profile, F^d can be solved using Rayleigh's expansion [254]:

$$F^d = \sum_n B_n \exp[i(\alpha_n x + \beta_n z)] \quad (\text{A.2.2})$$

with $\alpha_n = k \sin \theta + nK$ and $\beta_n = \sqrt{k^2 - \alpha_n^2}$ for $n \in U$ or become imaginary for $n \notin U$. U has P integers thus $|\alpha_n| < k$, and $\sum_n$ covers $n = -\infty$ to $+\infty$.

F^d consists asymptotic as well as evanescent diffracted field (F^{ad} and F^{ed}). F^{ad} can be considered as the total of coefficients of the terms in the F^d for $n \in U$. Due its evanescence nature, F^{ed} could be ignored in the far field region. Unlike normal expansion, by utilizing Chandezon's model, F^{ad} can be solved for the enclosed (valley) region of the profile:

$$F^{ad} = \sum_n B_n \exp[i(\alpha_n x + \beta_n z)] \quad (\text{A.2.3})$$

Inside the enclosed region, F^{ed} cannot be represented by a plane-wave expansion. However the energy efficiencies ratio between n^{th} order and incident value for $n \in U$ equals to:

$$\varepsilon_n = B_n B_n^* \cos \theta_n \sec \theta \quad (\text{A.2.4})$$

To simplify the mathematical form for continuity of EM at the interface, translation coordinate system is used in this method. The new coordinate system only changes the z direction: $z' = u = z - s(x)$ while x and y remain unchanged.

A.2.1. Expression of F^{ad} and F^{ed} in new coordinate system

In new coordinate system for $z > s(x)$, then the incident field is given by [254]:

$$F^i = \exp(-ik \cos \theta (u + s(x) - x \tan \theta)) \quad (\text{A.2.4})$$

And the second exponential of the Fourier series [254]:

$$F^i = \frac{\beta_0}{\exp(i\beta_0 u)} \sum_m L_m \exp(i\alpha_m x) \quad (\text{A.2.5})$$

$$\text{Where } L_m = \left[\frac{ie^{-i(s(x)+mKx)} 1}{\Lambda(s'(x) + mK)} \right]_0^\Lambda$$

$$\text{Similarly } F^{ad} = \sum_{n \in U} \sum_m (-\beta B)_n L_{m-n} \exp[i(\alpha_m x - \beta_n u)] \quad (\text{A.2.6})$$

The covariant components for TM mode in j^{th} medium: $F = H_y$ (μ_0/ε_0)^{1/2} and $G = -k\varepsilon_j E_x$.

For SPP generation, only TM-mode is considered. The partial differential equation (PDE) of first order in u can be derived from Maxwell's equations in covariant form.

For TM-mode the magnetic curl in certain layer:

$$\frac{\partial H_y}{\partial u} = -i\omega\epsilon_i(E_x - s'E_u) \quad (\text{A.2.7})$$

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

By rearrangement the PDE of first order for H:

$$\frac{\partial H_y}{\partial u} = \frac{s'}{1+s'^2} \frac{\partial H_y}{\partial x} + \frac{i}{1+s'^2} \omega\epsilon_i E_x = \frac{s'}{1+s'^2} \frac{\partial H_y}{\partial x} + \frac{i}{1+s'^2} G \quad (\text{A.2.8})$$

The similar re-arrangement in electric field curl:

$$\begin{aligned} -\frac{\partial E_x}{\partial u} &= \frac{\partial}{\partial x} \left(\frac{i}{\omega\epsilon_i(1+s'^2)} \frac{\partial H_y}{\partial x} \right) + i\omega\mu_0 H_y + \frac{\partial}{\partial x} \left(\frac{s'}{1+s'^2} E_x \right) \\ -\frac{\partial G}{\partial u} &= \frac{\partial}{\partial x} \left(\frac{i}{1+s'^2} \frac{\partial H_y}{\partial x} \right) + i\epsilon_i k^2 F + \frac{\partial}{\partial x} \left(\frac{s'}{1+s'^2} G \right) \end{aligned} \quad (\text{A.2.9})$$

s' is derivative of $s(x)$, $s'(x) = Ak\cos(kx)$. These PDEs need to be solved for every layers and the electric as well as magnetic field must be with continuous at boundary.

A.2.2. Solution of the mathematical problem

The problem in Eq. A.2.8 – A.2.9 can be solved by PDEs. The grating profile for PDE should be periodic: $C(x) = \frac{1}{1+s'^2}$ and $D(x) = C(x)s'$ which can be expanded in Fourier series:

$$C(x) = \sum_p C_p \exp(ipKx) \quad (\text{A.2.10})$$

The grating profile, $s(x)$ can be an arbitrary periodic function; as long as it is continuous, single value and the Fourier series is converged [270, 320].

Using Bloch–Floquet the solution for the PDEs is given by:

$$H_y = \sum_m H_m(u) \exp(i\alpha_m x) \text{ and } G = \sum_m G_m(u) \exp(i\alpha_m x) \quad (\text{A.2.11})$$

Putting in the previous expansions in the PDEs, for each medium [254]:

$$\sum_m \exp(i\alpha_m x) \frac{\partial H_m}{\partial u} = \sum_p \sum_n D_p i\alpha_n H_n \exp(i\alpha_n + px) + \sum_p \sum_n iC_p G_n \exp(i\alpha_n + px) \quad (\text{A.2.12})$$

with the position $n + p = m$, it becomes:

$$\sum_m \exp(i\alpha_m x) \left[-i \frac{\partial H_m}{\partial u} - \sum_n \alpha_n D_{m-n} H_n + C_{m-n} G_n \right] = 0 \quad (\text{A.2.13})$$

$$\text{with } -i \frac{\partial H_m}{\partial u} = \sum_n \alpha_n D_{m-n} H_n + C_{m-n} G_n$$

Similarly for the second PDE, it becomes:

$$\sum_m \exp(i\alpha_m x) \left[-i \frac{\partial G_m}{\partial u} - \sum_n \left(-\alpha_n \alpha_m C_{m-n} H_n + k^2 \varepsilon_i \delta_{mn} H_n + \alpha_m D_{m-n} G_n \right) \right] = 0 \quad (\text{A.2.14})$$

with: $-i \frac{\partial G_m}{\partial u} = \sum_n \left(-\alpha_n \alpha_m C_{m-n} H_n + k^2 \varepsilon_i \delta_{mn} H_n + \alpha_m D_{m-n} G_n \right)$. δ_{mn} is the Kronecker symbol. Thus the unknown H_m and G_m can be calculated.

To simplify the problem, vector $\xi(u)$ is introduced to include H and G from $-N$ to $+N$ such as [254]:

$$-i \frac{d\xi}{du} = \left\{ T \cdot \begin{pmatrix} R_2 & 0 \\ 0 & R_1 \end{pmatrix} \cdot \begin{pmatrix} R_1 & 0 \\ 0 & R_2 \end{pmatrix} \right\} \xi \quad (\text{A.2.15})$$

$$\text{where: } T = \begin{pmatrix} A & B \\ C & D \end{pmatrix}$$

$$A_{m,n} = \alpha_n D_{m-n}$$

$$B_{m,n} = C_{m-n}$$

$$C_{m,n} = -\alpha_m \alpha_n C_{m-n} + k^2 \varepsilon_j(u) \delta_{mn}$$

$$D_{m,n} = \alpha_m D_{m-n}$$

$$R_{1m,n} = \delta_{mn} / \sqrt{\varepsilon(u)}$$

$$R_{2m,n} = \delta_{mn} \sqrt{\varepsilon(u)}$$

The solution of linear equation is reduced to solving the eigenvectors and eigenvalues in every layers so that the $\xi(u)$ can be expanded [254]:

$$\xi(u) = \sum_{q=1}^{\infty} b_q^j \left(\begin{pmatrix} R_2 & 0 \\ 0 & R_1 \end{pmatrix} V_q^j \right) \exp(i\lambda_q^j u) \quad (\text{A.2.16})$$

where λ_q^j and V_q^j are the *eigenvalues* and *eigenvectors* in j^{th} layer. Constant b_q^j is related to the eigenvectors. Therefore for each layer [254]:

$$\xi(u) = \begin{pmatrix} R_2 & 0 \\ 0 & R_1 \end{pmatrix} V_q^j \phi^j(u) b^j \quad (\text{A.2.17})$$

where $\phi^j(u)$ is a diagonal matrix with $\phi_{mn}^j = \exp(i\lambda_m^j u) \delta_{mn}$. Now the constant b_q^j needs to be calculated for each layer.

A.2.3. Boundary Conditions

The continuity equation at the interface (boundary) is given by [254]:

$$M^j \phi^j(u_j) b^j = M^{j+1} \phi^{j+1}(u_j) b^{j+1} \quad (\text{A.2.18})$$

Each layer of the grating profile, the field can be represented by matrix $H^j = M^j \phi^j(d_j) (M_j)^{-1}$ and the equation can be given by [254]:

$$M^{M+1} b^{M+1} = H b^0 \text{ with } H = H^M H^{M-1} \dots H^1 M^0 \phi(-d) \quad (\text{A.2.19-2.20})$$

To solve the F^{ad} , the constant b^{M+1} needs to be calculated.

A.2.4. Outgoing-Wave

This requires some limits for the solutions in the first and outermost layers. The b^0 only consist of b_q^j where λ_q^j relates to a field whose intensity reduces at y near to negative infinity. While u is depend on $\exp(i\lambda_q^0 u)$, thus the imaginary component of λ_q^0 needs to be equal or smaller than 0 while the real part needs to be less than zero [254].

In the void the condition will be further complex because the incoming EM, F^{ad} and F^{ed} must be clearly defined, thus:

$$\xi^{M+1} = Hb^0 \phi^{M+1}(u) + e^{(-i\beta_0 u)l} + M' \phi'(u)B \quad (A.2.21)$$

where l is a vector from negative to positive infinity where $l'_m = L_m(\beta_0)$. B is an element of B_n ($n \in U$) with size P , $\phi(u)$ is a diagonal matrix with identical size. M' is a matrix with the limit when N approach infinity of matrix $\begin{pmatrix} M'' \\ M''' \end{pmatrix}$ and size of $(4N+2)$ multiple by P [254]:

$$M''_{mn} = L_{m-n}(-\beta_n) \text{ and } M'''_{mn} = \left[\beta_n - (m-n)K \frac{\alpha_n}{\beta_n} \right] M''_{mn} \quad (A.2.22)$$

$$\text{hence } Hb^0 = M^{M+1}b^{M+1} + 1 + M'B \quad (A.2.23)$$

A.2.4. Truncation

All equations and calculations need to be truncated. ξ can be substituted using matrix T with size $4N+2$. From matrix T , in each medium eigenvector has size of $2N+1$ hence b^0 will have equal size as λ_j^{M+1} . For the imaginary component, λ_j^{M+1} size is equal to $2N+1-P$, thus similarly with b^{M+1} . Given that B consists of P elements, A.2.23 turns into linear equation with size of $4N+2$. As the matrix order increases, the eigenvalue's solutions will be more sophisticated.

