Metal nanostructures for enhanced optical functionalities: Surface enhanced Raman spectroscopy and Photonic integration

by

Min Qiao
B.Sc., Lanzhou University, 2004
M.Sc., Lanzhou University, 2007

A Dissertation Submitted in Partial Fulfillment
of the Requirements for the Degree of

DOCTOR OF PHILOSOPHY

in the Department of Electrical and Computer Engineering

© Min Qiao, 2011
University of Victoria

All rights reserved. This thesis may not be reproduced in whole or in part, by photocopy or other means, without the permission of the author.
Supervisory Committee

Metal nanostructures for enhanced optical functionalities: Surface enhanced Raman spectroscopy and Photonic integration

by

Min Qiao
B.Sc., Lanzhou University, 2004
M.Sc., Lanzhou University, 2007

Supervisory Committee

Supervisor
Dr. Reuven Gordon, (Department of Electrical and Computer Engineering)

Departmental Member
Dr. Tao Lu, (Department of Electrical and Computer Engineering)

Outside Member
Dr. Alexandre Brolo, (Department of Chemistry)
Abstract

Supervisory Committee

Supervisor
Dr. Reuven Gordon, (Department of Electrical and Computer Engineering)

Departmental Member
Dr. Tao Lu, (Department of Electrical and Computer Engineering)

Outside Member
Dr. Alexandre Brolo, (Department of Chemistry)

As the developments in nanoscale fabrication and characterization technology, the investigation and applications of light in metal nanostructures have been becoming one of the most focused research areas. Metal materials allow to couple the incident light energy into electromagnetic waves propagating on the metal surface under certain configurations, which is called surface plasmon (SP). This feature tremendously expanded the application possibility of metals in optical regime, such as extraordinary transmission (EOT), near-field optics and surface enhanced spectroscopies. In this talk, various metal structures will be demonstrated which could control SP’s propagation, resonance and local field enhancement. A number of SP applications are benefited – the plasmonic bragg reflector (PBR), the frequency sensitive plasmonic microcavity, the subwavelength metallic taper, the long range surface plasmon (LRSP) waveguide and surface enhanced Raman spectroscopy (SERS). Especially for SERS, long-term effort was devoted into it to achieve the single molecule detection limit.
# Table of Contents

Supervisory Committee ............................................................................................................... ii
Abstract ........................................................................................................................................ iii
Table of Contents ....................................................................................................................... iv
List of Tables ............................................................................................................................. vi
List of Figures ........................................................................................................................... vii
Acknowledgments .................................................................................................................... xi
Chapter 1 Introduction .............................................................................................................. 1
Chapter 2 Background theory ................................................................................................. 4
  2.1 Surface plasmons ............................................................................................................ 4
      2.1.1 Dielectrics and conductors ............................................................................... 5
      2.1.2 Surface plasmon formation from Maxwell equations .................................... 7
      2.1.3 Excitation of surface plasmon ........................................................................ 10
  2.2 Extraordinary transmission ....................................................................................... 12
  2.3 Transmission matrix method..................................................................................... 14
      Application: Bragg reflectors .................................................................................... 17
  2.4 Surface enhanced Raman spectroscopy .................................................................. 19
      2.4.1 Raman spectroscopy ....................................................................................... 19
      2.4.2 Localized surface plasmon resonance ......................................................... 21
      2.4.3 SERS ............................................................................................................... 23
Chapter 3 Surface plasmon Bragg reflector ........................................................................... 25
  3.1 Focused ion beam (FIB) fabrication ........................................................................... 27
  3.2 Transmission measurement setup ............................................................................. 28
  3.3 Characterization of PBR layers ................................................................................. 29
      3.3.1 Variation in Depth of PBR Layers ................................................................. 29
      3.3.2 Variation in Number of Holes and Number of PBRs .................................. 31
      3.3.3 Discussion of Variation in Line Number and Depth ................................. 33
  3.4 Isolation using PBRs ................................................................................................. 36
      3.4.1 PBRs to Prevent Interference between Two Adjacent Nanohole Arrays .... 36
      3.4.2 PBRs for Blocking SPPs Launched from Dimple Array ............................ 37
      3.4.3 PBRs for Uniform Spectral Emission over a Superarray ....................... 39
  3.5 Summary ...................................................................................................................... 41
Chapter 4 Frequency sensitive plasmonic microcavity .......................................................... 42
  4.1 Experimental and calculation methods ..................................................................... 43
  4.2 Results and discussion ............................................................................................... 45
  4.3 Summary ...................................................................................................................... 51
Chapter 5 Subwavelength metallic taper ................................................................................. 53
  5.1 The SMM method in 2D ............................................................................................. 54
      5.1.1 Structure and Gap Mode Description ......................................................... 54
      5.1.2 Method .......................................................................................................... 55
      5.1.3 Results .......................................................................................................... 58
5.2 The SMM method in 3D

5.2.1 Structure and Gap Mode Description

5.2.2 Method

5.2.3 Results

5.3 Discussion

5.4 Summary

Chapter 6 Asymmetric long range surface plasmon waveguide

6.1 LRSP along an IMII slab structure (1D)

6.1.1 Geometry of the IMII slab waveguide

6.1.2 Theoretical model of the IMII: restored LRSP symmetry in the metal

6.1.3 Computations using the transfer matrix method

6.1.4 Comparison with TE and TM dielectric waveguide modes

6.2 LRSP along an IMII stripe structure (2D)

6.2.1 Geometry of the IMII stripe waveguide

6.2.2 Finite difference results

6.3 Summary

Chapter 7 Surface enhanced Raman spectroscopy: 2D substrate

7.1 Experimental and calculation methods

7.2 Results and discussion

7.3 Summary

Chapter 8 Surface enhanced Raman spectroscopy: 3D substrate

8.1 SERS measurement with multilayer substrates

8.1.1 SERS experimental setup

8.1.2 Extinction spectrum of silver nano-prisms

8.1.3 Theoretical calculation on phase reflection

8.1.4 SERS measurement results

8.2 FDTD simulation results

8.3 Discussion

8.4 Summary

Chapter 9 Conclusions and outlook
List of Tables

Table 6.1 Comparison of modal quantities for the LRSP supported by the IMII of interest (H$_2$O - Au - SiO$_2$ - air at 1310 nm), and by the corresponding IMI (H$_2$O-Au-H$_2$O), for the two metal slab thicknesses............................................................. 81
List of Figures

Figure 2.1 Permittivities of gold (left) and SiO₂ (right) at different frequencies. The blue line represents the real part of the permittivity, and the red is the imaginary part. .......... 6
Figure 2.2 Geometry for SPPs propagation at a single interface between a positive permittivity material and a negative permittivity material. ............................................. 7
Figure 2.3 Dispersion relation of SPPs at the interface between a Drude metal with negligible collision frequency and air (gray curves) and silica (black curves) [9]. .......... 8
Figure 2.4 Dispersion relation of SPPs at a silver/air (gray curve) and silver/silica (black curve) interface. Due to the damping, the wave vector of the bound SPPs approaches a finite limit at the surface plasmon frequency [9]}. ........................................................................... 9
Figure 2.5 Kretschmann configuration and Otto configuration for coupling light into the surface plasmon polaritons by attenuated total reflection. (a) Kretschmann configuration. (b) Otto configuration [10]. ...................................................................................... 10
Figure 2.6 Kinds of periodical nano structures (a) The famous nano-rings structure, (b) nano-grooves, (c) nanoholes \cite{lezec2002} ................................................................. 12
Figure 2.7 Diffraction and typical transmission spectrum of visible light through a subwavelength hole in an infinitely thin perfectmetal film. [12] ............................................................................. 13
Figure 2.8 Zero-order transmission spectrum of an Ag square hole array. The side length d = 150 nm. [11] ................................................................. 14
Figure 2.9 A schematic of a simple two-medium interface for transmission matrix method. ...................................................................................... 15
Figure 2.10 A scheme of a typical Bragg reflector. Light normally incidents into the reflector from left to right. ..................................................................................... 18
Figure 2.11 A typical wavelength dependent reflectivity of a Bragg reflector. .......... 19
Figure 2.12 The energy level scheme of two different types of Raman shifts: Stokes and anti-stokes shifts. ..................................................................................... 20
Figure 2.14 An illustration of the localized surface plasmon resonance effect [15]. .... 21
Figure 2.15 A quasi-static model for localized surface plasmon resonance. ............... 22
Figure 3.1 Experimental set-up for measuring linear transmission spectra of nanohole arrays. CCD: CCD camera, L: lens, BS: beam splitter, P: linear polarizer, O: microscope objective, NHA: gold slide with nanohole arrays, FO: fiber optic, S: spectrometer, XYZ: translation stages. The halogen source is replaced by a 780 nm laser for the isolation studies. ..................................................................................... 29
Figure 3.2 SEMs of the hole-arrays, diameter 150 nm and periodicity 600 nm with PBRs milled to a depth of the following. (a) 15 nm. (b) 45 nm. (c) 75 nm. ................. 30
Figure 3.3 Peak transmission of an array of nanoholes of periodicity 600 nm flanked by PBRs of varying depths (e.g., in Figure 3.2). ....................................................... 30
Figure 3.4 PBR enhancement (i.e., ratio between transmission with and without PBRs) as a function of size of array (i.e., number of holes along one edge). ..................... 31
Figure 3.5 SEMs of the hole-arrays, diameter 150 nm and periodicity 600 nm. (a) Without PBRs. (b) With two layers of PBRs. (c) With four layers of PBRs ............... 32
Figure 3.6 Transmission spectra of an array of nanoholes of periodicity 600 nm flanked by different numbers of PBRs (e.g., in Figure 3.5) ........................................................... 33
Figure 3.7 Transmission through subwavelength hole array for light incident over adjacent dimple array in the presence and absence of three PBRs. The light source is a 780 nm diode laser with the electric field polarized perpendicular to the lines of the PBR. The inset is an SEM of the structure with three PBR layers .................................................. 38
Figure 3.8 SEMs of superarrays with 600 nm periodicity. (a) Without PBRs. (b) With PBRs. ................................................................................................................................ 40
Figure 4.1 Scanning electron microscope image of w=1300 nm wide SP microcavity (200 nm depth) with central slit (180 nm width, 100 nm depth) and a schematic representation. ................................................................................................................................. 44
Figure 4.2 Measured transmission spectra for different surface plasmon microcavity widths ........................................................................................................................................... 46
Figure 4.3 FDTD calculated transmission spectra, normalized to power incident on slit, for different SP microcavity widths ........................................................................................................................................... 48
Figure 4.4 Transverse magnetic field (perpendicular to imaging plane) profile of 1300 nm structure for three wavelengths: (a) 640 nm, (b) 730 nm and (c) 840 nm. Scale bar is the same for all three images. ........................................................................................................................................... 50
Figure 5.1 The geometry of a 2D taper gap structure between two gold media. The widths $W_I$ and $W_f$ are fixed and the length $L$ varies for different taper angle $\theta$. For comparison with past works, $W_I = 316.4$ nm, $W_f = 1.512$ nm and the permittivity of gold $\varepsilon_w$ is $-16.2 + 0.5i$, $\varepsilon_v$ is 1 for vacuum ........................................................................................................................................... 55
Figure 5.2 The schematic diagram of the SMM model. The calculation step size in $x$-direction is 0.1 nm. $H_i$ and $H_r$ represent the incident and reflective transverse magnetic fields, respectively ........................................................................................................................................... 57
Figure 5.3 The SP wave vector $\beta$ at different widths in the taper gap. Blue line represents the real part of $\beta$, and red line is the imaginary part ........................................................................................................................................... 58
Figure 5.4 The dependence of the normalized optical transmission efficiency through the taper gap on the taper angle $\theta$. Blue line: with dissipation, in which $\varepsilon_w = -16.2 + 0.5i$; Red line: without dissipation, $\varepsilon_w = -16.2$. ........................................................................................................................................... 59
Figure 5.5 The dependence of the normalized optical transmission efficiency through the taper gap on the taper angle $\theta$. Blue line: with dissipation, in which $\varepsilon_w = -11.44 + 1.12i$; Red line: without dissipation, $\varepsilon_w = -11.44$. ........................................................................................................................................... 61
Figure 5.6 The model of a 3D gold taper rod structure in vacuum. Here $2 \times a = 600$ nm, $2 \times b = 10$ nm and the permittivity of gold $\varepsilon_w$ is $-11.44 + 1.12i$, $\varepsilon_v$ is 1 for vacuum. ........................................................................................................................................... 62
Figure 5.7 The schematic diagram of the SMM model in 3D gold rod. The calculation step size in $x$-direction is 0.1 nm. $H_i$ and $H_r$ represent the incident and reflective transverse magnetic fields, respectively ........................................................................................................................................... 63
Figure 5.8 The SP wave vector $\beta$ at different widths in the taper gap. Blue line represents the real part of $\beta$, and red line is the imaginary part ........................................................................................................................................... 65
Figure 5.9 The dependence of the normalized optical transmission efficiency through the gold taper rod on the taper angle $\theta$. Blue line: with dissipation, in which $\varepsilon_n = -11.44 + 1.12i$; Red line: without dissipation, $\varepsilon_n = -11.44$.

Figure 6.1 (a) Schematic of a 1D IMII slab waveguide; the layers from top to bottom are H$_2$O, Au, SiO$_2$ and air, respectively. (b) Sketch (not to scale) of the transverse magnetic field of the symmetry constrained LRSP (dashed curves) having identical field values along the upper and lower boundaries of the Au layer.

Figure 6.2 (a) Symmetry-constrained (blue curve) and cut-off (green curve) thicknesses for the LRSP in the IMII of interest (H$_2$O - Au – SiO$_2$ - air at 1310 nm). (b) Effective index (blue curve) and attenuation (red curve) of the symmetry-constrained LRSP in the IMII of interest (H$_2$O - Au – SiO$_2$ - air at 1310 nm) as a function of the Au slab thickness.

Figure 6.3 (a) Effective index (blue solid) and attenuation (red dashed) of the LRSP on the IMII of interest (H$_2$O - Au – SiO$_2$ - air at 1310 nm) for two thicknesses of the Au slab (20 and 50 nm) computed by the TMM. The values marked by the stars and the pentagons (green and magenta) were computed for the symmetry-constrained LRSP via Eq. (5). (b) Bulk ($\partial n_{\text{eff}} / \partial a$ - blue solid) and surface ($\partial n_{\text{eff}} / \partial a$ - red dashed) sensitivities, and (c) surface sensing parameter $G$ (blue solid) and $M_2$ figure of merit (red dashed), of the LRSP on the 1D IMII of interest. (d) Distribution of the $\mathbf{H}_y$ field component of the LRSP on the IMII of interest for $t = 50$ nm and $d = 341.7$ nm (Blue thick), and on the corresponding IMI (H$_2$O-Au-H$_2$O with $t = 50$ nm, red thin); the bottom boundary of the Au slab is located at $z = 0$.

Figure 6.4 (a) Effective indices for TE$_0$ (blue curve), TM$_0$ (red curve) and symmetry-constrained LRSP (green curve) modes as a function of SiO$_2$ thickness in the IMII of interest (H$_2$O - Au - SiO$_2$ - air at 1310 nm). (b) Same as Part (a), except using Si$_3$N$_4$ as the membrane (the refractive index of Si$_3$N$_4$ is ~2).

Figure 6.5 Sketch of a 2D IMII stripe waveguide of width $w$; the layers are the same as in Fig. 1.

Figure 6.6 Effective index (blue - solid) and attenuation (red - dashed) of the LRSP on the stripe IMII of interest ($w = 5 \mu m$, H$_2$O - Au - SiO$_2$ - air at 1310 nm) for two thicknesses of the Au stripe (20 and 50 nm) computed by the FDM.

Figure 6.7 Distribution of the transverse magnetic field ($\mathbf{H}_y$) of the symmetry-constrained LRSP over the cross-section of the stripe IMII of interest ($w = 5 \mu m$, H$_2$O - Au - SiO$_2$ - air at 1310 nm); (a) $t = 50$ nm, $d = 330$ nm; (b) $t = 20$ nm, $d = 380$ nm.

Figure 7.1 Scanning electron microscope image of a double-hole structure with concentric rings milled 50 nm into a 100 nm thick gold film. The inner ring has a radius of 900 nm, and the ring periodicity is 600 nm.

Figure 7.2 (a) SERS of oxazine 720 adsorbed on the concentric apex structure (900 nm inner radius and 600 nm periodicity) at two polarizations of the incident laser (defined in Figure 7.1). (b) Dependence of the SERS intensity of the 598 cm$^{-1}$ oxazine 720 band with the inner radii of the concentric apex structure.

Figure 7.3 FDTD-calculated electrical field intensity at the surface of a double-hole apex structure with a concentric rings concentric apex structure surface at 632.8 nm. Profile of
the \( z \)-component of the electrical field intensity (for the center region only) for (a) \( x \)-polarized incident light and (b) \( y \)-polarized incident light. Also shown are histograms, binned by field intensity, of the number of pixels over the whole surface area (blue bar) and the sum weighted by \( |E|^4 \) at each pixel (red bar) for (c) \( x \)-polarized incident light and (d) \( y \)-polarized incident light. All of the electrical field intensities were normalized by the source.

Figure 8.1 Silver nano-prisms over the multilayer SERS substrate. (a) Schematic of silver nano-prisms on TiO\(_2\) spacer layer over optically thick Au layer, where \( t \) is the thickness of TiO\(_2\) and \( d \) is the side length of a nano-prism. The illumination pattern is not to scale and the actual experiment has ~30 MNPs within the focus. (b) The SEM of the multilayer SERS substrate surface. The inset shows a TEM image of a single silver nano-prism.

Figure 8.2 Extinction spectrum of the silver nano-prisms used in the experiment in an aqueous environment, where the 673 nm extinction peak is clearly visible.

Figure 8.3 Experimental SERS spectra. (a) An example Raman spectra for the R6G dye using the silver nano-prisms. (b) Enhancement of SERS using silver nano-prisms for the 1509 cm\(^{-1}\) Stokes shift peak as a function of dielectric layer thickness, normalized by the SERS signal from a bare glass substrate. The blue bands indicate the first order and the second order SERS enhancement peaks.

