Hyperspectral Light-trapping within Graded Gratings Using Adiabatically Coupled Plasmonic Waveguide-Resonators

by

Arthur O. Montazeri

A thesis submitted in conformity with the requirements for the degree of Doctor of Philosophy
Graduate Department of The Edward S. Rogers Sr. Department of Electrical and Computer Engineering
University of Toronto

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Abstract

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Rainbow-trapping or slowing down broadband electromagnetic radiation over a subwavelength grating, provides new opportunities for light-matter interaction on a nanometer scale. Previous efforts have shown rainbow-trapping is possible on functionally graded structures. Here, a new gradient parameter is proposed for designing rainbow-trapping gratings, which takes advantage of the close correlation between the groove-width and the overlap of the evanescent fields within the grooves. In the suitable range ($\lesssim 150$ nm), this width parameter is as important as other known variables such as groove depth and materials composition, but with the added advantage that tailoring groove widths is remarkably more feasible in practice. This is shown to be the case through nanofabrication techniques described in this dissertation.

The effect of groove-width on the dispersion relation of the nano-groove is studied, resulting in an analytical solution for the effective index of the groove. Adjusting this effective index through the width-parameter establishes the basis for the graded-index gratings discussed herein, where groove-widths are tapered across the grooves of a grating. Accordingly, using groove-width as a design parameter gives rise to rainbow-trapping in linear, as well as other geometries such as bull’s eye type structures.

Furthermore, the extension of graded gratings to other geometries such as cylindrical and spiky spherical nanoparticles is studied through transformation optics. The case of spiky nanoparticles with a tapered spike geometry is closely examined
through Multiphysics simulations to predict the thermal effects of light-matter interaction in pico- and nanosecond timescales, as well as experiments conducted under continuous wave conditions. Using gold nanoparticles with diameters of (∼30-100 nm) and various spike aspect-ratios, enables exploiting both the plasmonic resonance of the spherical particle (Mie resonance), as well as the plasmons contributed and guided by the graded geometry of the spikes. The interaction of these two types of resonances results in an unprecedented and high-resolution control of the plasmonic field distribution and temperature profiles. This deeply sub-wavelength heat control allows the scalable genesis of self-dressing nanoparticles in a thermally triggered precursor of the shell under controllable laser illumination. The result is nanoparticles with controllable partial shell-formation, where the tips of gold spikes are left exposed. This is in contrast to the blanket coverage of the particle that can lead to mode suppression, by blocking light’s access to the spikes which are responsible for light-coupling to surface plasmons.

The derived analytical formula obtained through treating each nano-groove as a plasmonic waveguide resonator is compared with simulations, and near-field optical measurements in the visible and infrared regions. These results closely agree with numerical simulations, fabrication, and characterization results.
Dedication

To Prof. Nazir Kherani. I am grateful for every moment spent in the supportive and encouraging environment that you cultivated, all the tools you provided, and all the doors you opened. This work grew organically in that environment.

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I feel privileged to have worked with many great minds at the University of Toronto, UC Berkeley, and the Lawrence Berkeley National Laboratory during my PhD research. I am grateful to everyone who directly or indirectly helped me understand and made the understanding process fun and enjoyable. I am bound to forget a name or two, though I will not forget that your help was instrumental for this research.

Words fail to convey my gratitude to Prof. Nazir Kherani, my PhD supervisor, whose patient and unwavering support evoked and cultivated inspiration, depth of understanding, and direction to this work. It is quite unbelievable and in fact a bit surreal to me, that in about five years of working together while establishing a rather new area of research, I cannot recall a single uncomfortable moment in our interactions. He turned most ordinary interactions into sources of insight, inspiration, and enlightenment, leading me to the realization that these were not merely acts of kindness, but reflections of the largess of his character. I simply could not have imagined a more ideal advisor. For this, I will remain forever grateful.

My experience as a PhD student at the University of Toronto was one of the highlights of my life. Having seen many other schools, I consider UofT to be one of the best places I could have been at, if not the very first choice. The rich campus life, cultural activities, as well as the faculty and staff at UofT, were amazing and beyond my imagination. UofT and the ECE Department, supported me throughout my research in more ways that I can remember. I now understand the literal meaning of *alma mater* in Latin i.e., nourishing mother, and I consider myself fortunate to call UofT my *alma mater*. By way of example, I am much grateful to Darlene Gorzo, our Graduate Programs Administrator at the ECE Department at the University of Toronto. I have never come across anyone quite as efficient, alert, knowledgeable, helpful, organized, and with lightening speed, all at the same time. That kind of behind-the-scenes magic sometimes gives the impression that the obstacles were never there. I am much obliged for Darlene’s support and help, and of course the entire staff that includes Shawn Mitchell, and others.

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I am also grateful for the generous support of the Berkeley Synchrotron Infrared Structural Biology (BSISB) program under the direction of Dr. Hoi-Ying Holman for helping with this research and its applications for infrared imaging and spectroscopy.

I also acknowledge the support of the Molecular Foundry at the Lawrence Berkeley National Laboratory and the US Department of Energy through the User Facility program, where I spent the last two years on the nanofabrication of the devices described in this dissertation. Specifically, I would like to thank Dr. Stefano Cabrini, the Director of the Nanofabrication facility at the Molecular Foundry. Dr. Scott Dhuey, the resident expert on electron beam lithography, Dr. Hans Bechtel for teaching me the operation of the near-field setup at the Advanced Light Source at LBNL, and Dr. Fausto D’Apuzzo for his help in acquiring high-resolution images. I am also greatly thankful to Dr. Alex Polyakov, whose acquaintance led me to becoming familiar with the capabilities of LBNL. I am thankful for Dr. Peyman Sarrafi’s help for many useful discussions and collaborations, Dr. Arash Joushaghani, for his insights, Dr. Farshid Bahrami, for a collaboration related to gold nanoparticles, Yujin Kim for collaborating and helping on the plasmonic gold nanoparticles, and all my colleagues at the Advanced Photovoltaics and Devices (APD) Group at UofT.

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7.4 A linear grating is transformed through conformal optical transformation to a circular profile in the polar plane, while preserving its light-interaction properties.

7.5 A linear grating is transformed through conformal optical transformation to a circular profile in the polar plane, while preserving its light-interaction properties.
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(2.1) - Differential form of Maxwell’s equations. ......................................................... 9
\[ \nabla \cdot E = \frac{1}{\epsilon_0} \rho_{ext}, \quad \nabla \cdot B = 0, \quad \nabla \times E = -\frac{\partial B}{\partial t}, \quad \nabla \times B = \mu_0 \epsilon_0 \frac{\partial E}{\partial t} + \mu_0 J. \]

(2.2a) - Using electric displacement to include polarization. .............................. 11
\[ \nabla \cdot D = \rho_{ext}, \quad \nabla \times H = \mu_0 \epsilon_0 \frac{\partial D}{\partial t} + \mu_0 J. \]

(2.3) - The dielectric displacement term. ................................................................. 11

\[ D = \epsilon_0 E + P. \]

(2.4) - The magnetic field strength and magnetization. ................................. 11
\[ H = \frac{1}{\mu_0} B - M. \]

(2.2a) - Gauss’s law and charge density. ......................................................... 11
\[ \nabla \cdot E = \frac{\rho_{total}}{\epsilon_0}. \]

(2.6) - Material response to electric field - dielectric permittivity term. ............. 12
\[ D = \epsilon \epsilon_0 E. \]

(2.7) - Material response to magnetic field - magnetic permeability. ............... 12
\[ B = \mu \mu_0 H. \]
(2.8) - The first step to derive the wave equation from Maxwell’s equations.

\[ \nabla \times \nabla \times E = -\mu_0 \frac{\partial^2 D}{\partial t^2}. \]

(2.9) - Simplifying the fields using mathematical identity for \( \nabla \times \nabla \cdot \)

\[ \nabla \left( -\frac{1}{\epsilon} \nabla \cdot E \right) - \nabla^2 E = -\mu_0 \epsilon_0 \frac{\partial^2 E}{\partial t^2}. \]

(2.10) - Let there be light! - Arriving at the wave equation.

\[ \nabla^2 E = \frac{\epsilon}{c^2} \frac{\partial^2 E}{\partial t^2}. \]

(2.11) - Wave equation satisfied with exponential solutions.

\[ \nabla^2 E = -\frac{\omega^2}{c^2} \epsilon E. \]

(2.12) - Wave equation solution component along \( x \)-direction.

\[ \frac{\partial^2 E(x)}{\partial x^2} = (\beta^2 - k_0^2 \epsilon) E(x). \]

(2.13) - Including the magnetic term. General component-wise solution term. There exist 6 of these through cyclic permutation of the coordinates.

\[ \frac{\partial E_x}{\partial z} - \frac{\partial E_z}{\partial x} = i\omega \mu_0 H_y. \]

(2.14) - Component-wise solution set of Maxwell’s equations.

\[ \frac{\partial E_x}{\partial z} - i\beta E_z = i\omega \mu_0 H_y, \quad i\beta E_y = i\omega \mu_0 H_z, \quad \frac{\partial E_y}{\partial z} = -i\omega \mu_0 H_x, \]

\[ \frac{\partial H_x}{\partial z} - i\beta H_z = -i\omega \epsilon \epsilon_0 E_y, \quad i\beta H_y = -i\omega \epsilon \epsilon_0 E_z, \quad \frac{\partial H_y}{\partial z} = i\omega \epsilon \epsilon_0 E_x. \]

(2.15) - Wave equation for \( s \)-polarization.

\[ \frac{\partial^2 E_y}{\partial z^2} = (\beta^2 - k_0^2 \epsilon) E_y. \]
(2.16) - Wave equation for \( p \)-polarization. 
\[
\frac{\partial^2 H_y}{\partial z^2} = (\beta^2 - k_0^2 \epsilon) H_y.
\]

(2.17) - Damped harmonic oscillation of plasma electrons. 
\[
m\ddot{x} + m\gamma\dot{x} - eE = 0.
\]

(2.18) - The phase factor between electron oscillations and the driving field. 
\[
x(t) = \frac{e}{m(\omega^2 + i\gamma\omega)^2} E(t).
\]

(2.19) - The macroscopic electric displacement as a result of the response of electron oscillations and the polarization field. 
\[
D = (\epsilon_0 - \frac{\epsilon_0\omega_p^2}{\omega^2 + i\gamma\omega}) E.
\]

(6.2) - The complex dielectric function of the metal. 
\[
\epsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega} = \left(1 - \frac{\omega_p^2}{\gamma^{-2} + \omega^2}\right) + i\left(\frac{\omega_p^2}{\omega(\gamma^{-2} + \omega^2)}\right).
\]

(2.21) - SPP equation in dielectric. 
\[
E_x(z) = \Gamma_2 \frac{i}{\omega \epsilon_2 \epsilon_0} k_2 e^{i\beta x - k_2 z}, \quad E_z(z) = -\Gamma_1 \frac{\beta}{\omega \epsilon_2 \epsilon_0} k_2 e^{i\beta x - k_2 z}, \\
H_y(z) = -\Gamma_2 e^{i\beta x - k_2 z}.
\]

(2.22) - SPP equation in metal. 
\[
E_x(z) = -\Gamma_1 \frac{i}{\omega \epsilon_1 \epsilon_0} k_2 e^{i\beta x - k_1 z}, \quad E_z(z) = -\Gamma_2 \frac{\beta}{\omega \epsilon_1 \epsilon_0} k_2 e^{i\beta x - k_1 z}, \\
H_y(z) = -\Gamma_1 e^{i\beta x - k_1 z}.
\]

(2.23) - Single metallo-dielectric SPP dispersion relation. 
\[
\epsilon_1 k_2 = -\epsilon_2 k_1.
\]
(2.24) - Wave-vectors (propagation constant) in the two media.
\[ k_1^2 = \beta^2 - k_0^2 \epsilon_1, \quad k_2^2 = \beta^2 - k_0^2 \epsilon_2. \]

(2.25) - SPP dispersion relation and the effective permittivity of the metallo-dielectric waveguide.
\[ \beta = k_0 \sqrt{\frac{\epsilon_1 \epsilon_2}{\epsilon_1 + \epsilon_2}}. \]

(2.26) - Wave components at the core of a sandwich structure. (insulator-metal-insulator (IMI), or MIM)
\[
\begin{align*}
E_x(z) &= \Gamma \frac{i}{\omega \epsilon_D \epsilon_0} k_2 e^{i \beta x - k_D z} - \Gamma' \frac{i}{\omega \epsilon_D \epsilon_0} k_2 e^{i \beta x + k_D z}, \\
E_z(z) &= \Gamma \frac{\beta}{\omega \epsilon_2 \epsilon_0} k_2 e^{i \beta x - k_2 z} + \Gamma' \frac{\beta}{\omega \epsilon_2 \epsilon_0} k_2 e^{i \beta x + k_2 z}, \\
H_y(z) &= \Gamma e^{i \beta x - k_2 z} + \Gamma' e^{i \beta x + k_2 z}.
\end{align*}
\]

(2.27) - General dispersion relation of MIM waveguide, assuming identical cladding materials.
\[
e^{-k_M w} = \frac{k_M \epsilon_M}{\epsilon_M} + \frac{k_D \epsilon_D}{\epsilon_D} + \frac{k_M \epsilon_M}{\epsilon_M} - \frac{k_D \epsilon_D}{\epsilon_D}.
\]

(2.28) - Simplified dispersion relation of even and odd1 waveguided modes.
\[
\tanh(k_1 w) = -\frac{k_D \epsilon_M}{k_M \epsilon_D}, \quad \tanh(k_1 w) = -\frac{k_M \epsilon_D}{k_D \epsilon_M}.
\]

(3.1) - Coupled SPP cavity modes within the core.
\[
\begin{align*}
H_y &= Ce^{i \beta x} e^{k_1 z} + De^{i \beta x} e^{-k_1 z}, \\
E_x &= -i C \frac{1}{\omega_0 \epsilon_1} k e^{i \beta x} e^{k_1 z} + i D \frac{1}{\omega_0 \epsilon_1} k e^{i \beta x} e^{-k_1 z}, \\
E_z &= C \frac{\beta}{\omega_0 \epsilon_1} e^{i \beta x} e^{k_1 z} + D \frac{\beta}{\omega_0 \epsilon_1} e^{i \beta x} e^{-k_1 z}.
\end{align*}
\]
(3.4) - MIM cavity dispersion relation. .................................................. 27

\[ \tanh \left( \frac{k_1 w}{2} \right) = -\frac{k_1 \epsilon_1}{k_2 \epsilon_2}. \]

(3.5) - Cavity resonant condition ............................................................ 27

\[ \left( \frac{1}{4} + \frac{n}{2} \right) \lambda_{sp} = L. \]

(3.6) - Adiabaticity condition of a tapered groove. ................................. 33

\[ \gamma = \left| \frac{d\Re(\beta_{GSP})}{dz} \right| \approx \frac{1}{4} \sqrt{\frac{\lambda \sqrt{\epsilon'_{M}}}{\pi \epsilon_d w(z)}} \left| \frac{dw}{dz} \right| \ll 1. \]

(4.6) - Effective refractive index of resonant cavity. ............................... 42

\[ n_{eff} = \sqrt{\frac{\alpha^2 \epsilon_1 \epsilon_2^2 - \epsilon_1^2 \epsilon_2}{\alpha^2 \epsilon_2^2 - \epsilon_1^2}}. \]
## Acronyms

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1D</td>
<td>one-dimensional.</td>
</tr>
<tr>
<td>2D</td>
<td>two-dimensional.</td>
</tr>
<tr>
<td>3D</td>
<td>three-dimensional.</td>
</tr>
<tr>
<td>AFM</td>
<td>atomic force microscope.</td>
</tr>
<tr>
<td>ALS</td>
<td>Advanced Light Source.</td>
</tr>
<tr>
<td>AOA</td>
<td>abnormal optical absorption.</td>
</tr>
<tr>
<td>APD</td>
<td>Advanced Photovoltaics and Devices.</td>
</tr>
<tr>
<td>DOE</td>
<td>Department of Energy.</td>
</tr>
<tr>
<td>EBL</td>
<td>electron-beam lithography.</td>
</tr>
<tr>
<td>EM</td>
<td>electromagnetic.</td>
</tr>
<tr>
<td>FP</td>
<td>Fabry-Perot.</td>
</tr>
<tr>
<td>GRIN</td>
<td>gradient-index.</td>
</tr>
<tr>
<td>HF</td>
<td>hydrofluoric acid.</td>
</tr>
<tr>
<td>HSQ</td>
<td>hydrogen silsesquioxan.</td>
</tr>
<tr>
<td>IMI</td>
<td>insulator-metal-insulator.</td>
</tr>
<tr>
<td>IR</td>
<td>infrared.</td>
</tr>
<tr>
<td>KOH</td>
<td>potassium hydroxide.</td>
</tr>
<tr>
<td>LBNL</td>
<td>Lawrence Berkeley National Laboratory.</td>
</tr>
<tr>
<td>MIM</td>
<td>metal-insulator-metal.</td>
</tr>
<tr>
<td>MWIR</td>
<td>mid-wavelength infrared.</td>
</tr>
<tr>
<td>NIR</td>
<td>near infrared.</td>
</tr>
<tr>
<td>NSOM</td>
<td>near-field scanning optical microscopy.</td>
</tr>
<tr>
<td>PEC</td>
<td>perfect electric conductor.</td>
</tr>
<tr>
<td>QCL</td>
<td>quantum cascade laser.</td>
</tr>
<tr>
<td>rms</td>
<td>root-mean-squared.</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
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<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscope. xiv, xv, 54, 59–61, 63</td>
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<tr>
<td>SINS</td>
<td>synchrotron infrared nanospectroscopy. xvii, 65–67, 71</td>
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<td>SNOM</td>
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Chapter 1

Introduction

“There is a crack in everything. That’s how the light gets in.”
― Leonard Cohen, Anthem, 1992

A large portion of this dissertation is about creating nano-cracks on otherwise naturally impregnable surfaces such as metals, with the overriding aim to squeeze light into nanogrooves some two orders of magnitude smaller than the wavelength of light in space. Further, cracked surfaces with gradually changing properties are introduced, guiding light into predesignated loci of high-intensity localization.