A.2.5. Plasmonic Crystal Solution

Here the Chandenzon's method is used to solve EM on periodic function $z = s(x) = A \sin(kx + \varphi_1)$, with period $\Lambda = 2\pi/k$ and amplitude A . The Fourier's expansion $C(x)$ and $D(x)$ can be calculated as follow:

$$C(x) = \frac{1}{1 + A^2 k^2 \cos^2 kx} = \sum_{n=0}^{\infty} \frac{1}{n!} \left[\prod_{i=0}^{n-1} (-1-i) \right] (A^2 k^2 \cos^2 kx)^n \quad (A.2.24)$$

$$\text{where } \cos^{2n} kx = \sum_{p=0}^{2n} \frac{2n!}{p!(2n-p)!} \exp[2ikx(p-n)]$$

For position $2(p - n) = m$, where m is even value thus:

$$C_m = \sum_{n \geq \frac{m}{2}}^{+\infty} \frac{1}{n!} \left[\prod_{i=0}^{n-1} (-1-i) \right] (Ak)^{2n} \frac{(2n)!}{\left(\frac{m}{2} + n\right)! \left(n - \frac{m}{2}\right)!} \quad (\text{A.2.25})$$

Similarly $D(x)$ can be calculated. In this case $2(p - n) = m + 1$, where m is odd value.

The following Fourier's coefficients of the expansions till the fifth order.

$$C = C_0 + C_2 + C_4 = \left[1 - \frac{1}{2}(kA)^2 + \frac{3}{8}(kA)^4 \right] + \left[\frac{-(kA)^2 + (kA)^4}{4} \right] + \left[\frac{(kA)^4}{16} \right]$$

while $C_{(n=1, 3, 5, n>5)} = 0$

and

$$D = D_1 + D_3 + D_5 = \left[\frac{16kA - 4(kA)^3 + 5(kA)^5}{32} \right] + \left[\frac{-4(kA)^3 + 5(kA)^5}{32} \right] + \left[\frac{(kA)^5}{32} \right]$$

while $D_{(n=0, 2, 4, n>5)} = 0$

Since the amplitude of PCL is less than 10% of the periodicity thus third or fifth order will provide sufficient accuracy to simplify numerical calculation. The Fourier's coefficients $L_m(t)$ in new coordinate system needs to be calculated. Using Euler's and binomial series this coefficient can be calculated as follow [318]:

$$\begin{aligned} \exp[-its(x)] &= \exp\left[-\frac{tA}{2}(e^{ikx} - e^{-ikx})\right] \\ &= \sum_{n=p=0}^{+\infty} (-1)^n \frac{1}{n! p!} \left(\frac{tA}{2}\right)^{n+p} e^{i(n-p)kx} \end{aligned} \quad (\text{A.2.26})$$

Thus the condition for $n - p = m$ can be calculated

The Maxwell's equation based on Chadezon's theory [254] together with the azimuthal effect, φ is written in Mathematica in order to calculate angular reflectivity. There are several parameters that can be adjusted such as: grating periodicity, amplitude and metal thickness, refractive index of metals and medium, incident angle, wavelength, polarization and azimuthal angle. The function surface profile can also be adjusted based on the fabrication result by introducing certain phases and higher harmonic components as described in [270]

Appendix B

B.1. Variation in 1D PCL Profiles

The reflectivities' depth and efficiencies can be developed from different arrangements of different harmonic levels with phase φ_1 and φ_2 . This is the main reason that Fourier components of the PCL are important in the determination of the reflection spectrum of such profile. The perfect sinusoidal curve is demonstrated in Fig. B.1.1.

Figure B.1.1. A perfect sinusoidal profile, represented by sine function – undistorted profile.

Function 1 (black): $A \sin(\bar{g}x + \varphi_1)$ where $A=1$ and $\varphi_1=0$ is the main undistorted sinusoidal function (profile).

Figure B.1.2. Approximation of square wave function by adding the third harmonic function into a main sinusoidal function.

Function 1 (blue): $A \sin(\bar{g}x + \varphi_1)$ where $A=1$ and $\varphi_1=0$ is the main sinusoidal function (profile).

Function 2 (purple): $A_2 \sin(3\bar{g}x + \varphi_2)$ where $A_2/A=0.12$ and $\varphi_2=0$ (or $2\pi/3$, etc) is the third harmonic component (where the wavelength is one third of the main function).

The total Function (black): $S(x) = \sin(\bar{g}x) + 0.12\sin(3\bar{g}x)$

For square profile, the first term (main sinusoidal function) may at all times have biggest contribution both in total function as well as the transmitted diffracted order. For more square-like quality with sufficient accuracy, usually involves other higher harmonics term (Fourier component). One of the examples of better accuracy of square profile is

$S(x) = A\cos(\bar{g}x) - 0.2\cos(3 \cdot \bar{g}x) + 0.004\cos(5 \cdot \bar{g}x)$. The higher harmonic component in the sinusoidal profile will influence the crystal momentum in generating the surface plasmon mode on the PCL and thus alter the dispersion relation. In certain situation, it may form a plasmonic energy gap [144].

Figure B.1.3. PCL profiles of a) *top-blunt* and b) *bottom-blunt* sinusoidal wave function by adding the second harmonic function into a main sinusoidal function.

Function 2 (purple): $A_1 \sin(2\bar{g}x + \varphi_1)$ where $A_1/A=0.26$ and a) $\varphi_1 = \pi/4$ (or $5\pi/4$, etc) for *top-blunt* and b) $\varphi_1 = 3\pi/4$ (or $7\pi/4$, etc) for *bottom-blunt* is the second harmonic component (where the wavelength is half of the main function).

The total Function (black): a) $S(x) = \sin(\bar{g}x) + 0.26 \sin\left(2\bar{g}x + \frac{\pi}{4}\right)$ b)

$$S(x) = \sin(\bar{g}x) + 0.26 \sin\left(2\bar{g}x - \frac{\pi}{4}\right) \quad (\text{B.1.1})$$

For Fig. B.1.3 (a), if the amplitude is increased to 0.7, then the profile will look like this:

Function: $S(x) = \sin(\bar{g}x) + 0.7 \sin\left(2\bar{g}x + \frac{\pi}{4}\right)$ (B.1.2)

Some blazed profile can be modeled and shown in Fig. B.1.4.

Figure B.1.4. PCL profiles of a) *negative blazed* and b) *positive blazed* sinusoidal wave function by adding the second harmonic function into a main sinusoidal function.

Function 2 (purple): $A_1 \sin(2\bar{g}x + \varphi_1)$ where $A_1/A=0.4$ and a) $\varphi_1 = 0$ (or π , etc) for *negative blazed* and b) $\varphi_1 = \pi/2$ (or $3\pi/2$, etc) for *positive blazed* is the second harmonic component (where the wavelength is half of the main function).

The total Function (black): a) $S(x) = \sin(\bar{g}x) + 0.4\sin(2\bar{g}x)$ b)

$$S(x) = \sin(\bar{g}x) + 0.4\sin\left(2\bar{g}x + \frac{\pi}{2}\right) \quad (\text{B.1.3})$$

Figure B.1.5. Triangular profiles by adding the third harmonic function into a main sinusoidal function.

Function 2 (purple): $A_2 \sin(3\bar{g}x + \varphi_2)$ where $A_2/A=0.1$ and $\varphi_2 = \pi/3$ (or π , etc)

$$\text{The total Function (black): } S(x) = \sin(\bar{g}x) + 0.1\sin\left(3\bar{g}x + \frac{\pi}{3}\right) \quad (\text{B.1.4})$$

One of the examples of better accuracy of triangular profile is

$$S(x) = A\cos(\bar{g}x) + 0.111\cos(3 \cdot \bar{g}x) + 0.004\cos(5 \cdot \bar{g}x). \quad (\text{B.1.5})$$

Distorted PCL profiles of left and right sharp sinusoidal wave function is shown in Fig. B.1.6 and can be represented by adding the second harmonic function into a main sinusoidal function

Figure B.1.6. Distorted PCL profiles of a) left sharp and b) right sharp sinusoidal wave function by adding the second harmonic function into a main sinusoidal function.

Function 2 (purple): $A_2 \sin(3\bar{g}x + \varphi_2)$ where $A_2/A=0.3$ and a) $\varphi_2 = \pi/6$ (or $5\pi/6$, etc) for left sharp and b) $\varphi_2 = \pi/2$ (or $7\pi/6$, etc) for *positive blazed* is the first harmonic component (where the wavelength is half of the main function).

The total Function (black): a) $S(x) = \sin(\bar{g}x) + 0.3 \sin\left(3\bar{g}x + \frac{\pi}{6}\right)$ b)

$$S(x) = \sin(\bar{g}x) + 0.3 \sin\left(3\bar{g}x + \frac{\pi}{2}\right) \quad (\text{B.1.6})$$

The symmetry is very important in this case, in order to simplify the calculation during the simulation. For $\varphi_1 = \pi/4$ and $3\pi/4$, the $S(x) = S(-x)$, in which x is centered within $\pm \pi/4$ or $3\pi/4$. For $\varphi_1 = 0$ and π , the $S(x) = S(-x)$, where x is centered at $x=0$ or $\pi/2$. More complicated structures, for more accurate approximation can be mathematically represented using third and higher harmonic system.

B.2. Modified Lloyd's Mirror Configuration

The modified Lloyd's mirror configuration is based on development from J. Boor's paper [241] in which additional two to three mirrors are introduced so that the incident beam and its reflections from the mirrors generate a periodic-regular interference pattern on the photoresist. This modified method is more general as the angle between the mirrors (Fig. 3.11) can be tuned as desired to form specific lattice shapes. In addition the fourth beam is introduced to form more intricate structure as described in Fig. 3.11 (c).

For standard Lloyd's mirror configuration in Fig. 3.11 (a), the direct (from laser) and reflected (from mirror) wavevector is given by:

$$k_1 = k_0(-\sin \theta, 0, -\cos \theta) \text{ and} \quad (\text{B.2.1})$$

$$k_2 = R_\theta \cdot k_0(\sin \theta, 0, -\cos \theta) \quad (\text{B.2.2})$$

where R_θ is defined as a reflectivity coefficient of the mirror at certain incident angle and wavelength. The grating constant is given by:

$$\Lambda_C = \lambda / (2 \sin \theta) \quad (\text{B.2.3})$$

For modified Lloyd's configuration in Fig. 3.11 (b), the direct and reflected wavevectors is given by:

$$k_1 = k_0(-\sin \theta, 0, -\cos \theta), \quad (\text{B.2.4})$$

$$k_2 = R_\theta k_0 \left[\cos\left(\frac{\alpha}{2}\right) \sin \theta, -\sin\left(\frac{\alpha}{2}\right), -\cos\left(\frac{\alpha}{2}\right) \cos \theta \right] \text{ and} \quad (\text{B.2.5})$$

$$k_3 = R_\theta k_0 \left[\cos\left(\frac{\alpha}{2}\right) \sin \theta, \sin\left(\frac{\alpha}{2}\right), -\cos\left(\frac{\alpha}{2}\right) \cos \theta \right] \quad (\text{B.2.6})$$

For four beams Lloyd's modified setup as demonstrated in Fig. 3.11 (c), besides k_1 , k_2 and k_3 , the additional fourth beam wavevector is given by:

$$k_4 = k_0 (-\sin \theta, 0, \cos \theta) \quad (\text{B.2.7})$$

where α is the angle between two mirrors.