Figure 8.4 Finite difference time domain simulations of enhancement factor, for 80 nm side nano-prism in the same configuration as in Figure 8.3(b).

Figure 8.5 Simulated local electric field intensity distributions close to a nano-prism for varying dielectric thicknesses (\( t = 80 \text{ nm}, 160 \text{ nm}, 260 \text{ nm} \)) shown on a logarithmic scale. The dashed lines show the interfaces of the silver nano-prism, the dielectric layer and the gold ground plane.
Acknowledgments

I would like to express my sincere gratitude and appreciation to my supervisor Dr. Reuven Grodon for providing me the valuable opportunity to work in the research area of nano-photonics, for his mentorship and informative guidance, and for his understanding and untiring support. I also would like to thank Dr. Alexandre Brolo for inspiring discussions in the field of Chemistry. Additional appreciation is expressed to Dr. Tao Lu for his insightful suggestions and comments.

I am grateful to all my colleagues and friends at the University of Victoria. Their support, insightful discussions and friendship made the past four years memorable.

Finally, I would like to express my deepest appreciation to my family for their encouragement and moral support throughout my studies.
Chapter 1

Introduction

As the developments in nano-scale fabrication and characterization technology, the investigation and applications of light in metal nanostructures have been becoming one of the most focused research areas. Compared to those common dielectrics light media, metal materials allow to couple the incident light energy into the electromagnetic waves propagating on the metal surface under certain configurations, so called surface plasmon (SP). This feature tremendously expanded the application possibility of metals in optical regime, such as extraordinary transmission, near-field optics and surface enhanced spectroscopes.

Surface plasmon is essentially collective coherent electron oscillations existing at the interface between a dielectric and a metal, which was first predicted in 1957 by R.H. Ritchie [1]. From a photonics point of view, surface plasmon is a type of electromagnetic wave (or light) confined to the dielectric-metal interface, it is evanescent in the direction away from the interface. The existence of surface plasmon relies on the electrical properties of both material – metal has a permittivity with a large negative real part in optical regime, while dielectric has one with a positive real
part. The negative permittivity of metal is derived using a Drude model in Section 2.1.1, and surface plasmon is then derived from Maxwell’s equations and the permittivities of both materials in Section 2.1.2.

There are two types of surface plasmons, the surface plasmon polaritons (SPP) and localized surface plasmon (LSP).

SPP propagates along the metal-dielectric interface, and is evanescent in the direction perpendicular to the interface. As a property of the evanescent wave, SPP has a wavenumber larger than that of light in free space. This mismatch makes it difficult to directly couple light from a free space into SPP. Section 2.1.3 introduces different common methods to excite SPP. The decay length of SPP in the evanescent direction is typically hundreds of nanometers into the dielectric and tens of nanometers into the metal. In other words, the electromagnetic energy is densely bounded at the interface. This feature makes SPP suitable for sensing a very thin layer of material on the surface. The propagation of SPP is usually highly lossy due to the dissipation in metal, which greatly limits its application. By designing a multi-layer structure at the metal surface, the property of SPP can be optimized with a significantly enhanced propagation length. The design of this “long range surface plasmon” is discussed in details in Chapter 6.

LSP is a type of surface plasmon localized to a metal nano-particle surface. Unlike the propagating SPP, the energy of LSP is bounded in all spatial directions. By solving the boundary conditions at the metal particle surface, a resonant condition can be found with a dramatic local field enhancement. This local field enhancement near a
metal nano particle as a result of localized surface plasmon resonance (LSPR) is applied to many different fields. Chapter 7 and Chapter 8 discuss surface-enhanced Raman spectroscopy (SERS), a typical application to LSPR, with novel platform designs.

Overall, the whole thesis will be divided in 9 chapters. The first one is the introduction part, which will give a description of the problems I have been solving. The second chapter is about the background theories and the terms which were involved into the whole research. The third - eighth chapters are all about my research on surface plasmon, which are SP Bragg reflector, frequency sensitive microcavity, subwavelength metallic taper, asymmetric long range surface plasmon waveguide, and 2D and 3D surface enhanced Raman spectroscopy substrates, respectively. I will conclude at the chapter 9 and give out some outlook of my work.
Chapter 2

Background theory

2.1 Surface plasmons

As we talked in the previous chapter, surface plasmon is the phenomenon of a set of electrons oscillating on the metal and dielectric interface. This term is commonly mentioned together with “polaritons” and “resonance”, which are two main ingredients of surface plasmon. Surface plasmon polaritons are the propagations of the electrons oscillation energy on the metal surface in form of electromagnetic waves and surface plasmon resonance refers the case when standing waves of surface plasmon polaritons occur within certain metal nanostructure geometries and the plasmonic energy are highly confined to a quite small region, which is also called "localize surface plasmon". Surface plasmon resonance can create significant electric local field which is fairly advantageous for nonlinear optical applications, such as second harmonic generation.
Since the surface plasmon is an electromagnetic phenomenon occurring at the metal-dielectric interface, then the electric properties of the metal and the dielectric become evidently important if we want to clarify the concept “surface plasmon” well.

2.1.1 Dielectrics and conductors

The traditional optical devices have been developed are mainly based on dielectric materials, whereas metals are not always the first choice for optical applications because it always has energy loss within optical frequency regime. The reason accounting for this difference is that the electrons in dielectrics are confined, but the ones in metals are allowed to move around. To show the optical difference between the metals and the dielectrics mathematically, Drude model is utilized here.

The permittivity of a material can be write as

\[ \varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega} \] (2.1)

where \( \omega \) is the electromagnetic wave frequency, \( \omega_p^2 = \frac{n\varepsilon^2}{\varepsilon_0m} \) is the plasma frequency, and \( \gamma = 1/\tau \) is the reciprocal of free electron's mean relaxation time \( \tau \). \( n \) is the number density of free electrons in a material, \( e \) is the elementary charge, \( \varepsilon_0 \) is the vacuum permittivity and \( m \) is the mass of an electron. If we consider \( \varepsilon_1(\omega) \) and \( \varepsilon_2(\omega) \) are the real part and imaginary part of \( \varepsilon(\omega) \), respectively, then we have:

\[ \varepsilon_1(\omega) = 1 - \frac{\omega_p^2\tau^2}{1 + \omega^2\tau^2} \] (2.2)
\[ \varepsilon_2(\omega) = \frac{\omega_p^2 \tau}{\omega(1 + \omega^2 \tau^2)} \]  

(2.3)

Figure 2.1 shows the permittivity-wavelength relationships of gold and SiO\(_2\), which are typical metal and dielectric. It is shown that the permittivity of SiO\(_2\) doesn't change a lot at visible and near infrared regime, and the imaginary part is close to 0 which indicates that SiO\(_2\) is free of loss for electromagnetic wave in this condition. As a contrary, the absolute values of both the real and the imaginary part of the gold permittivity are getting larger when the wavelength getting bigger, and gold has a distinct imaginary part at the visible and infrared region which represents considerable loss for it. Because of the low loss of light, traditional optical instruments are usually made of dielectrics. However, the discoveries on surface plasmon recent years may change this situation completely and metal will show its unique importance in photonic applications, especially in near field optical applications.

Figure 2.1 Permittivities of gold (left) and SiO\(_2\) (right) at different frequencies. The blue line represents the real part of the permittivity, and the red is the imaginary part.
2.1.2 Surface plasmon formation from Maxwell equations

Physically, Surface plasmon polaritons (SPPs) are the oscillation states of the free electron gas at the material surface (note here localized surface plasmon (LSP) is considered as the SPP propagating in standing wave state). As its electromagnetic nature, here we use Maxwell equations to solve the SPPs mode first. As shown in Figure 2.2, the SPPs we study here propagating on the interface of a dielectric and a metal. Assume the EM field along $z > 0$ by applying a certain boundary condition which has a positive permittivity medium and a negative permittivity medium at each of the sides (shown in Figure 2.2).

![Figure 2.2 Geometry for SPPs propagation at a single interface between a positive permittivity material and a negative permittivity material.](image)

Then, the only supported TM mode is obtained [2].

\begin{align*}
H_y(z) &= Ae^{j\beta_x}e^{-k_z} \\
E_x(z) &= iA\frac{1}{\omega\varepsilon_0\varepsilon_2}k_ze^{j\beta_x}e^{-k_z} \\
E_z(z) &= -A\frac{\beta}{\omega\varepsilon_0\varepsilon_2}e^{j\beta_x}e^{-k_z}
\end{align*}

(2.4) \quad (2.5) \quad (2.6)

for $z > 0$, and
\[ H_y(z) = Ae^{i\beta z} e^{kz} \]  
\[ E_x(z) = -iA \frac{1}{\omega \varepsilon_0 \varepsilon_1} k_1 e^{i\beta z} e^{kz} \]  
\[ E_z(z) = -A \frac{\beta}{\omega \varepsilon_0 \varepsilon_1} e^{i\beta z} e^{kz} \]

for \( z < 0 \). Here, \( \omega \) is the frequency of SPPs, and \( \varepsilon_1 \) and \( \varepsilon_2 \) are permittivities of these two media. \( k_i \equiv k_{z,i} \ (i=1, 2) \) is the component of the wave vector perpendicular to the interface. \( A \) is the amplitude coefficient. By the boundary condition of continuity of \( H_y \) and \( \varepsilon_i E_z \) at the interface, the wave vector \( \beta \) is then determined by

\[ \beta = k_0 \sqrt{\frac{\varepsilon_1 \varepsilon_2}{\varepsilon_1 + \varepsilon_2}} \]

where \( k_0 = \omega / c \) is the wave vector of the propagating wave in vacuum. Equation (2.10) is the SPPs dispersion relation.

Figure 2.3 Dispersion relation of SPPs at the interface between a Drude metal with negligible collision frequency and air (gray curves) and silica (black curves) [2].
Figure 2.3 shows the calculated dispersion relations for SPPs in a Drude metal and dielectric interface with negligible collision. It could be seen that the SPPs have smaller group velocity than waves propagating in corresponding dielectrics. Especially when frequency comes to the characteristic surface plasmon frequency

\[ \omega_{sp} = \frac{\omega_p}{\sqrt{1 + \varepsilon_2}} \]  

(\(\omega_p\) is the plasma frequency of the metal), the group velocity goes to zero. That is why sometimes we call SPP wave “slow wave”, and this is also the point for localized SPPs realization. Note for real metals, it is not possible to achieve this zero group velocity limit because of dissipation (shown in Figure 2.4).

![Dispersion relation of SPPs at a silver/air (gray curve) and silver/silica (black curve) interface. Due to the damping, the wave vector of the bound SPPs approaches a finite limit at the surface plasmon frequency][2].

Note here we only discussed the surface plasmon mode on a two-layer interface, and in the practical applications, more complicated surface plasmon structures are needed, such as slab waveguides and cylindrical waveguides, whose modes will be discussed in more details in Chapter 5 and Chapter 6.
2.1.3 Excitation of surface plasmon

To excite SPPs, the most straightforward way is shining the light onto the interface which satisfies the boundary conditions in section 2.1.2. Unfortunately, the simple combination of normal light and normal interface does not give birth to SPPs due to the mismatch of wave momentum \( (\hbar k) \), where \( \hbar \) is the Planck's constant. Therefore, some momentum compensation strategies are required at this circumstance. There are two ways to achieve this goal in general -- attenuated total reflection (ATR) and periodic nano structures [3, 4].

The first approach sits on the fact that the total internal reflection can generate larger wave vector evanescent wave on the exit surface, which could be matched to the SPPs. Two configurations have been proposed to excite surface plasmons optically by employing a high refractive index prism (as shown in Figure 2.5), which are Kretschmann configuration and Otto configuration.

![Figure 2.5 Kretschmann configuration and Otto configuration](image)

Figure 2.5 Kretschmann configuration and Otto configuration for coupling light into the surface plasmon polaritons by attenuated total reflection. (a) Kretschmann configuration. (b) Otto configuration [3].
In the Otto configuration sketched in Figure 2.5 (b) a light beam is reflected off the base of a prism. Adjacent to the base is a gap of low refractive index material with a thickness of the order of the employed laser wavelength. Located on the other side of the gap is a metal layer of optically infinite thickness. TIR takes place for angles equal to or larger than the critical angle. Under the TIR condition, the evanescent field at the prism base can tunnel across the dielectric spacer and excite surface plasmon modes on the metal/dielectric interface.

The Kretschmann configuration (Figure 2.5 (a)) is more popular than Otto today to couple light to surface plasmons because of its relative simplicity and robustness. A light beam is reflected off the base of a high refractive index prism and the reflected intensity is measured. Metal and low refractive index dielectric layers swap roles compared to the previous method but with the advantage that the dielectric phase is readily accessible in the Kretschmann configuration. A thin metal layer is located on the prism base, followed by a bulk dielectric. For the appropriate metal film thickness the surface plasmon resonance can be excited on lower surface of the metal. Note that in the Kretschmann configuration, the metal layer thickness needs to be precisely controlled in order to obtain the most efficient coupling to the excitation.

Another approach takes advantage of periodic nanostructures. This method is more similar as creating a 2D photonic crystal which can give its lattice momentum to the incoming light in form of wave vector. Kinds of periodic structures have been made, shown in Figure 2.6. The excited SPPs wave vector $\beta$ should always follow the equation below [3]:

$$\beta = \frac{2\pi}{\lambda} n \sin \theta$$
Here, $k_0$ is the vacuum wave vector of incident light, $\theta$ is the light incident angle, $g$ is the reciprocal of the grating constant, and $n$ is an integer.

Figure 2.6 Kinds of periodical nano structures (a) The famous nano-rings structure, (b) nano-grooves, (c) nanoholes [5].

### 2.2 Extraordinary transmission

One main research direction of SPPs is the extraordinary optical transmission (EOT) when light travels through subwavelength apertures. In the case of a large metal aperture, there would be propagation modes in the aperture which allow the light to transmit through it. However, for a small aperture with $r$ much smaller than half wavelength $\lambda / 2$, all modes are cut-off in the aperture, little light energy can travel thought the subwavelength aperture. In 1944, Bethe arrived at an exact analytical solution for light transmission through a sub-wavelength circular hole in a perfectly conducting, infinitely thin screen. He derived a very simple expression for the transmission efficiency $T$ [6],

$$\beta = k_0 \sin \theta \pm vg = k_{sp}$$

(2.11)
where \( k = \frac{2\pi}{\lambda} \) is the norm of the wave number of the incoming light of wavelength \( \lambda \), and \( r \) is the radius of the hole. It is immediately apparent that \( T \) scales as \( \left( \frac{r}{\lambda} \right)^4 \) and that therefore we would expect the optical transmission to drop rapidly as \( \lambda \) becomes larger than \( r \), as shown in Figure 2.7. In addition, the transmission efficiency is further attenuated exponentially if the real depth of the hole is taken into account.

\[
T = \frac{64(kr)^4}{27\pi^2} \tag{2.12}
\]

Figure 2.7 Diffraction and typical transmission spectrum of visible light through a subwavelength hole in an infinitely thin perfect metal film [6].

However, the discovery of EOT is a surprising counter example to the usual inverse fourth power dependence of the transmitted power to the subwavelength aperture dimension. In 1998, Ebbesen reported the first EOT phenomenon through subwavelength hole arrays, and large transmission power was found at certain wavelengths below the cut-off frequency [4], as shown in Figure 2.8. In this case, the SPP exited at the hole array in metal surface is constructively interfered and the transmitted optical power is enhanced. Thereafter, more EOT examples were reported.
for arrays [7] and a single aperture with surrounding fringes [8]. EOT can also
without relying on SPP, for arrays [9] and a single aperture in a waveguide [10], as a
result of the divergent magnetic field of a cut-off TM mode. However, when SPPs
exist, they will always play a role in the transmission. EOT finds significant
applications in optical sensing [11], photodetectors [6] and nearfield optics [12].

![Graph showing zero-order transmission spectrum of an Ag square hole array. The side length d = 150 nm.](image)

**Figure 2.8** Zero-order transmission spectrum of an Ag square hole array. The side length $d = 150$ nm. [4]

2.3 Transmission matrix method

Transmission matrix method is essentially a matrix with which we could
demonstrate the input and output EM field on one side of a system in form of the EM
field on the opposite side.
In transmission matrix method, we relate the input and output EM field on both sides of a system using a transmission matrix.

![Figure 2.9 A schematic of a simple two-medium interface for transmission matrix method.](image)

As a simplest example, in Figure 2.9, we have two media 1 and 2 with permittivities $\varepsilon_1$ and $\varepsilon_2$. $E_{1+}^1$, $E_{1-}^1$ represent the input and the output EM fields in medium 1. $E_{2+}^2$, $E_{2-}^2$ are the output and the input EM fields in medium 2, respectively. The positive and the negative superscripts indicate the propagation directions of the electric field. Then we could have relations between $E_{1+}^1$, $E_{1-}^1$ and $E_{2+}^2$, $E_{2-}^2$,

\[
\begin{align*}
E_{1-}^1 &= r_{1,2} E_{1+}^2 + t_{2,1} E_{2-}^2 \\
E_{2+}^2 &= r_{2,1} E_{2-}^2 + t_{1,2} E_{1+}^1
\end{align*}
\]  \hspace{1cm} (2.13)

$r_{i,j}$ and $t_{i,j}$ is the reflection coefficient and the transmission coefficient from medium $i$ to medium $j$.

By reforming Equations (2.13),
\[
E_2^- = \frac{1}{t_{2,1}} (E_1^- - r_{1,2} E_1^+) \\
E_2^+ = \frac{r_{2,1}}{t_{2,1}} (E_1^- - r_{1,2} E_1^+) + t_{1,2} E_1^+ 
\]

(2.14)

and write (2.14) in form of a coefficient matrix, we achieve

\[
\begin{bmatrix}
E_2^+ \\
E_2^-
\end{bmatrix} = \begin{bmatrix}
t_{1,2} - \frac{r_{1,2} \cdot r_{2,1}}{t_{2,1}} & \frac{r_{2,1}}{t_{2,1}} \\
-\frac{r_{1,2}}{t_{2,1}} & 1 - \frac{r_{1,2}}{t_{2,1}}
\end{bmatrix} \begin{bmatrix}
E_1^+ \\
E_1^-
\end{bmatrix} 
\]

(2.15)

The coefficient matrix in Equation (2.15), denoted by \( T_{1,2} \), is called the transmission matrix.