But why does any of this matter?

We use light to extend our vision into smaller and smaller details of the world around us—such as peering into the machinery of life through microscopy. This requires ever smaller wavelengths of light in order to achieve sufficient optical precision to see smaller features of the object. One way to realize small wavelengths is to use photons of higher energy, since in general, higher energy interactions furnish a more detailed perspective of the substance under examination. Cranking the energy of light all the way up to X-rays for example, enables us to see the internal fractures in metallic parts, or inspect the contents of luggage at airports. Such high energy light gets in most materials just fine, and no additional cracks are required. Section 2.4, is in fact dedicated to describing
the frequency regions where metals exhibit their metallic behavior, above which metals effectively become dielectric, allowing light to pass through.

The critical dimensions of an object dictate the wavelength of light required for their imaging. That is, probing an object with a large number of long wavelength photons which are “blind” to the details of the sample, pointlessly increases the intensity without helping the resolution. This seemingly leaves us with only one variable to adjust, which is cranking the photon energy up so as to ensure that the wavelength of light is smaller than the dimensions of the object. Going higher and higher on the energy scale might be fine when the object is an inanimate suitcase, but high energy photons can damage living organisms and their workings. This becomes particularly important when the workings of a functional structure are examined, where the goal is to be as minimally disruptive as possible to the undisturbed natural behavior of the structure.

Fundamentally, the wavelength of the photons and not their energy, determines the resolution of optical systems. Further, the wavelength of photons can be changed without changing their energy. Taking advantage of wavelength-compression mechanisms thus provides a means of enhancing the resolution without increasing the energy. This bio-friendly route avails low-energy non-damaging photons for investigating the form and function of the machinery of life, and other applications where the interaction of high-energy photons with matter can change the integrity of the matter being observed.

Wavelength-compression takes place any time electromagnetic waves enter a medium with a larger refractive index—which is the basis of many optical phenomena. However, to really take advantage of wavelength-compression as a practical means for imaging, for example in the infrared range, very high effective indices are needed.\footnote{For example, glass has a refractive index of 1.5 for visible light, so it compresses the wavelength 1.5 times. However, using mid-infrared frequencies with the resolution of visible light, requires at least a 10:1 compression.} This is possible, but there is a caveat: light at these lower frequencies does not readily get in. It needs help, and that’s where the cracks come in handy—nano-cracks that is—which as it turns
out have an unintuitive and extraordinary ability to assist light with its conundrum of being shut out of matter. The next section introduces the interaction of surface plasmons which just offer such high indices.

1.1 Light-matter interaction at metallic surfaces

As we will further discuss in Chapter 2, the refractive index is not just a property of bulk materials such as the glass used in optical instruments, but waveguides, resonators, and indeed surfaces, such as the interface between a metal and a dielectric possessing an effective refractive index [1]. All such modes are thus capable of wavelength compression, which is the very heart and soul of high resolution microscopy, and other sensing techniques such as imaging and spectroscopy. The origin of the refractive index lies in the interaction of an external field with the contributions of secondary fields generated by the oscillating charges in matter—as the impinging wave sets them in motion. Modifying the nature of such oscillations in matter, via changing the field intensity profile for example, accordingly modifies the index. In general, the response of the microscopic oscillators within matter, is a frequency dependent phenomenon and is the basis of dispersion, where the equation for the index of refraction as a function of frequency is called the dispersion equation. So when the field is concentrated or shaped using waveguides, for instance through the geometric design of the surfaces supporting surface plasmons, the resulting index is accordingly altered. Chapter 4 will derive analytical expressions for this index modification for the case of extremely narrow nanogrooves on metallic surfaces.

Metals are a particularly interesting class of material in their interactions with light. In many ways they resemble a plasma, or a gas of charged particles, where these charged particles have a lot of freedom to roam around. Within the kingdom of metals they roam freely, however, their freedom ends where the boundary of the metal ends. For this reason, when there are electromagnetic fields present outside the metal, a large number of free electrons congregate at the surface. Unable to leave this frontier of
light-matter interaction, bound modes of electromagnetic (EM) waves are formed that are called surface plasmons. Under the right conditions as we will discuss in detail in Chapter 2, surface plasmons form, within a thin volume proximal to the metal interface, with intensities exponentially decaying away from the boundaries, and this thin volume becomes an intense locus of light-matter interaction and field enhancement.

1.2 Motivation & approach

The main focus of this dissertation is on wavelength-management of light, so that low energy photons could attain smaller and smaller effective wavelengths and thereby be suitably applied for high-resolution interaction with the nano-world. This enables high-resolution light-matter interactions without the deleterious effects of high energy photons. As we shall see, there are other benefits of using longer-wavelength photons such as infrared light, as they are able to penetrate deeper into biological tissue, conveying information from deep within living beings.\(^2\) Furthermore, infrared (IR) carries spectral signatures of compounds, crucial for identifying trace amounts of their presence \([2]\).

One mechanism of wavelength-management discussed and utilized here, is surface plasmon polaritons (SPPs), which are light waves coupled to the collective oscillations of free electrons of a metal, at a metal-dielectric interface. Interestingly, as is the case with SPPs, the coupling of light and matter\(^3\) can together result in stronger localized fields. This field enhancement however, comes at a price. The light-enhancement region is limited to the immediate vicinity of the interface of the dielectric and the metal, so that even a small departure from this interface will cause an exponential drop in the field strength. Secondly, the wavelengths of light are compressed, as the effective index at the interface now exceeds that of the dielectric alone \([3]\). There is also an in-plane momentum mismatch between the waves traveling in the dielectric (radiative modes) and the bound metalo-dielectric interface modes (bound modes) \([4]\). Overcoming such

\(^2\)Additionally, SPPs are generally better behaved, lower loss, and have longer propagation distances in the IR.

\(^3\)Charged matter in this case
a momentum mismatch, in order to transfer energy in and out of the surface plasmon mode, requires an arbitrator, typically a prism or a diffraction grating [5].

The approach taken here, is to utilize diffraction gratings for coupling of light to the SPP modes. These SPPs then travel within and without the very same grooves that assisted with the coupling of light to the SPP modes in the first place. As we shall see, when the groove dimensions are suitably chosen, the cavity space can additionally act as a resonator, within which surface plasmons can continue their existence. Grooves of different depth (resonator length), possess different resonant frequencies and trap light of corresponding frequency, as the wave bounces back and forth between two reflective surfaces.

Previous work has shown that uniform gratings, optimized to resonate at a particular frequency, can almost completely absorb light of a particular wavelength [1]. Other attempts have shown that by stringing a series of grooves of different depth, several corresponding wavelengths of light can be trapped, giving rise to multi-spectral or rainbow-trapping gratings [6]. There are two main challenges with these approaches; first, engraving, carving, and/or etching with nanometer precision, from one groove depth to the next is not an easy nanoengineering feat. Second, extending these approaches into other geometries and higher dimensions becomes even more challenging [7].

This dissertation focuses on revealing another dimension in the design of plasmonic cavity resonators, namely the width of the resonators, and once established, to extend this approach to other geometries and arrangements. A major part of the discussion on width-based gratings presented in Chapter 4 clarifies that the width dimension has very different underlying physics at work in contrast to length-variation. Unlike typical cavity-resonators where the energy of the vibrations is dispersed through the volume of the resonator, surface plasmons are so tightly bound to the interfaces that the energy stored in the resonator is mostly concentrated near the surfaces. Thus, the proximity
of these surfaces, when they become very close, influences the dispersion of the cavity mode [1]. This means very narrow cavities have to be designed with this principle in mind, but it also means that the cavity width is a legitimate design parameter in the right range [7]. The regime of this cross-over from the classical resonator, to an SPP-coupled cavity is defined by the field extension of the SPP’s exponential decay into the dielectric—which is typically around 50 nm in the visible range for plasmonic metals such as gold and silver. Advancements in the nanofabrication techniques, now routinely render these dimensions amenable to practical realization, and in fact structures with single digit nanometer grooves discussed in this dissertation are the direct offspring of this approach.

1.3 Chapter-by-chapter outline

This dissertation is comprised of theoretical and experimental works and have been divided into the following sections:

Chapter 2 (Background - SPPs) briefly reviews the background physics describing surface plasmons through the use of Maxwell’s equations leading to the non-radiative bound modes at the interface of a metal and a dielectric. It also discusses the physics of metals which is treated as a plasma of charged particles leading to the formation of plasmon polaritons, and in particular surface plasmon polaritons. Then it discusses the transition from a single interface to two or more interfaces that form sandwich structures, leading to metal-insulator-metal (MIM) or insulator-metal-insulator (IMI) waveguides. These components are the building blocks for the rest of this dissertation.

Chapter 3 (Plasmonic Cavity Resonators) discusses the formation of gratings based on simple structural units discussed in Chapter 2, such as extended surfaces and sandwiched interfaces. In this reductionist view of the gratings, the emergent properties of an extended structure is analyzed in terms of the response of a single structural unit.

Chapter 4 (Graded gratings) presents a departure from the reductionist view and discusses the individual characteristics of each resonator, that is each groove. Even
though each individual resonator is now specialized and optimized for a particular frequency of light, the large-scale harmony of the entire structure is preserved by making the successive tapering of properties so slowly (i.e., adiabatically), that the small impedance mismatch between immediate neighbors is tolerated by surface plasmon waves traveling on the surface of the grating.

Chapter 5 (Nanofabrication) presents the methods of fabrication of the graded gratings. The novelty of the width-based gratings lies in the power of creating the entire structure in a simple single-step lithography process. Various fabrication approaches and materials are discussed, and examples of fabricated devices are presented.

Chapter 6 (Characterization and Experiments) shows the measured response of the devices when examined with subwavelength precision. First the surface profiles and smoothnesses are examined with the atomic force microscope. Next, the devices are illuminated under a laser connected to an atomic force microscope configuration. This is followed by measurements taken when the atomic force microscope (AFM) tip channels broadband yet coherent synchrotron radiation. And the results of each findings are discussed.

Chapter 7 (Other Geometries & Higher Dimensions) takes the concept introduced in Chapter 4 to the next level, by introducing conformal transformation optics as the basis for structures inspired by the geometric gradients amenable to facile fabrication. Here bull’s eye structures and spiky nanostructures are discussed that are mathematically inspired by the concept of graded nano-structures, with adiabatically tapered feature sizes.

Chapter 8 (Conclusion) presents insights and implications emerging from the ideas and research discussed and reported herein in a summary form. This chapter also presents further direction of work as well as allied novel integration inspired by the research presented herein.
Chapter 2

Background - SPPs

SPPs, have now been studied for well over two decades, though their existence has been known long before they were named surface plasmons as they are valid solutions of Maxwell’s equations at the interface of a metal and a dielectric [3, 4, 8]. We will shortly review their properties and modes of excitation (Sec. 2.5). As the name suggests however, SPPs are surface waves that exponentially attenuate away from the surface and into the bulk. The maximal intensity of the field at the surface makes them particularly suitable for enhancement of phenomena that involve light-matter interactions at surfaces [9].

A brief overview of the nature of methods of excitation of SPPs is presented here. Section 2.1 is a primer on the theory of surface plasmons, and the conditions that must be met for their excitation.

The genesis of SPPs relies on the coupling of the electron density wave of a conductor to the incident electromagnetic radiation [3]. Accordingly, these quasi particles form at the interface of the conductor and the dielectric where, the free electrons of the conductor are confined to the metal.

The conduction electrons of a conductor can be modeled as a gas of charged particles for most of the visible and ultraviolet (UV) region. These particles (e.g. electrons,) are “free” to the extent that they can roam within the conductor, but their freedom is
ultimately impeded as they reach the boundary of the conductor, which they cannot, under ordinary circumstances, cross. Their escape from the metal requires energies in excess of the work-function of the metal, in order to photoelectrically facilitate their escape. Within the scope of the work considered here, the photon energies are less than the work-function of the metal. However SPPs have also been studied in the context of assisting with electron ejection from metals in the case of the free-election laser [10]. When the photons and electrons meet at the interface, and under appropriate conditions, they can become coupled resulting in a hybrid wave “tethered” and evanescently confined to the interface.

2.1 The theory of surface plasmon polaritons

For a plane interface of a metal and a dielectric, SPPs represent plane-wave solutions of Maxwell’s equations. In general these plane waves have complex wave vectors that determine both the field propagation and loss. A reasonable starting point for a mathematical description of SPPs, is perhaps with the following form of Maxwell’s equations:

\[
\begin{align*}
\nabla \cdot E &= \frac{1}{\epsilon_0} \rho_{\text{ext}} \quad \text{Gauss’s Law} \tag{2.1a} \\
\nabla \cdot B &= 0 \quad \text{Gauss’s Law for magnetism} \tag{2.1b} \\
\nabla \times E &= -\frac{\partial B}{\partial t} \quad \text{Faraday-Maxwell Law} \tag{2.1c} \\
\nabla \times B &= \mu_0 \epsilon_0 \frac{\partial E}{\partial t} + \mu_0 J \quad \text{Ampère-Maxwell Law} \tag{2.1d}
\end{align*}
\]

In 1835, Gauss formulated the behavior of the electric field resulting from the arrangement of charges in space [11]. In differential form this is given by Eq. 2.1a, stating that the divergence of the electric field \(E\), at any point in space, is proportional to the amount of charge at that point, where \(\epsilon_0\) is the vacuum permittivity, and \(\rho_{\text{ext}}\) is the volume charge density. Eq. 2.1b similarly states that the divergence of the magnetic
field is zero at all points, since there are no magnetic charges. Almost contemporaneously in 1831, Faraday discovered that a changing magnetic field through a closed circuit, gives rise to an electromotive force. Using the concept of fields, Maxwell’s generalized Faraday’s law of induction, and stated it in the form given by Eq. 2.1c, showing how a time-varying magnetic field will always be accompanied by a spatially varying electric field. That is, a time-varying magnetic field $B$, gives rise to an electric vector field $E$, whose rotation (curl) around that point is defined by the rate of change of $B$.

In the year 1823, less than a decade prior to the work of Faraday and Gauss, Ampère had discovered that wires carrying time-varying currents are attracted to magnets, where his law was limited to $\nabla \times B = \mu_0 J$, with $J$ denoting the electric current density, and $\mu_0$ the magnetic permeability. Nevertheless, in 1861, Maxwell rediscovered this law independently, in its complete form while adding the finishing touches that included in addition to the current density term, the effects of a time varying electric field [12]. Eq. 2.1d also displays the symmetry that exists with Faraday’s law. Once Maxwell completed the mathematical description of the laws given by the set of Eqs. 2.1, the complete picture was nothing short of miraculous. Not only is this set of laws able to describe phenomena such as light propagation in general, and even surface plasmons, but it is, as far as we know complete, even considering the effects later described by special relativity of Einstein.

2.2 A closer look at maxwell’s equations

When dealing with light-matter interactions such as surface plasmons, it is easier to first simplify the math by bundling the microscopic details of the material into bulk materials properties such as the permittivity.

There are of course a number of ways to formulate the set of equations 2.1. The integral form of which are intuitively easier to imagine, though, the differential form as stated here is easier to solve in many cases. Also, Eq. 2.1a, and Eq. 2.1d are often stated
in slightly different notation as

\[ \nabla \cdot D = \rho_{\text{ext}} \]  \hspace{1cm} (2.2a)
\[ \nabla \times H = \mu_0 \epsilon_0 \frac{\partial D}{\partial t} + \mu_0 J. \]  \hspace{1cm} (2.2b)

where \( D \) is the dielectric displacement, and \( H \) is the magnetizing field. The advantage of this approach, as intended, is to sweep under the carpet as much of the microscopic details of individual oscillators, as possible. To show that this is not to cut corners on the physics, but rather to conveniently include the effects of polarization alongside the electric field where matter is present, we start from the two equations:

\[ D = \epsilon_0 E + P, \]  \hspace{1cm} (2.3)
\[ H = \frac{1}{\mu_0} B - M, \]  \hspace{1cm} (2.4)

where \( M \) is the magnetization. Eq. 2.3 still explicitly includes the microscopic details of the oscillators within the medium as the microscopic dipoles within matter align with the external field to give rise to the polarization effect \( P \). The bound charges are fixed in lattice position and can just jiggle around a little, each with a little dipole moment. If each charge is displaced by a distance \( d \), then in a medium with a charge density of \( \rho_b \) for bound charges, the total polarization vector is \( P = \rho_b d \). It is also easy to see that we can state Gauss’s Law as \( \nabla \cdot P = -\rho_b \). Then conservation of charge which is \( \nabla \cdot J = -\frac{\partial \rho_b}{\partial t} \) can be rewritten as \( J = \frac{\partial P}{\partial t} \). With this, we can place 2.3 into 2.2a and obtain

\[ \nabla \cdot E = \frac{\rho_{\text{total}}}{\epsilon_0}. \]  \hspace{1cm} (2.5)

Now, we do not need to worry about the microscopic effects inside matter, and only keep track of charges and bulk materials properties that determine how a particular
material responds to the external electric field, namely:

\[ D = \varepsilon \varepsilon_0 \mathbf{E}. \]  

(2.6)

The electric field \( \mathbf{E} \), is now combined with the effects of polarization of matter. These two effects together, are now implicitly included under the umbrella of a new term called the **electric displacement field** \( \mathbf{D} \). Using \( \mathbf{D} \) instead of the \( \mathbf{E} \), reprieves us from having to diligently keep track of the external and internal fields and currents.

Similarly, Eq. 2.4 includes the details of magnetization of matter in the presence of a magnetic field. All throughout this work however, we will only be dealing with nonmagnetic materials, and as such will not consider \( M \). The magnetic counterpart of Eq. 2.6, is given by:

\[ \mathbf{B} = \mu \mu_0 \mathbf{H}, \]  

(2.7)

where as we are considering nonmagnetic materials, \( \mu = 1 \), and we are left to deal with \( \varepsilon \) which is the relative permittivity of the material interacting with light.