The grating constant is given by the distance between two adjacent intensity maxima formed by direct and any of reflected wavevectors (i.e. k_1 and $k_{2/3}$):

$$\Lambda = 2\pi / (k_1 - k_{2/3}) \quad (\text{C.2.8})$$

Hence the periodicity is given by:

$$\Lambda_M = \frac{\lambda}{(\cos(\alpha/2) + 1) \cdot \pi \sin \theta} \quad (\text{B.2.9})$$

The secondary periodicity formed by k_1 and k_4 is identical to standard Lloyd's Mirror (Eq. C.2.3). Generally periodicity by modified configuration will be larger than the one formed by conventional Lloyd's mirror configuration by:

$$\Lambda_M / \Lambda_C = \frac{2}{(\cos(\alpha/2) + 1)} \quad (\text{B.2.10})$$

References

1. V. M. Shalaev, *Plasmonic Nanophotonics: Coupling Light to Nanostructure via Plasmons*. LEOS, 2005(22-28): p. 280-281.
2. S. Vyawahare, S. Eyal, K. D. Mathews, and S. R. Quake, *Nanometer-scale Fluorescence Resonance Optical Waveguides*. Nano Lett., 2004. **4**(6): p. 1035-1039.
3. P. Berini, R. Charbonneau, N. Lahoud, and G. Mattiussi, *Characterization of long-range surface-plasmon-polariton waveguides*. J. Appl. Phys, 2005. **98**(4): p. 043109.
4. R. Zia, A. Chandran, and M. I. Brongersma, *Dielectric waveguide model for guided surface polaritons*. Optics Letters, 2005. **30**(12): p. 1473.
5. J. A. Dionne, L. A. Sweatlock, H. A. Atwater, and Polman, *Planar metal plasmon waveguides: frequency-dependent dispersion, propagation, localization, and loss beyond the free electron model*. Phys. Rev. B., 2005. **72**(7): p. 075405.
6. B. Steinberger, A. Hohenau, H. Ditlbacher, A. L. Stepanov, A. Drezet, and A.L. F. R. Aussenegg, and J. R. Krenn, *Dielectric stripes on gold as surface plasmon waveguides*. Appl. Phys. Lett., 2006. **88**(9): p. 094104.
7. J. A. Dionne, L. A. Sweatlock, H. A. Atwater and A. Polman, *Plasmon slot waveguides: Towards chip-scale propagation with subwavelength-scale localization*. Phys. Rev. B., 2006. **73**(3): p. 035407.
8. Y. S. Chu, W. H. Hsu, C. W. Lin, and W. S. Wang, *Surface Plasmon Resonance Sensors using Silica on Silicon Optical Waveguide*. Microw. Opt. Tech. Lett., 2006. **48**(5): p. 955.
9. M. Skorobogatiya, and A. V. Kabashin, *Photon crystal waveguide-based surface plasmon resonance biosensor*. Appl. Phys. Lett., 2006. **89**(14): p. 143518.
10. A. Kuzyk, M. Pettersson, J. J. Toppari, T. K. Hakala, H. Tikkanen, H. Kunttu, and P. Törmä, *Molecular coupling of light with plasmonic waveguide*. Optics Express, 2007. **15**(16): p. 9908.
11. B. H. Ong, X. Yuan, and S. C. Tjin, *Bimetallic Silver-Gold Film Waveguide Surface Plasmon Resonance Sensor*. Fiber and Integrated Optics, 2007. **26**(4): p. 229-240.
12. S. A. Maier, *Plasmonic Waveguide*, in *Plasmonic Fundamental and applications*, S.A. Maier, Editor 2007, Springer Science+Business Media LLC: New York.
13. H. A. Atwater, J. A. Dionne, and L. A. Sweatlock, *Subwavelength - Scale Plasmon Waveguides*, in *Surface Plasmon Nanophotonics*, M.L. Brongersma, and P.G. Kik, Editor 2007, Springer: Netherland. p. 87-104.
14. A. Hosseini, H. Nejati, and Y. Massoud, *Triangular lattice plasmonic photonic band gaps in subwavelength metal-insulator-metal waveguide structures*. Appl. Phys. Lett., 2008. **92**(1): p. 013116.
15. H. Xu, Z. Wang, J. Hao, J. Dai, L. Ran, J. A. Kong, and L. Zhou, *Effective-medium models and experiments for extraordinary transmission in metamaterial-loaded waveguides*. Appl. Phys. Lett., 2008. **92**(4): p. 041122.
16. M. Veith, K. G. Müller, S. Mittler-Neher, and W. Knoll, *Propagation and deflection of guided modes in planar waveguides via grating rotation* Appl. Phys. B: Lasers and Optics, 1995. **60**(1): p. 1-4.
17. P. Bakshi, and K. Kempa,, *A Plasmon Laser in Nanostructures*. Condensed Matter Theories, 1997. **12**(1): p. 399-412.
18. C. Sirtori, C. Gmachl, F. Capasso, J. Faist, D. L. Sivco, A. L. Hutchinson, and A. Y. Cho, *Long-wavelength (8–11.5 mm) semiconductor lasers with waveguides based on surface plasmons*. Optics Letters, 1998. **23**(17): p. 1366.
19. A. Tredicucc, C. Gmachl, F. Capasso, A. L. Hutchinson, D. L. Sivco, and A. Y. Cho, *Single-mode surface-plasmon laser*. Appl. Phys. Lett., 2000. **76**(16): p. 2164.
20. T. Okamoto, F. H'Dhili, and S. Kawata, *Towards plasmonic band gap laser*. Appl. Phys. Lett., 2004. **85**(18): p. 3968.

21. C. Ropers, G. Stibenz, G. Steinmeyer, R. Müller, D. J. Park, K. G. Lee, J. E. Kihm, J. Kim, Q. H. Park, D. S. Kim, and C. Lienau, *Ultrafast dynamics of surface plasmon polaritons in plasmonic metamaterials* Appl. Phys. B: Lasers and Optics, 2006. **84**(1-2): p. 183-189.
22. Q. Xie, M. H. Hong, H. L. Tan, G. X. Chen, L. P. Shi, and T. C. Chong, *Fabrication of nanostructures with laser interference lithography*. J. Alloys and Comp., 2008. **449**(1-2): p. 261-264
23. B. Liedberg, I. Lundstrom, and E. Stenberg, *Principles of Biosensing with an Extended Coupling Matrix and SPR*. Sensors and Actuators B, 1993(11): p. 63.
24. K. Ideta, and T. Arakawa, *Surface plasmon resonance study for the detection of some chemical species* Sensors and Actuators B: Chemical, 1993. **13**(1-3): p. 384-386
25. L. S. Jung, C. T. Campbell, T. M. Chinowsky, M. N. Mar, and S. S. Yee *Quantitative Interpretation of the Response of Surface Plasmon Resonance Sensors to Adsorbed Films*. Langmuir, 1998. **14**(19): p. 5636-5648.
26. A. V. Kabashin, V. E. Kochergin, and P. I. Nikitin, *Surface plasmon resonance bio- and chemical sensors with phase-polarisation contrast*. Sensors and Actuators B, 1999. **54**(1-2): p. 51-56.
27. J. Homola, Sinclair S. Yee and Günter Gauglitz, *Surface plasmon resonance sensors: review* Sensors and Actuators B: Chemical, 1999. **54**(1-2): p. 3-15.
28. R. L. Rich, and D.G. Myszka, *Survey of the year 2001 commercial optical biosensor literature*. J. Molec. Recog., 2002. **15**(6): p. 352-376.
29. J. Vörös, J. J. Ramsden, G. Csúcs, I. Szendr, S. M. De Paula, M. Textor, and N. D. Spencer, *Optical grating coupler biosensors* Biomater., 2002. **23**(17): p. 3699-3710
30. J. Homola, *Present and future of surface plasmon resonance biosensors*. Anal. Bioanal. Chem., 2003. **377**(3): p. 528-539.
31. N. L. Dmitruk, O. I. Mayeva, S. V. Mamykin, I. B. Mamontova, and O. B. Yastrubchak, *Contribution of Structure and Morphology of Design Constituents to Performance Improvement of Multilayer Polaritonic Photodetector*. Sensors, 2003. **3**(1): p. 480-490.
32. A. J. Haes, W. P. Hall, L. Chang, W. L. Klein, and R. P. Van Duyne, *A Localized Surface Plasmon Resonance Biosensor: First Steps toward an Assay for Alzheimer's Disease*. Nano Lett., 2004. **4**(6): p. 1029-1034.
33. D. Kim, *Effect of the azimuthal orientation on the performance of grating-coupled surface-plasmon resonance biosensors*. Appl. Opt., 2005. **44**(16): p. 3218.
34. F. Yu, and W. Knoll, *Surface Plasmon Diffraction Biosensor*. J. Nonlin. Optc. Phys. Mater., 2005. **14**(2): p. 149-160.
35. F. Liu, Y. Rao, Y. Huang, D. Ohnishi, W. Zhang, J. Peng, *A Novel LRSPB Based Refractive Index Sensor*. IEEE Conference Proceeding on Biophotonics, Nanophotonics and Metamaterials, 2006: p. 103-105.
36. S. Janz, J. Ctyroky, and S. Tanev, *Surface Plasmon resonance (SPR) Biosensors and Their Application in Food Safety and Security*, in *NATO Science Series II: Mathematics Physics and Chemistry*, J. Homola, Editor 2006, Springer Netherlands: Prague, Czech Republic.
37. J. Liu, X. Ding, X. Yu, and D. Wang, *Data analysis of surface plasmon resonance biosensor based on phase detection*. Sensors and Actuators B, 2006. **108**(1-2): p. 778-783.
38. S. Brantzen, F. Volklein, W. Knoll, and B. Menges, *A new sensor for the thermo-optical detection of surface plasmon resonance*. Sensors and Actuators A: Physical, 2007. **135**(2): p. 492-501.
39. K. L. Lee, C. W. Lee, W. S. Wang, and P. K. Wei, *Sensitive biosensor array using surface plasmon resonance on metallic nanoslits*. J. Biomed. Opt., 2007. **12**(4): p. 044023.
40. P. Adam, J. Dostálek, O. Telezhnikova, and J. Homola, *SPR sensor based on a bi-diffractive grating*, in *Optical Sensing Technology and Applications*, Francesco Baldini, Jiri Homola, Robert A. Lieberman, Miroslav Miler., Editor 2007, SPIE.
41. A. Lesuffleur, H. Im, N. C. Lindquist, and S. H. Oh, *Periodic nanohole arrays with shape-enhanced plasmon resonance as real-time biosensors*. Appl. Phys. Lett., 2007. **90**(24): p. 243110.