The reflection and transmission coefficients in Equation (2.15) can be expressed using Fresnel’s equations for both the TE and TM modes. For the TE mode,

\[
\begin{align*}
&\begin{cases}
r_{i,j} = \frac{k_{i,z} - k_{j,z}}{k_{i,z} + k_{j,z}} \\
t_{i,j} = \frac{2k_{i,z}}{k_{i,z} + k_{j,z}}
\end{cases} \\
\end{align*}
\]

(2.16)

where the EM wave vector along the z direction is \( k_z = \sqrt{\varepsilon_i (\cos \theta) \cdot \frac{2\pi}{\lambda}} \), \( \theta \) is the incident angle, and \( \lambda \) is the vacuum wavelength of the EM wave. With the reflection and transmission coefficients, the transmission matrix \( T_{i,j} \) can be represented in the way below,

\[
T_{i,j} = \frac{1}{2} \begin{bmatrix}
1 + \kappa_i & 1 - \kappa_i \\
1 - \kappa_i & 1 + \kappa_i
\end{bmatrix}
\]

(2.17)

where \( \kappa_i = \frac{k_{i,z}}{k_{j,z}} \).

Similarly for the TM mode,
\[ T_{i,j} = \frac{1}{2} \begin{bmatrix} 1 + \kappa_j \eta_i & 1 - \kappa_j \eta_i \\ 1 - \kappa_i \eta_i & 1 + \kappa_i \eta_i \end{bmatrix} \] (2.18)

in which \( \eta_i = \frac{\varepsilon_j}{\varepsilon_i} \).

If we expand the transmission matrix method to a multilayer system, then we have

\[
\begin{bmatrix} E_{n+1}^+ \\ E_{n+1}^- \end{bmatrix} = T_{n,n+1} \cdot T_{n-1,n} \cdots T_{1,2} \cdot T_{0,1} \begin{bmatrix} E_0^+ \\ E_0^- \end{bmatrix}
\] (2.19)

Transmission matrix method has been used widely in optical system calculation, here are two application involved in my work.

**Application: Bragg reflectors**

Bragg reflectors are widely used in waveguides as high reflectivity components, such as in optical fibers. It consists of multiple layers of alternating materials with varying permittivities (refractive indexes), or by periodic variation of some characteristic (such as height) of a dielectric waveguide, resulting in periodic variation in the effective refractive index in the guide (shown in Figure 2.10). Each layer boundary causes a partial reflection of the incident light. For light with wavelength close to four times the optical thickness of the layers (\( \lambda = 4 \cdot \sqrt{\varepsilon_i d_i} = 4 \cdot \sqrt{\varepsilon_j d_j} \)), the multiple reflections interfere constructively and the multiple transmission interfere destructively, therefore the layers act as a high-quality reflector. The range of wavelengths that are reflected is called the photonic stopband. Within this range of wavelengths, light is "forbidden" to propagate in the structure.
Figure 2.10 A scheme of a typical Bragg reflector. Light normally incidents into the reflector from left to right.

Figure 2.10 shows a scheme of a typical Bragg reflector. \( \varepsilon_1 \) and \( \varepsilon_2 \) are the permittivities of the alternating layers. \( \varepsilon_s \) is the substrate permittivity and \( \varepsilon_0 \) is the ambient permittivity. Light incidents from left side into the Bragg reflector and gets reflected back. Bragg reflector’s reflectivity can be achieved by using TMM method and Figure 2.11 shows a TMM method calculated reflectivity-wavelength dependence result.
2.4 Surface enhanced Raman spectroscopy

2.4.1 Raman spectroscopy

Raman spectroscopy was discovered by C. V. Raman in 1930, which has been utilized as a spectroscopic technique used to study vibrational, rotational, and other low-frequency modes in a system. It relies on inelastic scattering of monochromatic light from target molecules. The excitation light wavelength is usually around the visible, near infrared, or near ultraviolet range. For spontaneous Raman effects, photons excite the molecules from the ground state to a virtual energy state. When molecules return to different ground states photons with different wavelength will be emitted and the differences in energy between the original states and the final states lead to shifts in the emitted photon’s frequency away from the excitation wavelength. If the final vibrational states of the molecule is more energetic than the initial states,
then they will result in the longer wavelength emitted photons compared to the excitation photons, which are called Stokes shifts. If the final vibrational states are less energetic than the initial states, then the emitted photon will be shifted to a shorter wavelengths, and this is called anti-Stokes shifts (shown in Figure 2.12). A change in the molecular polarization potential with respect to the vibrational coordinate is required for a molecule to exhibit a Raman effect. The amount of the polarizability change will determine the Raman scattering intensity. The pattern of shifted frequencies is determined by the rotational and vibrational states of the sample.

Figure 2.12 The energy level scheme of two different types of Raman shifts: Stokes and anti-Stokes shifts.

Spontaneous Raman spectroscopy is fairly useful for the material distinguishing and characterization because of its uniqueness on different molecules. However, the Raman signal is often very weak due to its very small scattering cross-section, which makes the spontaneous Raman signal submerged into the noise spectrum such as
fluorescence spectrum and quite hard to detect. Therefore, special techniques were
developed to enhance spontaneous Raman signal and make it more detectable, such as
resonance Raman, SERS.

2.4.2 Localized surface plasmon resonance

It is necessary to talk about localized surface plasmon resonance (LSPR) before we
discuss SERS. LSPR are non-propagating excitations of the conduction electrons of
metallic nanostructures (such as a nano-particles or a curved nano-structure) coupled
to the electromagnetic field (shown in Figure 2.13) [2]. The curved surface of the
particle exerts an effective restoring force on the driven electrons, so that a resonance
can arise, leading to field amplification both inside and in the near-field zone outside
the particle. This resonance is called the localized surface plasmon resonance.

Figure 2.13 An illustration of the localized surface plasmon resonance
effect [13].

To estimate the electric field enhancement by the localized surface plasmon
resonance, we will take a look at the metal nano-sphere case here. Assume that
electric field $E_0$ around a tiny metal sphere with radius $a$ along $z$-direction as
shown in Figure 2.14. The permittivities of outside and inside the sphere are \( \varepsilon_0 \) and \( \varepsilon(\omega) \). Considering this tiny sphere as a dipole, and taking the advantage of the quasi-static approximation which allows Maxwell’s equations to be replaced by the Laplace equation of electrostatics [14], then we will obtain the expression of the electric potential of any location \( P \):

\[
V = \begin{cases} 
-E_i \cdot r \cos \theta & r < a \\
-E_0 \cdot r \cos \theta + \alpha E_0 \cos \theta & r > a
\end{cases}
\]

(2.20)

\( E_i \) is the electric field inside the sphere, \( r \) is the distance from the sphere center to the point \( P \), and \( \theta \) is the angle between the direction \( P \) and \( z \) direction. \( \alpha \) is the metal polarizability.

By applying the continuous boundary condition for electric potential \( V \), the tangential electric field \( E_{//} \) and the normal electric displacement vector \( D_\perp \) at the sphere interface, we reach the expression for the polarizability \( \alpha \),

\[
\alpha = \frac{\varepsilon(\omega) - \varepsilon_0}{\varepsilon(\omega) + 2\varepsilon_0} \cdot a^3
\]

(2.21)

Equation (2.21) represents how much electric field enhancement can be induced by the original field \( E_0 \) from the metal sphere. Note when metal permittivity \( \varepsilon(\omega) \)
equals to the ambient permittivity $-2\varepsilon_0$, the polarizability $\alpha$ tends to infinity, which means significant electric field enhancement is created. This is exactly the substance of localized surface plasmon resonance. Since the metal permittivity $\varepsilon(\omega)$ is wavelength dependent, the enhancement also varies with excitation EM wavelength.

2.4.3 SERS

Spontaneous Raman signal is weak due to its small scattering cross-section. One of the most effective ways to magnify the Raman signal is surface enhanced Raman spectroscopy, which allows the normal Raman signal magnified by orders of magnitudes with using a nano-structurized metal substrate.

However, the cause of SERS still remains in debate. There are two primary theories accounting for SERS – the electromagnetic enhancement mechanism and the chemical enhancement mechanism. These two mechanisms arise because the intensity of Raman scattering is directly proportional to the square of the induced dipole moment, which is in turn the product of the Raman polarizability $\alpha$, and the magnitude of the incident electromagnetic field. As a consequence of exciting the localized surface plasmon resonance of a nanostructured or nanoparticle metal surface, the local electromagnetic field $E$ is significantly enhanced. Since Raman scattering cross-section is approximately proportional to the forth power of the local electric field -- $E^4$, which means $E^4$ folds SERS enhancement will be generated.
There are two primary theories accounting for SERS – the electromagnetic theory and the chemical theory. The former theory believes the enhancement of Raman which is due to the existence of highly localized light fields in the near-field of metallic nanostructures which could increase the Raman scattering cross-section of suitable molecules. And the chemical theory involves charge transfer between the chemisorbed species and the metal surface which only applies in specific cases and probably occurs in concert with the electromagnetic mechanism. I will mainly talk about the electromagnetic mechanism in this thesis.

So far, the most significant SERS enhancement of single molecules have been recorded, with estimated enhancements of the scattering cross section by factors up to $10^{14}$ by using chemically rough-ened silver substrates [15, 16].

Despite such these enhancements, which made SERS orders of magnitude more sensitive than normal Raman spectroscopy, SERS substrates still suffer from the low reproducibility and the instability. This severely encumbers the way of SERS industrialization and application, which requests more stable and repeatable SERS substrates with high sensitivity in the future.
As talked in Section 2.2, a major milestone in the realization of SPPs was the ability to overcome the diffraction limit and confine light at the subwavelength scale [17]. It has been shown that single periodic nanohole array structures provide an extraordinary optical transmission (EOT) in thin-metal films [4]. EOT is also possible from a single hole or slit by using encompassing periodic surface structures [18-20]. The propagation of SPPs away from nanohole structures has been observed directly [21, 22]. This effect is important because it introduces both loss and cross talk between a series of EOT structures on the same film.

In this chapter, we are going to demonstrate surface plasmon Bragg reflectors (PBRs) which could effectively enhance the EOT intensity and eliminate the cross talk among different surface plasmon units based on our previous work [23]. A modulation of transmission through a nanohole array has been demonstrated by PBRs used in a resonant cavity configuration [24]. These works, by using the Bragg resonance condition for the SPPs, have adapted prior works on the use of surface corrugations to enhance coupling of SPPs into a single slit [25]. Separate to studies on EOT, investigations on the reflection of PBRs have shown that dispersion can be
minimized by tailoring the angle of incidence [26]. In addition, an optical confinement has been demonstrated from Bragg reflection of SPPs in metal-insulator-metal waveguides [27], and PBRs have been achieved by alternately stacking metal gap heterowaveguide structures [28].

Here we characterize the use of PBRs for the application of isolating adjacent structures on a single plasmonic device, thereby eliminating the cross talk. The effect of the variation of the number of PBR layers is studied, as well as the dependence on the depth of the PBR lines. The effect of isolation is shown directly for an array of dimples and an array of holes separated by different numbers of PBR layers. Finally, isolation is examined for multiple arrays separated by PBRs to produce a more uniform spectral output from a superarray. In section 3.1, we describe the fabrication of the nanohole array structures. In section 3.2, we describe the setup used for the linear transmission measurements. In section 3.3, we present our studies on the characterization of PBRs. First, we describe the effect of PBR depth on enhancement. Then we show the effect of the number of holes and the number of PBRs on the enhancement of EOT. Finally, we present a discussion of the results of the characterization experiments. In section 3.4, we study the use of PBRs for isolating adjacent plasmonic devices. First, we study the effect that PBRs have on interference patterns of pairs of closely spaced hole-arrays. Then we study the use of PBRs to isolate a hole-array from SPPs sourced by an array of partially milled dimples. Finally, we study the use of PBRs in isolating adjacent components of a superarray.
3.1 Focused ion beam (FIB) fabrication

The structures were fabricated by FIB milling of a 100-nm-thick gold film evaporated on a glass substrate. A 5-nm-thick chromium layer is present to provide adhesion between the gold and glass layers. A gallium ion beam current of 30 pA at 30 kV was used for milling. The gallium spot size was approximately 7 nm at a magnification of 5000×. A beam dwell time of 12 μs was used to mill completely through the gold and chromium layers.

The PBR layers consist of partially milled lines, with the beam dwell time varied to precisely control the depth of milling. To satisfy the Bragg reflection condition, the periodicity of the PBRs is chosen to be half the periodicity of the array. The first PBR layer is placed a half period away from the edge of the array in order to ensure reflection in phase with the EOT light, and thereby maximize the EOT enhancement, as shown previously [23].

For characterizing the effect of the number of reflector layers on the enhanced EOT, arrays of circular holes of diameter 150 nm and periodicity 600 nm were fabricated. The width of the PBRs was set to be 130 nm. For the study of PBRs for isolation, arrays of circular holes of diameter 150 nm and periodicity 700 nm were fabricated. The width of the lines forming the PBR was set to be equal to the diameter of the circles in the array of the isolation structures.
3.2 Transmission measurement setup

Figure 3.1 shows a schematic representation of the setup used to measure the white light transmission spectra of the structures. The transmission spectra were recorded using a fiber-optic coupled UV-visible spectrometer. The halogen source was focused with normal incidence onto the arrays. An illumination spot size of approximately 30 μm was obtained by using a combination of an iris and a 20× microscope objective. (A 60× objective was used for the superarray isolation experiment.) The zeroth-order transmission spectrum was collected with a 100 μm diameter core fiber placed approximately 5 mm from the sample. Precise positioning of the fiber core and the gold slide were achieved using XYZ translation stages. Images of the arrays in the sample and the spot were collected using a charge-coupled device (CCD) camera. For isolation studies, the halogen source was replaced by a laser with emission wavelength at 780 nm, corresponding to the (1, 0) resonance of the array.
3.3 Characterization of PBR layers

3.3.1 Variation in Depth of PBR Layers

Figure 3.2 shows SEMs of arrays of circular holes flanked by partially milled PBR layers of depths of 15, 45, and 75 nm, respectively. Figure 3.3 shows the variation of peak transmission intensity of the hole-arrays with different depths of the PBR layers. The 45 and 60 nm deep PBRs have the strongest transmission intensities. As will be
described, this can be attributed to the saturation of the reflection that comes from the skin depth of the SPP propagating in the gold; the optical energy was well confined within 45 nm below the gold surface. Structures of larger depth introduce more scattering losses, and therefore show lower reflection in multiple line PBRs. This behavior is demonstrated clearly by the 60 and 75-nm-deep PBRs, which have progressively less transmission than the 45 nm PBR. The extra scattering losses of deeper groove structures lead to a decay of the reflected surface wave.

![Figure 3.2 SEMs of the hole-arrays, diameter 150 nm and periodicity 600 nm with PBRs milled to a depth of the following. (a) 15 nm. (b) 45 nm. (c) 75 nm.](image)

**Figure 3.2** SEMs of the hole-arrays, diameter 150 nm and periodicity 600 nm with PBRs milled to a depth of the following. (a) 15 nm. (b) 45 nm. (c) 75 nm.

![Figure 3.3 Peak transmission of an array of nanoholes of periodicity 600 nm flanked by PBRs of varying depths (e.g., in Figure 3.2).](image)

**Figure 3.3** Peak transmission of an array of nanoholes of periodicity 600 nm flanked by PBRs of varying depths (e.g., in Figure 3.2).
3.3.2 Variation in Number of Holes and Number of PBRs

Figure 3.4 shows the enhancement of the transmission from PBRs as the number of holes in the array is increased. The transmission enhancement is defined as the ratio in the peak transmission with three PBR layers to the peak transmission without the PBRs. The number of holes is the number along one edge, not the total number in the array. It is clear that the effect of the PBR layers becomes less significant as the array size becomes larger, because the influence of the PBRs is confined to the edges.

![Figure 3.4 PBR enhancement (i.e., ratio between transmission with and without PBRs) as a function of size of array (i.e., number of holes along one edge).](image)

Figure 3.5 shows SEM images of arrays of circular holes flanked by different numbers of partially milled line PBRs. Figure 3.5 (a) shows an array of periodicity 600 nm without PBRs. Figure 3.5 (b) shows the same array flanked by two layers of PBRs, and Figure 3.5 (c) shows the array with four layers of PBRs. In accordance with the results of the last section, milling depth of 45 nm is shown; however, other depths have also been tested.
Figure 3.5 SEMs of the hole-arrays, diameter 150 nm and periodicity 600 nm. (a) Without PBRs. (b) With two layers of PBRs. (c) With four layers of PBRs.

Figure 3.6 shows the transmission spectra for 0, 1, 2, 3, and 4 PBR layers. The (1, 0) transmission resonance of the array at the gold-air interface is at 700 nm. The peak transmission intensity increases up to three PBR layers, which provide a maximum enhancement of 1.5 times the transmission intensity when compared to the same structure without PBRs. The transmission intensity shows little variance for the addition of subsequent PBR layers (these studies were extended up to 12 layers). As will be described in the next section, this saturation phenomenon may be attributed to the scattering losses arising at the PBR interfaces.
3.3.3 Discussion of Variation in Line Number and Depth

To optimize the performance of the PBRs, it is required to maintain minimal scattering losses at the downward and upward step-edges while maximizing the reflection. Full numerical calculations have been provided for SPPs at a step-edge discontinuity [29]. (Incidentally, the real part of the dielectric constant for silver at 632 nm is that the work is comparable to the real part of the dielectric constant for gold at the 700 nm resonance under study in this paper.) That work showed that the reflection at a downward step-edge saturates for a relatively small step, while the radiation losses increase dramatically.