### 2.3 The wave equation

We begin by deriving the wave equation at the interface of a metal and a dielectric—a simple flat interface. To do this, the wave equation is solved for each medium separately, that is metal and dielectric, and subsequently matched at the boundary. This is easier to accomplish in the differential form of Maxwell’s equation compared to the integral form. Individually or collectively, Maxwell’s equations are a description of waves, but rather the general behavior of the fields in the presence of charges and currents. Historically, Maxwell himself began by taking the curl of the curl of the electric field, and using the mathematical identity \( \nabla \times \nabla \times \mathbf{E} = \nabla (\nabla \cdot \mathbf{E}) - \nabla^2 \mathbf{E} \) and Eqs. 2.1c, and 2.1d to arrive
at
\[ \nabla \times \nabla \times \mathbf{E} = -\mu_0 \frac{\partial^2 \mathbf{D}}{\partial t^2}, \]  
(2.8)

leading to
\[ \nabla \left( -\frac{1}{\epsilon} \nabla \cdot \mathbf{E} \right) - \nabla^2 \mathbf{E} = -\mu_0 \epsilon_0 \epsilon \frac{\partial^2 \mathbf{E}}{\partial t^2}, \]  
(2.9)

where in source-free regions of space, \( \nabla \cdot \mathbf{E} = 0 \) and hence the first term vanishes. In general \( \epsilon \) is also a spatially dependent quantity, in other words \( \epsilon \equiv \epsilon(\mathbf{r}) \), however, we assume that this variation is negligible over small spatial distances, roughly on the same order as \( \lambda \). This assumption is clearly not justified in the case of metamaterials where the materials properties can vary at distances smaller than the wavelength. Though for simple interfaces of homogeneous materials the wave equation simplifies to:

\[ \nabla^2 \mathbf{E} = \frac{\epsilon}{c^2} \frac{\partial^2 \mathbf{E}}{\partial t^2}. \]  
(2.10)

Eq. 2.10, which states a second spatial derivative of a quantity is proportional to the second-order-time-derivative of the same quantity, provides a hint that the solutions are complex sinusoidals, or harmonics of the form \( \mathbf{E}(\cos(\omega t) - i \sin(\omega t)) \) or alternatively stated in exponential form \( \mathbf{E}(\mathbf{r}) e^{i\omega t} \), where \( \mathbf{E} \) is only a spatially varying quantity. This simplifies our wave equation to:

\[ \nabla^2 \mathbf{E} = -\frac{\omega^2}{c^2} \epsilon \mathbf{E}, \]  
(2.11)

known as the Helmholtz equation. This linear PDE\(^1\) can also be exactly solved by d’Alembert’s solution, through Fourier transform method, or using separation of variables. In any case, the solutions that satisfy Eq. 2.10 are superposition of the form \( a e^{i\beta x} \) and \( b e^{-i\beta x} \), where \( a \) and \( b \) are constants of integration. The solution space is thus a superposition of plane waves traveling in both \( x \) direction and \( -x \) direction. \( \beta \) is the

\(^1\)partial differential equation
called the propagation constant, which is the component of the $\frac{2\pi}{\lambda} \hat{r}$ wave vector projected from the direction of the wave propagation $\hat{r}$ onto the $x$ direction resulting in solutions of the form $E(r) = E_r \hat{r} e^{i(\beta x - \omega t)}$. A traveling wave in an arbitrary direction can thus be decomposed along the three spatial directions, and in fact our original wave Eq. 2.11 is not constrained to any particular direction. The solution space is now neatly organized along the principal axes $x, y, z$ into a set of plane waves that are either propagating along an axis or in the opposite direction. In the $x$ direction, this can be written as:

$$\frac{\partial^2 E(x)}{\partial x^2} = (\beta^2 - k_0^2 \epsilon) E(x).$$

Of course, a sister equation also exists for the magnetic field $H$, and $E$ and $H$ are related through Maxwell’s equations. Thus the complete set of solutions to Eq. 2.12 takes on the form:

$$\frac{\partial E_x}{\partial z} - \frac{\partial E_z}{\partial x} = i\omega \mu_0 H_y,$$

with cyclic permutations of $x \rightarrow y$, $y \rightarrow z$, and $z \rightarrow x$, giving a total of six equations. For a simplified geometry of propagation along an axis, say the $x$ direction with no $y$ variation, these equations simplify to:

$$\frac{\partial E_x}{\partial z} - i\beta E_z = i\omega \mu_0 H_y$$

$$i\beta E_y = i\omega \mu_0 H_z$$

$$\frac{\partial E_y}{\partial z} = -i\omega \mu_0 H_x$$

$$\frac{\partial H_x}{\partial z} - i\beta H_z = -i\omega \epsilon \epsilon_0 E_y$$

$$i\beta H_y = -i\omega \epsilon \epsilon_0 E_z$$

$$\frac{\partial H_y}{\partial z} = i\omega \epsilon \epsilon_0 E_x$$

This system admits two solutions with different polarizations called $p$ (or transverse magnetic (TM)), where the only nontrivial components of the $E$ field are $x$, and $z$
and the nontrivial components of the $H$ field has only the $y$ component. The second polarization is known as $s$ (or transverse electric (TE)), where the nonzero components of the electric and magnetic fields along the axes are flipped, namely, the only nonzero component of the $E$ field is along the $y$ direction, whereas the $H$ field has $x$, and $z$ components.

The corresponding wave equations for the $s$ and $p$ polarizations are respectively:

$$\frac{\partial^2 E_y}{\partial z^2} = (\beta^2 - k_0^2 \epsilon) E_y,$$  
(2.15)

and

$$\frac{\partial^2 H_y}{\partial z^2} = (\beta^2 - k_0^2 \epsilon) H_y,$$  
(2.16)

where the only difference is that the $E$ and $H$ fields are exchanged.

## 2.4 Plasma frequency of a metal as a gas of electrons

By treating the free electrons of a metal (i.e. the plasma sea) with a damped harmonic motion subject to a harmonic external driving electric field $E = E_0 e^{i\omega t}$, we can write:

$$m \ddot{x} + m\gamma \dot{x} - eE = 0,$$  
(2.17)

where a corresponding oscillation can be attributed to the electrons as $x = x_0 e^{i\omega t}$. Of course, the ponderable nature of electrons and the damping factor impose a lag, or a phase delay between the two harmonic oscillations: that of the electron, and the driving external force, given by the following factor:

$$x(t) = \frac{e}{m(\omega^2 + i\gamma \omega)^2} E(t).$$  
(2.18)
Since \( P = -ne x(t) \), the electric displacement as a result of this retardation factor given by Eq. 2.18, becomes:

\[
D = (\epsilon_0 - \frac{\epsilon_0 \omega_p^2}{\omega^2 + i\gamma \omega}) E, \tag{2.19}
\]

where \( \omega_p = \sqrt{\frac{ne^2}{\epsilon_0 m}} \) is the plasma frequency of the sea of free electrons of the conductor.

Finally, the dielectric function of this plasma is found to be:

\[
\epsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma \omega} = \left(1 - \frac{\omega_p^2}{\gamma^{-2} + \omega^2}\right) + i\left(\frac{\omega_p^2}{\omega(\gamma^{-2} + \omega^2)}\right), \tag{2.20}
\]

where \( \omega(t) \) is parsed into its real and imaginary components in the last term. It can be seen that when \( \omega < \omega_p \), metals will behave as very good conductors, and only when \( \omega \) becomes very large and close to \( \omega_p^2 \), the damping can be considered negligible, and the free electrons of the metal can be approximated as an undamped plasma of electrons. Of course in the case of real plasmonic meals such gold, and silver, the intraband transitions lead to deviations for this ideal model [13]. Finally, it is important to note that when \( \omega > \omega_p \), metals begin to exhibit dielectric-like behavior, as the oscillating frequencies are so fast that the electrons can all but jiggle a little, without producing significant fields to counteract the externally driving field. As a result, such high frequency radiation is not screened well, and can penetrate into the metal.

### 2.5 SPPs at a single metal-dielectric interface

After a component-wise analysis of the Maxwell’s equations for the \( s \), and \( p \) modes in a homogeneous medium, we can easily apply the wave equation solutions to the boundary of two media forming an interface as shown in Fig. 2.2, where the space is divided into the positive and negative \( z \) directions forming two half-spaces, one in the \( +z \) direction which is the dielectric, and the other in the \( -z \) direction into the metal. For the \( p \) polarization as discussed above, the exponential solutions of the field that satisfy the relevant components of the set of equations in the dielectric 2.14 yielding:

\( \omega_p \) is normally very large and in the UV range for most metals.
Figure 2.1: Plot of the dispersion relation of SPPs with respect to the light cones in vacuum and glass. The dispersion curve of the SPP always lies outside and to the right of the vacuum light cone; it does however intersect the glass light cone. The point of this intersection offers a $k$-vector for which the glass-metal interface, such as a prism, can become the impedance-matching mediator.

Figure 2.2: A slab of smooth metallic surface defining an interface between the dielectric and the metal. Vacuum itself can serve as a dielectric.

\[
E_x(z) = \Gamma_2 \frac{i}{\omega \epsilon_2 \epsilon_0} k_2 e^{i \beta x - k_2 z}, \quad (2.21a)
\]
\[
E_z(z) = -\Gamma_1 \frac{\beta}{\omega \epsilon_2 \epsilon_0} k_2 e^{i \beta x - k_2 z}, \quad (2.21b)
\]
\[
H_y(z) = -\Gamma_2 e^{i \beta x - k_2 z}, \quad (2.21c)
\]
where \( k_1 \) and \( k_2 \) are the \( z \) components of the wave vector in the two media, and in the metal they become:

\[
\begin{align*}
E_x(z) &= -\Gamma_1 \frac{i}{\omega \epsilon_1 \epsilon_0} k_2 e^{i\beta x - k_1 z}, \\
E_z(z) &= -\Gamma_2 \frac{\beta}{\omega \epsilon_1 \epsilon_0} k_2 e^{i\beta x - k_1 z}, \\
H_y(z) &= -\Gamma_1 e^{i\beta x - k_1 z},
\end{align*}
\]

Continuity of the magnetic field simply requires that the constants \( \Gamma_1 \), and \( \Gamma_2 \) are equal, and continuity of the tangential component of the electric field and the normal component of the dielectric displacement, scaled by the material’s permittivity, imposes the dispersion equation for the single metal-dielectric interface:

\[
\epsilon_1 k_2 = -\epsilon_2 k_1. \tag{2.23}
\]

Equations 2.15, and 2.16 require that in both media, a new wave vector be defined whose value is:

\[
\begin{align*}
k_1^2 &= \beta^2 - k_0^2 \epsilon_1, \\
k_2^2 &= \beta^2 - k_0^2 \epsilon_2,
\end{align*}
\]

and taking advantage of Eq. 2.23, a simple substitution results in the dispersion relation of the surface plasmon at the boundary of the two media as shown in Fig. 2.2, that is

\[
\beta = k_0 \sqrt{\frac{\epsilon_1 \epsilon_2}{\epsilon_1 + \epsilon_2}}, \tag{2.25}
\]
as though the interface were a medium whose effective index is the geometric average of the two permittivities $\epsilon_1$ and $\epsilon_2$, that is $\epsilon_{\text{eff}} = \sqrt{\epsilon_1 \epsilon_2}$, bearing in mind that the permittivities are in general complex quantities.

The characteristic lossiness of metals prevents electromagnetic radiation to travel within the body of the metal at any significant distance which exceeds a few nanometers. Beer’s law of absorption predicts that the fields fall off exponentially as $e^{-z/\delta}$, where $\delta$ is the skin-depth. However, the bound modes as described above, strike a cooperative union between a metal and a dielectric resulting in SPP modes with propagation distances of several micrometers in the visible and near infrared (NIR) range. In this case the skin depth exponentially increases in the dielectric while remaining more or less constant in metal, pinned to about 25 nm. Doubling up the metal-dielectric interface, by sandwiching either material into a waveguide, allows for even larger propagation distances of SPPs. Normally for such MIM waveguides, only the conventional waveguiding modes are accessed, however, these structures also boast plasmonic waveguiding modes once the transverse core dimensions are comparable to the SPP skin-depths in the dielectric [14]. The following section discusses the plasmonic MIM waveguides, and Chapter 4 will then undertake a systematic overview of creating gratings based on this principle of tapping the plasmonic modes of MIM waveguides.

### 2.6 Double metal-dielectric interface

Whether the structure is comprised of a metal sandwiched by a two layers of dielectric (Fig. 2.3), or vice versa, there exist two metallo-dielectric interfaces that are spatially separated. If their spatial separation is too large compared to the exponential tail of the SPP, the two interfaces are effectively decoupled and thus independent. Such a structure operates as a conventional waveguide. However, when the middle layer of the sandwich is comparable or thinner than the exponential tail of the SPP, the two SPP modes can become coupled and effectively reinforce each other, as will be discussed in detail in Section 4.2. We leave the details of their coupling to the aforementioned section, and
Figure 2.3: A metallic slab is sandwiched between two dielectric layers. This mode supports SPPs at both interfaces, and when the thickness of the metal becomes comparable to the exponential (evanescent) tail of the surface plasmons in the metal, these two SPPs can become coupled. This is referred to as the insulator-metal-insulator waveguide or IMI.

here only give the details of the geometry and the SPPs. It is noteworthy to mention that the structure can include many more layers than described here, and when the layers are much thinner than the decay length of the SPP, their effective fields can extend over several neighboring layers. Although, the metal skin depth is generally around 25 nm, and so this becomes a nanofabrication limit in practice. Since in the graded grating structures discussed in Chapter 4, the focus of our attention will be on the coupling through the dielectric sandwiched by two metallic claddings, the following is a description of an MIM structure.3

Let us make the assumption that the dielectric medium is labeled with subscript D. These solutions were already derived in Eq. 2.21, here we take the components in the middle dielectric layer, noting that reference of the z-axis is taken to be the center of the dielectric, and hence its sign is reflected accordingly:

---

3The mathematics of an IMI structure can be easily derived based on the discussion herein.
\[ E_x(z) = \Gamma \frac{i}{\omega \epsilon_M \epsilon_0} k_M e^{i\beta x - k_M z} - \Gamma' \frac{i}{\omega \epsilon_M \epsilon_0} k_M e^{i\beta x + k_M z}, \]  
\[ E_z(z) = \Gamma \frac{\beta}{\omega \epsilon_M \epsilon_0} k_M e^{i\beta x - k_M z} + \Gamma' \frac{\beta}{\omega \epsilon_M \epsilon_0} k_M e^{i\beta x + k_M z}, \]  
\[ H_y(z) = \Gamma e^{i\beta x - k_M z} + \Gamma' e^{i\beta x + k_M z}. \]

(2.26a)  
(2.26b)  
(2.26c)

The details can be found elsewhere such as Ref. [13], however, the solution of the system of linear equations that includes Eq. 2.24, as well as the continuity of the \( H_y \) components across the three media results in the dispersion relation of the waveguide as follows:\(^4\):

\[ e^{-k_M w} = \frac{k_M}{\epsilon_M} + \frac{k_D k_M}{\epsilon_D \epsilon_M} + \frac{k_D}{\epsilon_D}, \]

(2.27)

where \( k_M \) is the \( z \)-component of the \( k \)-vector in the metal, and \( w \) is the thickness of the metal. It can be seen that when \( w \) becomes very large this equation reduces to Eq. 2.23, which is two decoupled SPPs. Furthermore, we have assumed above that the two dielectrics sandwiching the metal are the same, thus Eq. 2.27 further simplifies to:

\[ \tanh(k_1 w) = -\frac{k_D \epsilon_M}{k_M \epsilon_D}, \]

(2.28a)  
\[ \tanh(k_1 w) = -\frac{k_M \epsilon_D}{k_D \epsilon_M}. \]

(2.28b)

These two equations describe the symmetric and antisymmetric modes (otherwise known as even and odd parities, respectively). Here, the particular modes of interest are the odd modes of the MIM structure, since these modes have no cutoff, which means no matter how small \( w \), these modes can still subsist within the structure. The discussion of Chapter 4, almost exclusively revolves around the odd modes of the system. Although, the even modes will not be discussed here, it is interesting to mention that their confinement has the opposite behavior, as they become less confined.

\(^4\)Here the two dielectrics surrounding the metal are considered the same material. For details see [13]
with \( w \) getting narrower, until in the limiting case the SPP modes vanish into plane waves in the dielectric [13].

It is worth mentioning that the symmetric and antisymmetric modes of the waveguide are the result of the energy-splitting when the degeneracy of the system is lifted. This occurs again and again in physics, and perhaps the most familiar example is that of the atomic orbitals splitting into molecular orbitals as they come together. At any rate, when the degeneracy is lifted, energy splitting results in energies that are above and below the degenerate energy of the system creating a bandgap. The odd modes occur at higher energy compared to the decoupled system (i.e., single-interface SPP modes), and the even modes are at lower energy compared to the decoupled system.

### 2.7 Methods of SPP excitation

There are several ways of exciting SPPs, and all require that the impedance matching criteria discussed in Section 2.5 be satisfactorily addressed. One method previously pointed out and shown in Fig. 2.2 is using the momentum matching afforded by a prism [3]. Schematically, this is shown in the top image of Fig. 2.4, where a total internal reflection creates evanescent waves whose in-plane \( k \)-vectors are impedance matched to the SPP modes of the waveguide, thus transferring part of the energy of the incident light through the prism to the SPP modes. Another way, shown in the middle image of the same figure is through the use of grating, and particularly subwavelength gratings whose non-specular diffraction orders (higher than zeroth order) are evanescent and thus have an in-plane momentum component impedance-matched to the SPP modes. It is also possible to bring a sharp tip such as an AFM tip, as is done in near-field scanning optical microscopy (NSOM) set ups, where the sharp tip has Fourier frequencies, some of which satisfy the impedance-matching requirement and are able to launch SPPs as illustrated [15]. Of course, a variation of this, with the same underlying physics is through the use of plasmonic nanoparticles, which act as a tip in a similar way. This is not shown
here, though in Chapter 7, we will rely almost exclusively on this means for launching SPP modes on nanoparticles [16].
Figure 2.4: (Top) Prism-coupling mechanism allows for impedance matching through total internal reflection at the boundary of the metal and the dielectric. This is known as the Kretschmann coupling. (Middle) Light can also use the momentum matching of various diffraction modes of a grating for SPP coupling. In the case of subwavelength gratings, other than the zeroth order mode, all higher modes are evanescent, meaning they are well-suited for launching SPPs. (Bottom) Of course, the near field components of the SPP-fields can also be directly excited through a near-field means such as an AFM tip acting as a waveguide, as is typical in NSOM set ups.
Chapter 3

Plasmonic Cavity Resonators

3.1 Resonator cavity

It is sometimes useful to consider subwavelength volumes such as nanogrooves as the building blocks of subwavelength gratings. In so doing, the pairwise coupling of neighboring grooves can result in energy transfer between them [17, 18]. This is quite evident in the case of identical grooves, as their impedance-matching is satisfied due to the fact that they are identical. However, as examined in detail in Chapter 4, the impedance-matching of perturbed graded grooves requires a few other considerations. This phenomenon is akin to coupled resonator optical waveguides (CROWs) [19, 20]. When all grooves are identical, the emergent optical response of the grating can often be analyzed based on a single groove’s response, and simple in-phase repetition does not change the solution space. As Chapter 4 will discuss, even in the case of non-identical grooves, under certain circumstances discussed in Chapter 4, this groove-wise analysis can be quite relevant and accurately portraying of the physics.