42. T. M. Squires, R. J. Messinger, and S. R. Manalis, *Making it stick: convection, reaction and diffusion in surface-based biosensors*. Nature Biotech, 2008. **26**(4): p. 417.
43. V. Berger, *From photonic band gaps to refractive index engineering*. Opt. Mater., 1999. **11**(98): p. 1331-142.
44. D. R. Smith, J. B. Pendry, and M. C. K. Wiltshire, *Metamaterials and Negative Refractive Index*. Science, 2004. **305**(5685): p. 788-792.
45. J. Dintinger, S. Klein, and T.W. Ebbesen *Molecule-surface plasmon interactions in hole arrays: enhanced absorption, refractive index changes, and all-optical switching*. Adv. Matter, 2006. **18**(10): p. 1267-1270
46. T. Rindzevicius, Y.A., M. Kall, W. A. Murray, and W. L. Barnes, *Long-Range Refractive Index Sensing Using Plasmonic Nanostructures*. J. Phys. Chem. C, 2007. **111**(32): p. 11806 -11810.
47. J. Y. Lee, H. C. Shih, C. T. Hong, and T. K. Chou, *Measurement of refractive index change by surface plasmon resonance and phase quadrature interferometry*. Opt. Comm., 2007. **276**(2): p. 283–287.
48. H. Raether, *Surface plasma oscillations and their applications* Phys. Thin Film, 1977. **9**: p. 145-261.
49. H. Raether, *Surface Plasmons on Smooth and Rough Surfaces and on Gratings* 1988, Berlin: Springer-Verlag.
50. S. A. Maier, M. L. B., P. G. Kik, S. Meltzer, A. A. G. Requicha, and H. A. Atwater, *Plasmonics - A Route to Nanoscale Optical Devices***. Adv. Mater., 2001. **13**(19): p. 1501.
51. S. A. Maier, and H. A. Atwater, *Plasmonics: Localization and guiding of electromagnetic energy in metal/dielectric structures*. J. Appl. Phys., 2005. **98**(1): p. 011101.
52. E. Ozbay, *Plasmonics: Merging Photonics and Electronics at Nanoscale Dimensions* Science, 2006. **311**(5758): p. 189-193
53. R. W. Wood, *On a Remarkable Case of Uneven Distribution of Light in a Diffraction Grating Spectrum*. Proc. Phys. Soc., 1902. **18**(1): p. 269-275
54. R. H. Ritchie, E. T. Arakawa, J. J. Cowan, and R. N. Hamm, *Surface-Plasmon Resonance Effect in Grating Diffraction*. Phys. Rev. Lett. , 1968. **21**(22): p. 1530 - 1533
55. G. P. Bryan-Brown, M. C. Jory, S. J. Elston, and J. R. Sambles *Diffraction Grating Characterization Via the Excitation of Surface Plasmons* J. Modern Opt., 1993. **40**(5): p. 959 - 964.
56. W. L. Barnes, T. W. Preist, S. C. Kitson, and J. R. Sambles, *Physical origin of photonic energy gaps in the propagation of surface plasmons on gratings*. Phys. Rev. B, 1996. **54**(9): p. 6227.
57. R. A. Watts, T. W. Preist, and J. R. Sambles, *Sharp Surface-Plasmon Resonances on Deep Diffraction Gratings*. Phys. Rev. Lett. , 1997. **79**(20): p. 3978-3981.
58. U. Schroter, and D. Heitmann, *Surface-plasmon-enhanced transmission through metallic gratings*. Phys. Rev. B, 1998. **58**(23): p. 15419.
59. M. M. J. Treacy, *Dynamical diffraction explanation of the anomalous transmission of light through metallic gratings*. Phys. Rev. B, 2002. **66**(19): p. 195105.
60. J. G. Rivas, M. Kuttge, H. Kurz, P. H. Bolívar, and J. A. S'anchez-Gil, *Propagation of surface plasmon polaritons on semiconductor gratings*. Appl. Phys. Lett., 2006. **88**(8): p. 082106.
61. Z. Chen, I. R. Hooper, and J. R. Sambles, *Coupled surface plasmons on thin silver gratings*. J. Opt. A: Pure Appl. Opt., 2008. **10**(1): p. 015007.
62. C. J. Alleyne, A.G.K., R. C. McPhedran, N. A. P. Nicorovici, and D. Maystre, *Enhanced SPR sensitivity using periodic metallic structures*. Opt. Express, 2007. **15**(13): p. 7.
63. W. L. Barnes, W. A. Murray, J. Dintinger, E. Devaux, and T. W. Ebbesen., *Surface plasmon polaritons and their role in the enhanced transmission of light through periodic arrays of subwavelength holes in a metal film*. Phys. Rev. Lett., 2004. **92**(10): p. 107401.
64. A. V. Zayats, L. Salomon, and F. de Fornel, *How light gets through periodically nanostructured metal films: a role of surface polaritonic crystals*. J. Microscopy, 2002. **210**(3): p. 344-349.

65. G. H. Derrick, R. C. McPhedran, D. Maystre, and M. Neviere, *Crossed Gratings: A Theory and its Applications*. Appl. Phys., 1979. **18**(79): p. 39-52.
66. N. E. Glass, A. A. Maradudin, and V. Celli, *Diffraction of light by a bigrating: Surface polariton resonances and electric field enhancements*. Phys. Rev. B 1983. **27**(8): p. 5150 - 5153.
67. N. E. Glass, and A. A. Maradudin, *Polariton resonant absorption in a bigrating - Exact theory compared to recent experiments and to perturbation theory*. Opt. Comm., 1986. **56**(1): p. 339-344.
68. N. E. Glass, *Perturbation theory for light diffraction with surface-polariton resonances on a bigrating*. Phys. Rev. B, 1987. **35**(6): p. 2647 - 2659.
69. J. B. Harris, T. W. Preist, J. R. Sambles, R. N. Thorpe, and R. A. Watts, *Optical response of bigratings*. J. Opt. Soc. Am. A, 1996. **13**(10): p. 2041.
70. P. T. Worthing, and W. L. Barnes, *Efficient coupling of surface plasmon polaritons to radiation using a bi-grating*. Appl. Phys. Lett., 2001. **79**(19): p. 3035.
71. N. E. Glass, A. A. Maradudin, and V. Celli *Theory of surface-polariton resonances and field enhancements in light scattering from bigratings*. J. Opt. Soc. Am., 2007. **73**(10): p. 1240.
72. F. Romanato, K. H. Lee, H. K. Kang, C. C. Wong, Y. Zong, and W. Knoll, *Azimuthal dispersion and energy mode condensation of grating-coupled surface plasmon polaritons*. Phys. Rev. B., 2008. **77**: p. 245435.
73. A. P. Hibbins, J. R. Sambles, and C. R. Lawrence, *Azimuth-angle-dependent reflectivity data from metallic gratings*. J. Modern Opt., 1998. **45**(5): p. 1019-1028.
74. A. V. Zayats, I. I. Smolyaninov, and A. A. Maradudin, *Nano-optics of surface plasmon polaritons* Phys. Rep., 2005. **408**(3-4): p. 131-314.
75. A. V. Krasavin, A. V. Zayats, and N. I. Zheludev, *Active control of surface plasmon-polariton waves*. J. Opt. A, 2005. **7**(2): p. S85-S89.
76. M. Xu, R. Moshrefzadeh, U. J. Gibson, G. I. Stegeman, and C. T. Seaton *Simple versatile method for fabricating guided-wave gratings*. Appl. Opt., 1985. **24**(19): p. 3155.
77. A. P. Hibbins, J. R. Sambles, and C. R. Lawrence *The coupling of microwave radiation to surface plasmon polaritons and guided modes via dielectric gratings*. J. Appl. Phys, 2000. **87**(6): p. 2677.
78. N. Felidj, J. Aubard, G. Levi, J. R. Krenn, G. Schider, A. Leitner, and F. R. Aussenegg, *Enhanced substrate-induced coupling in two-dimensional gold nanoparticle arrays*. Phys. Rev. B, 2002. **66**(24): p. 245407.
79. A. L. Baudrion, F. D. Leon-Perez, O. Mahboub, A. Hohenau, H. Ditlbacher, F. J. Garcia-Vidal, J. Dintinger, T. W. Ebbesen, L. Martin-Moreno, and J. R. Krenn *Coupling efficiency of light to surface plasmon polariton for single subwavelength holes in a gold film*. Opt. Express, 2008. **16**(5): p. 3420-3429.
80. A. Otto, *Excitation of nonradiative surface plasma waves in silver by the method of frustrated total reflection*. Zeitschrift für Physik A Hadrons and Nuclei, 1968. **216**(4): p. 398-410.
81. E. Kretschmann, *Decay of non radiative surface plasmons into light on rough silver films. Comparison of experimental and theoretical results* Opt. Comm., 1972. **6**(2): p. 185-187.
82. A. Bouhelier, Th. Huser, H. Tamaru, H.-J. Güntherodt, D. W. Pohl, Fadi I. Baida, and D. Van Labeke, *Plasmon optics of structured silver films*. Phys. Rev. B, 2001. **63**(15): p. 155404.
83. M. W. Tsai, T. H. Chuang, H. Y. Chang, and S. C. Lee, *Bragg scattering of surface plasmon polaritons on extraordinary transmission through silver periodic perforated hole arrays*. Appl. Phys. Lett., 2006. **88**(21): p. 213112.
84. C. Y. Chen, M. W. Tsai, T. H. Chuang, Y. T. Chang, and S. C. Lee, *Extraordinary transmission through a silver film perforated with cross shaped hole arrays in a square lattice*. Appl. Phys. Lett., 2007. **91**(6): p. 063108.
85. S. Tomita, T. Yokoyama, H. Yanagi, B. Wood, J. B. Pendry, M. Fujii, and S. Hayashi *Resonant photon tunneling via surface plasmon polaritons through one-dimensional metal-dielectric metamaterials*. Opt. Express, 2008. **16**(13): p. 9942-9950