While not attempting a full numerical calculation, here we consider the coupling across the metal-dielectric interface, retaining only the transmitted and reflections of
the SPPs mode. This approximate theory is consistent qualitatively with full numerical calculations for small steps [29], and even shows reasonable quantitative agreement. Matching for the electric field of the incident and reflected SPPs modes with the transmitted SPPs mode gives the following relation at the interface for the reflection \( r \) and the transmission \( t \) as

\[
1 + r = t I (d)
\]

(3.1)

and matching for the magnetic field gives

\[
1 - r = t I (d)
\]

(3.2)

where the field components for the SPPs are used in the integral

\[
I (d) = \int_{-\infty}^{\infty} E_z (z - d) H_y (z) dz
\]

(3.3)

with the normalization

\[
I (0) = 1
\]

(3.4)

Considering a step in a gold film in air at free-space wavelength of 700 nm, the reflection calculated in this way begins to saturate 50 nm, and it is fully saturated for a step of over 100 nm. We consider the power flow in the SPPs to interpret this saturation phenomenon.

The Poynting vector of an SPPs shows that the power travels in the forward direction above the metal surface and in the backward direction below the metal surface. This is due to the change of sign in the transverse electric field component at the metal-air boundary. As a result, a small downward step-edge naturally converts this backward-traveling portion of the wave below (i.e., the portion within the skin depth on one side of the step) from transmission into reflection. Therefore,
maximizing the reflection at a downward step requires only milling down just beyond the skin depth.

Comparing with the experiments, the optimum step height of 45 nm gives a reflection of 66% of the saturation value. For an upward step, the maximum reflection occurs for an infinite step, since the upward step acts like a large mirror to reflect the portion of the SPPs wave above the metal surface. For smaller steps, zeroth-order perturbation theory (where the field distribution is assumed to be well-represented by the SPPs mode only) may be employed to calculate the reflected portion analytically. This zeroth-order method readily shows that a downward step behaves in a similar way to a small upward step. As a result, to match the reflection for the downward and upward step, it is necessary to keep the height of the step comparable to the skin depth.

The experiments show that it is not beneficial to saturate the reflection by making a deep step, and this, we attribute to an increase in scattering losses for large steps. It is possible to estimate the scattering losses using this approach of retaining only the single surface plasmon polariton mode

$$L = 1 - |r|^2 - |t|^2$$

From this, it is found that the scattering losses increase in a way that is comparable to the reflection. It is found that the scattering losses at each interface are about 7% at the experimentally found optimum step-height of 45 nm. Since each groove has two steps (up and down), it is reasonable that the reflection saturates after only a few
periods, after which, scattering losses take over. Therefore, only three PBRs are sufficient to obtain maximum reflection.

It might be considered that, making the step smaller will reduce radiation loss, but it will also reduce reflection, and thereby make material absorption a dominant factor, as the SPPs have to travel a longer distance to build up the same amount of reflection from multiple facets. Another possible configuration is to have a single upward step, which acts as a mirror to give near-total reflection \[29]\; ; however, this is not practically feasible for the fabrication method that we considered.

### 3.4 Isolation using PBRS

#### 3.4.1 PBRS to Prevent Interference between Two Adjacent Nanohole Arrays

Here, the overall transmission from two closely spaced adjacent hole-arrays is considered to determine how well the PBR layers can isolate adjacent structures. Arrays were fabricated with separations corresponding to between one and five layers of PBRs. The structures were made both with and without PBRs. The PBRs have a periodicity equal to one half of the array pitch, an odd number of PBR layers will correspond to a whole multiple of array pitch, and an even number will not. Therefore, these odd and even PBR separations correspond to constructive and destructive interference of SPPs scattered between each of the arrays. The periodicity of the
arrays was chosen to be 700 nm to match the laser source for launching experiments in the next section. This periodicity has a (1, 0) transmission peak at 780 nm.

It was found that the intensity of the (1, 0) transmission peak at 780 nm changes by nearly 50% between odd and even numbers of PBR layers. In the case of odd numbers of PBR layers, the net transmission was seen to increase by 10% due to the introduction of line PBRs between the arrays. For the structures with odd numbers of PBRs, it is difficult to separate the isolation effect from the enhanced EOT coming from the PBRs. This difficulty arises due to the production of constructive interference even without the PBRs leading to the enhanced transmission with respect to a single array.

A more pronounced effect was observed for the even number of PBRs, where there is a destructive interference between the arrays. For even numbers of PBRs, the transmission without the PBRs is reduced at the resonance; however, it is increased by 30% when adding the PBRs.

### 3.4.2 PBRs for Blocking SPPs Launched from Dimple Array

To separate the effect of constructive and destructive interference due to adjacent hole-arrays from the isolation due to the PBR layers, another structure was fabricated. One of the two hole-arrays was replaced with an array of partially milled dimples, maintaining the geometric features of the hole-array, but not milling entirely through the gold. In studying these structures, the beam from a 780 nm diode laser was
focused onto the dimple array. The electric field polarization of the laser beam was chosen to be pointing between the dimple-array and the hole-array, so that the SPPs generated at the dimple-array would be launched toward the hole-array. This is due to the fact that scattered SPPs will propagate parallel to the direction of the electric field polarization from the normally incident light [30]. Due to the spot-size of the laser beam, there was some residual direct excitation of the hole-array by the laser source, and since the hole-array readily allows transmission and the dimple array does not, this residual excitation contributes significantly to the detected signal.

Figure 3.7 Transmission through subwavelength hole array for light incident over adjacent dimple array in the presence and absence of three PBRs. The light source is a 780 nm diode laser with the electric field polarized perpendicular to the lines of the PBR. The inset is an SEM of the structure with three PBR layers.

Figure 3.7 shows the transmission spectra from a 780 nm diode laser source in the presence and absence of three layers of PBRs. (All numbers of PBR layers between 2 and 5 were studied, and they showed similar results; however, the results for three layers were most pronounced, which is consistent with the optimization presented
previously in this section) An SEM of the structure with PBRs is shown in the inset. The transmission for the structure without PBRs is significantly higher than the one with PBRs. The change in transmission intensity shows that the PBR attenuates the SPPs launched from the dimple-array to the hole-array, and therefore it is capable of providing isolation for adjacent structures from launched SP waves.

**3.4.3 PBRs for Uniform Spectral Emission over a Superarray**

For certain applications, such as sensing over a large area, it may be desirable to concatenate several arrays into a superarray, thereby creating a large field. It is necessary to fabricate this in the form of a superarray due to the constraints of the nanofabrication process (e.g., the write field size of the FIB). For such applications, constructive and destructive interference between adjacent arrays, which arises from the inability to control the phase of separation with ~100 nm precision, will modify the transmission spectrum as recorded from separate local regions. Therefore, the interference will give nonuniform spectral transmission over the superarray.

Figure 3.8 shows the superarray structure studied, consisting of a $4 \times 4$ matrix of hole-arrays, each with circular holes of diameter 150 nm, periodicity 600 nm, and a transmission peak at 700 nm. Due to the field size of the FIB, each array must be milled separately. As a result, the distance between adjacent matrix elements is variable, resulting in interference that is not directly controllable. Figure 3.8 (b) shows a superarray made up of smaller arrays with three surrounding PBR layers. This latter
PBR-configuration was chosen to minimize the uncertainty of interference between adjacent arrays.

Using the transmission setup with a source spot size equal to the size of one matrix element, the spot was made to be incident over a single matrix element. The peak transmission intensity was taken for the four arrays around the center of the matrix. While the transmission resonance wavelengths did not change significantly, the variance in the transmission intensity of the individual arrays was reduced by 60% with the introduction of PBRs into the superarray. Therefore, isolating array elements within the superarray using PBRs provides increased control over the transmission.

The spectra for the structures without PBRs show slightly higher peak intensities due to the higher number of transmitting holes in the structure without PBRs. In the future, reducing the number of PBR layers will be attempted to overcome this discrepancy.

Figure 3.8 SEMs of superarrays with 600 nm periodicity. (a) Without PBRs. (b) With PBRs.
3.5 Summary

In this chapter, we have characterized PBRs for nanohole arrays. The effectiveness of PBRs in reflecting and enhancing the EOT has been shown to be dependent on the number and depth of PBR layers present. The enhancement was seen to saturate beyond three layers of PBRs. It was also seen that the ideal milling depth for the PBRs was 45 nm, beyond which no appreciable enhancement was observed. This is confirmed by calculations based on the skin depth, where scattering losses and the skin depth of the SPP were seen to play an important role in the performance of the PBR.

Experiments were presented to show the application of PBRs to isolating separate plasmonic structures. The PBRs were seen to considerably alter the interference pattern of a pair of adjacent hole-arrays, and isolate SPPs propagating from an array of partially milled dimples into a hole-array. It was seen that PBRs effectively minimize the interference between adjacent array elements of a superarray. The ability to have arbitrarily large surface areas for use in sensors and other applications using plasmonics is realized with this effect.
Chapter 4

Frequency sensitive plasmonic microcavity

Frequency sensitive optical devices are of importance in optics integration, which also stands in subwavelength regime. For an even more compact reflector device with resonant transmission, here we propose using the highly reflective gold as a simple mirror, and thereby forming a compact surface plasmon (SP) microcavity. The SP microcavity is created by trench milling in a gold film. Other narrower trench structures have been proposed for channel plasmon polaritons waveguides [31-33], those structures used a different polarization state and they relied on lateral guiding the SPPs [34], which is not the topic of this work. Here, the trench is used simply to form mirror side-walls, and thereby to create a microcavity. Due to the surface localization of the SPPs, the trench side-walls are good reflectors, even for depths of only a few hundred nanometers [29]. As a result, compact SP microcavities can be easily created using this approach. Recently, a theory was presented for enhanced coupling between plasmonic transmission lines by using a gold microcavity [35]. In
that work, the transverse resonances of a corresponding periodic slit-array were considered to explain the enhanced coupling.

In this chapter, we present experimental observations and calculations of a SP microcavity enhanced transmission through a slit for the case of free-space coupling. In this paper, we demonstrate the use of a SP microcavity formed in a gold film to resonantly enhance the transmission of light through a slit. The optical transmission is measured experimentally for SP microcavities fabricated with various widths, each having a central slit. The observed resonant transmission peak wavelengths agree well with finite-difference time-domain (FDTD) calculations. The FDTD calculations allow for near-field visualization of the SP standing waves within the SP microcavity. These near-field images elucidate the interaction between the SP microcavity and the slit in the center of the microcavity.

4.1 Experimental and calculation methods

Figure 4.1 shows the scanning electron microscope image of a fabricated SP microcavity with a slit and a schematic representation of the structure. Focussed ion beam (FIB) milling was used to fabricate the SP microcavity structures. The FIB milled through a 300 nm deep gold film evaporated on a glass substrate. There was a 5 nm thick chromium layer deposited to assist adhesion between the gold layer and glass substrate. A gallium beam current of 30 pA at 30 kV was used for milling. The gallium beam spot size was 7 nm. The mill rate of the gold film was calibrated using
energy-dispersive x-ray analysis and it was found to be 110 nm/ms. We fabricated six SP microcavity structures of 200 nm depth and of variable widths from 800 nm to 1300 nm. The length of these structures was 15 \( \mu m \). In the middle of each structure, a 180 nm slit was milled entirely through the gold film. From past work, the 200 nm high walls of the microcavity were estimated to give 50% reflection, while having strong coupling to the input radiation through scattering [29].

The transmission spectra were recorded using a fiber-optic coupled spectrometer. The source was focused with normal incidence onto the SP microcavity structure with a slit. An illumination spot size of 30 \( \mu m \) was obtained using a combination of an iris and a 20\( \times \) microscope objective. A polarizer was used to control the polarization of the incident light. The zeroth order transmission was collected with a 100 \( \mu m \) diameter core fiber placed 1.5 mm from the sample. Positioning of the fiber core and gold slide were achieved using XYZ translation stages.

![Figure 4.1 Scanning electron microscope image of w=1300 nm wide SP microcavity (200 nm depth) with central slit (180 nm width, 100 nm depth) and a schematic representation.](image)
FDTD was used to calculate electromagnetic transmission characteristics of the SP microcavity structure with a slit [36]. The dispersion of the gold was captured using a Drude model. A small mesh-size of 2 nm was chosen to accurately capture SP effects, as was verified by finite-difference mode calculations and repeating the calculations with varying grid sizes (both smaller and larger). Perfectly matched layer boundary conditions were used on all sides of the calculation domain. The Courant stability factor was 0.99. To reproduce the conditions of the experiment, a broadband plane wave source (500 nm to 900 nm) was normally incident on the top surface of the SP microcavity structure, with electric field polarization in the x-direction. Near-field and transmission monitors were used to visualize standing waves within the microcavity and to quantify the transmission spectrum.

4.2 Results and discussion

Figure 4.2 shows the measured transmission spectra from different width SP microcavities, with incident polarization in the x-direction, normalized to the white-light source spectrum. There was no additional normalization to account for the width of the microcavity; however, the lengths of all the structures were the same. All of the structures were measured under the same conditions and the results were repeatable. The transmission for a single slit in a 100 nm gold film without a microcavity is also shown for direct quantitative comparison. (For the orthogonal polarization, no transmission was detectable, which is expected because of the
reduced TE transmission through a subwavelength slit.) Resonant transmission peaks were observed with wavelength that increases as cavity width increases. For example, for a cavity width of 1300 nm, the transmission peak was at 750 nm wavelength (shown with the blue curve in Figure 4.2). This resonant transmission peak was approximately 170 nm wide. There appears to be some additional structurally-dependent transmission features for shorter wavelengths (below 600 nm); however, these effects were obscured by the transmission of gold close to the plasma frequency. The measured transmission is reduced at longer wavelengths due to greater diffraction from the slit. This is an experimental artefact that arises because the 100 μm core fiber collects the transmitted light 1.5 mm from the slit. In essence, this is a zeroth-order transmission measurement.

![Figure 4.2 Measured transmission spectra for different surface plasmon microcavity widths.](image)
Figure 4.3 shows the FDTD calculated transmission spectra for different SP microcavity widths for normal incidence and polarization in the x-direction. The transmission was normalized to the incident power on the width of the slit. There is good quantitative agreement between this calculation and the experimental results for the long wavelength transmission peak. For example, the 1300 nm wide SP microcavity had a calculated transmission peak at 730 nm, whereas the experimentally measured peak was at 750 nm. The small discrepancy can be attributed to fabrication tolerances and experimental error. As in the experiment, the peak transmission wavelength red-shifted when the SP microcavity width increased. The calculated transmission spectra also showed small short-wavelength transmission peaks below 600 nm; however, for these wavelengths, the Drude model does not accurately represent the gold dispersion and so the agreement with experiment is not as good [37]. For the 1100 nm, 1200 nm and 1300 nm wide structures, both experiments and calculations show transmission peaks below 600 nm. These peaks are expected as the next higher order standing wave resonances of the microcavity structure. For example, for the 1300 nm structure, the magnetic field has two nodes for the 730 nm wavelength, and four around 550 nm. The minima in transmission occur around where there is a node in the region of the slit, as will be discussed in more detail later (see Figure 4.3(a)).
The calculated resonant transmission peak widths were smaller than in the experiments, which may be attributed to additional losses from surface roughness that is present in real fabrication. We have repeated our calculations without the slit and we still observe strong SPPs resonances inside the cavity; for example, the 1300 nm wide slit showed 72% as large a transverse magnetic field without the slit as compared to with the slit. This implies that the side walls play an important part in coupling to the input radiation, as well as the coupling as the central slit.

From the experimental and calculation results, the SP microcavity shows a resonant enhancement of the optical transmission through a slit. The experiment showed a maximum transmission enhancement of $2 \times$ with respect to the single slit and the calculations showed a maximum enhancement of $2.6 \times$ both for the 1100 nm array. The discrepancy can be mostly attributed to fabrication tolerances (see Figure 4.1). There is good quantitative agreement in the wavelength of peak transmission between

Figure 4.3 FDTD calculated transmission spectra, normalized to power incident on slit, for different SP microcavity widths.
experiment and calculations. The resonant enhancement is expected from coupling of
the slit to standing-wave resonances of the SP microcavity, which is formed by the
200 nm tall side walls.

The SP microcavity is similar to the plane-wave microcavity, except that
plane-waves are replaced with SPPs. This should shift the resonances to longer
wavelengths; however, the transmission peak resonances were actually observed at
shorter wavelengths. To explore this further, we consider the field distribution within
the cavity for different wavelengths.

Figure 4.4 shows the near-field distribution of the transverse magnetic field squared
magnitude for the 1300 nm cavity. It should be noted that similar features have been
observed in a complimentary plasmonic cavity structure [38]. Figure 4.4(a) shows the
near-field for 640 nm -- a wavelength that is shorter than the transmission resonance
peak. It is clear from this figure that the intensity maxima are away from the slit (on
each side), which reduces the coupling to the slit and the overall transmission. Figure
4.2(b) is at the transmission resonance peak wavelength of 730 nm. It is clear from
this figure that the slit introduces a strong negative phase-shift and reflection to the
SPPs mode [39], which produces 3 peaks near the slit. There is also a strong intensity
variation seen within the slit, which corresponds to resonances within the slit from the
reflection at each end. These features are associated with the slit, and they perturb the
cavity to blue-shift the resonant wavelength away from the expected values of a
regular microcavity. Figure Figure 4.4 (c) shows the near-field distribution at 840 nm,
where the SPPs is closely matched to the second order resonance of the 1300 nm wide
cavity. While this does not give the largest transmission, since the coupling to the slit is not optimized, the standing wave within the cavity is seen clearly.

There may be additional resonance effects from changing the height of the cavity side walls coming from modes in the vertical z-direction in addition to resonant modes we observe in the horizontal x-direction [35]. This influences only slightly the resonance wavelength for the short and wide cavities considered here - the resonances are mainly from the transverse SPPs propagation. For example, we varied the depth of the sidewalls by 100 nm for the 1300 nm cavity in the FDTD calculations and found that the peak shift was only 20 nm.