The structural repeating unit of a grating such as the one shown in Fig. 3.1, is a rectangular cavity such as the one shown in Fig. 3.2. The incident light is $p$ polarized here, and in all subsequent gratings analyzed in this dissertation, unless specifically indicated otherwise. The defining dimensions of this cavity are given by the groove width $w$, and
3.2 Dispersion relation of resonant plasmonic cavities

We model a groove as an MIM waveguide. The non-oscillatory $p$-polarized bound modes of this waveguide result in the coupling of the localized modes in the core ($-\frac{w}{2} < z < \frac{w}{2}$) (for details see [13]). The electric and magnetic field-components of the coupled-
SPPs are given by solving Maxwell’s equations, as previously discussed:

\[ H_y = Ce^{i\beta x}e^{k_1 z} + De^{i\beta x}e^{-k_1 z}, \quad (3.1) \]
\[ E_x = -iC\frac{1}{\omega\epsilon_0\epsilon_1}ke^{i\beta x}e^{k_1 z} + iD\frac{1}{\omega\epsilon_0\epsilon_1}ke^{i\beta x}e^{-k_1 z}, \quad (3.2) \]
\[ E_z = C\frac{\beta}{\omega\epsilon_0\epsilon_1}e^{i\beta x}e^{k_1 z} + D\frac{\beta}{\omega\epsilon_0\epsilon_1}e^{i\beta x}e^{-k_1 z}, \quad (3.3) \]

where \( k_1 \) and \( k_2 \) are the components of the \( k \)-vector perpendicular to the intragroove surface (i.e., along the \( z \)-direction) in the core and the metal, respectively. \( k_1 = \sqrt{\beta^2 - \epsilon_1 k_0^2} \), and \( k_2 = \sqrt{\beta^2 - \epsilon_2 k_0^2} \); where \( k_0 = \frac{\omega}{c} \), and \( \omega \) is the frequency of the excitation. By adding the two solutions in the core region of thickness \( w \) and applying continuity conditions, the dispersion relation of the MIM waveguide is readily obtained; the odd modes of which are given by [13]:

\[ \tanh \left( k_1 \frac{w}{2} \right) = -\frac{k_1 \epsilon_1}{k_2 \epsilon_2}. \quad (3.4) \]

Note that these odd modes (i.e. symmetric mode) have no cutoff which means theoretically these modes will be accommodated by the waveguide even when the groove widths are extremely narrow well into the single digit nanometer regime [21].

The MIM SPP wavelength \( \lambda_{sp} = \frac{2\pi}{\text{Re}(\beta)} \), is calculated from Eq. (4.4) as a function of the core thickness \( w \) [1]. For bounded grooves such as shown in Fig. 3.2, applying the continuity conditions: \( E_{z1}|_{x=0} + E_{z2}|_{x=0} = 0 \) due to the perfect electric conductor at the bottom of the resonator, and \( \frac{\partial(H_{y1}+H_{y2})}{\partial x}|_{x=L} = 0 \) due to the near unity reflection from the top of the resonator where \( \beta \gg \sqrt{\epsilon k_0} \) yields the relation between the plasmonic wavelength, cavity length, and cavity modes:

\[ \left( \frac{1}{4} + \frac{n}{2} \right) \lambda_{sp} = L, \quad (3.5) \]
where \( n \) is an integer denoting mode order. Clearly, this resonant condition matches resonators as shown in Fig. 3.2, which are open-ended on top and terminate at the metal at the bottom. There is no transmission through those gratings, and they operate in reflection mode. It is straightforward to modify the resonant condition if the grooves were open-ended on both sides, as the dispersion relation does not change. Such grooves will act as subwavelength plasmonic gratings, whose individual and collective characteristics give rise to interesting phenomena such as light steering, and bending the path of propagation of light [22]. The case grooves that are only open on top, is discussed in this dissertation for clarity of illustration, otherwise, all the discussions made herein also apply to the case of transmission grooves as well.

### 3.3 Grooves as the structural repeating units

In Section 2.5, the condition for excitation of SPP at the interface was given, which is that the momentum matching criteria between the light cone in vacuum and the SPP
at a metallo-dielectric interface has to be addressed. This is a requirement for the energy of a traveling wave in a dielectric to be channeled to a waveguide mode such as the SPP on a metal surface. In order to mediate this impedance mismatch, typically a prism [23], or a grating [8] It is often said that subwavelength gratings have only the zeroth order diffraction mode, and all the higher modes are nonexistent. It is perhaps more useful to describe the higher order modes as evanescent, which in effect direct the oncoming wave energy onto the non-radiative modes at the interface of the grating material and the dielectric. In the case of subwavelength gratings, the in-plane\(^1\) \(k\)-vectors of all higher order modes, are adjusted by multiples of \(\frac{2\pi}{\Lambda}\), added or subtracted from the \(k\)-vector in free space; where \(\Lambda\) is the periodicity of the grating, also referred to as the grating pitch, which is the sum of the thicknesses of the gap \(w\) and the thickness of the metallic divider wall between.

Although the discussion here primarily focuses on varying the thickness of the dielectric \(w\), the same physics applies to the case where the thickness of the metal is varied. Although from a practical standpoint, since the SPP exponential tail extends much farther into the dielectric compared to the metal, there is so much more real-estate to work with the dielectric width as opposed to the metal. The metals widths required for such coupling is about 50 nm (\(\sim\) 25nm contributed from each SPP), which although not impossible is rather challenging. On the other hand the dielectric skin depths as large as \(\sim\) 150 nm\(^2\) can easily lead to accessing the plasmonic modes of the MIM waveguide.

### 3.4 Globally absorbing gratings

Le Perchec et al. have shown that gratings, and in particular subwavelength gratings with groove widths on the order of the exponential tail of the SPPs, i.e. \(w \sim 5 – 20\) nm, and \((L)\) less than a 100 nm deep, can lead to almost 100% absorption

\(^1\) i.e. plane of SPP propagation and specifically, in the direction orthogonal to the grooves shown as \(k_{||}\) in Fig. 3.3 (a).

\(^2\) even larger in the mid-wavelength infrared (MWIR) range
Chapter 3. Plasmonic Cavity Resonators

Figure 3.3: a) Schematic of the momentum matching between incident EM waves on a grating and a SPPs. The $E$ field has a component perpendicular to the grooves, i.e. parallel to the $k_{\parallel}$ as shown.

of the monochromatic light on (global) resonance as shown in Fig. 3.4 [1]. When all the nanogrooves are identical, the local and global resonances of the structures occur at the same frequency, thus leading to an extraordinary absorption of light, sometimes referred to as the abnormal optical absorption (AOA) [1]. This total absorption is controllable over a wide range from the near IR all the way up to the UV range, and can be attained by adjusting the dimensions of the nanogrooves [27].

It is noteworthy, and will be further discussed in Chapter 4 that the AOA case, takes place in resonators that are far shorter than the typical corresponding Fabry-Perot (FP) resonator length i.e. $\frac{\lambda}{4}$, which would be roughly a quarter of the wavelength of the visible region of light ($\sim$100-400 nm). But that is not the case here, as cavities only a few nanometers deep and wide can almost completely absorb light by becoming resonant at frequencies that is not typical of cavity resonators such as the FP type [1]. This has been attributed to the excitation of surface plasmon modes in the quasistatic regime.
Figure 3.4: Reflectivity plot of $p$-polarized EM plane wave impinging at normal incidence on a silver grating such as shown in the inset, analytically calculated for various heights of $h=30$ nm (black dot), $h=15$ nm (dashed line), and $h=5$ nm (+) with $w=5$ nm and $d=30$ nm. Solid black curve corresponds to the reflectivity of a film of silver much thicker than the skin-depth [1]. Reprinted with permission from Le Perchec et al., [1] ©2008 American Physical Society.

3.5 Introducing a gradient profile

Functionally graded materials, such as gradient-index (GRIN) optics, have long been used to attain a larger finesse over the propagation of light in a particular waveguide [28]. This is achieved by a gradual tapering of the refractive index of the material such as in fiber optics [29], flat lenses [30], and aberration correction [31,32]. Moreover, the tapering of the gradient can follow various functions such as linear, spherical, and so on [33]. In fact, this also occurs in nature, as the human eye has a GRIN of refraction that varies between 1.406 in the center of the lens to about 1.386 in the peripheral region [34]. The mirage appearing on a hot surface, is due to a temperature gradient, which produces a density gradient, which in turn produces a GRIN profile for the column of air which acts as a lens.
Figure 3.5: (TOP) A graded-grating structure with a depth gradient where the FP resonance length is changed. (BOTTOM) COMSOL simulation of the grating shown above with 30 THz radiation trapped at the location where the groove is resonant.

The functional gradient introduced by changing the resonant frequency of a series of FP resonators such as the one shown in Fig. 3.5 is also a functional gradient, however, in this case the effective index of the cavity stays the same, and the structure is just a series of resonators which are each resonant at a different wavelength. Of a slightly more interesting case however, is changing the groove width $w$, which truly modifies the effective index. As discussed in Sec. 3.4, there is an intricate link between the width
of exceedingly narrow cavities and the dispersion relation of the cavity, which is not attributable to a simple resonator structure such as a FP cavity. The equation for the effective groove index (Eq. 4.6) is derived and discussed in the next chapter. Thus, creating a chain of nanogrooves (under weak coupling), each with a slightly higher (or lower depending on the direction), effective index is truly a GRIN approach to plasmonic subwavelength graded gratings.

3.6 On adiabatic gradients

The next chapter, gives a detailed theoretical treatise of the plasmonic graded grating structures based on the tapering of the local effective index of each groove. This is accomplished not by changing the resonant condition of the grooves, but rather through changing the groove-widths which is ultimately related to the dispersion relation of the grooves [7].

Before commencing the study of the grating with simple rectangular cross-sections, it is useful to consider the case where the adiabatic geometric tapering is incorporated into the design of each groove as opposed to from one groove to the next. Though, only the latter case is studied in Chapter 4, the tapering of each plasmonic element discussed in Chapter 7, becomes a key factor in determining the response.

As illustrated in the graphical rendition of Fig. 3.6 (a), changing the groove width can lead to humpy gratings where each groove-width is tapered. Ref. [35] discusses the adiabatic condition (cross-sectional side view and pertinent variables shown in Fig. 3.6(b)). This condition can be given as [35]:

$$\gamma = \left| \frac{d\Re(\beta_{GSP})}{dz} \right| \approx \frac{1}{4} \sqrt{\frac{\lambda\sqrt{\epsilon_M}}{\pi\epsilon_0 w(z)}} \left| \frac{dw}{dz} \right| \ll 1, \quad (3.6)$$

where $\gamma$ is the adiabaticity, $\lambda$ is the EM wavelength in space, $\Re(\beta_{GSP})$ is the real part of the propagation constant of the groove surface plasmon (SP) mode, $w$ is given as a
function of the depth coordinate $z$, and $\epsilon'_M$ is the real part of the metal. To achieve a perfect broadband absorption, the gap-width at the bottom of the groove shown by $\delta$ in Fig. 3.6(b), has to vanish. This condition is difficult to achieve in practice, and thus a certain amount of reflection is practically inevitable as seen in the plot of reflectivity in inset (c) of the same figure, which shows the calculated reflectivity figures for a series of inclination angles (shown in Fig. 3.6(b) as $\alpha$). The solid lines are the case of $p$-polarized light, and the dash-dot lines are $s$-polarization in the two limiting cases of the normal incidence and a $12.5^\circ$ inclination angle. Reflectivity of a flat gold surface is the brown dashed line above the two said curves [35]. The resulting broadband absorption gives an absorbing grating in the visible part of the spectrum, where a gold surface can be turned black through the aforementioned adiabatic nano-texturing. In contrast to the case discussed in Section 3.4 where the rectangular grooves are strongly resonant FP grooves, in the case discussed here, absorption of the light takes place within grooves that are not simple cavity-resonators.

The next chapter will discuss the structure and response of gratings comprised of strongly resonant FP grooves with adiabatic tapering of their properties (such as width) along the propagation direction of an emergent wave that travels over the collection of grooves behaving as an effective medium; as the groove widths get narrower, the groove effective indices (dispersions) are modified. Although such a structure is a broadband absorber of light, the absorption regions are streamlined, and spatially resolved across the grating, enabling precise and subwavelength light-matter interaction with each spectral component of light.
Figure 3.6: (a) A graphical representation of curved groove profiles and incident EM plane wave. (b) Side-view of the curved groove profile along with parameters defining the groove.
Chapter 4

Graded gratings

Devi più dell’oro per quello che si ferma la luce.  

\(^a\)You owe more than just gold to the captivator of light.

Slowing down the group velocity of light to nearly zero, sometimes called light-trapping, enables an unprecedented window of opportunity for light-matter interaction. Small group velocities have been shown to enhance nonlinear processes [36] and hyperspectral light localization [37]. Pioneering efforts in light-trapping include using cold atomic gases [38], photonic crystal nanocavities [39], gradient index materials [40, 41], and geometric tapering of the structure [15]. Rainbow-trapping has been proposed as a means of localized storage of broadband electromagnetic radiation in metamaterials and plasmonic heterostructures [6, 42, 43], with proposed applications in optical memories and delays for computation.

The methods and structures needed for rainbow-trapping, however, remain a great challenge and are often quite elaborate and difficult to fabricate. A gradient in groove depth \((L\) in Fig. 4.2), for example, as reported by [6, 44], requires nanofabrication methods for controlling and customizing each groove depth with nanometer precision. In contrast, this chapter discusses achieving rainbow-trapping gratings using a new
Figure 4.1: The schematic diagram shows the structure of a graded grating, pieced together from grooves of gradually changing width, while the periodicity of the grating, i.e. the edge to edge distance, is constant. This transmission-type grating is designed to operate as plasmonic slits, where each MIM resonator space acts as a plasmonic cavity, the resonant dispersion relation of which is an extension of closed-ended cavities that operate in reflection mode. The underlying substrate is transparent to the transmission window of interest.

design parameter, amenable to a simple standard planar fabrication process over a large area. This new parameter, the groove width, is fundamentally linked to the surface plasmon polariton (SPP) interactions on the sidewalls of the groove (shown with downward arrows in Fig. 4.2).

4.1 SPP interactions within plasmonic grooves

As the name suggests, the energy of surface plasmon modes is concentrated very near the metal-dielectric interface and exponentially decays away from the boundary. Fig. 4.2 depicts $p$-polarized light impinging on a metallic grating comprised of grooves with width $w$ and depth $L$ and assumed infinitely long in the $y$ direction. When grooves become quite narrow and comparable in size to the exponential tail of SPPs, $w$ is conceived as an additional parameter modifying the dispersion relation of the resonant cavity, i.e., the
groove. This is unintuitive at first, because a typical FP cavity resonator is sensitive to $L$, not $w$. Therefore, at very small cavity widths, another mechanism is at play. Although this effect is known to exist in abnormal optical absorption [1, 45], we show here that extraordinary properties such as rainbow-trapping ensue when $w$ is used as a gradient parameter of a grating. Conversely, at groove-widths much larger than the exponentially decaying SPP tail in the dielectric, typically $\sim 50$ nm for a single metal-dielectric interface (or $\sim 100$ nm in an MIM structure such as the groove), the effect of the width on the response of the structure becomes negligible. This defines the interval wherein $w$ becomes unfrozen and takes on an active role in the cavity response. Beyond this interval, the contribution of $w$ to the groove dispersion relation again becomes negligible. Since most graded gratings reported thus far fall in the latter regime where $w$ is frozen, the use of $w$ as a design parameter of gratings has remained unintuitive and unexplored.

4.2 Width-based gratings

Working against this understanding, the use of $w$ is proposed here as a powerful design parameter for light-trapping applications. This approach renders a landscape of gratings for light-trapping and waveguiding, with $w$ in the design parameter space. Further, this approach naturally accounts for unintended variations in groove dimensions (both $L$ and $w$) that are sometimes unavoidable in practice. The development of a powerful analytic and predictive tool opens up the possibility of easily producible and large area surfaces for rainbow-trapping.

The approach introduced here not only explains the behavior of an individual groove, it also predicts rainbow-trapping over graded gratings comprised of grooves with gradually changing widths. Note that our groove-wise method of analysis differs from approaches treating the entire grating as a homogeneous effective medium approximation and field-localization as a spoof-SPP [9]. The power of the present approach is that a simple model for a single groove can explain the behavior of an entire functionally graded grating, with a non-homogeneous effective index. More
Figure 4.2: \(p\)-polarized radiation (\(E\)-field in the \(z\)-direction) can launch SPPs traveling in the \(x\)-direction into the grooves, as well as SPPs traveling in the \(z\)-direction on the top surface between grooves. In narrow grooves when \(w \lesssim 150\) nm, SPP fields within the grooves overlap, resulting in coupling of SPPs on the sidewalls (shown as a squiggly line between two down-traveling SPPs facing each other on the opposite walls of the groove). Likewise, SPPs can become coupled through the metal when \(d\) is comparable in size, to the skin depth of SPPs in the metal. However, coupling through the metal requires still smaller \(d\) values \(\sim 25\) nm, approximately the skin depth of SPPs in the metals in the visible and near infrared range.

specifically, the groove geometry changes across the grating, changing the effective index of the groove; the response of the extended structure follows suit in a totally predictable manner. Finally, the approach allows us to provide a simple and powerful pictorial representation of predicting the response of graded gratings without having to perform simulations.

