Optimizing the Plasmonic Enhancement of Light in Metallic Nanogap Structures for Surface-Enhanced Raman Spectroscopy

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by

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ABSTRACT

Technology based on the interaction between light and matter has entered something of a renaissance over the past few decades due to improved control over the creation of nanoscale patterns. Tunable nanofabrication has benefitted optical sensing, by which light is used to detect the presence or quantity of various substances. Through methods such as Raman spectroscopy, the optical spectra of solid, liquid, or gaseous samples act as fingerprints which help identify a single type of molecule amongst a background of potentially many other chemicals. This technique therefore offers great benefit to applications such as biomedical sensors, airport security, industrial waste management, water treatment, art/jewelry validation, and more. The primary setback of such techniques has been the difficulty of signal measurement, especially when the detected molecules are very sparse within a surrounding material, such as trace levels of a harmful chemical in a gas or liquid sample.

The ability to enhance light signals from such samples is key to developing affordable solutions to bring this type of optical sensing from being a research lab tool to an every-day technology. It has been found that local electric fields increase significantly by incorporating nanostructures onto surfaces containing the detected substances, thus increasing the signal strength measured at the detector. Using specially engineered metal nanostructures and their plasmonic resonance properties, signals such as Raman scattering from particles of interest can be enhanced to much more useable detection limits. This dissertation work employs two nanofabrication methods to engineer light enhancement to understand and improve real surface-enhanced Raman spectroscopy substrates that can predictably boost the identifying signals measured for probe molecules.
A lithography-based technique and a self-assembly process were studied for producing plasmonic nanostructures with at least one tunable geometrical parameter. These variable nanoscale features were the tuning knobs used during design engineering of optimal light enhancement through computational physics studies. Experimental enhanced Raman spectra were measured using plasmonic metasurfaces, with the signal enhancement found to corroborate theoretical calculations. The results demonstrated the effectiveness of the tunable devices as surface-enhanced sensing devices worthy of further development and study.
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To any reader of this work, never forget that you’re capable of what you may have once thought was impossible or what others may have told you was so. You’re not an imposter.

“Thoroughly conscious ignorance is the prelude to every real advance in science.”

– James Clerk Maxwell
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Chapter 1.
INTRODUCTION

1.1 Motivation for Optical Sensing

The original optical sensors, the eyeballs of homo sapiens, underwent millennia of evolutionary changes before reaching their current form, that which has detected visible light from flames burning in the distance, stars burning across the night sky, and lasers burning holes through thick metal sheets. Modifications have been made to these and other optical sensing devices ever since the advent of primitive glasses, telescopes, and other early geometrical optics tools. The ability for homo sapiens to study and understand the vast universe outside of the Earth’s atmosphere and the sub-macroscopic universe permeating the planet has been a direct result of the species’ technical advancements in optical and other sensing capabilities. Without telescopes and microscopes, many scientific discoveries and engineering breakthroughs of the past millennia, especially the past couple of centuries, would not have been possible. Clearly, with the development of ultrafast short-pulse lasers, particle colliders, and solar-powered telescopes that travel to other planets and beyond, the reach of sapiens’ sensing abilities has surpassed what was considered fathomable even in the 19th and 20th centuries.

The range of sensing technologies employed by humans covers the entire spectrum of light, as well as including other media such as sound, gravity, massive particles, gas pressures, weather events on Earth, and more. Detection of signals composed of light could arguably be the most ubiquitous and widely used technological advancement regarding sensing in 2018. Beyond the abilities to communicate using long wavelengths of light such as radio waves, look at the skeletal systems noninvasively using shorter wavelength light, and detect heat via infrared
radiation, modern advancements in optical sensing have provided the species with new ways to use normal old visible light.

Having replicated the human eye’s image capturing capability with even higher resolution in the form of digital cameras, humans also utilized the ability to predictably spread the colors of light over space, as demonstrated by Isaac Newton circa 1666 and by a popular rock band album cover circa 1973, allowing for even more useful methods of analyzing signals from various sources. The ability to analyze the spectrum of a light source quantitatively became known as the field of spectroscopy and has made possible the study of many optical phenomena such as how light is absorbed by, reflected from, or transmitted through an object at different wavelengths. This knowledge has enabled many technological advancements involving sensing, including the ability to detect the presence of chemicals that would otherwise be invisible in something such as a blood sample or a gas emanating from a power plant.

Optical sensing methods using spectroscopy have the potential to become valuable tools for medical diagnostics, drug and weapon residue detection, security and environmental monitoring, biochemistry, food safety, and forensics.1–4 Advancing the state-of-the-art to create highly sensitive optical sensors for any of these applications will prove beneficial to humanity and could save lives. Optical sensors offer many benefits such as remote detection and nondestructive measurement, even for many biological samples.