![Figure 4.4 Transverse magnetic field (perpendicular to imaging plane) profile of 1300 nm structure for three wavelengths: (a) 640 nm, (b) 730 nm and (c) 840 nm. Scale bar is the same for all three images.](image-url)

The reflection of a 200 nm step for a gold surface was calculated using FDTD. For 750 nm wavelength, the reflection was 0.76 and the phase of reflection was 171° (close to 180° expected for a perfect electric conductor, which contributes a 1.7% shift to the resonant wavelength). For the 1300 nm cavity, ignoring the influence of the slit and the SPPs loss, this gives an optimal quality factor (Q) of 6.6. Considering this, the FWHM of the transmission resonances should be approximately
110 nm. In the FDTD calculations for the 1300 nm cavity, the transmission peak FWHM (subtracting the slit-only transmission) was 150 nm, which is larger due to material loss and scattering loss from the slit. In the experiment, the FWHM of the 1300 nm cavity peak transmission (subtracting the slit-only transmission) was 15% larger still, likely due to roughness from fabrication. The transmission resonance has an asymmetric shape, which is characteristic of Fano resonances found in similar plasmonic systems [40]. The present structure was not optimized for achieving a large quality factor because of the additional losses necessary from the slit to measure the transmission. Without the slit, the quality factor (from calculations) increases to 14.3; however, there is an intrinsic limitation from metal losses that limits plasmonic microcavities. The SPPs propagation length divided by the SPPs wavelength is an approximate upper bound for the quality factor imposed by plasmonic damping.

4.3 Summary

The optical transmission through a slit was resonantly enhanced, by a factor of 2, by forming a SP microcavity around the slit. Wavelength tuning of the transmission maxima was achieved by varying the width of the microcavity. FDTD calculations were also performed that agreed quantitatively with the experiments. The resonance transmission wavelength was dependent on the cavity width, and influenced by the presence of the slit. The compact SP microcavity geometry proposed here is easily fabricated and it may be used to provide wavelength-sensitive transmission. By
extending the SP microcavity approach presented here, it is easy to envision future devices for enhancing local electromagnetic fields and for providing refractive index sensitive peak shifts. Those optimized SP microcavity structures can be applied to surface-enhanced Raman scattering, nonlinear optics and surface plasmon resonance sensors [41-46].
Chapter 5

Subwavelength metallic taper

Subwavelength metallic taper structures allows for significant field enhancement towards the end of the taper and therefore efficiently coupling light into nanoscale devices [47-49]. Since the coupling efficiency of taper structure is dependent on the taper angle, optimizations to these structures have considered solving for the optimal angle. Two methods have been reported to calculate the optimal angle of the taper structures: the finite-difference time-domain method (FDTD) and the adiabatic theory [48, 50, 51]. FDTD is a comprehensive fully-vectorial method that can achieve accurate results; however, plasmonic structures require small grid sizes, and for stability, small time-steps. Therefore, FDTD is computationally intensive and time-consuming, which is a limitation in large structures in 2D, such as a gradual taper, and 3D structures. The adiabatic method is fully-analytic and efficient, but only accurate when the taper structure satisfies adiabaticity. Further calculations are required to ensure that there is negligible reflection.

In this chapter, we propose a simple single mode matching (SMM) method that allows for rapid calculation of the optical transmission efficiency through both 2D and
3D taper structures. This method calculates the reflection and transmission of the lowest order mode at a stepped-interface, including the influence of material loss in each segment. By comparison with past results, it is verified that the SMM method can efficiently achieve accurate results under different configurations, including both loss and reflection. Examples of a 2D gold taper gap and a 3D gold taper rod are presented, which have been calculated in the past by FDTD and the adiabatic method [50, 51]. Our results compare well quantitatively with those works. The proposed method can be easily extended to more complex structures.

5.1 The SMM method in 2D

5.1.1 Structure and Gap Mode Description

To demonstrate the SMM method, we analyze in detail a tapered gap in 2D. The analyzed structure is shown in Figure 5.1. All the configurations are exactly the same as previous work for comparison [50]. A vacuum taper gap is formed between two gold media. The initial width of the taper \( W_i \) is 316.4 nm, and the final width \( W_f \) is 1.512 nm. The relative permittivity for the gold \( \varepsilon_m \) is set to -16.2+0.5i, and for vacuum \( \varepsilon_v \) is 1. This structure is uniform and infinite in \( z \)-direction.

The wave mode in the taper gap used to calculate the optical transmission efficiency is the lowest order TM surface plasmon (SP) mode, which has the transverse magnetic field component in \( z \)-direction and electric field component in
$x$- and $y$-directions. The wavelength in vacuum $\lambda_\nu$ is 632.8 nm. Only the $y$-component electric field and $z$-component magnetic field are considered, because they are the transverse components required for formulating the orthogonality relations.

![Figure 5.1](image)

**Figure 5.1** The geometry of a 2D taper gap structure between two gold media. The widths $W_i$ and $W_f$ are fixed and the length $L$ varies for different taper angle $\theta$. For comparison with past works, $W_i = 316.4$ nm, $W_f = 1.512$ nm and the permittivity of gold $\varepsilon_m$ is -16.2 + 0.5i, $\varepsilon_\nu$ is 1 for vacuum.

### 5.1.2 Method

The methodology here is based on the mode matching theory truncated to a single mode [1]. The taper gap is divided into small steps along $x$-direction (as shown in Figure 5.2), and the method is then implemented on each two adjacent steps to calculate the transmission matrix $M_t$. A 0.1 nm step size is applied here.

Assuming two adjacent steps, step 1 and step 2, in which

\[
\begin{align*}
E_i^y &= A_i E_{ii}^y + B_i E_{ir}^y \\
H_i^z &= A_i H_{ii}^z - B_i H_{ir}^z
\end{align*}
\]  

(5.1)
\[\begin{align*}
E_2^y &= A_2 E_{2i}^y + B_2 E_{2r}^y \\
H_2^z &= A_2 H_{2i}^z - B_2 H_{2r}^z
\end{align*}\] (5.2)

\(E_1^y, \ E_2^y, \ H_1^z, \ H_2^z\) represent \(y\)-component electric field and \(z\)-component magnetic field in each step, respectively. Subscript \(i\) and \(r\) indicate the incident wave and the reflected wave. \(A_1, \ A_2, \ B_1, \ B_2\) are the elements of transmission matrix \(M_t\),

\[M_t = \begin{bmatrix} A_1 & B_1 \\ A_2 & B_2 \end{bmatrix}\] (5.3)

and can be solved using Equation (5.1) and Equation (5.2) and the orthogonality relations:

\[\begin{align*}
\int_{-\infty}^{\infty} (E_1^y \times H_1^z) dy &= \int_{-\infty}^{\infty} (E_2^y \times H_2^z) dy \\
\int_{-\infty}^{\infty} (E_2^y \times H_1^z) dy &= \int_{-\infty}^{\infty} (E_2^y \times H_2^z) dy
\end{align*}\] (5.4)
Figure 5.2 The schematic diagram of the SMM model. The calculation step size in $x$-direction is 0.1 nm. $H_i$ and $H_r$ represent the incident and reflective transverse magnetic fields, respectively.

To take into account the influence of the dissipation in each step, the propagation matrix $M_p$ should be considered, which is formed by

$$M_p = \begin{bmatrix} e^{-j\beta \Delta x} & 0 \\ 0 & e^{j\beta \Delta x} \end{bmatrix}$$  \hspace{1cm} (5.5)$$

$\beta$ is the SP wave vector, and $\Delta x$ is the distance SP propagating in a step.

The transmission efficiency result can be achieved by

$$T_{total} = \prod_{\alpha} (M_{pu} \cdot M_{ut}) \cdot \begin{bmatrix} 1 \\ 0 \end{bmatrix}$$  \hspace{1cm} (5.6)$$

Subscript $\alpha$ indicates the step number. For this 2D taper gap structure, the magnetic and electric fields can be expressed by the function of the gap width $w$,

$$H^z = \begin{cases} C_1 \cdot \cosh(-\sqrt{\beta^2 - \varepsilon_n k_y^2} \cdot y) \cdot e^{-j\beta x} & |y| \leq \frac{w}{2} \\
C_2 \cdot \exp(-\sqrt{\beta^2 - \varepsilon_n k_y^2} \cdot (|y| - \frac{w}{2})) \cdot e^{-j\beta x} & |y| > \frac{w}{2} \end{cases}$$  \hspace{1cm} (5.7)$$
and

\[
E^y = \begin{cases} 
-\frac{\beta}{\omega \epsilon_v} H^z & |y| \leq \frac{w}{2} \\
-\frac{\beta}{\omega \epsilon_v \epsilon_m} H^z & |y| > \frac{w}{2}
\end{cases}
\]  \quad (5.8)

where \( C_1 \) and \( C_2 \) are the normalization coefficients, \( \omega \) is the angular frequency of SP wave and \( k_v \) is the wave vector in vacuum. The wave vector in the taper gap \( \beta \) is also a function of \( w \) and can be determined by equation [39],

\[
\tanh(\sqrt{\beta^2 - k_v^2} \cdot \frac{w}{2}) = \frac{-\epsilon_v \sqrt{\beta^2 - \epsilon_m k_v^2}}{\epsilon_m \sqrt{\beta^2 - \epsilon_v k_v^2}}
\]  \quad (5.9)

5.1.3 Results

![Figure 5.3 The SP wave vector \( \beta \) at different widths in the taper gap.](image)

Blue line represents the real part of \( \beta \), and red line is the imaginary part.

Figure 5.3 shows the dependence of the wave vector \( \beta \) on the gap width. The real part (blue line) of \( \beta \) is close to vacuum wave vector \( k_v \) when the gap width \( w \) is...
above $0.3\lambda$, and then becomes large as $w$ decreases. Similar to the real part, the imaginary part (red line) of $\beta$ is very small ($\sim 0.001k_v$) when $w$ is $0.5\lambda$, and increase rapidly when $w$ is close to 0. For the imaginary part of wave vector is related to the dissipation, it can be seen that the wave loss is significant with small even the permittivity imaginary part of the gold is only 0.5 in this example.

Figure 5.4 The dependence of the normalized optical transmission efficiency through the taper gap on the taper angle $\theta$. Blue line: with dissipation, in which $\varepsilon = -16.2 + 0.5i$; Red line: without dissipation, $\varepsilon = -16.2$.

Figure 5.4 shows the dependence of the normalized optical transmission efficiency through the taper gap structure on the taper angle $\theta$, calculated using Equation (5.1) - (5.9). Both the cases with dissipation and without dissipation are calculated. For the case without dissipation, the imaginary part of the relative permittivity is set to zero. Without dissipation (red line), the transmission efficiency is unity when $\theta$ is zero because there is negligible back-scattering for this adiabatic taper. The transmission efficiency decreases as the taper angle becomes larger due to backscattering. With the
dissipation (blue line), the transmission efficiency goes to zero for 0°, since longer
tapers have greater material losses. The transmission efficiency increases to maximum
about 0.71 when $\theta$ is 14°. This is the optimum angle for the trade-off between
back-scattering that dominates for large angles and losses that dominate for small
angles. For the limit situation, the whole structure is equivalent to an infinite 2D
subwavelength waveguide at 0° taper angle which is corresponding to infinite
dissipation and a gold plate with a 1.512 nm wide slit at 180° which is corresponding
to maximum reflection. This optimum angle for the 2D taper gap agrees well with the
previous work using comprehensive FDTD calculations where the value of 13.5° was
found as the optimum [50].

For consistency within this work, the optical transmission efficiency of a 2D taper
gap with another gold permittivity ($\varepsilon_m$ is -11.44 + 1.12i) has also been investigated
[37, 51], which is shown in Figure 5.5. It can be seen that this taper gap structure has
larger transmission efficiency at high taper angle condition than the former one due to
its smaller reflection, but lower transmission peak (0.58 at 22.5°) due to loss.
To further test the validity of the SMM method, a 3D gold taper rod is considered below.

5.2 The SMM method in 3D

5.2.1 Structure and Gap Mode Description

Figure 5.6 shows the model of the 3D gold taper rod structure in vacuum. The vacuum wavelength $\lambda_v$ is 632.8 nm. The initial diameter $2 \times a$ and the final diameter $2 \times b$ are 600 nm, 10 nm, respectively. The gold permittivity $\varepsilon_m$ is
-11.44+1.12i, and the vacuum permittivity $\varepsilon_v$ is 1. (Note that the different value of the relative permittivity here is used for direct comparison with past numerical calculations).

![Diagram of a 3D gold taper rod structure in vacuum.](attachment:diagram.png)

**Figure 5.6** The model of a 3D gold taper rod structure in vacuum. Here $2\times a = 600$ nm, $2\times b = 10$ nm and the permittivity of gold $\varepsilon_m$ is -11.44 + 1.12i, $\varepsilon_v$ is 1 for vacuum.

The SP wave mode used here is the lowest order surface plasmon TM mode, whose magnetic field is parallel to the azimuthal direction in the cylindrical coordinate system. Therefore, the $\phi$-component of magnetic field and the $r$-component of electric field are considered for the orthogonality relations. The vacuum wavelength $\lambda_v$ of SP wave is also 632.8 nm. All the configurations are the same as a recent work [51].

Figure 5.7 shows the schematic diagram of the SMM mode in 3D gold taper rod. The calculation step in $x$-direction is 0.1 nm as shown.
Figure 5.7 The schematic diagram of the SMM model in 3D gold rod. The calculation step size in $x$-direction is 0.1 nm. $H_i$ and $H_r$ represent the incident and reflective transverse magnetic fields, respectively.

5.2.2 Method

A similar methodology is applied in this example as in the 2D case. Instead of $E^y$, $H^z$, the $r$-component electric field $E^r$ and $\varphi$-component magnetic field $H^\varphi$ are considered:

$$H^\varphi = \begin{cases} 
C_1 \frac{j\omega\varepsilon_m}{p_m} I_1(p_m r) & r \leq \rho \\
-C_2 \frac{j\omega\varepsilon}{p_v} K_1(p_v r) & r > \rho 
\end{cases}$$

(5.10)

and
\begin{equation}
E^r = \begin{cases} 
-\frac{\beta}{\omega \varepsilon_m} H^\varphi & r \leq \rho \\
-\frac{\beta}{\omega \varepsilon_v} H^\varphi & r > \rho 
\end{cases}
\tag{5.11}
\end{equation}

$C_1, C_2$ are the normalization coefficients, $I$ and $K$ are the first kind and the second kind of modified Bessel functions, respectively, and the subscripts indicate the orders [12]. $\omega$ is the angular frequency of SP wave and $\rho$ is the rod radius at certain position. $p$ is defined as
\begin{equation}
\begin{cases} 
    p_v^2 = \beta^2 - k_v^2 \\
    p_m^2 = \beta^2 - k_m^2
\end{cases}
\tag{5.12}
\end{equation}

$k_v, k_m$ are the wave vectors in vacuum and gold, respectively. Using the boundary condition, SP wave vector $\beta$ can be achieved by equation below [12],
\begin{equation}
\frac{K_0(p_m \rho)}{I_0(p, \rho)} + \frac{\varepsilon_m p_v}{\varepsilon_v p_m} \frac{K_1(p_m \rho)}{I_1(p, \rho)} = 0
\tag{5.13}
\end{equation}

Here the orthogonality relations are in form as:
\begin{equation}
\begin{cases} 
    \int_0^{2\pi} d\varphi \int_0^{\infty} (E_1^r \times H_1^\varphi) r dr = \int_0^{2\pi} d\varphi \int_0^{\infty} (E_2^r \times H_1^\varphi) r dr \\
    \int_0^{2\pi} d\varphi \int_{-\infty}^{0} (E_1^r \times H_1^\varphi) r dr = \int_0^{2\pi} d\varphi \int_{-\infty}^{0} (E_2^r \times H_2^\varphi) r dr 
\end{cases}
\tag{5.14}
\end{equation}

5.2.3 Results

Figure 5.8 shows the dependence of the wave vector $\beta$ on the diameter $2\rho$. The real part (blue line) of $\beta$ is close to $k_v$ when diameter is over 0.2 wavelength but increases rapidly when the diameter is made very small. The imaginary part (red line) is $0.01k_v$ when the diameter equals to half $\lambda_v$ and increases rapidly to $k_v$ when the taper rod diameter decreases to $0.01\lambda_v$. 
Figure 5.8 The SP wave vector $\beta$ at different widths in the taper gap.

Blue line represents the real part of $\beta$, and red line is the imaginary part.

Figure 5.9 shows the dependence of the normalized optical transmission efficiency through the gold taper rod structure on the taper angle $\theta$, as calculated using the same basic method as in Equations (5.1) - (5.5), but with modification to the cylindrical geometry as represented by Equations (5.10) - (5.14). Without dissipation, the transmission efficiency decreases from 1 at zero degree to 0.42 at $\theta = 60^\circ$. For there is lossless-metal, mode reflection in this case is larger than the 2D taper gap case, which contributes to the larger optimal taper angle. With dissipation (blue line), the optical transmission efficiency reaches a maximum of 0.44 at $\theta = 32^\circ$. As is consistent with the 2D case, the transmission is zero at $0^\circ$ due to material losses over an infinitely long taper. Therefore, the optimal taper angle is bigger than in 2D, which is due to the combined effects of greater loss and greater mode reflection.
Figure 5.9 The dependence of the normalized optical transmission efficiency through the gold taper rod on the taper angle $\theta$. Blue line: with dissipation, in which $\varepsilon_{\infty} = -11.44 + 1.12i$; Red line: without dissipation, $\varepsilon_{\infty} = -11.44$.

In a recent work, the adiabatic method has been applied to small taper angle realm and the FDTD method to large taper angle realm. The optimal taper angle for maximum electric field at exit side was 35°, which is in good agreement with the result of this paper [51].

5.3 Discussion

Two other methods have been used to calculate the SP wave propagation properties through metal taper structures: the FDTD method and the adiabatic method. Both of them have very distinct advantages and drawbacks as discussed above. Here we add
the SMM method. The SMM method introduced by this paper considers both the mode reflection and dissipation, which allows for operation over a wide range of angles (approximately 0° - 70°, as discussed below). This method inherently contains the physics associated with the lowest-order mode, so that it is easy to interpret the results in terms of the properties of that mode, and to make generalizations to other geometries. Furthermore, the method is very efficient due to its analytic nature.

Considering past FDTD calculations, there is discrepancies with the SMM work for angles greater than 90° [51]. In particular, the FDTD calculations show a faster reduction in the transmitted light than the SMM method. This error is due to the truncation of the SMM method to a single mode only, whereas there is scattering to higher order modes for highly-angled tapers. While in principle, this problem can be solved by adding higher modes into the calculation, this will remove the benefit of simplicity in the proposed approach. Therefore, we suggest that this method may be applied for tapers in the range of approximately 0°-70°, and for larger angles, comprehensive numerical methods should be used. Neglecting higher-order modes also removes the possibility of coupling to anti-symmetric modes in systems where there is symmetry breaking.