Further, there is another advantage of using the odd modes of sandwich plasmonic MIM waveguides. Unlike, single-interface SPP modes which support excitations near the plasma frequency of the metal, the MIM modes can attain and sustain excitations well outside the plasma frequency and into the MWIR region. This makes such geometric arrangements an invaluable asset for research in the IR region, aligned with the aims of this dissertation as stated in the opening of the first chapter. Furthermore, plasmonic
materials, whether metals, metal-oxides, or doped-semiconductors are fundamentally less lossy in the MWIR region than the visible and IR [46].

In general, when there is a refractive index gradient within an optical structure, light is naturally guided along the direction of the increasing index. At the same time, an optical resonator near the resonance significantly decreases the group velocity of light propagating through the resonant medium. (This condition is realized, for instance, near the band edges of periodic structures such as photonic crystals [47]). If $w$ is smoothly tapered, both the groove effective index $n_{\text{eff}}$ and the cavity resonance can be gradually and adiabatically shaped across the grating, enabling control of propagation and the trapping of radiation over the grating.

### 4.3 The waveguiding nature of grooves

We model a groove as a plasmonic MIM waveguide. The non-oscillatory $p$-polarized bound modes of this waveguide result in the coupling of the localized modes in the core ($-\frac{w}{2} < z < \frac{w}{2}$ in the inset of Fig. 4.3) (for details see [13]). The electric and magnetic field-components of the coupled-SPPs are given by solving Maxwell’s equations:

\begin{align*}
H_y &= Ce^{i\beta z}e^{k_1 z} + De^{i\beta z}e^{-k_1 z}, \\
E_x &= -iC\frac{1}{\omega\varepsilon_0\varepsilon_1}ke^{i\beta z}e^{k_1 z} + iD\frac{1}{\omega\varepsilon_0\varepsilon_1}ke^{i\beta z}e^{-k_1 z}, \\
E_z &= C\frac{\beta}{\omega\varepsilon_0\varepsilon_1}e^{i\beta z}e^{k_1 z} + D\frac{\beta}{\omega\varepsilon_0\varepsilon_1}e^{i\beta z}e^{-k_1 z},
\end{align*}

where $k_1$ and $k_2$ are the components of the $k$-vector perpendicular to the intragroove surface (i.e., along the $z$-direction) in the core and the metal, respectively. $k_1 = \sqrt{\beta^2 - \varepsilon_1 k_0^2}$, and $k_2 = \sqrt{\beta^2 - \varepsilon_2 k_0^2}$; where $k_0 = \frac{\omega}{c}$, and $\omega$ is the frequency of the excitation. By adding the two solutions in the core region of thickness $w$ and applying continuity conditions, the dispersion relation of the MIM waveguide is readily obtained;
the odd modes of which are given by [13]:

\[ \tanh \left( k_1 \frac{w}{2} \right) = - \frac{k_1 \epsilon_1}{k_2 \epsilon_2}. \] (4.4)

### 4.4 The resonant nature of each groove

Fig. 4.3 shows the MIM SPPs wavelength \( \lambda_{sp} = \frac{2\pi}{\text{Re}(\beta)} \), calculated from Eq. (4.4) as a function of the core thickness \( w \) [1]. For bounded grooves such as shown in the inset of Fig. 4.3, applying the continuity conditions: \( E_{z1} |_{x=0} + E_{z2} |_{x=0} = 0 \) due to the perfect electric conductor at the bottom of the resonator, and \( \frac{\partial (H_{y1} + H_{y2})}{\partial x} |_{x=L} = 0 \) due to the near unity reflection from the top of the resonator where \( \beta \gg \sqrt{\epsilon k_0} \) yields the relation between the plasmonic wavelength, cavity length, and cavity modes:

\[ \left( \frac{1}{4} + \frac{n}{2} \right) \lambda_{sp} = L, \] (4.5)

where \( n \) is an integer denoting the mode order. It can thus be expected that for very narrow grooves, the evanescent SPP fields from each metal-insulator interface of the MIM waveguide (groove) add up mathematically, as shown in Eq. (4.1-4.3), and squeeze \( \lambda_{sp} \) of the MIM bound modes within the groove. This, in turn, enables the compression of evens very large wavelengths into grooves as thin as 3 nm, as experimentally demonstrated in [21] for a single waveguide. As \( w \) gets larger, the \( \lambda_{sp} \) approaches that of a cavity resonator where the two metal-insulator interfaces are decoupled. In this regime, the resonant modes are independent of \( w \) and simply determined by \( L \). The existing rainbow-trapping approaches based on the variation of groove-depth operate in this decoupled regime and are, hence, insensitive to \( w \) (as, for example, shown in ref. [6]).

### 4.5 Modeling grooves as waveguide-resonators

Together, the groove waveguide dispersion Eq. (4.4) and the cavity resonance Eq. (4.5) give rise to the generalized resonant-dispersion of the groove. As shown in Fig. 4.3, the
Chapter 4. Graded gratings

4.6 Examining the extremes of the width parameter

When $w \to 0$ (bringing the metallic walls closer and shrinking the dielectric gap), $n_{eff} \to \sqrt{\epsilon_2}$ and the effective index of the metal is recovered, as expected. For the most part, metals shield electromagnetic radiation up to UV frequencies, with a skin-depth of
around 25 nm \[13\]. This prevents electromagnetic fields from profoundly penetrating such high index media. However, the grooves waveguide the field and extend it much deeper into the metal. Although not the focus of this dissertation, it is worth mentioning that the field extension takes place even in the absence of SPPs within the groove, compensating for the naturally weak fields in the metals and giving rise to spoof-SPPs \[9\]. In addition to the field extension caused by the waveguiding behavior of grooves, the SPP-coupling inside the grooves discussed here, significantly enhances the spoof-SPP effect. This SPP-assisted field-extension plays a key role in the infrared range by strengthening the weak-but-still-existing field penetration in metals \[48\]. Finally, in the terahertz range, when the metal behaves as a perfect electric conductor (PEC), real surface plasmons can no longer form, and the waveguiding property of the grooves alone gives rise to spoof-SPPs \[49\].

At the other extreme, \( w \to \infty \) (separating the groove walls from each other and resulting in a single vertical wall) leads to \( n_{\text{eff}} = \sqrt{\frac{\epsilon_1 \epsilon_2}{\epsilon_1 + \epsilon_2}} \), a flat metal-insulator interface \[50\]. Engineering a grating with a graded \( n_{\text{eff}} \) through slow variation or adiabatic tapering of \( w \), therefore, results in a metasurface with a spatially varying effective index. This gradient index property guides light in the direction of an increasing index, until the resonant nature of the groove no longer admits the wave. The resulting dispersive medium has a strong frequency dependence, reaching resonance at different spatial positions and engendering a rainbow effect.

### 4.7 A mnemonic key for quick structure design

Tailoring gratings using this SPP coupling through a \( w \)-variation, as shown above, enables the rainbow-trapping structures illustrated in the inset of Fig. 4.4. The area shown under the horizontal dotted line (b) in Fig. 4.4 represents a grating comprised of grooves numbered with Latin numerals (i through v). Each point of the dotted line corresponds to a single groove of the grating, with dimensions immediately known from the plot. The position of each point with respect to the resonant-dispersion curve predicts the groove response to the excitation. Grooves i and ii are below resonance, groove iii is...
Figure 4.4: Plot of the fundamental cavity mode \((n=0)\) as a function \(L\) and \(w\) for a single frequency. Dotted lines (a) and (b) outline the discrete nature of the grating possessing linear gradients in \(L\) and \(w\), respectively, with each point corresponding to a nano-groove of particular dimensions \((w_{ng}, L_{ng})\). Inset (a): a grating with a linear gradient in depth variation corresponding to the vertical dotted line (a). Inset (b): a grating corresponding to the horizontal dotted line (b), where the gradient is strictly based on groove width. Inset (c) plots the resonant dispersion curve for several frequencies in the visible range. Each spectral component intersects at a different location with the horizontal dotted line pictorially representing the grating. The result is the formation of a rainbow trapping effect over the grating.

At resonance (positioned exactly on the resonant dispersion curve), and grooves iv and v lie above resonance. Consequently, grating (b) is a uniform-depth grating comprised of grooves of identical depth \(L\) but gradually changing width \(w\). Light is guided from groove v in the -z direction by grooves that are above the cutoff until it reaches the location of a resonant groove iii where it is trapped; beyond which the grooves are below the cutoff and impede the propagation of light.

As we are considering gratings with spatial gradients along the z-direction, it is useful to reintroduce \(L\) and \(w\) as functions of \(z\), as in Fig. 4.4. This is easily accomplished by scaling \(L\) and \(w\) axes by the same gradient functions as those defining the spatial gradation of \(L\) and \(w\) for a grating. For example, if for a particular grating, the groove
Figure 4.5: The figure shows a graphical illustration of how a hyperspectral surface separates the wavelengths of light, just like a grating, or a prism would do. However, for subwavelength gratings where first and higher order modes are evanescent, the energy is coupled to the SPP modes. Carefully designing grooves that can trap and spatially separate these SPP modes leads to hyperspectral light trapping such as shown here. A broadband source of light, such as white light results in a rainbow-trapping outcome as illustrated.

widths increase by 2 nm per each nanometer in the $z$-direction, the abscissa is accordingly scaled by a 2:1 factor.

As a result, the coordinates of a point such as point iii on the horizontal dotted line (b) of Fig. 4.4, simultaneously convey the dimensions of a single groove and the relative location of the groove within the grating. That is, dotted line (b) outlines a light-trapping graded grating while preserving complete information about the dimensions of individual constituent grooves.

### 4.8 Comparison with simulations

Therefore, successive points shown on the plot of Fig. 4.4, when taken individually, correspond to the responses of single grooves to light of frequency $f$, and when taken
collectively outline the contour of a rainbow-trapping grating, such as the two gratings depicted right next to the dotted lines (a) and (b). By maintaining the one-to-one correspondence between the groove geometry and its placement within the grating, the intersection of the resonant dispersion plot in Fig. 4.4 with the dotted lines, reveals the locus of light-trapping over that grating. Whereas the single plot of Fig. 4.4 is for a single frequency of light, the inset shows the resonant dispersion curves across multiple frequencies in the visible part of the spectrum. For this reason Fig. 4.4 serves as a powerful mnemonic representation of light-trapping gratings with groove width \( w \), groove depth \( L \), or an arbitrary combination of the two. The following procedure can be used to design light trapping structures in a particular region of interest. First, draw the outline of the desired grating based on the gradient profile. Next, position this dotted line with respect to the resonant dispersion plot so that their intersection, which represents light-trapping, occurs in the region of interest. This can involve an arbitrary combination of \( L \) and \( w \) and should certainly take into account the feasibility constraints and fabrication methods of choice. The resulting dotted line provides the detailed design parameters of the light-trapping grating, without having to resort to simulations. It is worth mentioning that the dotted lines outlining the grating profiles given here are simple examples; arbitrary grating profiles (such as nonlinear profiles) can be just as easily analyzed.

Fig. 4.6 shows the simulated electric field for ten different overlaid simulated in COMSOL Multiphysics using permittivity values from Johnson & Christy [51] and Rakić [52]. These simulations assume silver as the grating material and air as the dielectric, at an excitation wavelength of 1 \( \mu m \). The position of the trap over the grating corresponds to the location of the maximum field intensity within the resonant grooves, as shown in insets (a) and (b) of Fig. 4.6. The horizontal error bars in Fig. 4.6 are based on the spatial field distribution at the location of resonance (trap), which spatially extends over a few adjacent grooves on either side of the principal resonant groove. The full-width-at-80%-maximum of the trapped field distribution is taken as
the error bar values in determining the trap location. The values for two such points are shown above the gratings in insets (a) and (b).

The darker regions indicate high field localization or light-traps. Each simulation is performed with a structure having a constant profile of $w$ variation. $L$ is successively increased in each subsequent simulation from 0.5 $\mu$m to 1.5 $\mu$m. This sweeps a long horizontal line representing a width-based grating (similar to the dotted line (b)), over the resonant dispersion plot, revealing the loci of light-trapping. When the resulting curve is compared to the analytical model of Fig. 4.6, the agreement is remarkable.

The simulated values are very slightly higher than the theory, as expected, since the theory only includes the coupling of surface plasmons within the groove and ignores any coupling between the neighboring grooves. In reality, there is a weak but nontrivial coupling between the adjacent grooves.

Width-based gratings may prove useful tools for waveguiding and light trapping with applications in bio-imaging, optoelectronics, infrared sensors, optical memories, and energy devices. The theory developed here accounts for a generalized combination of groove width and groove depth, as a combination of both is often inescapably present in practice. A further advantage of gratings whose design is based on this non-intuitive parameter, i.e. width, is facile fabrication.
Figure 4.6: Ten simulation frames are overlaid to produce this compound image. The width-gradient profile is constant across all frames ($w$ changing from 3 nm to 35 nm). That is, the structures in each frame utilize only groove width as the gradient parameter. In each successive frame the structure gets deeper; that is, the length ($L$) of the structure increases from left to right. Points (a) and (b) show the loci of light-trapping for two such frames. For example, point (a) in the figure shows a structure with a depth ($L$) of 1.1 µm, and the location of the trap at a groove with a width of 11 nm, corresponding to the grating shown in inset (a); the same logic applies for inset (b). The solid curve on the main plot shows the exact analytical solution of $\lambda_{sp}$ as a function of $L$ and $w$ (groove dimensions). Insets (a) and (b) show the field distribution of the trap over the structures that corresponds to points (a) and (b) on the main graph. The locations of the trap determined from the simulation, closely agree with the analytical solution.
Chapter 5

Nanofabrication

The realization of structures theoretically outlined in the previous chapters require precise nanofabrication techniques for successful implementation. For highest precision light-trapping outcomes, the surfaces must possess outstanding smoothnesses and conform as closely as possible to the theoretical and simulation-based dimensions.

Regardless of the details of the method used, the first requirement is to prepare ultra-flat surfaces that will later turn into ultra-flat interfaces for supporting the surface plasmons. This means neither etching nor sputtering of metallic surfaces onto a substrate is ordinarily possible, as the root-mean-squared (rms) roughnesses of the resulting surfaces are typically a few nanometers, which would radiatively couple the energy of the surface plasmons into space. Although, it should be mentioned that at the Advanced Photovoltaics and Devices (APD) Laboratory at the University of Toronto, ultra-smooth silver films of a few nanometers with rms roughnesses below one nanometer have been recently demonstrated, and the test samples prepared using this approach seem to be promising alternatives to metal evaporation. A sample device is shown in Section 5.3.2. In the case of silver a protection layer, typically Al₂O₃, is used to prevent reacting with oxygen and other species such as sulfur. In this chapter
however, we will discuss the details of devices fabricated using gold at the Molecular Foundry facilities of the Lawrence Berkeley National Laboratory (LBNL).

This chapter discusses the details of the fabrication process and the steps taken for fabricating high-resolution gratings with extreme dimensions up to single digit nanometer, and atomically smooth interfaces. Section 5.1 discusses the process of preparing the substrate and spin-coating the resist ready for electron-beam lithography (EBL). Section 5.2 will subsequently discusses the process of device fabrication using hydrogen silsesquioxan (HSQ) from the beginning to the end, and show pictorially the steps required. Section 5.4 discuss the peel-off process, and the experiments conducted to improve the process for transfer onto various substrates including flexible and thin film substrates. Section 5.3 will show the metalization process for gold deposition, as well as the experimental work with sputtering ultra-thin silver on the developed EBL resist. Section 5.7 discusses the alternative techniques used for the nanofabrication of ultra-high resolution gratings that were experimented with.

5.1 Pattern transfer using HSQ template and EBL

In order to create a stencil from of the resist material, first surfaces with atomic smoothnesses are prepared. One way to accomplish this is to use prime Si wafers whereupon the electron beam resist is deposited by spin-coating. This resist is then exposed and developed, leaving surfaces of Si for metal patterning. This metalization step is performed using electron beam evaporation of gold in a vacuum environment where gold is deposited onto Si (where the resist was removed) and onto the resist where it was left in place. The surface at the interface of the gold and silicon preserves extraordinary smoothness of the atomically smooth Si surface. In this case, high resolution HSQ electron beam resist was used which allows resolutions of up to single digit nanometer lines, in a single pass of the electron beam during lithography. The thickness of the resist in this case is critical as it determines the depth of the fins, or the grooves after developing the patterns. The nature of the uniform-depth graded
structures in the lamellar geometry is quite forgiving to proportional design and fabrication drifts, namely to proportionate widening or narrowing of gaps. This would mean that the center frequency designed to be at the center of the device would shift in case of fabrication errors, and only a portion of the usable bandwidth of the structure would be lost. The process of working on lamellar gratings was thus quite fruitful as it allowed to fine-tune the recipe requirements of the devices that were later exploited in the case of bull’s eye gratings, a geometry less forgiving to fabrication related errors. In the case of HSQ on a cleaned prime silicon, the resist was diluted as required by the specifications using isobutyl ketone (MIBK) to achieve thicknesses between 50nm and a few hundred nanometers. HSQ is quite sensitive to the time between coating, and EBL exposure, and this time must be minimal to achieve high-quality results. It is thus best to expose the sample as soon as it is spin coated. The process is schematically shown in Fig. 5.1.

The recipe used for spin coating HSQ is as follows:

**Recipe I: Spin coating HSQ for e-beam lithography**

1. **RCA cleaning**: a solution of NH\(_4\)OH:H\(_2\)O\(_2\):DI water in 1:1:5 ratio at 75°C for 15 mins, followed by a 5 mins DI water bath, then gently blow dried with N\(_2\).
2. 10 min heating of the sample on a hotplate at 180°C.
3. 10 min cleaning under ozone.
4. HSQ of proper dilution (e.g. 2%) spin coated at 100 rmp (resulting in a 60 nm layer)
5. Thermal curing of the HSQ on a hotplate at 100°C.