All signs relating to the field of optical sensing and detection point to significant increases in production and market size over the next decade. The global optical sensors market was estimated by Global Market Insights to be valued at 15.4 billion U.S. dollars (USD), with a compound annual growth rate (CAGR) of 7.5% expected for 2016 through 2024, reaching $30 billion. Growth specifically in the aerospace and defense sector was anticipated to grow at
Another report by MarketsandMarkets™ estimated a more conservative optical sensing market valuation of 1.12 billion USD with a CAGR of 15.47% expected to bring the market to 3.46 billion USD from 2017 to 2023. A significantly more liberal report claims that the global optical sensing market recorded revenue of $25.65 billion in 2017 and is expected to grow at a 8.99% CAGR through 2023. The global biomedical sensing market was valued at 9.55 billion USD in 2017 with an expected CAGR of 3.75% to reach 11.91 billion USD by 2023 in a report by Research and Markets Ltd. Biomedical sensors were claimed to have held 12% of the market share in 2015, with massive growth expected over the projected timeline. Though no mention is made of special rings nor special agents capable of remotely sensing the rings when worn by unsuspecting users, Mordor Intelligence reports that the global chemical sensing market was worth $18.56 billion in 2017 and projects a 7.20% CAGR raising the value to $28.16 billion by 2023.

Thus, it is clear that the overall market for light detection devices is increasing. This has largely been due to the increased demand for cameras on smart phones, lidar and radar systems for mapping and remote sensing in the aerospace and autonomous vehicle sectors, and other types of sensing technology that have made use of shrinking systems and cheaper technology.

Two of the most common and furthest advanced methods of optical detection are, broadly, fluorescence and vibrational spectroscopies. Both techniques involve shining a light onto a sample and detecting light emitted/scattered from the sample via a spectrometer or camera. Fluorescence is often used in imaging and studying biochemical processes and, through various advancements since its first use, has been used in the imaging of single molecules. This has proven to be a powerful tool for biochemical analysis and has even been used to observe single molecules, but relies on the use of special marker molecules and in many cases,
post-analysis of signal data.\textsuperscript{13,14}

This dissertation work focuses on the ability to use light to detect the presence of various chemical entities via their optical spectra. Methods applied to molecular sensing include fluorescence spectroscopy and localized surface plasmon resonance refractive index sensing. Fluorescence requires special “label” molecules to be attached to the analyte of interest, which can change its dynamics, typically very crucial in biomedical imaging studies. The ability to detect the presence of specific analytes therefore requires the proper chemistry for fluorescence to be of use. Refractive index sensing can be useful to detect the presence of a substance in cases where known refractive index changes occur, but in the common situation of unknown analyte concentration, this can produce misleading results.

Fluorescence is a powerful tool for tracking the location of microscopic biological entities \textit{in vitro} and \textit{in vivo}. Raman scattering and IR absorption, two complementary types of vibrational spectroscopy, provide additional benefits that are lacking in fluorescence methods, however. Raman spectroscopy identifies the presence of different chemicals in a sample by spectroscopic vibrational fingerprints unique to each type of molecule.\textsuperscript{15,16} Raman therefore requires no special modification of the sample molecules being detected. While Raman can be used in most environments for solid, liquid, or gas samples, it suffers from the issue of having a weak measurable signal. Enhancing the signal is necessary for practical use of Raman spectroscopy, especially due to the often significantly low concentrations of probe molecules within a given sample.

Surface-enhanced Raman spectroscopy (SERS) uses various strategies to modify a detector to increase the signal strength of Raman spectroscopy, vastly improving its usefulness toward the aforementioned applications.\textsuperscript{17} One way to enhance a surface is to incorporate
metallic nanostructures with dimensions on the order of the wavelength of the light. These so-called plasmonic structures manipulate the electric field of the light at the sample surface, increasing its intensity and resulting in a signal that is more easily detected. While modern technology has allowed for the fabrication of a diverse array of surface enhancements, SERS has not yet been developed for common cost-effective commercial applications. This is due to the combined issues of cost-prohibitive fabrication methods with a high degree of control over nanoscale features and easier, more scalable methods that lack sufficient tunability or robustness.

The ability of Raman spectroscopy to remotely sense the presence of specific molecules in a sample is a very powerful tool that has been applied to a wide variety of detection methods. The medical field can apply this strategy to detect different chemicals in the blood, for example as a blood glucose sensor used by diabetics. Airport security personnel and soldiers in warzones can detect, from a safe distance, trace levels of explosives, gunpowder, or chemical/biological warfare substances before an incident occurs. Industrial plants, labs, and other locations where potentially harmful liquids and gases may be utilized in large quantities need the ability to sense dangerous levels of these substances in the event of a leak or spill.