86. R. Biswas, S. Neginhal, C. G. Ding, I. Puscasu, and E. Johnson, *Mechanisms underlying extraordinary transmission enhancement in subwavelength hole arrays*. J. Opt. Soc. Am. B, 2007. **24**(10): p. 2589.
87. S. J. Elston, G. P. Bryan-Brown, T. W. Preist and J. R. Sambles, *Surface-resonance polarization conversion mediated by broken surface symmetry*. Phys. Rev. B., 1991. **44**(7): p. 3483-3485.
88. J. R. Sambles, G. W. Bradbery, and Fuzi Yang, *Optical Excitation of Surface Plasmons : an Introduction*. Contemp. Phys., 1991. **32**(3): p. 173-183.
89. R. A. Watts, J. Roy Sambles, and M. C. Hutley, *Optical characterization of a complex grating profile*. J. Modern Opt., 1998. **45**(3): p. 639-651
90. A. P. Hibbins, B. R. Evans, and J. R. Sambles, *Experimental Verification of Designer Surface Plasmons*. Science, 2005. **308**: p. 670.
91. N. E. Glass, *Enhanced Smith-Purcell radiation from a bigrating surface through multiplasmon excitation*. Phys. Rev. A, 1987. **36**(11): p. 5235-5250
92. T. W. Ebbesen, H. J. Lezec, H. F. Ghaemi, T. Thio, and P. A. Wolff, *Extraordinary optical transmission through subwavelength hole arrays*. Nature, 1998. **391**(6668): p. 667-669.
93. E. Popov, M. Nevie`re, S. Enoch, and R. Reinisch, *Theory of light transmission through subwavelength periodic hole arrays*. Phys. Rev. B, 2000. **62**(23): p. 16100.
94. L. Martín-Moreno, J. García-Vidal, H. J. Lezec, K. M. Pellerin, T. Thio, J. B. Pendry, and T.W. Ebbesen, *Theory of Extraordinary Optical Transmission through Subwavelength Hole Arrays*. Phys. Rev. Lett., 2001. **86**(6): p. 1114.
95. S. Enoch, E. Popov, M. Neviere, and R. Reinisch, *Enhanced light transmission by hole arrays*. J. Opt. A: Pure Appl. Opt., 2002. **4**(5): p. S83–S87.
96. R. Gordon, A. G. Brolo, A. McKinnon, A. Rajora, B. Leathem, and K. L. Kavanagh, *Strong polarization in the optical transmission through elliptical nanohole arrays*. Phys. Rev. Lett., 2004. **92**(3): p. 037401.
97. K. J. K. Koerkamp, S. Enoch, F. B. Segerink, N. F. van Hulst, and L. Kuipers, *Strong Influence of Hole Shape on Extraordinary Transmission through Periodic Arrays of Subwavelength Holes*. Phys. Rev. Lett., 2004. **92**(18): p. 183901.
98. A. Degiron, and T. W. Ebbesen, *The role of localized surface plasmon modes in the enhanced transmission of periodic subwavelength apertures*. J. Opt. A: Pure Appl. Opt. , 2005. **7**(2): p. S90-S96
99. C. Humeyra, B. Irfan ; O. Ekmel *Plasmonic structures with extraordinary transmission and highly directional beaming properties*. Microw. Opt. Tech. Lett., 2006. **48**(12): p. 2491-2496
100. E. A. Shanera, J. G. Cederberg, and D. Wasserman, *Electrically tunable extraordinary optical transmission gratings*. Appl. Phys. Lett., 2007. **91**(18): p. 181110.
101. P. B. Catrysse, and S. Fan, *Near-complete transmission through subwavelength hole arrays in phonon-polaritonic thin films*. Phys. Rev. B, 2007. **75**(7): p. 075422.
102. Y. M. Strelniker, *Theory of optical transmission through elliptical nanohole arrays*. Phys. Rev. B, 2007. **76**(8): p. 085409.
103. A. Battula, S. Chen, Y. Lu, R. J. Knize, and K. Reinhardt, *Tuning the extraordinary optical transmission through subwavelength hole array by applying a magnetic field*. Opt. Lett., 2007. **32**(18): p. 2692.
104. H. K. Kang, C. C. Wong, and F. Romanato, *1D to 2D Transitional Structure of Plasmonic Crystals: Fabrication and Characterization*. Appl. Phys. B, 2009. **97**(3): p. 8.
105. M. Farhoud, J. Ferrera, A. J. Lochtefeld, T. E. Murphy, M. L. Schattenburg, J. Carter, C. A. Ross, and H. I. Smith, *Fabrication of 200 nm period nanomagnet arrays using interference lithography and a negative resist*. J. Vac. Sci. Technol. B, 1999. **17**(6): p. 3182.
106. M. E. Walsh, *Nanostructuring Magnetic Thin Film using Interference Lithography*, in *Electrical Engineering 2000*, Massachusetts Institute of Technology: Boston. p. 86.
107. Y. Lu, H. Ling, C. J. Brinker, T. M. Niemczyk, and G. P. Lopeza *Chemical sensors based on hydrophobic porous sol-gel films and ATR-FTIR spectroscopy* Sensors and Actuators B: Chemical, 1996. **36**(1-3): p. 517-521.

108. E. Wang, K. F. Chow, V. Kwan, T. Chin, C. Wong, and A. Bocarsly, *Fast and long term optical sensors for pH based on sol-gels*. *Analytica Chimica Acta*, 2003. **495**(1): p. 45-50.
109. P. Innocenzi, G. Brusatin, M. Guglielmi, and R. Bertani, *Chem. Mat.*, 1999. **11**: p. 1672-1679.
110. N. L. Jeon, S. K. W. Dertinger, D. T. Chiu, I. S. Choi, A. D. Stroock, and G. M. Whitesides, *Generation of solution and surface gradients using microfluidic systems*. *Langmuir*, 2000. **16**(22): p. 8311-8316.
111. Y. E. Sarov, I. Capek, T. B. Ivanov, K. Zh. Ivanova, V. A. Sarova, and I. W. Rangelow, *On Total Internal Reflection Investigation of Nanoparticles by Integrated Micro-Fluidic System*. *Nano Lett.*, 2008. **8**(2): p. 375.
112. T. T. Ehler, N. Malmberg, and L. J. Noe, *Characterization of Self-Assembled Alkanethiol Monolayers on Silver and Gold Using Surface Plasmon Spectroscopy*. *J. Phys. Chem. B*, 1997. **101**(8): p. 5.
113. S. Y. Wu, H. P. Ho, W. C. Law, and C. L. Lin, *Highly sensitive differential phase-sensitive surface plasmon resonance biosensor based on the mach-Zehnder configuration*. *Opt. Lett.*, 2004. **29**: p. 3.
114. J. A. Woollam Co. Inc, *Spectroscopic Ellipsometry - Data Acquisition and Analysis in A Guide to use WVASE 322006*.
115. I. R. Hooper, and J. R. Sambles, *Sensing using differential surface plasmon ellipsometry*. *J. Appl. Phys.*, 2004. **96**(5): p. 3004.
116. F. Romanato, K. H. Lee, G. Ruffato, and C. C. Wong *The role of polarization on surface plasmon polariton excitation on metallic gratings in the conical mounting*. *Appl. Phys. Lett.*, 2010. **96**: p. 3.
117. U. Fano, *The Theory of Anomalous Diffraction Gratings and of Quasi-Stationary Waves on Metallic Surfaces (Sommerfeld's Waves)*. *J. Opt. Soc. Am. A*, 1941. **31**(3): p. 213-222.
118. C. J. Powell, and J. B. Swan, *Origin of the Characteristic Electron Energy Losses in Magnesium*. *Phys. Rev.*, 1959. **116**(1): p. 81-83.
119. C. J. Powel, and J. B. Swan, *Effect of Oxidation on the Characteristic Loss Spectra of Aluminum and Magnesium*. *Phys. Rev.*, 1960. **118**(3): p. 640-643.
120. W. L. Barnes, A. Dereux, and T. W. Ebbese, *Surface plasmon subwavelength optics*. *Nature*, 2003. **424**(6950): p. 7.
121. M. G. Moharam, and T. K. Gaylord *Rigorous coupled-wave analysis of metallic surface-relief gratings*. *J. Opt. Soc. Am. A: Optics, Image Science, and Vision*, 1986. **3**(11): p. 1780-1788.
122. J. M. Steele, C. E. Moran, A. Lee, C. M. Aguirre, and N. J. Halas, *Metallodielectric gratings with subwavelength slots: Optical properties*. *Phys. Rev. B*, 2003. **68**(20): p. 205103.
123. E. Hecht, *Light Polarization*, in *Optics* 1990, Addison Wesley
124. J. D. Jackson, *Classical Electrodynamics* 1998: Wiley.
125. R. Petit, *Electromagnetic Theory of Gratings* 1980: Springer.
126. W. Knoll, *Interfaces and thin films as seen by bound electromagnetic waves*. *Ann. Rev. Phys. Chem.*, 1998. **49**(1): p. 569-638.
127. J. B. Pendry, D. Schurig, and D. R. Smith, *Controlling electromagnetic fields*. *Science*, 2006. **312**(5781): p. 1780-1782.
128. M. Born, and E. Wolf, *Principles of Optic: Electromagnetic Theory of Propagation, Interference and Diffraction of Light*. 7th ed. *Principles of Optic* 1999: Cambridge University Press.
129. S. Kupratakul, and G. C. Fletcher, *Electron band structure of gold*. *J. Phys. C: Solid State Phys.*, 1969. **2**(10): p. 3.
130. P. Johnson, and R. Christy, *Optical constant of the noble metals*. *Phys. Rev. B*, 1972. **6**(12): p. 10.
131. M. A. Ordal, L. L. Long, R. J. Bell, S. E. Bell, R. R. Bell, R. W. Alexander Jr., and C. A. Ward, *Optical properties of the metals Al, Co, Cu, Au, Fe, Pb, Ni, Pd, Pt, Ag, Ti, and W in the infrared and far infrared*. *Appl. Opt.*, 1983. **22**(7): p. 21.
132. M. Suffczynski, *Optical Constants of Metals*. *Phys. Rev.*, 1960. **117**(3): p. 9.

133. G. P. Bryan-Brown, J. R. Sambles, and M. C. Hutley *Polarisation Conversion through the Excitation of Surface Plasmons on a Metallic Grating* J. Modern Opt., 1990. **37**(7): p. 1227-1232.
134. S. A. Maier, *Plasmonics: fundamental and applications* 2007, New York: Springer.
135. T. A. Kelf, *Light-matter interactions on nano-structured metallic films*, in *Engineering, Science and Mathematics* 2006, University of Southampton: Southampton.
136. M. P. Connolly, and P. Dawson *Optimization of the slow-mode plasmon polariton in light-emitting tunnel junctions* J. Appl. Phys., 1995. **78**(9): p. 5522.
137. P. Dawson, B. A. F. Puygranier and J-P. Goudonnet, *Surface plasmon polariton propagation length: A direct comparison using photon scanning tunneling microscopy and attenuated total reflection*. Phys. Rev. B, 2001. **63**(20): p. 10.
138. B. Rothenhäusler, and W. Knoll, *Total internal diffraction of plasmon surface polaritons*. Appl. Phys. Lett., 1987. **51**(11): p. 783.
139. E. Kretschmann, and H. Raether, *Radiative decay of nonradiative surface plasmons excited by light*. Z. Naturforsch. Teil A, 1963. **23**: p. 2135–2136.
140. E. D. Palik, *Handbook of Optical Constants of Solids*. Vol. 1. 1997, San Diego: Academic Press.
141. A. J. Ward, and J. B. Pendry *Refraction and Geometry in Maxwells Equations*. J. Mod. Opt., 1996. **43**(4): p. 773-793.
142. C. Ropers, C. C. Neacsu, T. Elsaesser, M. Albrecht, M. B. Raschke, and C. Lienau, *Grating-Coupling of Surface Plasmons onto Metallic Tips: A Nanoconfined Light Source*. Nano Lett., 2007. **7**(9): p. 2784-2788.
143. H. Raether, *The dispersion relation of surface plasmons on rough surfaces; a comment on roughness data*. Surf. Sci., 1983. **125**: p. 11.
144. S. C. Kitson, W. L. Barnes, and J. R. Sambles, *Full Photonic Band Gap for Surface Modes in the Visible*. Phys. Rev. Lett., 1996. **77**(13): p. 2670.
145. C. Hu, and D. Liu, *High-performance Grating Coupled Surface Plasmon Resonance Sensor Based on Al-Au Bimetallic Layer*. Mod. Appl. Sci., 2010. **4**(6): p. 6.
146. C. Kuo, J. Shiu, and P. Chen, *Size- and Shape-Controlled Fabrication of Large-Area Periodic Nanopillar Arrays*. Chem. Mater., 2003. **15**: p. 2917.
147. J. S. Shumaker-Parry, H. Rochholz, and M. Kreiter, *Fabrication of Crescent-Shaped Optical Antenna*. Adv. Matter., 2005. **17**(17): p. 2131-2134.
148. A. Pistore, M. Guglielmi, G. Brusatin, H. K. Kang, C. Ferraris and F. Romanato, *Active sol gel thin film on nanostructured plasmonic surface*. Solid State Sci. in press, 2010.
149. Y. Fu, Y. Zeng, E. Berglind, L. Thylen, and H. Agren., *Nanoscale excitonic-plasmonic optical waveguiding by metal-coated quantum dots*. IEEE, 2006. **6**.
150. A. N. Al-Ahmadi, and S. E. Ulloa, *Extended coherent exciton states in quantum dot arrays*. Appl. Phys. Lett., 2006. **88**(4): p. 043110.
151. C. Y. Chang, H. Y. Chang, C. Y. Chen, M. W. Tsai, Y. T. Chang, and S. C. Lee, *Wavelength selective quantum dot infrared photodetector with periodic metal hole arrays*. App. Phys. Lett., 2007. **91**(16): p. 163107.
152. E. M. Yeatman, *Resolution and sensitivity in surface plasmon microscopy and sensing*. Biosensors and bioelectronics 1996. **11**(6-7): p. 148.
153. A. Haes, and R. P. Van Duyne, *A unified view of propagating and localized surface plasmon resonance biosensors* Analytical and Bioanalytical Chemistry,, 2004. **379**(7-8): p. 920-930.
154. K. H. Yoon, M. L. Shuler, and S. J. Kim, *Design optimization of nano-grating surface plasmon resonance sensors*. Optics Express, 2006. **14**: p. 4842.
155. E. Kretschmann, *Determination of optical constants of metals by excitation of surface plasmon sensing*. Sensors and Actuators B, 1996. **35**: p. 212.