### 5.2 Exposure and developing the resist

After exposure HSQ turns into SiO\(_2\) and can therefore be treated and removed exactly as silicon dioxide, using for example HF-etch or buffered oxide etch (BOE). Also, in
Figure 5.1: (A) On a prime Si wafer, HSQ resist is spin coated, exposed and developed, resulting in a series of fins as shown. (B) Gold is thermally evaporated over the fins to fully coat around the fins, and fill up the gaps. (C) Evaporation continues past the fins to form a continuous film behind the grating with a typical film thickness of $\sim 150$ nm. (D) A thin film of epoxy is applied over gold layer, and peeled off to remove the grating formation from the Si substrate. The sample is then cleaned with HF to remove any residual HSQ which is converted to SiO$_2$ and dissolved away.

comparison with plasma-enhanced chemical vapor deposition (PECVD) deposited oxide, the etch rate of the exposed-HSQ oxide via the EBL exposure is much faster, and tens of nanometers can be removed in on second or less.

5.3 Metal deposition

Whether the stencil for the devices has been developed using HSQ resist as the template or an anisotropically etched silicon wafer, the next step to create a plasmonic interface is to deposit a plasmonic metal on the surface of the grating. This is
accomplished by either electron beam evaporation, or a highly well-developed and controlled sputtering environment. In Sec. 5.3.1 the process of metalization using gold is detailed, and Sec. 5.3.2 will subsequently discuss the state-of-the-art sputtering used for silver deposition, that given the high quality of closed thin films is able to create ultra-smooth surfaces as well.
5.3.1 Gold evaporation

The majority of the devices fabricated in this work were metalized with gold through an electron beam assisted evaporation directly onto the template as described in Sec. 5.2. For devices with small openings, which is especially the case in gratings with small width and large depth (i.e. aspect ratios 1:5 up to 1:10), the process of evaporation requires great care. A particular point of care is the rotation of the sample as the process of e-beam evaporation is quite directional. For high aspect ratio structures, it is also beneficial to tilt the sample by a 45° angle which due to the stage rotation would shift back and forth between a -45° and 45° [53]. The deposition was performed at a rate of 2 Å/s for the first 50 nm, and increased to 4 Å/s for the remaining 100 nm. This step yielded devices of high quality.

5.3.2 Silver sputtering

Using silver as the plasmonic material of the gratings has both great advantages and complications. Silver is not a material that normally forms closed form thin films under sputtering, and instead prefers to form islands. In order to form high-quality and ultra-smooth surfaces, great optimization efforts have to be taken, and the process has to be done under nitrogen. Recently, at the APD group, we have developed a recipe for depositing closed-form films with thicknesses as low as 6 nm, and rms surface roughnesses of under one nanometer. These devices permitted experimenting with plasmonic gratings that are usually not amenable to silver deposition due to high surface roughnesses that scatter any coupled non-radiative SPP modes on the surface. The details of this fabrication was as follows:

Recipe II: Ultra-thin silver sputtering

1. DI water clean.
2. 5 min of sonification in acetone.
3. IPA clean.
4. 10 min of RCA cleaning. Note: RCA cleaning outlined in Recipe I.
5. IPA cleaning.
6. Spin-coating SU8\(^1\) resist at 3000 rpm.
7. Heating the sample at 100 for 1 min.
8. Exposing the sample by EBL.
9. Developing the resist.
10. Sputtering ultra-smooth silver of 100 nm thickness.
11. Peel-off using epoxy and pattern transfer onto a Si substrate.

5.4 Metal peel-off from the developed template

As stated in the beginning of this chapter, the goal of a template-stripping process is to create stencils that are ultra-smooth, and thereby taking advantage of this, to deposit metals that conform to this smoothness, yet do not form a strong bond with the substrate. Once the metal is deposited either through an e-beam evaporation of gold or by sputtering silver onto the template, it has to be mechanically peeled off to expose the ultra-smooth patterned metal surface which is the grating. This process is quite simple in the case of gold and a silicon (oxide) template as discussed in Section 5.7, as the adhesion of gold and SiO\(_2\) is very poor. In the case of HSQ used here, the process is quite similar as HSQ turns into SiO\(_2\) upon processing. Using HSQ, the peeling process was successful every time. An SU8 resist was also tested, which resulted in satisfactory peel-off. However, the details of the surfaces were not fully examined, although these devices were measured using a near field NSOM which showed light trapping as expected, and as further discussed in Chapter 6.

The first step of the lift-off process is to prepare a support structure. In the work performed here, several substrates were successfully experimented with, for the lift-off process. This includes glass, silicon, scotch tape, self-adhesive conductive copper tape,

\(^1\)A commonly used epoxy-based negative EBL resist and photoresist.
Figure 5.3: SEM image of devices fabricated using SU8 and sputtered with silver. Devices are shown post template-stripping. The feature sizes were quite satisfactory as this was the only sample processed using this technique. The light-trapping performance of this sample is further discussed in Sec. 6.2.2. Residues seen are attributed to unprotected silver film reacting in the ambient environment, and further blistering due to the presence of micobubbles are further discussed in Sec. 5.4.

and Kapton tape. They all managed to peel off structures that maintained their functional integrity, though the issues related to each is discussed in Sec. 5.5.

In the case of glass and silicon as the substrate the cleaning up process involved the following steps:

Recipe III: Cleaning glass and Si prior to adhesion

1. DI water clean.
2. 5 min of sonification in acetone.
3. IPA clean.
4. 10 min of RCA cleaning. *Note: RCA cleaning outlined in Recipe I.*
5. IPA cleaning.
6. 10 mins under UV ozone environment.

After the substrate is prepared using the above recipe, the adhesive is prepared. The best practice in this case was to minimize the time between the last step of the cleaning recipe and the application of the epoxy. A small amount of a two part epoxy is prepared and thoroughly mixed. A small spherical dab of the mixture is then placed on the part of the substrate where the pattern is to be transferred to. All care must be taken to avoid bubbles in the mixture. This is important for two reasons, one is that it may cause roughness on the surface, and secondly, small bubbles can damage the sample by expanding and blistering the gold film, when and if the sample is placed in a vacuum chamber, for example in the case of imaging, or further processing such as metal deposition. On the other hand achieving excellent adhesion between the metal film and the substrate ensures proper support of the structure in vacuum, as well as preserving the smoothness of the devices.

### 5.5 Choice of substrate for pattern transfer

For most applications concerning this research, a smooth rigid surface was the best option, and in this sense Si wafers were the best choice. However, the lift-off process was found to be quite friendly experimentation with adhesives, and the poor adhesion of gold and Si, resulted in successful lift-off using scotch tape, and other sticky tapes such as Kapton tape and conductive copper tape typically used for SEM. To this end, a few remarks are necessary: surfaces with rough adhesives created wrinkles and creases on the gold film attributed to 1- the flexibility of the tape as well as its stretching and pulling as the tape was applied to and subsequently peeled off from the gold surface, 2- the roughness of the sticky material of the tape. The conductive copper tape in this case was the worst choice as the roughness of the copper itself was already imaged in the adhesive
Figure 5.4: Epoxy preparation is crucial to the successful sample transfer. The most important step is that the epoxy resin of the two-part adhesive are properly mixed, resulting in consistent crosslinking throughout. Presence of uncured individual parts of the epoxy will lead to the evaporation/expansion that can be seen as blisters in the image. Additionally the presence of bubbles in sample will also cause blistering. Finally, ensuring that enough time is given for curing of the epoxy ensures there is no uncured adhesive remaining. Note that this is only an issue when the sample is exposed to negative pressures such as SEM or deposition chambers.

that had already been in long-term contact with copper, and this yielded a gold surface that traced the roughness of the copper after transfer. However, it is worth noting, that in spite of the roughnesses, the grating still performed well, and on the nanoscale, it was still smooth. Most of the bumps and crevices of the copper tape were mesoscopic with roughly micron size features.

5.6 Fabricating more complicated geometries using HSQ

The template stripping using an etched prime silicon wafer yields both highest quality surfaces as well as a reusable stencil, both of which are invaluable when it comes to extreme nanodimensions involved here. However, this technique relies on the anisotropic etch of silicon, whole (111) crystalline axis runs in only one direction on a $<110>$ prime
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Figure 5.5: SEM image of an array of 2D graded gratings in the bull’s-eye geometry. A line crossing the center of the structure has a graded grating profile as discussed in detail in the previous chapter. The circular symmetry of this structure allows capturing light, with arbitrary orientation of the E-field in the plane of the image, thus leading to a higher sensitivity, compared to gratings discussed in Chapter 4. The response of these structures are further discussed in this chapter.

substrate. This simply means that straight lines such as the gratings thus far studied can be fabricated using this technique, however, the pattern cannot deviate from straight lines, nor change directions. For this reason, using HSQ patterned and developed by EBL has a tremendous advantage which allows for any pattern to be used and turned into a template.

5.7 Alternative methods for nano-templating

Both negative (such as HSQ) and positive resists (e.g. PMMA) allow creation of grooves whose depth is defined by the thickness of the resist. This allows for relatively easy fabrication of aspect ratios that are not very high ($\sim 1:5$). On the other hand, when aspect ratios are 1:10 or higher, an alternative approach is required. To this end,
Figure 5.6: A high-resolution SEM image of a single bull’s-eye graded grating structure, from the array shown in Fig. 5.5. This is the image of the HSQ template that will be metalized as discussed in Sec. 5.3.1.

anisotropic etch of a nano-patterned silicon allows for higher aspect ratio patterns that do not easily collapse compared to the softer material of the resists.

5.7.1 Anisotropically etched Si stencil

Silicon has a face-centered diamond-cubic crystal structure, and it is chemically etched at astonishingly different rates along different crystallographic directions [54]. For example, the (100) direction in Si etches away some 200 times faster than the (110) direction in a potassium hydroxide (KOH) solution. Over the years researchers have realized that they can take advantage of this property in order to create high aspect ratio Si-patterns that are etched out along the (100) direction, and in so doing maintain undesired etching along the (100) direction to less than 1% [54]. In order to accomplish this, all that needs to be done is to selectively protect the (110) direction, as the unprotected surfaces along the (110) direction will quickly get etched, while the (111)
Figure 5.7: Extreme aspect ratio grooves of above 1:16 width-to-height ratios have been fabricated at the Molecular Foundry of LBNL. The as-etched profile of Si fins using the anisotropic KOH etch are shown [53]. Reprinted with permission from Polyakov et al., [53] ©2011 American Vacuum Society.

direction of the silicon takes care of protecting itself. The (110) protection is done using silicon oxide, often thermally grown or using a prime wafer with the proper thickness of oxide.

Silicon is affordable, high quality, available in many wafer sizes and, more importantly Si forms an extremely weak adhesion with gold. This makes nano-templates made out of silicon an excellent reusable stencil for the linear gratings discussed earlier in this chapter. However, this will not accommodate patterns where the direction of the design deviates from the direction of the fast-etch axis; so circular designs or other curved shapes, are not amenable to this method for their fabrication. For all those designs, the approach described in Section 5.1 is the method of choice.
Chapter 6

Characterization and Experiments

In Chapter 5 several designs were presented and the SEM images of the corresponding fabricated structures were shown. In this section we will examine the devices in more detail including their near-field response to various light sources.

6.1 AFM profile of devices

This section we examines the surface smoothnesses and the profiles of the fabricated grating structures using AFM. In subsequent sections, the AFM tip is used as a subwavelength excitation probe for mediating light-matter interaction with graded gratings, through acquiring near-field images and the corresponding hyperspectral nano-spectrographs.

As previously mentioned, surfaces plasmons are bound and non-radiative modes, however, the presence of subwavelength surfaces roughnesses as well as sharp edges, gives them a way to escape by coupling to propagating (i.e. radiative) modes. The efforts taken to produces ultra-smooth surfaces will thus be paid off in terms of higher field intensities at the resonant interfaces. The process of fabrication of the graded gratings was optimized to yield surfaces approaching atomic smoothness. The main facilitator of achieving ultrasmooth surfaces is the use of prime silicon wafers for
patterning and subsequent transferring of patterned interfaces through low adhesion of gold and silicon oxide.

Fig. 6.1 shows the AFM acquired nano-topography of an even-spaced grating. The 2D image of the surface is shown on top with the legend colors denoting the structure’s depth variation. The middle image is a three-dimensional (3D) rendition of the same data showing the surface nano-topography. The bottom image shows the detailed depth profiles of a single linescan cutting across the grating revealing the dimensions of individual nanogrooves. Similarly, Fig. 6.2, shows the corresponding details of the surface topography for a graded grating structure with a width variation from 70 nm to 150 nm. Both even-spaced and graded gratings possess remarkably smooth surfaces over the flat portion of the metal. This can be observed for example in the bottom inset of Fig. 6.1, where in the range of 0-0.4 microns, the roughness variations are sub-nanometer, as indeed observed over most of the non-patterned metallic surface of the transferred pattern. The width of the even-spaced grating was chosen as the smallest dimensions of the graded grating (where the light-trapping takes place), so as to serve as a control sample for the measurements described in the following sections.

6.2 Near-field interaction with light

SPP modes, as discussed previously, are by nature non-radiative. They can be made to radiate near sharp edges and discontinuities, but when they are released into radiative modes they become diffraction limited in the far field. However, as discussed in detail in the following two sections, the strong near-field interactions leave a trail of their footprint in the higher harmonics space that can be detected in the far-field. In order to preserve the subwavelength resolution of IR SPPs in the far-field signal, some clever arrangements are needed. One such contrivance is a mechanism for scanning a subwavelength probe such as an AFM tip, with a spatial resolution that exceeds the native IR wavelength\(^1\), across the sample. This is often accommodated through the use of piezoelectric stages that translate

\(^1\)i.e. free-space wavelength
the tip relative to the sample. The scattered far-field signal of such an interaction will still preserve distinguishable near-field features of the sample with subwavelength resolution. Another mechanism, is to use a secondary near-field probe, such as another AFM tip brought close to the sample, in order to collect the radiation resulting from the interaction of the excitation with the sample. The latter set up is sometimes referred to as the true collection mode [56].

6.2.1 Measurements with synchrotron IR source

Fig. 6.3 shows the schematic of the setup of the SINS at the ALS Beamline 5.4. ALS is a third-generation synchrotron light source maintaining electrons of 1.9 GeV energy in a circular orbit with a circumference of 196.8 m that give rise to a constant current of 500 mA. In the infrared branch at Beamline 5.4, approximately 500 \( \mu \)W of IR radiation is channeled through a KBr beamsplitter, and partly directed onto a gold-plated parabolic mirror that concentrates the radiation onto a platinum-coated Si, or platinum silicide AFM tip. The brightness of the IR radiation from Beamline 5.4 is compared to other sources in Fig. 6.4 highlighting both the broadband and high spectral irradiance of the synchrotron IR radiation compared to other IR sources [55].

The nonlinear dependence of the near-field scattered signal on the tip-sample distance results in generation of several higher harmonics of the tapping-frequency [55]. The subwavelength features are thus identified in the far-field by looking for the strength and phase of the higher harmonics using a lock-in amplifier. The other portion of light reflected by the beamsplitter, is channeled to the moving mirror of an FTIR spectrometer, which can compensate for the phase-drifts in real-time during signal acquisition from the NSOM. Light scattered from the AFM tip of the NSOM is combined with the adjustable mirror of the FTIR at the beamsplitter and directed to a mercury cadmium telluride (MCT) detector, which is liquid nitrogen cooled. The responsivity of the MCT detector is in the range of 700-5000 inverse centimeters (2-13 \( \mu \)m range). The AFM tip of this modified commercial setup operates in non-contact mode, and the field scattered off the
The tip is demodulated at the tapping frequency of the tip which is $\sim 300$ kHz, using a lock-in amplifier. The mirror speed and the lock-in time constant are typically around 0.15 cm/s, and 200 $\mu$s, respectively. This enables the acquisition of a single interferogram in about 4 seconds at the resolution of 4 inverse centimeters. This scheme is a heterodyne detection and is based on the idea that the uncontrolled background field is replaced by controlled reference signal $E_r$, that is frequency shifted with respect to the field scattered by the tip $E_t$, the use of the lock-in amplifier then eliminates the $E_r$. This can be better understood by considering that the total field present is the interaction of three fields: the field of the tip, which is sought here, the reference field, and the background. This results in a far-field detected intensity of [59]:

$$I = (E_b + E_t + E_r)(E_b^* + E_t^* + E_r^*), \quad (6.1)$$

the result is that there are now six intensity terms [59]:

$$I = I_1 + I_2 + I_3 + I_4 + I_5 + I_6 =$$

$$= |E_b|^2$$

$$+ |E_r|^2$$

$$+ |E_t|^2$$

$$+ 2|E_b||E_t|\cos(\phi_b - \phi_t)$$

$$+ 2|E_b||E_r|\cos(\Delta \omega t + \phi_r - \phi_b)$$

$$+ 2|E_t||E_r|\cos(\Delta \omega t + \phi_r - \phi_t). \quad (6.2)$$

The first three terms of this equation are just the intensities of the corresponding fields, amongst which only the third intensity $I_3 = |E_t|^2$ is time-dependent and hence can be extracted using a lock-in amplifier, which effectively filters out $|E_b|$ and $|E_r|$. $I_4$ terms is the interference between the background and the field scattered by the tip. Since the tip operates in the tapping mode, the frequency of the tapping modulates this $I_4$. The
fifth term is the interference between the background and the reference field and has a characteristic beating frequency at $\Delta\omega$. In fact, this term is used experimentally to adjust and align the interferometer through the observation of this beating phenomenon. The sixth term, is what we seek and it is the superposition of the tip field and the reference field, regardless of the background field. It is found by using a different frequency of lock-in at $nf - \Delta\omega/2\pi$, where $f$ is the tapping frequency of the tip.