Advanced fabrication methods need to be further studied to reach the goal of cost-effective commercial SERS devices. When SERS becomes feasible for use in the wide variety of applications mentioned, the benefits to the safety and health of humanity will be great. The dissertation work is thus motivated to engineer nanostructures via recently developed, advanced fabrication methods for the advancement of tunable SERS substrate technology.

1.2 Dissertation Outline

This dissertation is ordered to walk the reader through the research process, starting by
developing the foundational understanding of the science, moving through the research methods, discussing the results, and addressing future work to further advance the projects conducted herein. Chapter 2 describes the background information required to understand the physics and engineering considerations related to the research, as well as some of the advanced techniques and technologies applied during the work. This includes introductions to electromagnetic theory, plasmonics, nanoscale effects, Raman and cathodoluminescence spectroscopies, and computational electromagnetics. Chapter 3 discusses fabrication of SERS structures that make use of nanoscale features and provides details regarding the two nanofabrication techniques associated with the development of SERS enhancement during this work. Chapter 4 discusses the computational electromagnetic models used to engineer enhancement for specific nanostructure geometries. As tunable geometries were the focus of this work, optimization of different geometrical parameters via computational sweeps is discussed in this chapter. Chapter 5 discusses the experimental characterization of fabricated samples using cathodoluminescence and Raman spectroscopy. The design and construction of the custom Raman spectroscopy setup used in this portion of the work is described as well. Chapter 6 discusses conclusions of the research and addresses future work that will help to further the research conducted in this work. The appendices provide additional information about the potential benefits and importance of the work, the methods and techniques used, and publications resulting from the author’s time working on the dissertation project(s).
Chapter 2.

BACKGROUND

This dissertation work requires the reader to have a firm grasp on the workings of nanoscale fabrication processes, optical phenomena, electromagnetic fields, spectroscopy, and other fields that may need some introduction. The following chapter outlines relevant background information regarding optics, spectroscopy, nanofabrication, and computational electromagnetics. The setup of electromagnetics is important to understanding the mechanism of plasmonics and how it relates to Raman spectroscopy, and specifically, SERS.

2.1 Light as an Electromagnetic Wave

The field of optics is the study of light and its interaction with matter in different configurations. Ray optics treats the passage of light through transparent materials and reflection from reflective materials by way of straight “rays” and their points of intersection. This treatment is sufficient in many cases in everyday life, at least for students of University Physics I courses or some experimental optics researchers, for which the wavelength of light is much smaller than the material entities involved. However, light may also be described using waves, like sound or ocean waves except in describing what exactly is doing the “waving”. In the case of light, it is the electric field (and magnetic field, simultaneously) that oscillates back and forth as it travels through space (and time). This is the same electric field that is generated in a static configuration by all charged particles, including electrons and protons, which are the constituents of all matter with which light is interacting in nearly all discussions of optics. In fact, oscillating electrons produce oscillating electric and magnetic fields, thus giving off light. The inverse is also true,
light causes electron oscillations within conductive materials. These two interactions and their useful properties and effects are the focus of this dissertation work.

Thus, more formally, light is an oscillatory electromagnetic wave that propagates in space and time in the classical view as established and understood mathematically by Maxwell’s equations (Equation 1 through Equation 4). Shown here in differential free-space form, this set of equations describes the relationship between electric charges and electromagnetic fields. These fields are a mathematical construct used by humans to describe continuous regions in which a force would be exerted on an object by another object without the two objects necessarily coming into contact. Electric charges experience forces when located within electric and magnetic fields (caused by other charged objects), much like how objects with mass experience forces when located within gravitational fields (caused by other massive objects).

The first equation is Gauss’ law for electrostatics (Equation 1), which directly results from Coulomb’s law describing the force between charges. Second is Gauss’ law for the absence of magnetic monopoles in the known universe (Equation 2). More relevant to the development of electromagnetic wave theory, and therefore this work, are Faraday’s induction law (Equation 3), which describes how a changing magnetic field induces a current of charges or a changing circular electric field, and the Ampère–Maxwell circuital law (Equation 4), which describes how a circular magnetic field is produced by a current or a changing electric field.

\[
\nabla \cdot \mathbf{E}(\mathbf{r}, t) = \frac{\rho}{\varepsilon_0} \quad \text{(Equation 1)}
\]

\[
\nabla \cdot \mathbf{B}(\mathbf{r}, t) = 0 \quad \text{(Equation 2)}
\]
\[ \nabla \times \mathbf{E}(\mathbf{r}, t) = -\frac{\partial \mathbf{B}(\mathbf{r}, t)}{\partial t} \]  
(Equation 3)

\[ \nabla \times \mathbf{B}(\mathbf{r}, t) = \mu_0 \left( \mathbf{J} + \varepsilon_0 \frac{\partial \mathbf{E}(\mathbf{r}, t)}{\partial t} \right) \]  
(Equation 4)