The SMM method described here can be generalized to other structures, not only simple linear tapers. For example, it is possible to consider a nonlinear taper structure that would reduce the back scattering and enhance the transmission efficiency. For the 3D gold taper rod, at the optimum angle 32°, 28% of the transmission loss is from
back scattering, which means there is room for further the enhancement in the transmission efficiency by optimizing the taper geometry with a nonlinear taper.

Another possible extension of this work is the application of the SMM method to periodic structures. These structures are interesting for potential Bragg resonances [52, 53]. This would require using periodic conditions (or scaled periodic conditions when including losses) in the matrix calculations.

Finally, an interesting extension of this work would be to deduce analytic results for the optical transmission based on the SMM method. Since the method is semi-analytic in the present form, a parametric description of the mode-matching and propagation would allow for a fully-analytic treatment. While that proposal is a challenging endeavour, beyond the scope of this present investigation, it has the potential benefit of allowing for a fully analytic determination of the optimum structure simply by taking a derivative.

5.4 Summary

In this chapter, a simple SMM method is presented to calculate the optical transmission efficiency through subwavelength metal taper structures. It is found that a 14° optimal angle with 71% transmission efficiency for the 2D taper gap structure in gold and a 32° optimal angle with 44% transmission efficiency for the 3D taper gold rod structure, which both agree well with the previous results [50, 51]. The method is more efficient than comprehensive numerical calculations and more accurate than
adiabatic methods; it retains the influence of reflection and losses simply by multiplying out 2-by-2 matrices. The SMM method may be extended to other nonlinear geometries, for example, to optimize the subwavelength squeezing of light or to enhance Bragg resonances. Many applications that presently use plasmonic field enhancements stand to benefit from the SMM method, such as SERS which allows the technique to be sensitive enough to detect single molecule [15, 16, 54-57].
Chapter 6

Asymmetric long range surface plasmon waveguide

While surface plasmons are of great interest for many applications [22], including biosensors [46, 58-65], waveguides and circuits [66-78], a major challenge remains overcoming propagation losses, for which long-range surface plasmons (LRSPs) have been investigated extensively [79]. The long propagating lengths achievable with LRSPs potentially enable numerous applications, including biosensors having a high sensitivity and a low detection limit [63].

Past work on LRSPs was based mainly on symmetric insulator-metal-insulator (IMI) structures which use a thin metal slab (infinite width) or stripe (finite width) to achieve low loss [79]. (The LRSP in the thin metal slab and stripe correspond to the sb and ssb0 modes respectively [79].) Allowing the structure to become slightly asymmetric introduces cut-off conditions for the LRSP, constraining the dimensions of the metal slab or stripe, or the operating wavelength [80-85]. As the LRSP in an asymmetric structure approaches cut-off, its propagation length increases, but its confinement rapidly vanishes as does its coupling efficiency to finite-sized beams.
In practice, such symmetric (or slightly asymmetric) LRSP waveguides are not always convenient. Within the context of biosensors for example, matching the refractive index of an aqueous sensing solution requires a cladding material having a refractive index of about 1.31 - 1.33 (depending on the operating wavelength). Few candidate materials exist satisfying this requirement; two are Teflon and Cytop. Teflon has an index that is slightly below that of de-ionised water and Cytop has an index that is slightly above. Both have been used to support metal slabs or stripes propagating LRSPs through aqueous solutions [86-89].

Enlarging the set of materials that could be used requires finding structures that are physically asymmetric but still support LRSPs. One approach involves combining thin layers of materials, as in [90] where a Teflon/Ta$_2$O$_5$ bi-layer system was used to match (effectively) the index of the aqueous environment on the other side of an Au slab. A second approach involves combining a finite 1D photonic crystal, which can support Bloch surface waves in the bandgap, with an Au slab (and the bounding medium on the other side) such that a symmetric LRSP field distribution is achieved throughout the structure [91]. A third approach is to minimally perturb the symmetry by using an ultrathin freestanding dielectric membrane to support the metal film and allowing the sensing environment to bound both sides of the structure [92, 93].

Building on these ideas, we propose in this paper a novel asymmetric insulator-metal-insulator-insulator (IMII) structure that can support LRSP waves. The IMII waveguide works by effectively restoring the symmetry of the LRSP transverse fields within the metal film. The generic 1D IMII slab waveguide is investigated
analytically first, and a TM (transverse-magnetic) transcendental equation that ensures LRSP propagation is derived. Cases implemented with specific materials are then verified quantitatively by the transfer matrix method (TMM), by which the surface sensitivity [63] and the figure of merit [94] of the proposed waveguide are also obtained. The corresponding 2D metal stripe structure is then investigated by the finite difference method (FDM), which shows parametric regimes where effective LRSP guiding can be accomplished. Results are given for a candidate structure relevant to biosensing, consisting of an H\textsubscript{2}O - Au - SiO\textsubscript{2} - air suspended structure which has a potential advantage over the membrane waveguide of [92, 93] in that integration with microfluidic channels should be easier to achieve.

6.1 LRSP along an IMII slab structure (1D)

6.1.1 Geometry of the IMII slab waveguide

The 1D IMII structure is studied first in order to provide insight into the conditions under which the LRSP may be supported. Figure 6.1(a) shows an example implementation of a structure that is of interest for bio-sensing. All layers are infinite in the x and y directions. The LRSP is assumed to propagate along the +x-direction at a vacuum wavelength of \( \lambda_0 = 1310 \text{ nm} \) according to \( e^{j\beta x} (e^{-j\omega t} \text{ time dependence assumed}) \). The H\textsubscript{2}O region is semi-infinite and its relative permittivity is \((1.3159 + j1.639\times10^{-5})^2\). The second layer is a Au slab, which has a
relative permittivity of $-86.08 + j8.322$ and a thickness $t$. Beneath the Au slab is a supporting dielectric membrane of thickness $d$, such as SiO$_2$ having a relative permittivity of 2.0932. The bottom semi-infinite layer is air, having a relative permittivity of 1. (The values of relative permittivity originate from [93]).

This structure is practical, provided that the SiO$_2$ layer is thick enough to be mechanically stable and deposited without too much compressive strain. It can be fabricated by etching through an underlying Si substrate (not shown) to release the SiO$_2$ layer, thereby creating a free-standing SiO$_2$ membrane supported around its perimeter (following [92]). The sensitivity of the LRSP in this structure to changes in an adlayer located at the Au/H$_2$O interface is high, based on results obtained for similar structures [63], and based on computations given below.

Figure 6.1 (a) Schematic of a 1D IMII slab waveguide; the layers from top to bottom are H$_2$O, Au, SiO$_2$ and air, respectively. (b) Sketch (not to scale) of the transverse magnetic field of the symmetry constrained LRSP
(dashed curves) having identical field values along the upper and lower boundaries of the Au layer.

6.1.2 Theoretical model of the IMII: restored LRSP symmetry in the metal

In the symmetric IMI structure, the transverse LRSP mode fields are symmetric about the centre plane bisecting the metal slab, so a transverse field is identical along its top and bottom boundaries. Building on this point, the approach to obtaining a low-loss IMII structure is to find the thickness of the dielectric layer d that restores the symmetry of the transverse LRSP mode fields within the metal slab. Practically, this is achieved by enforcing that the transverse magnetic field (and transverse electric field) be identical along its boundaries, as sketched in Figure 6.1(b). Although field symmetry over the full cross-section is not achieved, symmetry within the metal slab is achieved, thus capturing an IMII configuration that supports a LRSP; this LRSP shall henceforth be referred to as the "symmetry-constrained LRSP".

First, we write the transverse magnetic field in the different layers $H_{i,y}$ for a TM mode:

$$
\begin{align*}
H_{1,y} &= Ae^{-k_1 \left(\frac{z-d}{2}\right)} & \text{in } H_2O \\
H_{2,y} &= Be^{-k_3 \left(\frac{z-d}{2}\right)} + Ce^{k_3 \left(\frac{z-d}{2}\right)} & \text{in } Au \\
H_{3,y} &= De^{-k_3 \left(\frac{z+d}{2}\right)} + Fe^{k_3 \left(\frac{z+d}{2}\right)} & \text{in } SiO_2 \\
H_{4,y} &= Ge^{k_4 \left(\frac{z+d}{2}\right)} & \text{in } Air
\end{align*}
$$

(6.1)

The corresponding longitudinal electric field in each layer $E_{i,x}$ is obtained from:
\[ E_{ix} = -j \frac{1}{\omega \varepsilon_0 \varepsilon_i} \frac{\partial H_{iy}}{\partial z} \] (6.2)

\( A, B, C, D, F, G \) are the amplitude coefficients for \( H_{iy} \) and \( E_{ix} \) at the boundaries. Subscripts 1-4 indicate the \( \text{H}_2\text{O}, \text{Au}, \text{SiO}_2 \) and air layers, respectively, and
\[ k_i = \left( \beta^2 - k_0^2 \varepsilon_i \right)^{1/2} \] where \( k_0 \) represents the vacuum wavenumber, \( \varepsilon_i \) is the complex relative permittivity of the \( i^{th} \) layer and \( \beta \) is the complex TM mode wavenumber. Then by applying the boundary conditions (tangential fields must match) to Equations. (6.1) and (6.2), we obtain the \( \beta - d - t \) transcendental equation for TM modes on this structure:
\[ e^{2k_3 d} = \frac{r_3 (Re^{k_2 t} + e^{-k_2 t}) - r_2 (Re^{k_2 t} - e^{-k_2 t}) (r_3 - r_4)}{r_3 (Re^{k_2 t} + e^{-k_2 t}) + r_2 (Re^{k_2 t} - e^{-k_2 t}) (r_3 + r_4)} \] (6.3)

where \( r_i = \frac{k_i}{\varepsilon_i} \) and \( R = \frac{r_2 + r_1}{r_2 - r_1} \).

In the lossless case \((\text{Im} \{\varepsilon, \beta\} = 0)\) mode cut-off occurs when \( \beta = k_0 \varepsilon_1^{1/2} \) (mode wavenumber equals the wavenumber of plane waves in \( \text{H}_2\text{O} \)). Substituting this condition into Equation (6.3) yields the following equation which constrains \( d \) and \( t \) at the cut-off point of the TM modes:
\[ e^{2k_3 d} = \frac{(r_3 \cosh(k_2 \cdot t) - r_2 \sinh(k_2 \cdot t)) (r_3 - r_4)}{(r_3 \cosh(k_2 \cdot t) + r_2 \sinh(k_2 \cdot t)) (r_3 + r_4)} \] (6.4)

As mentioned above, the transverse magnetic field of the LRSP must be identical along the boundaries of the metal slab if the field is to be symmetric therein; this implies \( B = C \). Adding this constraint to the boundary conditions (tangential fields must match), and applying them to Equations. (6.1) and (6.2) yields:
\[ e^{2k_3d} = \frac{(r_1 \cosh(k_2 \frac{t}{2}) - r_2 \sinh(k_2 \frac{t}{2})) \cdot (r_3 - r_4)}{(r_1 \cosh(k_2 \frac{t}{2}) + r_2 \sinh(k_2 \frac{t}{2})) \cdot (r_3 + r_4)} \quad (6.5) \]

and:

\[ \tanh(k_2 \frac{t}{2}) = -\frac{k_1 \varepsilon_2}{k_2 \varepsilon_1} \quad (6.6) \]

Thus, the introduction of the additional constraint \( B = C \) yields two transcendental equations, instead of one (Equation (6.3)) as is usually the case. Equation (6.6) is generated from the field solutions in the \( H_2O \) and Au layers only \( (H_{1x}, H_{2y}, E_{1x}, E_{2x}) \), and is the same as for the LRSP of the symmetric IMI [81]. The symmetry-constrained LRSP satisfies Equations. (6.5) and (6.6) simultaneously in the lossless case only \( (\text{Im} \{\varepsilon_i, \beta\} = 0) \). A solution strategy then consists of first solving Equation (6.6) using a root-finding algorithm to determine \( \beta \) for a value of \( t \), and then inserting both values into Equation (6.5) to determine \( d \) directly. Equations. (6.5) and (6.6) are thus useful for generating \( t, d \) pairs for which the LRSP is symmetry-constrained. Equation (6.3) always holds (including losses) so the complex mode wavenumber (including attenuation) can then be readily determined for a particular design.

Figure 6.2(a) shows the collection of thicknesses \( t \) and \( d \) satisfying Equation (6.5) for the LRSP in the IMII considered \( (H_2O - Au - SiO_2 - air \text{ at } 1310 \text{ nm}) \) in the lossless case, and so corresponds to designs for which the LRSP is symmetry-constrained. Note that the thinner the Au slab, the thicker the SiO\(_2\) layer must be to compensate for the index discrepancy between \( H_2O \) and air. For example, for a 50 nm thick Au slab, a
342 nm thick SiO$_2$ layer is needed, but for a 20 nm thick Au slab, a 382 nm thick SiO$_2$ layer is needed. The other curve in Figure 6.2(a) corresponds to cut-off configurations obtained using Equation (6.4), below which there is no purely bound LRSP. The symmetry-constrained designs are above cut-off but as the metal slab thickness decreases, cut-off is approached.

![Figure 6.2(a)](image1.png)  
![Figure 6.2(b)](image2.png)

**Figure 6.2** (a) Symmetry-constrained (blue curve) and cut-off (green curve) thicknesses for the LRSP in the IMII of interest (H$_2$O - Au - SiO$_2$ - air at 1310 nm). (b) Effective index (blue curve) and attenuation (red curve) of the symmetry-constrained LRSP in the IMII of interest (H$_2$O - Au - SiO$_2$ - air at 1310 nm) as a function of the Au slab thickness.

Figure 6.2(b) shows the effective index ($n_{eff}$) of the symmetry-constrained LRSP computed using Equation (6.5), which increases with Au thickness as expected, approaching limiting values when the Au thickness is larger than ~100 nm. When the Au layer is thinner, the effective index is close to the refractive index of H$_2$O.

6.1.3 Computations using the transfer matrix method
The transfer matrix method (TMM) is broadly used for solving the modes of multilayer slab waveguides. The formulation reported in [95] was applied to verify the theory presented in Subsection 6.1.2.

Figure 6.3(a) shows the effective index and attenuation of the LRSP in the IMII of interest as a function of the membrane thickness for 20 and 50 nm thick Au slabs computed via the TMM. There is excellent quantitative agreement in the effective index between the TMM results (curves) and the theory for the symmetry-constrained LRSP (Equation (6.5) - stars). When the Au slab is 50 nm thick, the symmetry-constrained LRSP occurs at \( d = 341.7 \) nm and its effective index and attenuation (TMM) are 1.324633 and 31.39 dB/mm, respectively. When the Au slab is 20 nm thick, the symmetry-constrained LRSP occurs at \( d = 381.5 \) nm and its effective index and attenuation (TMM) are 1.3182884 and 3.26 dB/mm, respectively.

The lowest attenuation does not occur for the symmetry-constrained LRSP, but rather for a slightly asymmetric LRSP at a nearby membrane thickness. Further away from the symmetry-constrained design, the LRSP becomes increasingly localised to the Au/H_2O interface for increasing \( d \), and to the Au/SiO_2 interface for decreasing \( d \). The LRSP tends towards cut-off with decreasing \( d \), explaining the decreasing effective index.

Figure 6.3(b) plots the bulk (\( \frac{\partial n_{\text{eff}}}{\partial n_c} \)) and surface (\( \frac{\partial n_{\text{eff}}}{\partial a} \)) sensitivities of the LRSP computed using the TMM. \( n_c \) denotes the refractive index of the carrier fluid, in this case H_2O, and \( a \) denotes the thickness of a thin biochemical adlayer of refractive index 1.5 placed on the metal slab at the Au/H_2O interface [63]. The trends
in the sensitivities with $d$ follow the trends of the mode fields described in the preceding paragraph. In the case of the $t = 20$ nm thick Au slab, the bulk sensitivity increases as $d$ decreases below the symmetry-constrained design because the mode nears cut-off, and as it does its fields extend deeply into the higher index medium which is H$_2$O. The sensitivities are larger for the $t = 50$ nm slab because of the stronger mode confinement.

**Figure 6.3** (a) Effective index (blue solid) and attenuation (red dashed) of the LRSP on the IMII of interest (H$_2$O - Au – SiO$_2$ - air at 1310 nm) for two thicknesses of the Au slab (20 and 50 nm) computed by the TMM. The values marked by the stars and the pentagons (green and magenta) were computed for the symmetry-constrained LRSP via Eq. (5). (b) Bulk ($\partial n_{\text{eff}} / \partial n_i$ - blue solid) and surface ($\partial n_{\text{eff}} / \partial a$ - red dashed) sensitivities, and (c) surface sensing parameter $G$ (blue solid) and $M_2$ figure of merit (red dashed), of the LRSP on the 1D IMII of interest. (d) Distribution of the $H_y$ field component of the LRSP on the IMII of interest for $t = 50$ nm and $d = 341.7$ nm (Blue thick), and on the corresponding IMI (H$_2$O-Au-H$_2$O with $t = 50$ nm, red thin); the bottom boundary of the Au slab is located at $z = 0$. 
Figure 6.3(c) shows the surface sensing parameter $G$ and the $M_2$ figure of merit [63, 94] for different SiO$_2$ membrane thicknesses, calculated using the TMM. $G$ is the ratio of the surface sensitivity to the normalised attenuation ($k_{\text{eff}}$), and is particularly relevant for surface sensing [63]. $M_2$ measures the confinement-to-loss ratio where confinement is defined as the mode's distance from the light-line [94]. Both $G$ and $M_2$ are maximised at the same membrane thickness, which is fairly close to the symmetry-constrained design. For example, when the Au slab thickness is $t = 50$ nm, $G$ and $M_2$ peak at $d = 350$ nm (the symmetry-constrained membrane thickness in this case is $d = 341.7$ nm). Thus the symmetry-constrained structure generates good designs for sensing applications.