The demodulated signal is then analyzed using a commercial FTIR spectrometer and combined with the nanotopography of the sample (AFM signal). Fig. 6.5 shows the phase of the second harmonic of the far-field signal obtained as described in detail above. The red-lines on the AFM images on the top-right and top-left insets show the scan-line of the tip over the grating. While the tip dwells over each point, several (in this case 64) measurements in the spectral range of (700-5500 cm$^{-1}$) are taken by the detector, and averaged to produce each horizontal line of the phase-plots shown in the insets right beside the AFM profiles on the top row. Each of these horizontal lines corresponding to the spatial position along the red-line (denoted by the coordinate x on the ordinate axis of the top plots), is plotted in the line-graph below, showing the normalized phase value of the SINS signal as the AFM tip moves from the outside edge towards the center of the grating (following the red-line). While the plots on the left corresponding to the an even-spaced grating with a uniform gap size of 70 nm shows no resonance at any frequency in the detection range, the graded grating shown on the right has a strong resonance in the (2800-3500 cm$^{-1}$) range. This indicates broadband light trapping by the graded grating and can be used to enhance the near-field interaction of IR radiation with a sample that has a resonance in this range. As a practical example, the C-H stretching (corresponding to the sp$^3$ orbital) of amide groups has an infrared signature around the 3000 cm$^{-1}$ region. The gratings shown here were designed and optimized to serve as a substrate for enhancing the sensitivity of IR spectroscopic systems for the detection of trace amounts of amides.
6.2.2 Measurements with IR laser light

The near-field AFM set up of the SINS, detailed in the previous section also accommodates IR lasers such as quantum cascade lasers (QCLs). This allows cranking up of the light intensity at a particular wavelength by a couple of orders of magnitude, revealing a more detailed study of light-matter interactions. Following the discussion in the previous section, higher intensities enable exciting and detecting higher harmonics of the near-field light-matter interaction, thus revealing finer features of the sample under examination. In this study a QCL laser source with a 6,000 nm wavelength and a continuous wave (CW) power of 300 mW was used, for the near field mapping of the structures.

Fig. 6.6 shows the collected and demodulated signal from the interaction of the AFM tip under 6 μm radiation in three modalities of the third harmonic of the tapping frequency (top image), the fifth harmonic (middle), and the tapping phase (bottom). All three figures show a general field-enhancement mostly around the outer diameter rings. At the same time, because the scanning near-field optical microscopy (SNOM) tip has an out-of-plane polarization, traveling SPPs can be launched within the circular channels leading to whispering gallery-type modes, which further complicate the direct correspondence of the far-field signal to the near-field enhancement due solely to the width-based variation discussed in this dissertation. Further work is currently underway to examine a large array of these bull’s-eye gratings illuminated by an incandescent light source with radial polarization through a microscope objective, and analyzing far-field the spectral absorption. The current patterns were too sparse to yield a detectable signal in the far-field, when the illumination was low-intensity compared to a laser or synchrotron radiation. As the laser intensity and coherence is much higher than the synchrotron radiation, higher harmonics can be accessed leading to higher resolution reconstruction of the near-field data. The synchrotron images typically the second harmonic signal due

\footnote{Using the lock-in amplifier setup as described in the previous section.}
to lower spectral irradiance of the source. Also, as the bandwidth of interaction when using a QCL source is much narrower, the signal acquisition is much faster than when the broadband radiation from ALS is used.
Figure 6.1: (top) AFM profile of a non-graded grating fabricated using the techniques described in Chapter 5. The structure is gold deposited on an HSQ template and subsequently peeled off, resulting in a grating with ultra-smooth surfaces. (middle) 3D topography of the surfaces of the grating shown. (bottom) The quantitative plot of the AFM profile showing the consistency of the groove spaces and their depth. Note that the depth determined using an AFM tip in this case is limited to the distance the pyramidal shape of the tip can enter without encountering the sidewalls. Also at the distance of 0 to about 0.4 microns as shown on the plot, the surface possesses extraordinary smoothnesses as can be seen.
Figure 6.2: (top) AFM profile of a graded grating fabricated using the techniques described in Chapter 5. The structure is gold deposited on an HSQ template and subsequently peeled off, resulting in a grating with ultra-smooth surfaces. (middle) 3D topography of the surfaces of the grating shown. (bottom) The quantitative plot of the AFM profile showing the consistency of the groove spaces and their depth. Note that the depth determined using an AFM tip in this case is limited to the distance the pyramidal shape of the tip can enter without encountering the sidewalls. Also at the distance of 0 to about 0.2 microns as shown on the plot, the surface possesses extraordinary smoothnesses as can be seen.
Figure 6.3: Layout of the SINS experimental setup at the ALS IR Beamline 5.4 of LBNL. Emission from synchrotron is channeled and focused onto an AFM tip using which the samples can be probed [55]. The scattered filed is then scoured for the footprints of the near-field signal using an FTIR spectrometer with an adjustable mirror and a lock-in amplifier connected to the MCT detector. Reprinted with permission from Bechtel et al. [55], ©2014 National Academy of Sciences.

Figure 6.4: Bandwidth and spectral irradiance of synchrotron-based IR radiation at Beamline 5.4 vs. other IR sources (calculated profile is shown in dashed red line, and experimental detection limited by the sensitivity of the detector is shown in solid red line). A laser source with an optical parametric oscillator (OPO) [57], a supercontinuum laser source (blue) [58], and a 1,000-K blackbody source (black). [55]. Reprinted with permission from Bechtel et al. [55], ©2014 National Academy of Sciences.
Figure 6.5: The AFM images on the top-left and top-right show the two gratings whose near-field spectral response is probed using the synchrotron light which is channeled through an AFM tip. The vertical red lines indicate the path of the tip scan comprised of 256 pixels. While the tip dwells on each point in near-field, the detector acquires 64 spectral readings in the far-field that are averaged for a more accurate reading. Each of these broadband acquisitions correspond to the x-position along the red-line and are shown as horizontal line-scans in phase-plots of the top row. While the non-graded grating shows no signal enhancement in the range of 700-5,500 cm\(^{-1}\), the graded grating shows an enhancement in the 2,800-3,500 cm\(^{-1}\) region which is ideal for measuring the C-H stretching of amides. The bottom row plots correspond to the line-plots of each line-scan shown in the phase-plots of the top row revealing the size of the phase swing.
Figure 6.6: (Top image): the third harmonic, (middle image): the fifth harmonic, and (bottom image): the tapping phase (bottom) of the collected and demodulated signal is shown resulting from the interaction of the AFM tip illuminated with 6 µm radiation from a QCL laser. All three figures show a general field-enhancement mostly around the outer diameter rings.
Chapter 7

Other Geometries & Higher Dimensions

7.1 2D gratings with radial symmetry

One dimensional graded gratings described in Chapter 4 can be transformed to geometries with radial symmetry, through a rotation about the x-axis as shown in Fig. 4.2. This results in a bull’s eye shape structure as shown in Fig. 7.1, where groove widths are tapered in the radial direction, and light is localized within grooves in a circular ring about the center.

Fig. 7.1, (A) shows the SEM image of the HSQ resist post exposure and development, but prior to metalization. The circular rings shown protrude outside the page, and will form the groove after metalization. The smallest feature sizes are 20 nm in the center and gradually increase to 80 nm radially outward. Inset (B) shows the near-field response of the grating to the excitation at 6,000 nm wavelength using a QCL source, along the diameter of the structure. The structure is excited and measured using the same SINS set up described in detail in the previous chapter. The peaks of this graph correspond to the field-enhancements within the grooves, and the strongest signal in this case is seen at the fourth ring from the center, the corresponding near-field image of the entire
In addition to the light-trapping due to the dispersion engineering of the grooves through width-adjustment, these bull’s eye structures can also give rise to whispering gallery mode resonances, as the SPPs of the MIM waveguiding modes can continue to go around the circular trench and reinforce each other in phase. Although the loss nature of SPPs mostly limits the contribution of whispering gallery modes, in two cases this effect can become noticeable. First, when the circular trenches become very narrow, and the SPP modes take on a long-range SPP character and, second, when the radii are small, and SPPs can make it around a complete turn.

**Figure 7.1:** (A) SEM image of the HSQ resist post exposure and development. The circular rings shown protrude outside the page, and will form the groove after metalization. (B) Near-field response of the grating to the near field excitation at 6,000 nm wavelength using a QCL source, along the diameter of the structure. (C) Near-field image of field-enhancement as a result of excitation with the same source. (D) AFM image of the bull’s eye structure post-metalization.

structure is shown in (C), and (D) shows the AFM topography of the bull’s eye structure post-metalization.
7.2 Extension through conformal transformations

Transformation optics is a powerful mathematical tool for gaining insight into structures that are difficult to analyze in a particular frame of reference or in a particular geometric arrangement, by transforming the problem to a new and simpler domain. At the same time, the power of transformation optics can be revealed by taking a well-understood and simple geometry, and transforming it to more complicated arrangements, that can be explained by transforming the solution of the mother problem along.

Conformal transformations allow the interesting physics of electromagnetic fields that include SPPs, and their interactions to be translated to geometries that are seemingly quite different than the original problem. This chapter discusses one such problem, and pursues the idea though the entire production line from the theory to multi-physics simulations, fabrications, applications, and measurements.

A conformal mapping, is a transformation $w=f(z)$ that preserves local angles. A general analytical function is said to be conformal at a point, if it has a nontrivial derivative. There are countless conformal transformations, however, a specific conformal transformation of interest is $z \rightarrow w = e^{iz}$, where $z$ is a function in Cartesian system, and $w$ is the transformed (mapped) polar correspondence. This will be used to map certain periodic linear functions of interest onto periodic polar functions. Taking an arbitrary function $x = f(y)$ we apply the conformal transformation above, which results in $w = e^{f(y)} e^{iy}$. Expressing the result in polar coordinates we get $r = e^{f(y)}$ and $\theta = y$. Therefore, we have have the equation $r = e^{f(\theta)}$. To ensure that the equation remains periodic, $f(y)$ is taken to be $\frac{2\pi}{\alpha}$-periodic.

\footnote{Also known by the names conformal transformation, angle-preserving transformation, or biholomorphic map}
Let a particular class of periodic functions be defined by:

\[ x \equiv f(y) = \frac{\cos(ny)^k}{\Delta}, \]  

(7.1)

with \( n \) and \( k \) as integers, which defines a curve on the complex plane as plotted in Fig. 7.2, where the function is shown on the left and the corresponding conformal transformation on the right. Note that the plot of the function on the left is rotated 90° for convenience of establishing the visual correspondence between the planar and polar representations of the grating. It can thus be seen, that planar gratings have a mathematical kinship with cylindrical and spherical structures such as spiky nanoparticles, the latter case being the focus of this chapter.

The structure of the spikes embodies an adiabatic tapering, which allows launching SPPs along the spike. The traveling SPPs launched by the sharp tip can move towards the spherical body of the nanoparticle, where the smooth tapering of the spike’s base, can transfer some of their energy to the spherical particle, and onto other spikes. As discussed in Section 2.7, sharp tips carry all spectral (Fourier) components of the wave, and are capable of launching SPPs. This chapter will further discuss the role of sharp tips in SPP excitation, as well as SPP-mediated heat generation, to form partial shells over selective regions of the nanoparticle, without covering the sharp tips that are essential for light coupling.

Fig. 7.4 shows the conformal transformation of a linear grating into polar coordinates. In the figure, \( p \) is the periodicity (pitch) of the grating, \( w \) is the width of the groove, \( R \) is the radius as shown, and \( \Omega \) is the polar angle. The linear grating on the left is assumed to be infinitely long comprised of a periodic groove structure. Clearly, such a transformation cannot have a unique solution in the polar coordinates as the number of grooves in the transformed polar map have to be finite. This criterion requires that \( N \) or the number of unit structures (teeth) in the polar coordinate be defined. However, the repeating
Figure 7.2: Conformal transformation optics establishes an equivalence between geometries that can be seemingly quite different. The Figure shows that a linear grating is transformed to a circular cross-section shape in the polar coordinates. Thus, the analyses applied to the case of 1D simple gratings are transformable, for instance, to a nanoparticle with a spiky profile. This allows for the extension of the graded grating research into spiky nanoparticles.

Figure 7.3: The illustration of a transformation optics that convert a grating discussed in detail herein, to include shapes that possess a radial symmetry, such as rods with grooves, as well as spherical nanoparticles with spikes as discussed in detail in this chapter.

nature of structure in the polar coordinates preserves the phase matching amongst the finite grooves resulting the same field distribution as the linear grating. That is, a wave circumnavigating $2\pi$ radians around the circle, arrives in phase, as though it has traversed
Figure 7.4: The illustration of a transformation optics that convert a grating discussed in detail herein, to include shapes that possess a radial symmetry, such as rods with grooves, as well as spherical nanoparticles with spikes as discussed in detail in this chapter.

an infinite grating. The corresponding conformal transformation coordinates in this case are: $\xi = \frac{2\pi}{Np} x$ and $\eta = \frac{2\pi}{Np} y$.

This class of conformal transformations is useful for the study of nanostructures that exhibit unique optical properties. One such property is the collective electronic oscillations that takes place upon photoexcitation of spherical nanoparticles, known as localized surface plasmon resonance (LSPR). Heat dissipated through the LSPR effect has been employed as a means of inducing controlled chemical phase transitions on the nanoscale [60]. The LSPR heating of nanoparticles placed within a heat-activated liquid or gaseous precursor has resulted in a shell that surrounds the plasmonic particle [61]. The subwavelength size of the plasmonic particles however, has thus far prevented precision structuring of the shell over individual nanoparticles, resulting instead in blanket coverage of nanoparticle, thereby, suppressing many interesting plasmonic modes. Achieving fabrication control on the sub-particle length scale can not only revive these modes but has the potential to revolutionize the synthesis of next-generation composite nanomaterials with simultaneously tunable physical, chemical, and optical properties. The core, which is the energetic engine of the composite, needs to retain direct contact with the excitation light as well as its chemical and physical environment, thus directly benefiting the applications in sensing
Figure 7.5: The illustration of a transformation optics that convert a grating discussed in detail herein, to include shapes that possess a radial symmetry, such as rods with grooves, as well as spherical nanoparticles with spikes as discussed in detail in this chapter.

and catalysis. As previously stated, the spikes act as nano antennae, that absorb and convert the radiative energy into SPPs which subsequently interact with the nanoparticle and its immediate surroundings.

When the entire particle is uniformly resonant—as is typical of Mie resonance—there is no sub-particle control of the heating profile and any resulting heat-activated structuring fully covers entire particles. In contrast, nanoparticles exhibiting resonant modes with sub-particle features, as shown in the second row of Fig. 7.7, dissipate heat in plasmonic hotspots below the diffraction limit. The wavelength-dependent heat profiles of multi-mode plasmonic particles are selectable by choosing the right wavelength of
Figure 7.6: The striking similarity of the \( E \)-field profiles within and about the grooves is preserved through the conformal transformation. This allows the extension of the grating theory to structures with radial symmetry such as spiky nanoparticles.

excitation, out of several peaks as shown in the third row of the same figure. Selective excitation of each mode, allows concentrating heat in different spatial arrangements, e.g., near peaks or valleys. This wavelength selectivity enables a bottom-up self-assembly process while the choice of design template is communicated from top-to-bottom though proper wavelength and pulse duration. Accordingly, multi-mode plasmonic particles suspended in a thermally-activated precursor of the shell, self-dress into designer clothing whose pattern follows an externally selectable template. For the reasons mentioned, short-sleeve designs which leave the extremities of these spiky nanoparticles exposed, are of particular interest for plasmonic enhancement of the shell functionality, such as plasmonic enhancement of TiO\(_2\) catalyst shells around gold nanostars.

To illustrate this capability, we utilize multi-mode gold nanostars that have selectively excitable modes, as described. When under illumination at the right resonant wavelength, the fields can be selectively enhanced at the valleys between the spikes, as shown in mode \( b_1 \) of the spiky nanoparticle \( b \), illustrated in Fig. 7.8. Unlike the case of fully enclosed core-shell nanoparticles where the plasmonic core’s access to light is cut off by blanket coverage of the core, precision design of a shell reported here, covers the valleys while leaving the core still exposed, thus, enhancing and streamlining the interaction of light with the designer nanoparticles. The resulting heterostructure boasts plasmonically
Figure 7.7: (a) A spherical gold nanoparticle has a well-known plasmonic resonance as a function of its diameter. The figure underneath the schematic shows the field distribution over the particle with at the excitation frequency of 530 nm. The peak resonance for the spherical particle depicted (diameter of 35 nm) is around 650 nm as shown in the absorption cross-section plot underneath. The bottom TEM image shows the structure of the spherical nanoparticle. (b) Gold nanostars with an equal spike base-to-height ratio (labeled as 1:1 in the Fig), have a field distribution that concentrates the light differently in the peaks and valleys of the nanostars. And as seen in the absorption plot, the particle resonance peak splits into two sharper resonant peaks. The SEM images of these nano-meatball images are shown below. (c) As the spikiness of the nanostars increases in 1:2 nanostars, the resonant peak-splitting is more pronounced, and both peaks are red-shifted compared to 1:1 nanostars. (d) The redshift of the resonant peaks continues in the case of 1:3 nanoparticles for both resonant peaks. (e) Finally, when the peak aspect ratios are randomly distributed, the resonant peaks span a range bracketed by the nanostars of various aspect ratios as discussed.

enhanced functionality, such as catalytic capability, beyond what can be accomplished by shape effects (e.g. aspect ratios etc.), and choice of materials. For the general case of spherical plasmonic nanoparticles, the extinction cross section can be found by applying
the dipole-approximation of Mie’s theory [62]:

\[
\sigma_{\text{ext}} \propto \frac{\epsilon_r^{3/2} a^3}{\lambda} \frac{\epsilon_i(\lambda)}{(\epsilon_r(\lambda) + 2\epsilon_{\text{out}})^2 + \epsilon_i(\lambda)^2},
\]

(7.2)

where \(\epsilon_r\) and \(\epsilon_i\) are the real and imaginary parts of the metal dielectric function, \(\epsilon_{\text{out}}\) is the dielectric constant of the medium, \(a\) is the size of the particle, and \(\lambda\) is the wavelength of excitation. The term \(\epsilon_r(\lambda) + 2\epsilon_{\text{out}} = 0\), approximates the peak of the LSPR resonant condition, when \(\epsilon_i(\lambda)\) is relatively small or weakly dependent on \(\lambda\).