Here, \( \mathbf{E} \) is the electric field vector, \( \mathbf{r} \) is the position vector for the location in which the field is observed, \( t \) is the time at which the observation occurs, \( \rho \) is the charge density present in the region, \( \varepsilon_0 \) is the electric permittivity of free space, \( \mathbf{B} \) is the magnetic flux density vector, \( \mathbf{J} \) is the current density, and \( \mu_0 \) is the magnetic permeability of free space. The free space permittivity and permeability values, obtained via classical experiments, are as follows:\textsuperscript{20,22}

\[ \varepsilon_0 = 8.85 \times 10^{-12} \frac{F}{m} \]  
(Equation 5)

\[ \mu_0 = 4\pi \times 10^{-7} \approx 1.26 \times 10^{-6} \frac{H}{m} \]  
(Equation 6)

For now, the \((\mathbf{r}, t)\) will be dropped from the notation, but these dependencies are still implied in \( \mathbf{E} \) and \( \mathbf{B} \). Equation 1 means that the amount of charge in an area with a certain “reluctance to permit” the presence of an electric field is directly proportional to the strength of divergence (convergence) of the electric field from (into) the region surrounding the charge. Equation 2 means that the same type of diverging or converging of fields has no magnetic analog, as there are no such things as magnetic charges or monopoles. Equation 3 says that any change in the magnetic flux density with time causes an electric field that points circularly around a line pointing in the direction of the changing magnetic field. Equation 4, conversely, says that a changing electric field or a current cause a circularly pointing magnetic field to wrap
around the current or around a line pointing in the direction of the electric field.

This set of first-order partial differential equations for \( \mathbf{E} \) and \( \mathbf{B} \) can be decoupled by manipulating Equation 3 and Equation 4, first by applying the curl to each equation.\(^{23}\)

\[
\nabla \times (\nabla \times \mathbf{E}) = \nabla \times \left( - \frac{\partial \mathbf{B}}{\partial t} \right) \quad \text{(Equation 7)}
\]

\[
\nabla (\nabla \cdot \mathbf{E}) - \nabla^2 \mathbf{E} = - \frac{\partial (\nabla \times \mathbf{B})}{\partial t} \quad \text{(Equation 8)}
\]

In free space, there are no free charges or currents, so \( \rho = 0 \) and \( \mathbf{J} = 0 \). Thus, Equation 1 and Equation 4 become

\[
\nabla \cdot \mathbf{E} = 0 \quad \text{(Equation 9)}
\]

\[
\nabla \times \mathbf{B} = \mu_0 \varepsilon_0 \frac{\partial \mathbf{E}}{\partial t}. \quad \text{(Equation 10)}
\]

Plugging Equation 9 and Equation 10 into Equation 7 and Equation 8 gives a partial differential equation only in terms of \( \mathbf{E} \), thus decoupled from \( \mathbf{B} \). The same procedure using converse substitution produces an identical result to decouple \( \mathbf{B} \) from \( \mathbf{E} \).

\[
\nabla^2 \mathbf{E} = \mu_0 \varepsilon_0 \frac{\partial^2 \mathbf{E}}{\partial t^2}, \quad \nabla^2 \mathbf{B} = \mu_0 \varepsilon_0 \frac{\partial^2 \mathbf{B}}{\partial t^2} \quad \text{(Equation 11)}
\]

In Equation 11, both \( \mathbf{E} \) and \( \mathbf{B} \) are second-order differential equations describing simultaneous variations in space and time. In fact, they take the exact form of the three-dimensional wave equation,
Here, the change in a function $F$ over space (the Laplacian) is directly related to the change of the same function over time and inversely to a constant $v$, the speed of travel of the wave. This means that to fit the wave equation, both $E$ and $B$ must be waves traveling with a speed of $\frac{1}{\sqrt{\mu_0 \varepsilon_0}} = 2.998 \times 10^8$ m/s. Fortunately, during Maxwell’s time around the early 1860s, experimental measurements had been conducted to measure the speed of light, defined as $c$, and the results matched well with this theoretically obtained value. This led to the conclusion that light is a wave of electric and magnetic fields oscillating in space and time as it propagates forward with velocity $c$.