It is instructive to compare the symmetry-constrained LRSP in the IMII of interest with the LRSP supported by the corresponding IMI. Figure 6.3(d) plots the distribution of the associated $H_y$ fields, showing that they are identical for $z > 0$, i.e., within the metal slab and in the H$_2$O region. The field below the metal slab in the case of the IMII is more confined due to the SiO$_2$ and Air layers. Table 1 summarises the modal quantities for $t = 20$ and 50 nm. The effective indices are similar, through not identical, but the attenuation of the LRSP in the IMII is significantly larger. Although the field distribution in the metal is identical to that of the corresponding IMI (Figure 6.3(d)), the mode overlap with the metal is stronger because of the increased confinement in the SiO$_2$ and air regions, leading to the larger attenuation. The overlap with the biochemical adlayer is also larger for the LRSP on the IMII (due to the same reason) leading to a larger surface sensitivity. However, the $G$ parameters
end up being similar. (Only one adlayer was assumed for the IMI in the sensitivity calculations.)

Table 6.1 Comparison of modal quantities for the LRSP supported by the IMII of interest (H₂O - Au - SiO₂ - air at 1310 nm), and by the corresponding IMI (H₂O-Au-H₂O), for the two metal slab thicknesses.

<table>
<thead>
<tr>
<th>Structure</th>
<th>$n_{eff}$</th>
<th>Att (dB/mm)</th>
<th>$\partial n_{eff}/\partial a$ (nm⁻¹)</th>
<th>$G$ (nm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IMI (t = 50 nm)</td>
<td>1.324683</td>
<td>20.07</td>
<td>0.00011</td>
<td>0.22</td>
</tr>
<tr>
<td>IMII (t = 50 nm, d = 341.7 nm)</td>
<td>1.324633</td>
<td>31.39</td>
<td>0.00018</td>
<td>0.23</td>
</tr>
<tr>
<td>IMI (t = 20 nm)</td>
<td>1.318295</td>
<td>2.23</td>
<td>0.00006</td>
<td>1.07</td>
</tr>
<tr>
<td>IMII (t = 20 nm, d = 381.5 nm)</td>
<td>1.318288</td>
<td>3.26</td>
<td>0.00011</td>
<td>1.29</td>
</tr>
</tbody>
</table>

6.1.4 Comparison with TE and TM dielectric waveguide modes

The existence of TE and TM modes in the corresponding dielectric slab waveguide (i.e., the IMII without the Au slab) can lead to leakage in the case of the 2D metal stripe waveguide (Section 6.1.3). This occurs when the effective index of the LRSP on the IMII becomes less than that of the dielectric slab modes on either side of the Au stripe [93].

Figure 6.4(a) shows the effective index of the symmetry-constrained LRSP in the IMII of interest (H₂O - Au - SiO₂ - air at 1310 nm), and of the TE₀ and TM₀ modes in the corresponding dielectric slab waveguide. When the thickness of the membrane ($d$) is less than 390 nm, the LRSP has a larger effective index than the TE₀ and TM₀ modes. From Figure 6.2(a), this range of thickness ($d < 390$ nm) corresponds to an
Au slab thickness \((t)\) that is greater than 18 nm. It is therefore expected that the corresponding metal stripe waveguide will support a purely bound (non-radiative) symmetry-constrained LRSP for \(d < 390\) nm and \(t > 18\) nm (approximately). Note that this additional constraint leads to a lower bound on the Au thickness, and thus a lower bound on the achievable attenuation.

![Figure 6.4](image)

**Figure 6.4** (a) Effective indices for TE\(_0\) (blue curve), TM\(_0\) (red curve) and symmetry-constrained LRSP (green curve) modes as a function of SiO\(_2\) thickness in the IMII of interest (H\(_2\)O - Au - SiO\(_2\) - air at 1310 nm). (b) Same as Part (a), except using Si\(_3\)N\(_4\) as the membrane (the refractive index of Si\(_3\)N\(_4\) is \(\sim 2\)).

The effective indices for the case of Si\(_3\)N\(_4\) as the membrane are also computed, as shown in Figure 6.4(b). In this case, the effective index of the TE\(_0\) mode is larger than that of the symmetry-constrained LRSP over the entire range of membrane thickness, suggesting that Si\(_3\)N\(_4\) is not a good choice for the corresponding metal stripe waveguide.

### 6.2 LRSP along an IMII stripe structure (2D)
6.2.1 Geometry of the IMII stripe waveguide

For waveguide and integrated optics applications, a stripe geometry providing confinement in the plane transverse to the direction of propagation is typically preferred to a slab. Figure 6.5 shows the stripe structure that corresponds to the slab of Figure 6.1. The metal stripe of width $w$ provides additional confinement in the $y$ dimension, and propagation occurs along the stripe in the $x$ dimension. The same material parameters and operating wavelength (as in Subsection 6.1.1) are retained and the width of the Au stripe is selected as being $w = 5 \, \mu m$. Due to the geometrical complexity of the structure, theoretical and TMM approaches are not suitable for analysis, so the finite-difference method (FDM) implemented in commercial software [36] was used to compute the LRSP mode characteristics.

6.2.2 Finite difference results
Figure 6.6 shows the effective index and attenuation of the LRSP in the IMII as a function of the membrane thickness for 20 and 50 nm thick Au stripes computed via the FDM. Similar trends are noted as in the corresponding slab waveguide (Figure 6.4), however, the effective index is lower and the attenuation is higher in the case of the stripe for the same membrane and metal slab thicknesses \((d, t)\) (also observed in [93]). Features are evident in the MPA curves due to variations in the mode fields (perturbations) as the membrane thickness \((d)\) varies (also observed in [93]).

The symmetry-constrained LRSP occurs at \(d \sim 330\) and 380 nm in the case of the 50 and 20 nm thick Au stripes, respectively (as shown in Figure 6.7), similarly to the slab waveguide (Figure 6.4). One reason for the similarity is the large width selected for the stripe \((w = 5 \, \mu m)\) which reduces the interaction of the LRSP fields with the stripe corners. Another reason is the relatively small contrast between the selected membrane material (SiO\(_2\)) and H\(_2\)O. Indeed assuming Cytop [89] for the membrane (which has an index close to H\(_2\)O) renders the slab and stripe results essentially indistinguishable. Also, the lower the index of the membrane the larger the design space for the stripe waveguide because radiation into the TE\(_0\) and TM\(_0\) modes of the dielectric slab (on either side of the stripe) occurs over a smaller range of membrane thickness.

The similarity of the results to the 1D case is interesting because it allows use of the 1D theory (Subsection 6.1.2) to find good initial symmetry-constrained designs for the stripe waveguide.
Figure 6.6 Effective index (blue - solid) and attenuation (red - dashed) of the LRSP on the stripe IMII of interest ($w = 5 \, \mu m$, $H_2O - Au - SiO_2 - air$ at 1310 nm) for two thicknesses of the Au stripe (20 and 50 nm) computed by the FDM.

Figure 6.7 shows the transverse magnetic field distribution ($H_y$) of the LRSP over the cross-section of a stripe IMII with symmetry-constrained thicknesses as computed by the FDM. For a Au stripe thickness of $t = 50 \, nm$, the symmetry-constrained LRSP occurs for a membrane thickness of $d = 330 \, nm$, and for $t = 20 \, nm$, then $d = 380 \, nm$. The $H_y$ field along the top boundary of the Au stripe is identical to that along its bottom boundary as observed.

Figure 6.7 Distribution of the transverse magnetic field ($H_y$) of the symmetry-constrained LRSP over the cross-section of the stripe IMII of interest ($w = 5 \, \mu m$, $H_2O - Au - SiO_2 - air$ at 1310 nm); (a) $t = 50 \, nm$, $d = 330 \, nm$; (b) $t = 20 \, nm$, $d = 380 \, nm$. 
6.3 Summary

In this chapter, we demonstrated that LRSPs are supported in a physically asymmetric IMII thin slab structure, consisting of a low index medium on a metal slab on a dielectric layer (membrane) over air, as a suspended waveguide. An analytic formulation was derived in 1D yielding a transcendental equation that ensures symmetry of the transverse fields of the LRSP within the metal slab by constraining the thicknesses of the metal slab and the membrane. Mode characteristics obtained via the formulation for this "symmetry-constrained" LRSP are in quantitative agreement with TMM calculations for a candidate slab waveguide consisting of an H₂O-Au-SiO₂-air suspended structure. We found that the symmetry-constrained LRSP exhibits fairly low attenuation at a particular metal slab thickness. Furthermore, its attenuation and confinement decreased with decreasing metal thickness, following the conventional IMI. We also found that the thinner the metal slab, the thicker the dielectric layer needs to be to satisfy the symmetry constraint because the LRSP extends further into the dielectric for a thinner metal slab. As expected, the LRSP in this IMII waveguide has a high surface sensitivity as well as high figures of merit (G for surface sensing and M₂ for waveguiding) supporting its potential for sensing applications.

The FDM was used to analyze metal stripes (instead of metal slabs) on the same suspended structure. A symmetry-constrained LRSP confined in the plane transverse
to the direction of propagation was found thereon, but the metal stripe design space is more limited than that of the corresponding metal slab because of an additional constraint to non-radiative LRSP guiding: the effective index of the LRSP must remain above those of the TE$_0$ and TM$_0$ modes supported by the dielectric slabs on either side of the stripe to ensure no lateral radiation into these modes. This constraint places upper bounds on the thickness and the refractive index of the membrane, and on how thin the stripe may be, thereby also placing a lower bound on the LRSP attenuation. Despite these constraints, practical stripe designs have been found for the candidate structure (\(w = 5 \, \mu\text{m}, \, t = 20 \, \text{nm}, \, d = 380 \, \text{nm},\) yielding a symmetry-constrained LRSP attenuation of \(~3.27 \, \text{dB/mm at } \lambda_0 = 1310 \, \text{nm}~\)).

The structures are promising for sensors that operate with an aqueous solution and would otherwise require a low refractive index matched substrate to achieve LRSP guiding.
Chapter 7

Surface enhanced Raman spectroscopy: 2D substrate

In Section 2.4, we have introduced SPPs in nanostructured metals can generate highly concentrated electromagnetic fields which are responsible for the surface enhanced Raman scattering phenomenon. In this chapter, we propose and demonstrate the use of an isolated double-hole indentation with concentric rings as a highly efficient SERS substrate. The concentric rings couple the incident light into SPPs and then focus the electromagnetic field to the location of the double-hole [96-98]. The double-hole indentation has a set of apexes (sharp tips) where the holes overlap, which serve to further concentrate the electromagnetic field to length scales of 30 nm [99]. As a result, significant Raman enhancement was measured at the apex tips both from oxazine 720 (oxa) and from rhodamine 6G (R6G), which could be controlled by the excitation light polarization since the apex focusing is polarization-dependent [100, 101]. Finite-difference time-domain (FDTD) calculations were used to estimate the electric field enhancement and compare it with the SERS observations [36]. From
these calculations, it is estimated that the polarization-dependent SERS enhancement of 60% is from only ~1300 molecules at the metal surface in the vicinity of the apex tips.

7.1 Experimental and calculation methods

Figure 7.1 shows the scanning electron microscope image of a double-hole indentation structure with apexes surrounded by concentric rings. The structure was created by a focused ion beam (FIB) milling partially through the 100 nm thick gold film to a depth of 50 nm; therefore, the double-hole is not an aperture, but rather, it is an indentation. Several structures with different periodicities and inner ring radii for the concentric rings were fabricated. Each structure had five rings to scatter normally incident light into SPPs. This concentric ring structure has been considered previously for single holes [96]. All of the patterns had a milling depth of only 50 nm into the gold film, so that only the reflection (backscattering) geometry was used. A gallium beam current of 50 pA at 30 kV was used for milling. The gallium beam spot size was 10 nm. A milling time of 300 ns was applied for all of the patterns with a milling rate of 150 nm/ms, which was calibrated using energy-dispersive X-ray analysis. For the double-hole indentation, each hole had a diameter of 220 nm, and the center-to-center spacing was 210 nm. The double-hole structure is useful because it provides two sharp apexes with a radius of curvature of ~20 nm at the tip that can be readily fabricated from two larger holes.
SERS properties were investigated by modifying the surface of the nanostructure with organic dyes commonly used as SERS probes. Oxa (Lambdachrome) and R6G (Lambdachrome) were drop-casted on the metallic nanostructure. A 10 µM solution of oxa (in methanol) was deposited on the sample, the solvent was allowed to evaporate, and then, the surface was rinsed with a copious amount of ultrapure water (18.2 MΩcm from a Barnstead NANOpure Diamond water purification system). To measure the SERS from a different dye, R6G was deposited by following the same procedure; however, 20 µM of the dye was drop-casted three times onto the nanostructure.

Figure 7.2(a) shows the SERS spectra of oxa dye adsorbed on an array with 600 nm periodicity patterns and an inner radius of 900 nm (as shown in Figure 7.1) with different incident light polarizations. A polarized 35 mW He Ne laser was used as the excitation source (wavelength of 632.8 nm). The laser was focused at the sample.
using a 50× ultralong working distance objective, leading to a 5 µM spot size that illuminated the nanostructure completely. Additional details about our Raman setup have been published elsewhere [99]. The measurement was repeated to verify that the dependence on the Raman intensities was not due to the photodecomposition of the dye. During the FIB milling, the long axis of the nanostructure was aligned parallel to the edges of the square gold-on-glass slide. Therefore, different polarizations were accessed by manually rotating the sample, and this was sufficient to observe strong variations in the SERS intensities. The experiments were repeated several times (and with different dyes) to ensure that the polarization dependence was reproducible. Moreover, experiments with arrays of circular holes were also performed using the same procedure, and no significant polarization dependence was observed. The rotation of the sample was preferred over using a half-wave plate to avoid any polarization effect introduced by the reflections in the microscope.

Figure 7.2 (a) SERS of oxazine 720 adsorbed on the concentric apex structure (900 nm inner radius and 600 nm periodicity) at two polarizations of the incident laser (defined in Figure 7.1). (b) Dependence of the SERS intensity of the 598 cm⁻¹ oxazine 720 band with the inner radii of the concentric apex structure.
There is a strong Raman scattering peak at 598 cm⁻¹ for both polarizations in Figure 7.2, which corresponds to the main vibrational modes of the phenoxazine ring of the dye. The peak Raman scattering intensity for the \( x \)-polarization of the laser was 60% higher than that for the \( y \)-polarization. Since the only part of the structure without rotation symmetry is the double-hole apex at the center, this is expected to be the source of the polarization dependence of the Raman enhancement (as will be explored in further detail below using comprehensive electromagnetic calculations). It should be noted that the \( y \)-polarization still provides significant signal enhancement due to the presence of the concentric ring nanostructure; for the conditions of this experiment, the signal from the bare gold was not detectable above the noise.

Figure 7.2(b) shows the dependence of the SERS intensity peak at 598 cm⁻¹ with the inner radius of the nanostructure. The maximum signal occurs for inner radius values of 600 and 900 nm, which corresponds to the standing wave maxima of the surface plasmons that are scattered by the 600 nm concentric rings of the structure. The experiments were repeated with 500 and 700 nm periodicity rings, which showed similar polarization dependence, but overall, SERS intensities were an order of magnitude lower than those for the 600 nm concentric rings.

Oxa has an internal electronic transition at 620 nm (in ethanol), which is resonant with the laser excitation source at 632.8 nm (He-Ne). Hence, the results presented so far contains additional contributions to the enhancement from a resonance Raman mechanism, surface-enhanced resonance Raman scattering (SERRS). In order to isolate the effect of the nanostructure from the resonance Raman contribution to the
overall enhancement, we have performed further experiments with R6G. R6G absorbs at 530 nm in ethanol; therefore, its internal electronic transition is nonresonant at the excitation wavelength. The results confirmed the efficiency of the substrate by generating intense SERS from R6G. The polarization-dependent enhancement observed for oxa was seen for the rhodamine 6G as well, with good quantitative agreement.

FDTD calculations were carried out to reveal the electromagnetic field-enhancement mechanism of the polarization dependence [100]. A small mesh size of 5 nm was chosen to accurately capture SP effects, as was verified by finite-difference mode calculations and repeating the calculations with varying grid sizes (both smaller and larger). To reproduce the conditions of the experiment, a 632.8 nm Gaussian wave source was normally incident on the top surface of the double-hole structure. A near-field monitor was used to obtain the electric field distribution at the surface. Perfectly matched layer boundary conditions were used on all sides except for below the gold surface, which was set to be a perfect electric conductor (since the electromagnetic field does not penetrate that far into the gold). The ring structure acts as a focusing grating to couple the incident light into the SPPs toward the center of the rings [8]. To quantify the focusing ability of the ring structure, additional FDTD simulations were performed without the rings, and the peak electric field intensity was reduced by two orders of magnitude. Clearly, the ring structure is important to obtain the SERS enhancement seen in this work.
7.2 Results and discussion

Figure 7.3(a) and (b) shows the FDTD-calculated $z$-component of electrical field at the surface of the concentric apex structure surface for the $x$ and $y$ incident polarization source at the 632.8 nm wavelength. (The $z$-component was chosen for visualization because it is characteristic of the surface plasmon excitation and it is not present in the excitation source.) The periodicity was 600 nm, and the inner ring radius was 900 nm, to match the experimental configuration with the greatest SERS signal. The FDTD calculations showed that the 600 nm ring structure had a field intensity maximum at 620 nm with a FWHM of 32 nm. This peak is wide enough to encompass both the source and Raman scattered photons. It is clear that the surface plasmon waves are concentrated at the sharp apex region for the $x$-polarization, which leads to strong electrical field enhancement in that region. For $y$-polarization, the local electric field intensity enhancement was seven times lower, and the most intense electrical fields were distributed in the lateral sides. Considering these comprehensive numerical calculations, it appears that the double-hole apex structure provides strong subwavelength focusing that is responsible for the observed Raman enhancement observed in the experiments above.