156. J. Homola, *Surface Plasmon Resonance Based Sensors*. Chemical Sensors and Biosensors, ed. J. Homola. Vol. 4 2006: Springer
157. J. Homola, *Surface Plasmon Resonance Sensors for Detection of Chemical and Biological Species*. Chem. Rev., 2008. **108**(2): p. 32.
158. D. A. Schultz, *Plasmon Resonant particles for biological detection*. Current Opinion in Biotech, 2003. **14**: p. 13-22.
159. S. G. Nelson, K. S. Johnston and S. S. Yee, *A High sensitivity surface plasmon resonance sensor based on phase detection*. Sens. Actuat. B, 1996. **35**(1-3): p. 5.
160. J. Dostálek, A. Kasry, and W. Knoll, *Long range surface plasmons for observation of biomolecular binding events at metallic surfaces*. Plasmonics, 2007. **2**(3): p. 97-106.
161. K. A. Willets, and R. P. Van Duyne, *Localized Surface Plasmon Resonance Spectroscopy and Sensing*. Annu. Rev. Phys. Chem., 2007. **58**: p. 267-297
162. R. Karlsson, and R. Stahlberg, *Surface Plasmon Resonance Detection and Multispot Sensing for Direct Monitoring of Interactions Involving Low-Molecular-Weight Analytes and for Determination of Low Affinities* Analyt. Biochem. **228**(2): p. 274-280.
163. A. Kasry, and W. Knoll, *Long range surface plasmon fluorescence spectroscopy*. Appl. Phys. Lett., 2006. **89**(10): p. 101106.
164. <http://www.biacore.com/lifesciences/index.html>.
165. <http://www.xantech.com>.
166. <http://www.metrohm-autolab.com/Products/SPR/>.
167. http://www.biosensingusa.com/biosensing_instrument_review.html.
168. T. M. Chinowsky, J. G. Quinn, D. U. Bartholomew, R. Kaiser, and J. L. Elkind, *Performance of the Spreeta 2000 integrated surface plasmon resonance affinity sensor*. Sens. Actuat. B, 2003. **91**(1-3): p. 9.
169. http://www.optrel.de/products_multiskop.html.
170. <http://www.kmac.to/eng/products.php?cid=sprlab>.
171. <https://www.thermoscientific.com/wps/portal/ts/products/detail?productId=12706119&groupType=PRODUCT&searchType=0>.
172. http://www.labmate-online.com/news/laboratory-products/3/reichert_inc/leaders_in_spr_systems_and_refractometers/9827/.
173. <http://www.reichertspr.com/products.html>.
174. <http://www.ibis-spr.nl/>.
175. <http://www.plasmonic.de>.
176. <http://www.gwcinstruments.com/gwcSPRImager.htm>.
177. <http://www.nanofilm.de/application-package-SPR>.
178. http://www.dkktoa.net/spr_20.pdf.
179. <http://www.biosuplar.com/index.htm>.
180. <http://www.genoptics-spr.com/content.php?idcontent=sprplex2&lg=en>.
181. http://www.sierrasensors.com/index.php?option=com_content&task=view&id=68&Itemid=102.
182. K. Matsubara, S. Kawata, and S. Minami, *A compact surface plasmon resonance sensor for measurement of water in process*. Appl. Spectrosc., 1988. **42**: p. 5.
183. H. Q. Zhang, S. Boussaad, and N. J. Tao, *High-performance differential surface plasmon resonance sensor using quadrant cell photodetector*. Rev. Sci. Instrum., 2002. **74**(1): p. 4.
184. C. T. Campbell, and G. Kim, *SPR microscopy and its applications to high-throughput analyses of biomolecular binding events and their kinetics* Biomat., 2007. **28**(15): p. 13.

185. M. Piliarik, L. Párová, and J. Homola, *Towards parallelized surface plasmon resonance sensor platform for sensitive detection of oligonucleotides* Sens. Actuat. B, 2007. **121**(1): p. 7.
186. G. G. Nenninger, M. Piliarik, and J. Homola, *Data analysis for optical sensors based on spectroscopy of surface plasmons*. Meas. Sci. Tech., 2002. **13**(12): p. 9.
187. J. Homola, H. B. Lu, and S. S. Yee,, *Dual-channel surface plasmon resonance sensor with spectral discrimination of sensing channels using dielectric overlayer*. Electron. Lett., 1999. **35**: p. 2.
188. J. Guo, P. D. Keathley, and J.T. Hastings, *Dual-mode surface-plasmon-resonance sensors using angular interrogation*. . Opt. Lett., 2008. **33**: p. 3.
189. H. Kawazumi, K. V. Gobib, K. Oginoc, H. Maeda, and N. Miurab, *Compact surface plasmon resonance (SPR) immunosensor using multichannel for simultaneous detection of small molecule compounds* Sens. Actuat. B, 2005. **108**(1-2): p. 7.
190. T. M. Chinowsky, J. G. Quinn, D. U. Bartholomew, R. Kaiserc, and J. L. Elkindb, *Performance of the Spreeta 2000 integrated surface plasmon resonance affinity sensor*. Sens. Actuat. B, 2003. **91**(1-3): p. 9.
191. J. Melendez, R. Carr, D. U. Bartholomew, K. Kukanskis, J. Elkind, S. Yee, C. Furlong, and R. Woodbury, *A commercial solution for surface plasmon sensing*. Sens. Actuat. B, 1996. **35**: p. 5.
192. J. Melendez, R. Carr, D. U. Bartholomew, H. Taneja, S. Yee, C. Jung, and C. Furlong,, *Development of a surface plasmon resonance sensor for commercial applications*. Sens. Actuat. B, 1997. **38-39**: p. 5.
193. W. Lukosz, and K. Tiefenthaler, *Embossing technique for fabricating integrated optical components in hard organic waveguiding materials*. Opt.Lett., 1983. **8**: p. 3.
194. H. Raether, *Surface Plasmon on Rough Surfaces*. Il Nuovo Cimento B., 1977. **39B**(2): p. 6.
195. H. C. Pedersen, W. Y. Zong, M. H. Sorensen, and C. Thistrup, *Integrated holographic grating chip for surface plasmon resonance sensing*. Opt. Eng., 2004. **43**(11): p. 6.
196. D. C. Cullen, and C. R. Lowe, *A direct surface plasmon-polariton immunosensor: Preliminary investigation of the non-specific adsorption of serum components to the sensor interface*. Sens. Actuat. B, 1990. **1**(1-6): p. 4.
197. M. Piliarik, H. Vaisocherová, and J. Homola, *A new surface plasmon resonance sensor for high-throughput screening applications* Biosens. and Bioelec., 2004. **20**(10): p. 7.
198. O. Telezhnikova, and J. Homola *New approach to spectroscopy of surface plasmons*. Opt. Lett., 2006. **31**(22): p. 3.
199. M. Piliarika, M. Valaa, I. Tichýa, and J. Homola, *Compact and low-cost biosensor based on novel approach to spectroscopy of surface plasmons*. Biosens. and Bioelec., 2009. **24**(12): p. 6.
200. Y. H. Cho, and Y. H. Jin, *SPR Sensor Chips with Polymer Nanogratings*. Surf. Sci. Nanotech., 2009. **7**: p. 7.
201. D. Cai, Y. Lu, K. Lin, P. Wang, and H. Ming, *Improving the sensitivity of SPR sensors based on gratings by double-dips method (DDM)*. Opt. Express, 2008. **16**: p. 5.
202. W. Kubo, and S. Fujikawa, *Au Double Nanopillars with Nanogap for Plasmonic Sensor*. Nano Lett., 2010. **Article ASAP**.
203. J. Becker, A. Truegler, A. Jakab, U. Hohenester and C. Soennichsen, *The Optimal Aspect Ratio of Gold Nanorods for Plasmonic Bio-sensing* Plasmonics, 2010. **5**(2): p. 7.
204. N. Liu, M. Mesch, R. Weiss, M. Hentschel and H. Giessen, *Infrared Perfect Absorber and Its Application As Plasmonic Sensor*. Nano Lett., 2010. **10**(7): p. 7.
205. H. Gao, J. C. Yang, J. Y. Lin, A. D. Stuparu, M. H. Lee, M. Mrksich and T. W. Odom *Using the Angle-Dependent Resonances of Molded Plasmonic Crystals to Improve The Sensitivity of Biosensors*. Nano Lett., 2010. **10**(7): p. 6.
206. Y. Pang, C. Genent and T. W. Ebbesen, *Optical transmission through subwavelength slit apertures in metallic films* Opt. Comm., 2007. **280**(1): p. 6.
207. D. E. Grupp, H. J. Lezec, T. W. Ebbesen, K. M. Pellerin, and Tineke Thioa, *Crucial role of metal surface in enhanced transmission through subwavelength apertures*. Appl. Phys. Lett., 2000. **77**(11): p. 1569.