Mathematically, the solution to the differential wave equation (Equation 12) is a sinusoidal function. This provides a way to represent waves, or other periodic phenomena, with a convenient notation for the amplitude $A$, frequency $f$, wavelength $\lambda$, and phase of the oscillation $\phi$. The speed of propagation is related to the frequency and wavelength by $v = f\lambda$. The frequency is typically represented as a radial frequency $\omega \equiv 2\pi f = kv$, which results in a phase when multiplied by time $t$. The wavenumber is similarly defined as $k \equiv \frac{2\pi}{\lambda}$. This periodicity with time is referred to as harmonic time dependence. For a wave propagating in the $z$-direction at some position $z$, Equation 13 describes the wave without consideration of a polarization direction, which would require vector notation.

$$F = A \cos(kz - \omega t + \phi)$$  \hspace{1cm} (Equation 13)

More generally, the wave should be represented using vector notation where the variation in space is accounted for by the wave vector in the direction of propagation $k$, which for
Equation 13 would be \( k\hat{z} \), and the position vector for the point of observation \( r \). Thus, the real field representation in sinusoidal form appears as Equation 14, where \( \hat{n} \) defines the plane in which the electric field is polarized (transverse to the direction of propagation defined by \( k \)). The magnetic field or, as shown here, the magnetic flux density takes the same form with a polarization direction transverse to that of both \( E \) and \( k \) and with magnitude reduced by a factor of \( c \) (Equation 15).

\[
E = E_0 \cos(k \cdot r - \omega t + \phi)\hat{n} \quad \text{(Equation 14)}
\]

\[
B = \frac{1}{c} E_0 \cos(k \cdot r - \omega t + \phi)(k \times \hat{n}) \quad \text{(Equation 15)}
\]

Any harmonic function in this form can also be represented in exponential form through Euler’s formula (Equation 14), which offers the advantage of simpler mathematical manipulation in many cases.

\[
e^{i\theta} = \cos \theta + i \sin \theta \quad \text{(Equation 16)}
\]

From Equation 16, the real part of the function provides the real amplitude information of the wave as a function of time and position. Thus, for electromagnetic plane waves, one can write the complex wave equation, making use of the sinewave accent to denote complex values, as

\[
\tilde{E} = Re[E_0 e^{i(kr - \omega t + \phi)}\hat{n}] = Re[\tilde{E}_0 e^{i(kr - \omega t)}\hat{n}] = Re[\tilde{E}_0 e^{i(kr - \omega t)}]. \quad \text{(Equation 17)}
\]

Here, the field amplitude absorbs the phase term, and thus becomes the complex amplitude, \( \tilde{E}_0 \), as well as absorbing the vector notation for polarization direction.
It is often helpful to define the electric flux density \( \mathbf{D} = \varepsilon_0 \mathbf{E} \), also called the electric displacement field, and the relation between magnetic flux density \( \mathbf{B} = \mu_0 \mathbf{H} \) and magnetic field \( \mathbf{H} \). Implementing these, Maxwell’s equations may take a form (Equation 18) and (Equation 19) in which the sometimes-pesky material property terms need not be carried through the mathematics. Here, \( \mathbf{H} \) is the actual magnetic field.

\[
\nabla \cdot \mathbf{D}(\mathbf{r}, t) = \rho \quad \text{(Equation 18)}
\]

\[
\nabla \times \mathbf{H}(\mathbf{r}, t) = \mathbf{J} + \frac{\partial \mathbf{D}(\mathbf{r}, t)}{\partial t} \quad \text{(Equation 19)}
\]

This second form can be handy in cases such as electromagnetic wave propagation in free space, but in this work, electromagnetic fields in and near matter are considered, so material properties are an important consideration.

### 2.2 Light-matter Interaction

Light propagating through a vacuum has no matter interactions, barring gravitational lensing or other astronomical phenomena, which could alter the properties of the electromagnetic wave in any way. Thus, light can propagate across the vast distances of outer space to reach the telescopes of humanity on planet Earth after traveling for billions of years. The vacuum, or free space, is thus considered to be truly lossless, meaning the amplitude of the wave is not lessened to any degree during light’s propagation through free space. Often in optics and electromagnetics as studied by humans on Earth, light propagates through air as opposed to a vacuum, but the relatively low density of gaseous air particles compared with that of a solid or liquid allow for
the treatment of air as free space in terms of material properties $\varepsilon_0$ and $\mu_0$.