To further quantify this enhancement in terms of the number of molecules contributing to the SERS, we consider histograms taken over the simulation area. Figure 7.3(c) and (d) shows with blue the binning of the numerical calculation pixels (mesh-points) as a function $|E|^2$ for the $x$ and $y$ source polarizations. Shown in
red is the binning for the number of pixels multiplied by $|E|^4$ as a weighting factor. The different $|E|^2$ scaling for Figure 7.3(c) and d should be noted. One feature that stands out from this figure is that only 32 pixels (around the apexes of the double-hole) provide more than a third of the $|E|^4$ weighted contribution for the $x$-polarization. We have considered the effect of the bin width on the histograms presented in Figure 7.3. The effect of the hot spots on Figure 7.3(c) will be smeared out for high values of bin size. We then decided to use a bin size (750 for Figure 7.3(c) and 100 for Figure 7.3(d) that emphasizes the role of the hot spots for the $x$-polarization.

Figure 7.3 FDTD-calculated electrical field intensity at the surface of a double-hole apex structure with a concentric rings concentric apex structure surface at 632.8 nm. Profile of the $z$-component of the electrical field intensity (for the center region only) for (a) $x$-polarized incident light and (b) $y$-polarized incident light. Also shown are histograms, binned by field intensity, of the number of pixels over the whole surface.
area (blue bar) and the sum weighted by \(|E|^4\) at each pixel (red bar) for (c) \(x\)-polarized incident light and (d) \(y\)-polarized incident light. All of the electrical field intensities were normalized by the source.

Using these results, we can estimate the number of molecules contributing to the 60% increase in SERS with changes in polarization, that is, from focusing by the double-hole nanostructure. The electromagnetic contribution to the total SERS enhancement is commonly considered to be proportional to the fourth power of the field enhancement factor [102, 103].

\[
R = \frac{|E_{\text{loc}}|^4}{|E_0|^4}
\]  

(7.1)

Using this equation, from the red bars of Figure 7.3, it shows that an enhancement of 113% can be expected from the \(x\)-polarization excitation compared to that from the \(y\)-polarization. This is larger than the 60% enhancement measured in the experiments, and the discrepancy is likely due to imperfections (including duller apexes) in the fabricated nanostructure sample. Furthermore, more than 1/3 of the \(x\)-polarization signal comes from only 32 of the pixels with an intensity between 4500 and 6000 (normalized to incident field). There are 32 pixels in hot spots (in which \(|E|^2 > 4500\)), and each pixel represents a 25 nm\(^2\) area.

The number of molecules that contribute to the polarization effect observed can be estimated by considering a monolayer of oxa, the molecular dimensions of the dye as 1.2 nm (long axis) and 0.9 nm (short axis), and adsorption onto the gold along the long axis (where the nitrogen atoms are located). Each molecule occupies an area of around 0.6 nm\(^2\) in this adsorption mode, which leads to the highest packing. The
number of adsorbed molecules would be even smaller if a flat orientation was considered. The number of molecules in the hot spots is then 1300 within these assumptions. It is these molecules alone that lead to the 60% Raman enhancement under different incident light polarization. Considering that the standard deviation of the noise in Figure 7.3(a) is 50, the estimated limit of detection (defined as three times the standard deviation of the noise) for oxa from the best-case configuration is about 20 molecules.

7.3 Summary

In summary, we demonstrated the use of an isolated double-hole indentation in a metal film with concentric rings for surface plasmon focusing for SERS. Due to the symmetry of the double hole, which has strong subwavelength focusing at the apexes where the indentations overlap, the SERS enhancement factor was found to be strongly polarization-dependent. Using FDTD calculations of the fabricated nanostructure, an intense field was observed at the sharp apex region under the appropriate incident mode polarization, which is responsible for the polarization-dependent SERS enhancement. On the basis of these calculations, it was estimated that only 1300 molecules provide a 60% increase in the SERS when the incident polarization of the laser source coincides with the apexes and that the limit of detection is about 20 molecules. These results show that the isolated double-hole
indentation is a promising nanostructure for SERS that, with suitable optimization, may approach the ultimate goal of reliable and predictable single-molecule SERS.
Chapter 8

Surface enhanced Raman spectroscopy: 3D substrate

In Chapter 7, we managed a distinct SERS signal by applying a double-hole structured metal substrate. However, the SERS sensitivity of this sophisticated 2D substrate is still lower than the single molecule detection limit. Then there comes the question: Can we try to utilize one more dimension advantages and make a 3D substrate?

Previous works show that a dielectric spaced metal layer could enhance the SERS signal for evaporated silver islands about 10-fold by tuning their plasmon resonance frequency [104-108] and changing the local density of states [9, 109-112]. However, further improvements are required to boost the SERS to the level of the randomly roughened surface case and ultimately to detect the single molecule Raman signal [15, 16, 113].

In this chapter, we use the colloidally synthesized silver nano-prisms on top of a gold ground plane spaced by a TiO$_2$ dielectric layer as a 3D substrate to coherently
enhance the SERS signal of rhodamine 6G (R6G). Over 50× SERS enhancement is achieved. Theoretical calculations and FDTD simulations verify the experimental results and indicate more room for further SERS amplification with this configuration.

8.1 SERS measurement with multilayer substrates

8.1.1 SERS experimental setup

Figure 8.1(a) shows the schematic of the multilayer SERS substrate. An optically thick 100 nm Au layer was used as a ground plane (EMF Corp.). This was coated with a TiO$_2$ spacing layer evaporated by 7.5 kV electron beam source in an Angstrom Engineering physical vapor deposition system. The TiO$_2$ layer refractive index was measured to be 2.19 via white light reflection measurements. The purpose of the spacer layer was to tune the phase of the reflected light from the gold mirror as a function of thickness $t$. For each thickness, we fabricated three different samples to ensure reproducibility.
Silver nano-prisms were synthesized in water by white-light assisted conversion of spherical nanoparticles [114]. This yielded an ensemble of prisms with average length on a side, \( d \), of 80 nm, shown as the inset in Figure 8.1(b). A solution containing silver nano-prisms and dye were drop-cast (0.02 mL) on the substrates, where the concentration of the R6G dye was 1 \( \mu \text{M} \). The sample was then allowed to dry for 5 hours. Ultra-pure water with a resistivity of 18.2 \( \text{M}\Omega \text{cm} \) (from Barnstead
NANOpure Diamond water purification system) was used throughout the experiments.

The Raman spectra of the dye were taken using a Renishaw inVia Raman microscope with a 785 nm diode laser of 0.5 mW power illumination and an estimated density of 30 nano-prisms within the laser focus, as determined by scanning electron micrograph (SEM) studies of the surface - shown in Figure 8.1(b). The backward Raman scattered light was collected by a 20× objective (NA=0.4) with a total integration time of 30 s. All the measurements were repeated at least 4 times in each experiment and all the experiments were repeated on several different days in order to ensure the consistency and the stability of the results.

**8.1.2 Extinction spectrum of silver nano-prisms**

![Figure 8.2 Extinction spectrum of the silver nano-prisms used in the experiment in an aqueous environment, where the 673 nm extinction peak is clearly visible.](image)
The spectral dependence of the plasmon resonances were examined in solution, because of their relevance to SERS [115, 116]. Figure 8.2 shows the extinction spectrum (Cary 5 UV-VIS-NIR Spectrophotometer) of the nano-prisms used in the experiment. Three extinction peaks were observed at 337 nm, 413 nm, and 673 nm, of which the 673 nm peak has the strongest extinction.

8.1.3 Theoretical calculation on phase reflection

The primary objective of this experiment was to find the optimized dielectric spacer layer thickness for SERS enhancement. To coherently enhance the SERS, the reflected light from the ground plane should constructively interfere with the incident light beam. Upon reflection at the interface of a perfect electric conductor (PEC) and a dielectric, there is a phase shift of the electric component. The optimal thickness is corresponding to the in-phase reflection configuration which is expected to be [117]:

$$ (2 \times d) n_d = \left( m + \frac{1}{2} \right) \lambda $$

(8.1)

Here, $n_d$ is the TiO2 refractive index which is measured to be 2.19, $\lambda$ is the excitation wavelength equal to 785 nm, and $m$ is a whole number. The first and the second orders of optimized thicknesses $d$ are determined to be 90 nm and 270 nm. Note here the PEC assumption will lead to discrepancies between the theory and experiment, and this will be captured with the FDTD simulation results below.
8.1.4 SERS measurement results

Figure 8.3(a) shows a sample SERS spectrum from the multilayer SERS substrate. Three Raman shift peaks were observed, which are 1312 cm\(^{-1}\), 1364 cm\(^{-1}\), and 1509 cm\(^{-1}\), respectively. The full analysis was performed on the 1509 cm\(^{-1}\) peak because no deconvolution was necessary (although the other peaks showed the same general enhancement behaviour).

Figure 8.3(b) shows the enhancement of SERS using silver nano-prisms as a function of dielectric layer thickness. The enhancement is with respect to a bare glass substrate with the same drop-casting of silver nano-prisms and dye. The uncertainty for each thickness was calculated from the standard deviation from at least four SERS measurements at different locations on the sample. Furthermore, the measurements were repeated on two additional samples, each with the same thickness, showing the same results. It can be seen that the enhancement factor changes with thickness variation, and the peak enhancements (45.4 ± 1.6 and 51.6 ± 4.7) were achieved when the TiO\(_2\) equalled 40 nm and 200 nm, respectively. The uncertainty in these values comes from standard deviation over multiple measurements over randomly distributed nano-prisms. The difference in the thickness between the two peaks is 160 nm, which is close to the theoretical prediction of 179 nm. Also, the values are offset from the prediction of Equation (8.1), which will be discussed further below.

To ensure the generality of the enhancement for different MNPs, we repeated the experiments using Au nano-rods [118] instead of Ag nano-prisms, and similar
enhancement factors and dielectric thickness dependencies were observed (not shown).

![Figure 8.3 Experimental SERS spectra. (a) An example Raman spectra for the R6G dye using the silver nano-prisms. (b) Enhancement of SERS using silver nano-prisms for the 1509 cm⁻¹ Stokes shift peak as a function of dielectric layer thickness, normalized by the SERS signal from a bare glass substrate. The blue bands indicate the first order and the second order SERS enhancement peaks.]

8.2 FDTD simulation results

In the experiment, the situation is complicated from the simple picture presented above by other factors such as the absorption of the metal ground-plane, coupling into the modes of the finite dielectric layer underneath the MNPs, multiple reflections by the dielectric layer and ground-plane and a finite collection aperture. In addition, the finite wavelength difference between the excitation and Stokes wavelengths should be considered. For a more comprehensive understanding, we used FDTD numerical analysis for comparison with experiments.
The Au permittivity values were taken from a previous work [37], and the Ag permittivity values were taken from a different work [36], and these are two commonly used references for those materials, respectively. A 2 nm mesh was also used around the silver nano-prism to ensure that plasmonic effects were accurately captured, as verified by convergence studies. The simulation region was enclosed with perfectly-matched layer boundaries in the direction perpendicular to the gold ground plane, and with 200 nm periodic boundaries in the directions parallel to the ground plane. The theoretical results were invariant to changes in periodicity. A plane wave was injected from the top of the structure.

Figure 8.4 Finite difference time domain simulations of enhancement factor, for 80 nm side nano-prism in the same configuration as in Figure 8.3(b).

Figure 8.4 shows the resulting simulation of the SERS signal and its TiO$_2$ thickness dependence. To obtain the theoretical enhancement factor, we compare the near-field intensity of the nano-prism above the Au ground using different TiO$_2$ layer thicknesses to the control where the nano-prism was placed directly on a glass
substrate without the Au ground. The SERS intensity $I_{\text{sers}}$ is proportional to the localized electric field intensity both at the excitation wavelength $E_{\text{ex}}^2$ and the Raman wavelength $E_{\text{Raman}}^2$ [102, 119]:

$$I_{\text{sers}} \propto E_{\text{ex}}^2 \times E_{\text{Raman}}^2 \quad (8.2)$$

To consider the size distribution of the Ag nano-prisms, we sample 60 nano-prisms from a TEM image of the sample in a location where we performed the SERS. We perform FDTD simulations using nano-prisms of different sizes, and obtain the near field enhancement by summing the SERS intensity weighted by the nano-prism size distribution, and comparing the cases with and without the Au ground. The first order and the second order SERS enhancement peaks occur at 80 nm and 260 nm TiO$_2$ thicknesses, which are slightly less than the PEC theoretical results because we used Au in the FDTD model instead of PEC for the ground plane in our theoretical computation. Since the finite skin depth of Au for 785 nm wavelength light leads to penetration into the metal, there is an additional phase shift at the metal-dielectric interface. The enhancement factors of these two in-phase thicknesses are approximately 40.36 and 32.85, which are smaller than the experiment.
Figure 8.5 Simulated local electric field intensity distributions close to a nano-prism for varying dielectric thicknesses ($t = 80 \text{ nm}, 160 \text{ nm}, 260 \text{ nm}$) shown on a logarithmic scale. The dashed lines show the interfaces of the silver nano-prism, the dielectric layer and the gold ground plane.

Figure 8.5 shows the electric field intensity around a 80nm prism (the average size), the dielectric layer and the reflector (outlined with dashed white lines) in the $xz$-plane. The local field intensity in the resonant cases of 80 nm and 260 nm thicknesses are one order of magnitude larger than the off-resonant case (160 nm). This results from the constructive and destructive interference of the image excitation created by the Au ground plane reflector.

8.3 Discussion

The experiment and calculations give comparable enhancement factors and spacer layer thickness dependencies. Aside from the finite penetration of light into the metal, the additional offset with respect to the theoretically expected optimal spacer layer
thickness values remains an uncertainty in the experiment, but can be attributed to (at least in part) dye accumulation beneath the MNPs, off-axis excitation by the focusing objective and uncertainty in the dielectric thickness. The SERS signal peak values of experiment results are close to those given by the FDTD simulation. In the measurements, we measured locations of the sample where there was no obvious aggregation, as observed under the optical microscope. Even so, some aggregation may be present, and we cannot accurately capture that effect within our simple simulation.

Moreover, it is possible to envisage more advanced multilayer SERS schemes [120-122], such as a right corner reflector, which in the optimal geometry leads to an enhancement factor of 4 in terms of the localized field around the nano-prisms. As compared to the present system, the flat ground plane only has an enhancement factor of 2 [123]. Considering the SERS signal intensity is approximately proportional to the fourth power of the localized field [102, 119], then 16 times greater SERS signal enhancement is expected for the corner reflector substrate. Even more advanced schemes, such as the Yagi-Uda shaped MNPs, may be implemented to increase the enhancement still further. Based on these considerations, it is expected that at least 3 orders of magnitude enhancements in the MNP Raman should be possible through configuration optimization. Such boosts in the electric field could make single-molecule Raman demonstrations viable with MNPs [15, 16, 113].
8.4 Summary

We have demonstrated that the combination of simple substrate engineering and silver nano-prisms can enhance SERS by a factor of 50. Both the experiment and the theoretical calculations give comparable enhancement factor dependence on the dielectric spacer layer thickness. Similar results were also observed for Au nano-rods which indicate this multilayer substrate is a generic approach to boost the SERS signal for different MNPs grown in solution. FDTD simulations also verified this SERS enhancement quantitatively. With more advanced schemes utilizing corner reflectors or Yagi-Uda antennas, it is expected that MNP SERS can be enhanced by 3 orders of magnitude to the regime of signal molecule detection. Obvious benefits will arise from this sensitivity boost for many applications including the use of MNPs as Raman biolabel markers, the development of more reliable Raman-enhanced templates, and the improvement of Raman-based pathogen sensors.
Chapter 9

Conclusions and outlook

In this work, we explored various metal structures for controlling surface plasmon, propagation, resonances and local field enhancement. This has applications to a number of fields, such as nonlinear optics, single photon emitters and surface enhanced Raman scattering. In this work, we focused predominantly on applications in SERS as a desirable spectroscopy tool to approach the single molecule limit of detection. Here is a summary of contributions to the understanding of plasmonic structures and SERS:

We characterized PBRs for nanohole arrays by measuring the EOT at different conditions. It shows a dependence of PBRs enhanced EOT on the number and depth of PBR layers around the arrays. The EOT enhancement was maximized when three layers of PBRs present with 45 nm depths. PBRs also show the isolation ability on plasmonic structures, which could significantly reduce the SPPs interference between different plasmonic units.

We also constructed SP microcavities on the metal surface which could 2 times enhance the EOT through a subwavelength slit. The experiment shows the maximum
EOT wavelengths are tuned by the microcavity widths, and this will be beneficial for those frequency sensitive SP applications and the future SP photonic integration.

A SMM method was presented to calculate the optical transmission efficiency through subwavelength metal taper structures. The optimal angles and the corresponding transmission efficiencies were found. For 2D gold taper gap, it is 14° optimal angle with 71% transmission efficiency, and for 3D gold taper rod, it is 32° optimal angle with 44% transmission efficiency. The SMM method shows more efficient than comprehensive numerical calculations and more accurate than adiabatic methods, which could be extended more complex geometries.

An asymmetric long range surface plasmon waveguide was demonstrated for bio-sensors that operate with an aqueous solution. This waveguide shows fairly low propagation attenuation with reasonable mode confinement, which lead to the LRSP in this IMII waveguide has a high surface sensitivity as well as high figures of merit (G for surface sensing and M2 for waveguiding) supporting its potential for sensing applications. This asymmetric configuration puts forward an effective solution when a low refractive index matching layer is not convenient to achieve LRSP waveguiding.

We invested surface enhanced Raman spectroscopy, which can be divided into two parts. A concentric ring with double hole SERS substrate was designed and fabricated to achieve single molecule SERS detection by highly localizing the SP field into the small double hole tips. As a result, this structure shows a 20-molecule detection limit. To conquer this limit, we then developed a 3D reflection SERS system, which is utilizing a metal plane as an EM mirror to reflect the light field back to microscope.
The distance between the molecule (metal nanostructures) and the metal plane was optimized for in phase interference which finally achieved about 50 times enhancement compared to without the reflection configuration. By using more complex reflectors, SERS can be enhanced by 3 orders of magnitude to the regime of signal molecule detection.

In the future, my research could possibly go to many different applications. For LRSP biosensor, we could build it up in practice with our calculated configuration to improve the sensor performance; for SERS, a fairly promising way is try to combine the double-hole structure or other optimized nano-antenna structure and the reflection Raman system together to achieve the high sensitive single molecule detection [124]. These potential applications will significantly contribute to the SPP society and all the related research fields.
Reference