208. F. Miyamaru, S. Hayashi, C. Otani, K. Kawase, Y. Ogawa and H. Hoshida, *Terahertz surface-wave resonant sensor with a metal hole array*. Opt. Lett., 2006. **31**(8): p. 3.
209. A. G. Brolo, R. Gordon, B. Leathem, and K. L. Kavanagh, *Surface Plasmon Sensor Based on the Enhanced Light Transmission through Arrays of Nanoholes in Gold Films*. Langmuir, 2004. **20**: p. 3.
210. K. M. Byun, S. J. Kim, and D. Kim, *Grating-coupled transmission-type surface plasmon resonance sensors based on dielectric and metallic gratings*. Appl. Opt., 2007. **46**: p. 6.
211. A. A. Yanik, M. Huang, O. Kamohara, A. Artar, T. Geisbert, J. H. Connor and H. Altug, *An Optofluidic Nanoplasmonic Biosensor for Direct Detection of Live Viruses from Biological Media*. Nano Lett., 2010. **10**(12): p. 8.
212. N. Liu, T. Weiss, M. Mesch, L. Langguth, U. Eigenthaler, M. Hirscher, C. Sonnichsen and H. Giessen, *Planar Metamaterial Analogue of Electromagnetically Induced Transparency for Plasmonic Sensing*. Nano Lett., 2010. **10**(4): p. 5.
213. F. Abelès, *Surface electromagnetic waves ellipsometry*. Surf. Sci. , 1976. **56**: p. 15.
214. X. Yu, D. Wang, X. Wei, X. Ding, W. Liao, and X. Zhao, *A surface plasmon resonance imaging interferometry for protein micro-array detection*. Sens. Actuat. B, 2005. **108**: p. 7.
215. P. P. Markowicz, W. C. Law, A. Baev, P. N. Prasad, S. Patskovsky, and A. Kabashin, *Phase-sensitive time-modulated surface plasmon resonance polarimetry for wide dynamic range biosensing*. Opt. Express, 2007. **15**: p. 10.
216. S. Y. Wu, L. C. M. Wu, H. P. Ho and C. Lin. *A differential measurement approach for improving surface plasmon resonance phase sensing performance*. in *The Sixth Chinese Optoelectronics Symposium*. 2003. IEEE
217. H. P. Chiang, H. T. Yeh, C. M. Chen, J. C. Wu, S. Y. Su, R. Chang, Y. J. Wu, D. P. Tsai, S. U. Jen, and P. T. Leung, *Surface plasmon resonance monitoring of temperature via phase measurement*. Opt. Comm., 2004. **241**(4-6): p. 10.
218. J. V. Gent, P. V. Lambeck, H. J. M. Kreuwel, G. J. Gerritsma, E. J. R. Sudhölter, D. N. Reinhoudt, and T. J. A. Popma, *Optimization of a chemooptical surface plasmon resonance based sensor*. Appl. Opt. , 1990. **29**(19): p. 7.
219. R.C. Jorgenson, and S.S. Yee, *A fiber-optic chemical sensor based on surface plasmon resonance*. Sens. Actuat. B, 1993. **12**: p. 8.
220. J. Homola, *Optical fiber sensor based on surface plasmon resonance excitation*. Sens. Actuat. B, 1995. **29**: p. 5.
221. R. Slavík, J. Homola, and J. Čtyroký, *Single-mode optical fiber surface plasmon resonance sensor*. Sens. Actuat. B, 1999. **54**: p. 6.
222. C. Rashleigh, *Origins and control of polarization effects in single mode fibers*. J. Lightwave Technol., 1983. **LT-1**: p. 20.
223. R. Slavík, J. Homola, J. Čtyroký, and E. Brynda, *Novel spectral fiber optic sensor based on surface plasmon resonance*. Sens. Actuat. B, 2001. **74**(1-3): p. 6.
224. M. Piliarik, J. Homola, Z. Manikova, and J. Čtyroký, *Surface plasmon resonance based on a polarization-maintaining optical fiber*,. Sens. Actuat. B, 2003. **90**: p. 7.
225. M. H. Chiu, S. F. Wang, and R. S. Chang, *D-type fiber biosensor based on surface-plasmon resonance technology and heterodyne interferometry*. Opt. Lett., 2005. **30**(3): p. 3.
226. H. Y. Lin, Y. C. Tsao, W. H. Tsai, Y. W. Yang, T. R. Yan, and. B. C. Sheu, *Development and application of side-polished fiber immunosensor based on surface plasmon resonance for the detection of legionella pneumophila with halogens light and 850 nm-LED*. Sens. Actuat. B, 2007. **A138**: p. 7.
227. J. Dostálek, J. Čtyroký, J. Homola, E. Brynda, M. Skalský, P. Nekvindová, J. Špírková, J. Škvor, and J. Schröfel, *Surface plasmon resonance biosensor based on integrated optical waveguide*. Sens. Actuat. B, 2001. **76**: p. 4.
228. Y. Kim, W. Peng, S. Banerji, and K. S. Booksh, *Fiber-optic surface plasmon resonance for vapor phase analyses*. Opt. Lett. , 2005. **30**: p. 3.

229. L. J. Sherry, R. Jin, C. A. Mirkin, G. C. Schatz, and R. P. Van Duyne, *Localized Surface Plasmon Resonance Spectroscopy of Single Silver Triangular Nanoprisms*. Nano Lett., 2006. **6**(9): p. 2060-2065.
230. W. Hui, D. W. Brandl, L. Fei, P. Nordlander, and N. J. Halas, *Nanorice: A Hybrid Plasmonic Nanostructure*. Nano Lett., 2006. **6**(4): p. 6.
231. J. B. Lassiter, H. Sobhani, J. A. Fan, J. Kundu, F. Capasso, P. Nordlander, N. J. Halas, *Fano Resonances in Plasmonic Nanoclusters: Geometrical and Chemical Tunability*. Nano Lett., 2010. **10**(8): p. 6.
232. M. Svedendahl, S. Chen, A. Dmitriev and M. Käll, *Refractometric Sensing using Propagating versus Localized Surface Plasmons: A Direct Comparison*. Nano Lett., 2009. **9**(12): p. 6.
233. H. C. Guo, D. Nau, A. Radke, X. P. Zhang, J. Stodolka, X. L. Yang, S. G. Tikhodeev, N. A. Gippius, and H. Giessen, *Large-area metallic photonic crystal fabrication with interference lithography and dry etching*. App. Phys. B, 2005. **81**(2-3): p. 271-275.
234. T. B. O'Reilly, and H. I. Smith, *Linewidth uniformity in Lloyd's mirror interference lithography systems*. J. Vac. Sci. Technol. B, 2008. **26**(6): p. 2131-2134
235. S. Y. Chou, P. R. Krauss, and P. J. Renstrom, *Nanoimprint lithography*. J. Vac. Sci. Technol. B, 1996. **14**(6): p. 4129.
236. H. Tan, A. Gilbertson, S. Y. Chou, P. R. Krauss, and P. J. Renstrom, *Roller nanoimprint lithography*. J. Vac. Sci. Technol. B, 1998. **16**(6): p. 3926.
237. R. Pelzer, C. Gourgon, S. Landis, and P. Kettner. *Nanoimprint Lithography - Full Wafer Replication of Nanometer Features*. in *Micro- and Nanotechnology: Materials, Processes, Packaging, and Systems II*. 2005. Bellingham, WA: SPIE.
238. B. Wang, W. Zhao, A. Chen, and S. J. Chua, *Formation of nanoimprinting mould through use of nanosphere lithography*. J. Cryst. Growth, 2006. **228**: p. 200-204.
239. W. Wu, E. Kim, E. Ponizovskaya, Y. Liu, Z. Yu, N. Fang, Y. R. Shen, A. M. Bratkovsky, W. Tong, C. Sun, X. Zhang, S. Y. Wang, and R. S. Williams, *Optical metamaterials at near and mid-IR range fabricated by nanoimprint lithography* Appl. Phys. A, 2007. **87**(2): p. 143-150.
240. Y. Fan, A. Bourov, L. Zavvalova, J. Zhou, A. Estroff, N. Lafferty, and B. W. Smith. *ILSim – A compact simulation tool for interferometric lithography*. in *Optical Microlithography XVIII*. 2005. SPIE.
241. J. Boor, N. Geyer, U. Gösele, and V. Schmidt *Three-beam interference lithography: upgrading a Lloyd's interferometer for single-exposure hexagonal patterning*. Optics Lett., 2009. **34**(12): p. 3.
242. M. Sugawara, *Plasma Etching Fundamentals and Applications* 1998: Oxford University Press.
243. M. A. Lieberman, and A. J. Lichtenberg,, *Principles of Plasma Discharges and Materials Processing* 1994: Wiley.
244. Y. Xia, and G. M. Whitesides, *Soft Lithography*. Angew. Chem. Int. Ed., 1998. **37**: p. 550-575.
245. http://www.microresist.de/products/ormocers/ormostamp_en.htm.
246. J. Lin, and C. W. Brown, *Sol-gel glass as a matrix for chemical and biochemical sensing* TrAC Trends in Analytical Chemistry, 1997. **16**(4): p. 200-211
247. R. Yamada, and K. Uosaki, *In Situ, Real Time Monitoring of the Self-Assembly Process of Decanethiol on Au(111) in Liquid Phase. A Scanning Tunneling Microscopy Investigation*. Langmuir, 1997. **13**(20): p. 4.
248. R. Yamada, H. Wano, and K. Uosaki, *Effect of Temperature on Structure of the Self-Assembled Monolayer of Decanethiol on Au(111) Surface*. Langmuir, 2000. **16**(13): p. 3.
249. D. Fischer, A. Curioni, and W. Andreoni, *Decanethiols on Gold: The Structure of Self-Assembled Monolayers Unraveled with Computer Simulations*. Langmuir, 2003. **19**(9): p. 5.
250. D. K. Schwartz, *Mechanism and Kinetics of Self Assembled Monolayer Formation*. Annu. Rev. Phys. Chem, 2001. **52**(1): p. 31.
251. S. M. Mendoza, *Exploiting molecular machines on surfaces*, in *Faculty of Mathematics and Natural Sciences* 2007, University of Groningen: Groningen.
252. B. E. A. Saleh, and M. C. Teich, *Fundamentals of photonics*. Pure and applied optics, ed. B.E.A. Saleh 2007: Wiley-Interscience.

253. G. Granet, *Analysis of diffraction by surface-relief crossed gratings with use of the Chandezon method: application to multilayer crossed gratings*. J. Opt. Soc. Am. A, 1998. **15**(5): p. 11.
254. J. Chandezon, M. T. Dupuis, G. Cornet and D. Maystre, *Multicoated gratings: a differential formalism applicable in entire optical region*. J. Opt. Soc. Am., 1982. **72**(2): p. 8.
255. J. Chandezon, G. Raoult and D. Maystre, *A new theoretical method for diffraction gratings and its numerical application*. J. Opt. , 1980. **11**(4): p. 235-241
256. F. J. Garcia-Vidal, and L. Martín-Moreno, *Transmission and focusing of light in one-dimensional periodically nanostructured metals*. Phys. Rev. B., 2002. **66**(15): p. 10.
257. S. Yuferev, and N. Ida, *Surface Impedance Boundary Condition: A Comprehensive Approach*, ed. T.a.F. Group 2009, Boca Raton: CRC Press.
258. <http://www.lumerical.com/fdtd.php>.
259. *Finite Elements Frequency Domain code COMSOL Multiphysics*
260. K. S. Yee, *Numerical solution of initial boundary value problems involving Maxwell's equations in isotropic media*. IEEE Trans. Ant. Propag., 1966. **14**(3): p. 6.
261. J.A. Woollam Co., I., *Spectroscopic Ellipsometry - Data Acquisition and Analysis in A Guide to use WVASE 322006*.
262. J. V. Coe, J. M. Heer, S. Teeters-Kennedy, T. Hong, and K. R. Rodriguez, *Extra ordinary Transmission of Metal Films with Arrays of Subwavelength Holes*. Annu. Rev. Phys. Chem, 2008. **59**(1): p. 24.
263. J. B. Pendry, D. Schurig, and D. R. Smith, *Controlling Electromagnetic Fields*. Science, 2006. **312**(5781): p. 1780 - 1782.
264. P. T. Worthing, and W. L. Barnes, *Coupling efficiency of surface plasmon polaritons to radiation using a corrugated surface; angular dependence*. J. of Mod. Opt., 2002. **49**(9): p. 10.
265. <http://www.wolfram.com/mathematica/>.
266. A. Nemetz, and W. Knoll *Raman Spectroscopy and Microscopy with Plasmon Surface Polaritons* J. Raman Spectros., 1998. **27**(8): p. 587-592.
267. R. A. Watts, J. R. Sambles, and M. C. Hutley, *Optical characterization of a complex grating profile*. J. of Mod. Opt., 1998. **45**(3): p. 13.
268. W. C. Liu, *High sensitivity of surface plasmon weakly-distorted metallic surfaces*. Opt. Express, 2005. **13**(24): p. 8.
269. R. A. Watts, A. P. Hibbins, and J. R. Sambles, *The influence of grating profile on surface plasmon polariton resonance recorded in different diffracted orders*. J. of Mod. Opt., 1999. **46**(15): p. 30.
270. L. Li, J. Chandezon, G. Granet, and J. P. Plumey, *Rigorous and Efficient Grating-Analysis Method Made Easy for Optical Engineers*. Appl. Opt., 1999. **38**(2): p. 10.
271. E. Kretschmann, *The angular dependence and the polarisation of light emitted by surface plasmon on metals due to roughness*. Opt. Comm., 1972. **5**(5): p. 6.
272. Pockrand, I., *Coupling of surface plasma oscillations in thin periodically corrugated silver films*. Opt. Comm., 1975. **13**(3): p. 3.
273. W. Cai, U. K. Chettiar., A. V. Kildishev, and V. M. Shalaev, *Optical cloaking with metamaterials*. Nature Photonics, 2007. **1**: p. 224-227
274. V. M. Shalaev, *Optical negative-index metamaterials*. Nat. Photonics, 2006. **1**(1): p. 41-48.
275. F. J. Garcia-Vidal, L. Martín-Moreno, and J. B. Pendry, *Surfaces with holes in them: new plasmonic metamaterials*. J. Opt. A: Pure Appl. Opt, 2005. **7**(2): p. S97-S101
276. I. I. Smolyaninov, *Two-dimensional plasmonic metamaterials*. Appl. Phys. A, 2007. **87**(2): p. 227-234.
277. R. Jin, Y. Cao, C. A. Mirkin, K. L. Kelly, G. C. Schatz, and J. G. Zheng, *Photoinduced Conversion of Silver Nanospheres to Nanoprisms* Science, 2001. **294**(5548): p. 1901-1903.
278. J. J. Mock, D. R. Smith, and S. Schultz *Local Refractive Index Dependence of Plasmon Resonance Spectra from Individual Nanoparticles* Nano Lett., 2003. **3**(4): p. 485-491.