When a light wave propagates through materials other than free space, the material parameters $\varepsilon = \varepsilon_r \varepsilon_0$ and $\mu = \mu_r \mu_0$ must be used in place of the free space constants. Here, $\varepsilon_r$ and $\mu_r$ are the relative permittivity and permeability, respectively, compared to the free space values. For non-magnetic materials, on which this work exclusively focuses, $\mu = \mu_0$, so this is assumed throughout the dissertation work. Often used from a ray or geometric optics perspective, the index of refraction $n = \frac{c}{v}$ is another way of describing the dispersion of waves passing through a medium, as it compares the speed of light in free space to the speed of propagation $v$ in the medium. The refractive index often simplifies mathematical expressions such as Snell’s law slightly, due to its relation to relative permittivity.

$$n = \sqrt{\varepsilon_r \mu_r} \approx \sqrt{\varepsilon_r}. \quad \text{(Equation 20)}$$

Another definition of relative permittivity is $\varepsilon_r = 1 + \chi_e$ where $\chi_e$ is the electric susceptibility, typically used in considerations of the polarization resulting from an electric field within the material. The polarization is the separation of negative and positive charges, which manifests as electrons separating from their nuclei by some distance, causing an electric field between each charge pair in the atomic lattice, resulting in a field that opposes the incident field driving the polarization. This phenomenon is described by the vector quantity $\vec{P}$, also assumed to be complex (sinusoidally varying), as follows,

$$\vec{P} = \varepsilon_0 \chi_e \vec{E}. \quad \text{(Equation 21)}$$

The ability of a material to resist the presence of an electric field via polarization of the atoms stems from the ability of electrons within the material to respond to the field. This directly
depends on the material’s free electron density \( n_e \) which directly affects its conductivity \( \sigma \). As follows, the conductivity is obtained as a direct consequence of Ohm’s law, which relates electric fields and potentials to electric currents or current densities \( J \) (Equation 22).

\[
J = -nev_d = \frac{n_e e^2}{m_e} \tau_c E = \sigma E
\]  

(Equation 22)

Here, \( e \) is the electron charge, \( v_d \) is the drift velocity of electrons moving through the atomic lattice, \( m_e \) is the electron mass, and \( \tau_c \) is the mean free time, which denotes the average interval between collisions. The conductivity is therefore dependent on the above parameters as

\[
\sigma \equiv \frac{n_e e^2}{m_e} \tau_c.
\]  

(Equation 23)

The conductivity is thus an experimentally obtainable value, now well-known for many materials from poorly conducting insulators (also known as dielectrics) to high-\( \sigma \) conductors (typically metals); semiconductors are controllably doped to fall somewhere in the middle by changing the density of carriers.

The conductivity affects the optical properties of materials by manifesting in Ampère’s law through the current density term (Equation 19).

\[
\nabla \times \vec{H}(\vec{r}, t) = \sigma\vec{E} + \varepsilon \frac{\partial \vec{E}}{\partial t} = \sigma\vec{E} + j\omega \varepsilon \vec{E} = j\omega \left(\varepsilon - j \frac{\sigma}{\omega}\right) \vec{E}
\]  

(Equation 24)

This motivates the definition of a complex, frequency-dependent permittivity,\(^{25}\)

\[
\varepsilon(\omega) \equiv \varepsilon_0 \varepsilon_r = \varepsilon_0 (\varepsilon' - j\varepsilon'') = \varepsilon' - j\varepsilon'' = \varepsilon(\omega) - j \frac{\sigma}{\omega}
\]  

(Equation 25)

where \( \varepsilon' \) and \( \varepsilon'' \) are the real and imaginary parts, respectively. Thus, the conduction loss
mechanism is accounted for by \( \varepsilon'' = \frac{\sigma}{\omega} \) and the frequency-dependent, real, absolute permittivity is \( \varepsilon(\omega) \). One can now see that the permittivity, often referred to as the dielectric constant, is not, in fact, a constant but varies with the frequency of the electromagnetic wave.

The index of refraction also then takes a complex form, \( \tilde{n} = n + i\kappa \), where \( n \) is still the real part as defined previously and \( \kappa \) is called the extinction coefficient. The relationships between components of \( \tilde{n} \) and \( \tilde{\varepsilon} \) are shown in Equation 26 through Equation 31 with the implied \( (\omega) \) dropped after the first equation for readability.²⁶

\[
\tilde{\varepsilon}_r(\omega) = \varepsilon'_r(\omega) + j\varepsilon''_r(\omega) = \tilde{n}(\omega)^2 = (n(\omega) + i\kappa(\omega))^2 \quad \text{(Equation 26)}
\]

\[
\varepsilon'_r = n^2 - \kappa^2 \quad \text{(Equation 27)}
\]

\[
\varepsilon''_r = 2n\kappa \quad \text{(Equation 28)}
\]

\[
|\tilde{\varepsilon}| = \sqrt{\varepsilon'_r^2 + \varepsilon''_r^2} \quad \text{(Equation 29)}
\]

\[
n = \sqrt{\frac{|\tilde{\varepsilon}| + \varepsilon'_r}{2}} \quad \text{(Equation 30)}
\]

\[
\kappa = \sqrt{\frac{|\tilde{\varepsilon}| - \varepsilon'_r}{2}} \quad \text{(Equation 31)}
\]