While this dipole-based approximation does not account for more complicated particle shapes, where quadrupole and higher order modes are also excited, it does provide a baseline for the red-shift seen as the nanostars become increasingly spikier (Fig. 7.7).2

The presence of the sharp peaks—which excite traveling SPPs along the spikes—hybridizes the traveling SPPs together with the Mie LSPR resonant, resulting in distinct heat distribution patterns shown in the second row of Fig. 7.7. Selective excitation of the plasmonic modes of these spiky nanoparticles suspended in a heat-activated precursor of a compound generates partial shell-formations conformal to the super-resolution heat distribution map over the particle. This allows surpassing the already small structure of nanoparticles by crossing over into the subwavelength regime, paving the way for super-resolution synthesis of tailored functional materials. Such unprecedented super-resolution tailoring has direct applications in optics, materials sciences, medicine, sensing, imaging, and more. Of recent interest are freestanding metal-transition metal oxide (metal-TMO) nanocomposites with core-shell geometries that carry great promise across many fields such as surface enhanced Raman scattering (SERS) [63], catalysis [64], biomedicine [65], energy storage [66], and water splitting [67].

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2By spikier it is meant that the ratio of spike height to base is increased
Figure 7.8: Top row illustrates four particles with the same spherical core of 35 nm. (a) The single-peak resonant curve of the spherical particle (≈650 nm) is shown in the absorption cross-section plot below. The heat dissipation simulation above the peak shows the corresponding resonant mode of the particle. (b) Spikiness and surface texturing proliferates the single resonance into several peaks, as for a nanostar with a spike base-to-height ratio of 1:2. The resulting multiplicity of resonant peaks is shown in the absorption cross-section plot underneath. The three most prominent peaks clearly illustrate the unique excitation patterns (heat dissipation profiles) corresponding to the peaks and valleys that can be preferentially excited using the corresponding wavelength. This results in a controllable heat distribution over the particle through the choice of excitation wavelength. Insets $b_1$, $b_2$, and $b_3$, clearly demonstrate that heat can concentrated in various positions over the particle, for example at the valleys ($b_1$) using excitation wavelength of 630 nm, as opposed to spike tips ($b_3$), using excitation wavelength of 950 nm. This preferential excitation is a powerfully precise tool for designing particles, for example nanocomposite $c$, where the valleys are covered with a sintered crystalline material yet the tips still exposed. In order to accomplish this, nanostars of type $b$ are suspended in a liquid precursor of the desired shell material (such as TiCl$_4$ for TiO$_2$ synthesis), and exposed to a 633 nm laser (in order to excite a type $b_1$ mode.) This results in sintering of a partial TiO$_2$ shell in valleys as shown in inset $c$. The presence of this new partial dielectric shell now alters the response of the particle whose main modes are depicted in the absorption plot with three peaks $c_1$, $c_2$, and $c_3$, showing the resulting heat dissipation pattern at 533 nm, 800 nm, and 980 nm, respectively.

7.3 Experimental setup and results

The experimental setup is divided into two sections. The first half focuses on the use of plasmonic effect to fabricate the super-resolution nanoheterostructures mediated
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by the selectable plasmonic modes. The second half of the experimental results discusses the geometries, materials and the characterization of the emergent super-resolution nanoheterostructures.

### 7.3.1 Plasmonic-fabrication & plasmonic-activation

The appropriate particle size and aspect ratios were determined from 3D simulations, and the optimized aspect ratio gold nanostars were synthesized per Ref. [68]. The simulations were performed using COMSOL Multiphysics, where the data for dielectric properties of gold were adopted from Johnson and Christy [51], and the heat capacity of gold adopted from Ref. [69]. The medium surrounding gold was set to be water, with the refractive data taken from Ref. [70]. The cubic computational domain is surrounded on all sides by a perfectly matched layer (PML) boundary condition. The simulations were performed first using single physics, to derive the fields and heat dissipation maps as shown in Fig. 7.7, and Fig. 7.7. The excitation source is a plane wave excitation, with linear polarization. Subsequently, a time dependent physics study was added to the problem, allowing for the heat-diffusion equation to evolve in time, up to the desired pulse duration. This is shown in Figs. 7.11, 7.12, and 7.13, with the time indicated above the figure.

These nano-mace\textsuperscript{3} shaped spiky nanoparticles with a peak base-to-height aspect ratio of 1:2, are depicted in the third column of Fig. 7.7. The corresponding SEM images of particles are shown underneath in the bottom row. The absorption cross-section of the 1:2 nano-maces exhibits three distinct peaks, the first of which is around 630 nm. Inset $b_1$ in Fig. 7.8 shows the corresponding heat-dissipation with the highest intensity at base of the peaks, i.e., in the valleys. These nano-maces were suspended in the aqueous solution of the precursor (in this case TiCl$_4$ was used as the precursor of the resulting TiO$_2$ shells), and subsequently irradiated with a CW 633 nm He-Ne laser source through the microscope objective, of a Raman microscope set up.

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\textsuperscript{3}Named after their resemblance to the mace of a mace-and-chain flail.
Column c of Fig. 7.8 illustrates the post-illumination formation of heterostructure particles—which is a largely self-terminating process as the partial coverage of the nanostars with the TiO$_2$ shell, shifts the response out of the 630 nm region. The newly fabricated plasmonic particles boast a designer crystalline vest covering the valleys and exposing the arms, as shown in Fig. 7.9, and corresponding to the time-transient heat distribution simulation of Fig. 7.13.

The most interesting activation mode of these newly formed nanoheterostructures is now near 800 nm, where, there is an intense field-enhancement in the TiO$_2$ shell shown in the inset c$_2$ of Fig. 7.8. This newly formed resonance peak now offers a unique window of opportunity for plasmonically enhanced interface between gold and TiO$_2$ enhancing the catalytic properties of the TiO$_2$ film. This is largely due to the fact that the exposed gold peaks act as nano-antennae, enabling the excitation of SPPs via the peaks. This field-enhancement can increase the plasmon-assisted electron transfer from gold to the conduction band of the shell, further enhancing the electric field at the Schottky barrier between gold and TiO$_2$. In contrast, when the nanoparticles, are completely covered in a TiO$_2$ shell as shown in inset d of Fig. 7.8, the resonance peak of interest (∼800 nm) is suppressed, bringing about excitation modes that are minimally interactive with the shell.

The shell formation experiment was conducted under a Raman microscope setup, equipped with a 633 nm laser and collimated through a microscope objective (50x and 100 x). Both the plasmon assisted chemistry and the Raman measurements of the shell-formation at each point were carried out by the same light source. With Raman laser source doubling as the plasmonic subwavelength heat source, the sample position remains the same, ensuring that the location of the chemical reaction and the corresponding Raman signal match. This allows real-time measurements of the Raman shift during the light-assisted plasmon chemistry of nanoshell formation. Fig. 7.10 shows the time evolution of the Raman shift as the TiO$_2$ shell formation proceeds around the gold
Figure 7.9: (A) TEM image of Au nanostar after irradiation under 785nm laser in 1M TiCl$_4$ (the aqueous precursor of TiO$_2$). Plasmonically-induced sintering of crystalline TiO$_2$ takes place as shown in inset (c) of Fig. 3, partially covering the valleys and leaving a significant portion of the tips exposed to interact with radiation without interference from TiO$_2$. The enlarged image of the rectangular region in (A) is shown in inset (B); the TEM image of selectively deposited anatase TiO$_2$ wedged in between the bases of two spikes.

nanostars suspended in the liquid TiCl$_4$. The Raman signal is measured in 0.1 sec increments while the focal point is scanned across a line that crosses a cluster of gold nano-maces. In the absence of nano-maces, the Raman shift only shows the presence of the precursor. However, at the location of the gold nano-maces, the spectral signatures of anatase TiO$_2$ appear as the shell formation reaction proceeds. Scanning past the gold nano-maces, restores the background signature of the precursor as seen in Fig. 7.10.

7.3.2 Chemistry experiments

Titanium tetrachloride (TiCl$_4$) precursor (from Sigma-Aldrich), was diluted into a 2M stock solution by drop-wise introduction into DI water cooled in ice-bath while constantly stirred. This reaction vigorously releases hydrochloric gas, and was performed under an appropriate fume hood. The resulting translucent and yellowish color solution was stored in freezer at -20°C. This stock solution was diluted as required and immediately before each experiment, to prevent spontaneous hydrolysis in the presence of water that leads to the formation of TiO$_2$ over time.
All gold nanostar particles were prepared from a seed solution following Ref. [68], beginning with a 10 mM stock solution of chloroauric acid (HAuCl₄ 99.999% purity obtained from Sigma-Aldrich). 50 ml of the stock solution was then mixed in a 3:1 volumetric ratio with nitric acid for 15 minutes, until the color change from light yellow

Figure 7.10: The Raman response along the line-scan shown as the black solid line in the inset. The Raman signatures of anatase titania seen at the center of the path corresponding to the production of TiO₂ thought by the plasmonic effect initiated by the SPP excitation with the Raman laser.
Figure 7.11: Simulated temperature profile of a gold nano-mace irradiated at 428 nm radiation for 150 femtoseconds, showing the heat concentration is mostly at the tips. This is the case for most wavelengths of excitation away from the Mie resonance of the nano-mace. When Mie resonance is present and hybridizes with tip SPPs, high field intensities can be brought to the valleys. Temperatures are shown in degrees Kelvin.

to deep orange was observed. The beaker containing the mixture was then heated at 100 °C under vigorous stirring. 5 ml of prepared sodium citrate solution ($C_6H_8Na_3O_7\cdot2H_2O$ from Sigma-Aldrich) was added drop-wise to the boiling solution containing chloroauric acid and mixed while boiling for 15 minutes. A deep red color change follows and the seed solution is cooled to room temperature and filtered with a nylon filter of .4 µm to remove any residues. The seed solution has spherical gold nanoparticles with an average diameter of 11 nm, confirmed by TEM imaging.

A 40 ml solution of 0.2mM HAuCl$_4$ was prepared from stock solution. 20 µl of 1M HCl solution was added to the prepared chloroauric solution. While the two mixtures were being stirred, 200 µl of the gold seed solution was added to the container. Next 400µl of silver nitrate (AgNO$_3$ from Sigma Aldrich) at 0.5 mM concentration, and 200
Figure 7.12: Simulated localized heating after a one picosecond pulse at 633 nm after around. the field concentration is mostly at the valleys and tips are largely cool. This configuration leads to the structures of interest when irradiated while immersed in a thermally activated precursor of titania. The resulting structures boast a partial shell near the core, while leaving the tips exposed.

μl of ascorbic acid (C₆H₈O₆ from Sigma-Aldrich) at 80 mM concentration were added together to the container. The solution turns from light yellow to a deep blue and suggest the formation of gold nanostars. After 30 seconds, the solution was centrifuged for 12 minutes at 6,700 rpm. The pellets were re-dispersed in 10 ml of DI water and sonicated.

The structure of prepared gold nanoparticles were characterized using SEM (SEM, Hitachi S-5200) and transmission electron microscopy (TEM) (TEM, Hitachi HF-3300). In-situ characterization of TiO₂ crystal formation under laser irradiation was studied by observing time evolution Raman spectra (Horiba LabRam) for various nanoparticles under three different lasers: 532nm, 638nm, and 785nm.
Figure 7.13: An example of wavelength selectivity, where the temperature profile of a gold nano-mace is shown after a 240 femtosecond exposure to light of 500 nm, which for this particle excites mostly a Mie LSPR response.
Chapter 8

Conclusion

Recent nanofabrication advancements draw a realistic road map towards availing subwavelength structures of nanometer features for a broad range of research applications. Subwavelength structures that incorporate metals and dielectrics on subwavelength scale engender novel composite materials for light-matter interaction. The potential applications of such structures are far-reaching, extending across many areas of research from metamaterials, to super-resolution optics to biological spectroscopy. Normally, such high-resolution interactions are reserved for high-energy photons, however such photons carry deleterious side effects that is only exacerbated by small interaction volumes of subwavelength dimensions\(^1\).

This dissertation studies a specific class of subwavelength plasmonic gratings comprised of grooves which are both waveguides and resonators. As MIM waveguides, they operate in two distinct regimes, first, as dielectric slab waveguides due to the refractive index differential between the metal and the dielectric, and second, as plasmonic MIM waveguides, due to the fact that two metallo-dielectric interfaces are conjoined on the dielectric side. Which of these two waveguiding modes dominates, is determined by the transverse core thickness. In this work, we carefully examine the latter plasmonic waveguide mode, which becomes dominant at core thicknesses below

\(^1\)Due to phototoxicity
∼150 nm—a measure related to the dielectric skin-depth of the SPPs in the visible and NIR. As for the resonant nature of the grooves, they behave as typical Fabry-Perot cavity resonators, with their resonant condition determined by the groove length.

When all the grooves of a grating are identical, and resonant with an external frequency $f_0$, the entire grating surface will resonantly absorb the external radiation. However, an interesting case is made when a functional gradient is introduced, to gradually change the response of each groove along the grating. It is an intuitive expectation that such a functional gradient results in an interaction gradient with light. An example of this functional gradient is the gradual tapering of the length of each resonator (i.e. groove), resulting in deepening of grooves across the grating. Such a structure uses the Fabry-Perot length of the cavity as a design criteria, forming a series of grooves each with a unique resonance. Hence, light of a single frequency $f_e$ will cause resonance in only one of the grooves, as the EM wave travels over the grating from the shallow end to the deep end of the grating. Through the successive coupling of neighboring grooves, the grating becomes an effective medium for the propagation of a wave launched over the grating. Such a structure, is an intuitive embodiment of a graded grating and has been demonstrated in prior art as a method of light trapping.

This dissertation takes another, less intuitive approach for introducing a functional gradient capable of light trapping. This is attained by adjusting the waveguiding nature of grooves as opposed to their resonant cavity length, thus revealing a second design dimension for creating light trapping gratings. Conveniently, the waveguiding dispersion is related to the groove width, so at first glance it appears as though changing groove-width is a trivial extension of prior art from depth-variation\(^2\). However, it is shown in this dissertation that this is not so. The width parameter belongs in a different category altogether, than the depth parameter. Whereas the length is directly tied to the Fabry-Perot resonant condition, the width parameter arises from the

\(^2\)i.e. the Fabry-Perot resonant length of each groove
strength of the SPP coupling within a plasmonic waveguide. As one may recall, there
are two waveguiding regimes of the structure, the conventional waveguiding mode, and
the plasmonic waveguiding mode. The width parameter is specifically related to the
dispersion of the plasmonic waveguiding mode, which as previously stated, has an onset
at around 150 nm. It is thus not surprising that this width parameter has previously
gone unnoticed to serve as a gradient design-parameter of subwavelength gratings, since
most existing subwavelength graded gratings are of larger widths.\(^3\)

Conventional dielectric slot waveguides with their well-know modes, play a key role
in gratings with groove widths above \(\sim 150\) nm. However, below this range, the groove
structures can no longer support the conventional waveguiding modes, and light will be
diffracted without admittance into the grooves. That is of course, unless the grooves
also exhibit plasmonic waveguiding that enables light coupling to the SPP modes of
the structures. Additionally, the odd modes of plasmonic MIM waveguides have no
cut-off, allowing wavelength-compression in grooves to reach all the way into the single-
digit-nanometer dielectric widths. This squeezing of light into the deeply subwavelength
regime is of great interest where high-resolution light-matter interactions are sought.

Yet, perhaps the most significant outcome of uncovering the width parameter is
from a practical point of view. Width-based structures are incomparably easier to
fabricate than depth based gratings. A single fabrication step yields a large number of
gratings (thousands to hundreds of thousands) on the same chip, with light-trapping
center-frequency of each grating anywhere in the visible to MWIR range. The
importance of this achievement can hardly be overemphasized in the quest for devices
comprised of subwavelength light-trapping pixels in a broad range of the EM spectrum.
It is also gratuitous that the gratings directly couple external radiation to the
plasmonic modes of the structure, without the need for designing additional
impedance-matching mechanisms.

\(^3\)It is possible that this is partly to avoid this, up to now, anomalous range.
Chapter 8. Conclusion

The resonant nature of the structures follows typical cavity resonance condition, but takes on a whole new meaning in light of dispersion engineering of the grooves. Whereas before uncovering the width-parameter, the cavity length had to be changed to accommodate the range of wavelengths of interest, the advent of the width parameter means that the effective dielectric function within each groove can be tuned instead. As a result, grooves of different widths, compress light into SPPs of different wavelengths $\lambda_{SP}$, and it is $\lambda_{SP}$ that has to satisfy the groove resonant condition. Since each groove gives a different $\lambda_{SP}$ according to its width-based dispersion, in a grating comprised of gradually changing groove widths$^4$, the depth can stay the same, and the right $\lambda_{SP}$ will cause resonance in the right groove.

Together, the ability to utilize both the width and depth parameters, gives a powerful landscape of subwavelength plasmonic structures for light trapping in a wide range of visible to MWIR. This allows for designing light-trapping structures that can now be extended to other geometries and higher dimensions, such as bull’s-eye type structures, spiky nanoparticles, as well as geometries that introduce a gradient along the third dimension ($y$-direction in Fig. 4.2), resulting in 3D plasmonic cavity resonators with a finite length in all three dimensions. Such structures include graded bow-tie structures, as well as gratings with adiabatic tapering of their profile along the $y$-direction. As well, one can envision spherical metallic shells alternating with dielectric shells, with radial openings whose apertures are tuned at each layer, for example in the form of inverted cones. The metallic shells with the dielectric sandwiched within, act as resonant cavities whose resonance is tuned by the surface area of the sphere, which is controlled by the size of the aperture(s) introduced. Such onion-like structures allow controlling the heat dissipation along the radial direction, and can enclose a heat sensitive capsule in the center that is activated only by the radiation of the right wavelength.

$^4$In the plasmonic range of $\lesssim 150\text{nm}$ groove widths.
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