279. J. Nelayah, M. Kociak, O. Stéphan, F.J. Garcia de Abajo, M. Tencé, L. Henrard, D. Taverna, I. Pastoriza-Santos, L.M. Liz-Marzan, C. Colliex, *Mapping surface plasmons on a single metallic nanoparticle*. Nature Phys., 2007. **3**: p. 348-353.
280. L. Yin, V. K. Vlasko-Vlasov, J. Pearson, J. M. Hiller, J. Hua, U. Welp, D. E. Brown, and C. W. Kimball, *Subwavelength Focusing and Guiding of Surface Plasmons*. Nano Lett., 2005(5): p. 1399-1402.
281. D. B. Shao, and S. C. Chen, *Direct Patterning of Three-Dimensional Periodic Nanostructures by Surface-Plasmon-Assisted Nanolithography*. Nano Lett., 2006. **6**(10): p. 5.
282. T. Inagaki, J.P. Goundonnet, J. W. Little, and E. T. Arakawa, *Photoacoustic study of plasmon-resonance absorption in bigrating*. J. Opt. Soc. Am. B, 1984. **2**(3): p. 7.
283. N. E. Glass, A. A. Maradudin, and V. Celli, *Theory of surface-polariton resonance and field enhancement in light scattering from bigratings* J. Opt. Soc. Am., 1983. **73**(10): p. 9.
284. K. H. Yoon, M. L. Shuler and S. J. Kim, *Design optimization of nano-grating surface plasmon resonance sensors*. Opt. Express, 2006. **14**(11): p. 8.
285. J. M. Brockman, a.S.M.F., *Grating-coupled surface plasmon resonance for rapid, label-free, array based sensing*. Am. Lab., 2001. **33**: p. 4.
286. A. V. Kats, and I. S. Spevak, *Analytical theory of resonance diffraction and transformation of light polarization*. Phys. Rev. B., 2002. **65**(19): p. 195406.
287. M. Kreiter, S. Mittler, W. Knoll, and J. R. Sambles *Surface plasmon-related resonances on deep and asymmetric gold gratings*. Phys. Rev. B, 2002. **65**(12): p. 13.
288. I. R. Hooper, and J. R. Sambles, *Dispersion of surface plasmon polaritons on short-pitch metal gratings*. Phys. Rev. B, 2002. **65**(16): p. 9.
289. H. F. Ghaemi, T. Thio, D. E. Grupp, T. W. Ebbesen, and H. J. Lezec, *Surface plasmons enhance optical transmission through subwavelength holes*. Phys. Rev. B, 1998. **58**(11): p. 6779.
290. K. L. van der Molen, F. B. Segerink, N. F. van Hulst, and L. Kuipers, *Influence of hole size on the extraordinary transmission through subwavelength hole arrays*. Appl. Phys. Lett., 2004. **85**(19): p. 4316.
291. C. Genet, and T.W. Ebbesen *Light in Tiny Holes*. Nature, 2007. **445**(7123): p. 8.
292. K. Busch, G. von Freymann, S. Linden, S. F. Mingaleev, L. Tkeshelashvili, and M. Wegener, *Periodic Nanostructures for Photonics*. Phys. Report, 2007. **444**(3-6): p. 101.
293. D. Crouse, and P. Keshavareddy, *Polarization independent enhanced optical transmission in one-dimensional gratings and device applications*. Opt. Express, 2007. **15**(4): p. 12.
294. P. Lalanne, J. P. Hugonin, and J. C. Rodier *Theory of Surface Plasmon Generation at Nanoslit Apertures*. Phys. Rev. Lett., 2005. **95**(26): p. 4.
295. S. A. Darmanyan, and A. V. Zayats, *Light tunneling via resonant surface plasmon polariton states and the enhanced transmission of periodically nanostructured metal films: An analytical study*. Phys. Rev. B, 2003. **67**(3): p. 035424.
296. N. P. Johnson, A. Z. Khokhar, H. M. Chong, R. M. D. L. Rue, T. J. Antosiewicz, and S. McMeekin, *A Review of Size and Geometrical Factors Influencing Resonant Frequencies in Metamaterials*. Opto-Electronics Review, 2006. **14**(3): p. 187-191.
297. S. Collin, F. Pardo, R. Teissier and J. L. Pelouard *Horizontal and vertical surface resonances in transmission metallic gratings*. J. of Opt. A, 2002. **4**(5).
298. J. W. Lee, M. Seo, K. S. Khim, D. S. Kim, S. C. Jeung, J. H. Kang and Q. Park *Transmission Resonances by Combined Effects of Fabry-Perot and Surface Plasmons in the THz Region of Metallic Gratings in Microwave Photonics*, 2005. 2005. IEEE.
299. L. Cai, G. Li, Z. Wang, and A. Xu *Interference and horizontal Fabry-Perot resonance on extraordinary transmission through a metallic nanoslit surrounded by grooves*. Opt. Lett. , 2010. **35**(2): p. 3.
300. Z. B. Li, Y. H. Yang, X. T. Kong, W. Y. Zhou and J. G. Tian, *Fabry-Perot resonance in slit and grooves to enhance the transmission through a single subwavelength slit* J. of Opt. A, 2009. **11**(10): p. 4.

301. J. W. Lee, M. A. Seo, D. J. Park, S. C. Jeoung, Q. H. Park, Ch. Lienau, and D. S. Kim *Terahertz transparency at Fabry-Perot resonances of periodic slit arrays in a metal plate: experiment and theory*. Opt. Express, 2006. **14**(26): p. 7.
302. H. J. Lezec, and T. Thio, *Diffraction evanescent wave model for enhanced and suppressed optical transmission through subwavelength hole arrays*. Optics Express, 2004. **12**(16): p. 3629.
303. <http://chemicaland21.com/specialtychem/finechem/3-MERCAPTOPROPIONIC%20ACID.htm>.
304. K. L. Lee, C. W. Lee, W. S. Wang and P. K. Wei, *Sensitive biosensor array using surface plasmon resonance on metallic nanoslits*. J. of Biomed. Opt., 2007. **12**(4): p. 5.
305. S. Zhu, and W. Zhou, *Sensitivity of Triangular Hybrid Au-Ag Nanostructure Array*. J. of Comp.Theoretic. Nanosci., 2010. **7**(8): p. 4.
306. K. L. Lee, W. S. Wang and P. K. Wei, *Comparisons of Surface Plasmon Sensitivities in Periodic Gold Nanostructures* Plasmonics, 2008. **3**(4): p. 7.
307. X. Zhang, and Z. Liu, *Superlenses to overcome the diffraction limit*. Nat. Mater., 2008. **7**: p. 7.
308. P. C. A. Jerónimo, A. N. Araújo, and M. C. B. S. M. Montenegro, *Optical sensors and biosensors based on sol-gel films* Talanta, 2006. **72**(1): p. 13-27
309. H. Xie, J. Wei and X. Zhang, *Characterisation of Sol-gel Thin Films by Spectroscopic Ellipsometry*. J. Phys., 2006. **28**(1): p. 95-99.
310. Z. W. He, C. M. Zhen, X. Q. Liu, W. Lan, D. Y. Xu, and Y. Y. Wang, *Microstructural characterization of low dielectric silica xerogel film*. Thin Solid Film, 2004. **462-463**(5): p. 168-171.
311. A. Pistore, M. Guglielmi, G. Brusatin, H. K. Kang, C. Ferraris and F. Romanato, *Active sol gel thin film on nanostructured plasmonic surface*. Solid State Sci., 2010. **12**(11): p. 5.
312. K. Lin, Y. Lu, J. Chen, R. Zheng, P. Wang and H. Ming, *Surface plasmon resonance hydrogen sensor based on metallic grating with high sensitivity*. Opt. Express, 2008(16): p. 6.
313. G. Ruffato, *Surface Plasmon Polaritons on 1D-Gratings*, in *Department of Physics*, 2008, University of Padova: Padova
314. K. H. Lee, H. K. Kang, F. Romanato and C. C. Wong *Polarization optimization for a full sensitivity in azimuthal grating coupled surface plasmon resonance*. Sens. Actuat. B, 2010. **148**(1): p. 5.
315. F. Romanato, K. H. Lee, H. K. Kang, G. Ruffato, and C. C. Wong, *Sensitivity Enhancement in Grating-Coupled Surface Plasmon Resonance by Azimuthal Control*. Opt. Exp., 2009. **17**: p. 4.
316. <http://www.originlab.com/index.aspx?go=Products/Origin/DataAnalysis/BatchProcessing&pid=57>.
317. <http://hyperphysics.phy-astr.gsu.edu/HBASE/math/gaufcn.html>.
318. K. H. Lee, *Double Surface Plasmon Polaritons (SPPs) for Sensing Purposes*, School of Materials Engineering, 2011, Nanyang Technological University: Singapore.
319. A. H. Nicol, *Grating coupled Surface Plasmon Enhanced Fluorescence Spectroscopy*, Departement of Chemistry and Pharmacy, 2005, University of Mainz: Mainz.
320. L. Li, *Multilayer-coated diffraction gratings: differential method of Chandezon et al. revisited*. J. Opt. Soc. Am. A, 1994. **11**(11): p. 13.
321. F. Romanato, H. K. Kang, K. H. Lee, G. Ruffato, M. Prasciolu, C. C. Wong, *Interferential lithography of 1D thin metallic sinusoidal gratings*, Micro. Elec. Eng., 2009. **86**: p. 573.
322. H. K. Kang, K. H. Lee, Y. L. Wu and C. C. Wong, *The role of Polarization on 2D Plasmonic Crystal*, Plasmonics, 2011. **6**: p. 373.