The wave vector describing the wave’s spatial variation now also takes the frequency-dependent complex form, given by the dispersion relation \( k = k_0\tilde{n} = k_0(n(\omega) + i\kappa(\omega)) \) where
\[ k_0 = \frac{\omega}{c} = \frac{2\pi}{\lambda_0} \] is the wave number in vacuum. Thus, the refractive index represents the effects of the medium on the propagation of the wave, while \( \kappa \) describes the decay of the wave as it propagates through the medium. When inserted into Equation 17, assuming propagation in the \( z \)-direction, the imaginary term clearly results in a decaying exponential component as in Equation 32.\(^\text{20}\)

\[
\bar{E} = \text{Re}\left[ \bar{E}_0 e^{i(k\cdot r - \omega t)} \right] = \text{Re}\left[ \bar{E}_0 e^{i\left(\frac{2\pi(n+i\kappa)z}{\lambda_0} - \omega t\right)} \right] = e^{-\frac{2\pi\kappa}{\lambda_0}} \text{Re}\left[ \bar{E}_0 e^{i\kappa z - \omega t} \right] \quad \text{(Equation 32)}
\]

Since the intensity of the wave is proportional to \( E^2 \) and therefore to \( e^{-2\kappa z} \), it is useful to define the absorption coefficient \( \alpha \equiv \frac{4\pi\kappa}{\lambda} \). The skin depth \( d \equiv \frac{1}{\alpha} \) is the distance that it takes to attenuate the electric field amplitude by a factor of \( 1/e \), which is a good indication of a material’s opacity.

The refractive index and permittivity can be used interchangeably, for example in computations of electric fields in different situations containing multiple material types, depending on the data available. However, it may make more sense to use permittivity for certain materials, such as metals, and refractive index for dielectric materials. This is largely due to additional terms affecting the permittivity, considered in Section 2.3, in the case of plasmonic materials.

### 2.3 Plasmonic Nano-optics

Nanoscale optics, also known as nano-optics or nanophotonics, involves the study and application of light’s interaction with objects on the order of 1 to 100 nm, at which point unique phenomena occur. Visible light antennae, photonic crystal waveguides, metamaterials,
optoelectronics, and plasmonics all involve the study and use of nanoscale optical effects.\textsuperscript{27–29}

Engineering useful devices with unique optical properties involves choosing materials based on their optical properties, as described previously in Section 2.2. While dielectric materials are primarily used for their electrical insulation and optical transparency in various applications, the field of plasmonics, in particular, relies heavily on the optical response of materials under exposure to incident electromagnetic irradiation. This field studies the effects of light-matter interactions with consideration of the mutual effects between the electromagnetic wave and the free-flowing ‘electron gas’ within the material.

The electrons on a metal surface are free to move essentially as a fluid or gas of negative charge, akin to a plasma. A plasma is an ionized gas made of charged particles and capable of electrical conduction, examples of which include the gas inside of manmade fluorescent tube lights (Ne, Ar, Hg, etc), the aurora borealis and australis, and bolts of lightning. Charges experience a force in the presence of an electric field. Thus, when light interacts with a metallic surface, its oscillating electric field, as described in Sections 2.1 and 2.2, causes a collective vibration in the electron fluid, and the frequency of this oscillation is related to the frequency of the incident light. The natural resonance of the electron plasma, called the plasma frequency, is given by Equation 33.

\[
\omega_p = \frac{2\pi c}{\lambda_p} = \frac{n_e e^2}{\sqrt{\varepsilon_0 m_e}} = \sqrt{\frac{\sigma}{\varepsilon_0}}
\]  
(Equation 33)

As a plasma is a gaseous version of this phenomenon of collectively moving charges, the quantized oscillation of electrons bound to a metallic surface is called a plasmon. The study and use of plasmons for various applications is known as plasmonics.\textsuperscript{30} A plasmon can be localized on a small metallic structure (typically nanoscale structures), or can propagate along the interface
between a metal and a dielectric (such as air). These two situations are shown in Figure 2.3.1 with localized plasmon resonance shown to the left for a metal nanosphere and surface plasmon propagation shown to the right for a metallic surface.

Figure 2.3.1. Depiction of incident wave causing localized and surface plasmon resonances.

As thoroughly described by Etchegoin and Le Ru, metallic nanostructures are beneficial to light enhancement applications such as enhanced spectroscopy due to their complex dielectric functions. Due to the complex dielectric functions of noble metals like Ag and Au, these materials are ideally suited for plasmonic enhancement over the wavelength range of visible light. Commonly cited experimental data obtained from Johnson and Christy for $\varepsilon'(\lambda)$ and $\varepsilon''(\lambda)$ are plotted in Figure 2.3.2. Negative values for the real component of the electric permittivity mean that light is not able to penetrate deeply into the surface of metals. These significantly negative permittivity values for Ag and Au are responsible for the high reflectivity of these materials and, therefore, the high potential for strong local electric field intensity enhancement outside the metal surfaces.

Further developing the dielectric function to more accurately model the experimentally measured parameters, Paul Drude, in the year 1900, introduced a formula to treat the valence
electrons as a gas of free-flowing particles moving about fixed ion cores (the atomic nuclei).\textsuperscript{32} Crucially, this model considers the interactions between electrons, but leaves out the interactions between the electron gas and the ion cores. While the original Drude model approximates relatively well the permittivity at optical frequencies and below, the main differences between experimental and theoretical values are better reconciled when the interactions with the ion cores of the metal lattice are also considered. This manifests as a restoring force, such as in an oscillating two-mass spring system, with the electromagnetic wave as the excitation source. In the early 1900s, Hendrik Lorentz modified the model to this end, incorporating the so-called Lorentz oscillator term, a resonance frequency $\omega_0$.\textsuperscript{33}

\begin{figure}[h]
\centering
\includegraphics[width=0.75\textwidth]{diagram.png}
\caption{Real and imaginary dielectric functions of Au and Ag over visible wavelengths.}
\end{figure}

The derivation of the Lorentz oscillator model for dielectric permittivity can be followed
simply by starting from the differential equation form of Newton’s second law and Hooke’s law describing a general damped oscillator such as a mass-spring system. A force $F_{spring}$ causes a mass $m$ to accelerate back and forth in the $y$ direction, dependent on a resistance to motion $k$ as follows,

$$F_{spring}(x) = m \frac{d^2 y}{dt^2} = -ky.$$  \hspace{1cm} (Equation 34)

As with the electric field of a light wave described in Section 2.1, the result of this differential equation is a sine wave, this time describing a motion with a resonance frequency $\omega_0 = \sqrt{k/m}$. The damping of this motion is described by a force proportional to the velocity of the motion, $F_{damping} = -m\gamma \frac{dy}{dt}$ where $\gamma$ is the damping coefficient of the motion. Now the acceleration of the mass is described by the force driving the motion $F_{driving}$, the spring force, and the damping force (Equation 35).

$$m \frac{d^2 y}{dt^2} = F_{driving} + F_{damping} + F_{spring} = F_{driving} - m\gamma \frac{dy}{dt} - m\omega_0^2 y$$  \hspace{1cm} (Equation 35)

$$F_{driving} = m \frac{d^2 y}{dt^2} + m\gamma \frac{dy}{dt} + m\omega_0^2 y$$  \hspace{1cm} (Equation 36)

In the case of the metallic electron gas in an oscillating electric field, the driving force is given by $F_{driving} = -e\vec{E}$ with the field given as previously described. Rewriting the differential equation describing the particle motion with $\vec{E}$ is convenient if the polarization is also incorporated (Equation 37). The damping coefficient is now $\gamma_c = 1/\tau_c$, which is related to the time between collisions $\tau_c$ as defined in Section 2.2.
\[
\frac{ne^2}{m_e} \tilde{E}(\omega, t) = \frac{d^2 \tilde{P}(\omega, t)}{dt^2} + \gamma_c \frac{d \tilde{P}(\omega, t)}{dt} + \omega_0^2 \tilde{P}(\omega, t) \quad \text{(Equation 37)}
\]

The plasma frequency replaces the coefficient on the left-hand side, giving

\[
\varepsilon_0 \omega_p^2 \tilde{E}(\omega, t) = \frac{d^2 \tilde{P}(\omega, t)}{dt^2} + \gamma_c \frac{d \tilde{P}(\omega, t)}{dt} + \omega_0^2 \tilde{P}(\omega, t). \quad \text{(Equation 38)}
\]

As this differential equation is with respect to time, the complex values are expressed in view of their time dependency (Equation 39), the derivatives are carried out (Equation 40), and \( \tilde{P}(\omega) \) is written in terms of \( \tilde{E}(\omega) \) (Equation 41).

\[
\varepsilon_0 \omega_p^2 \tilde{E}(\omega)e^{i\omega t} = \frac{d^2 [\tilde{P}(\omega)e^{i\omega t}]}{dt^2} + \gamma_c \frac{d [\tilde{P}(\omega)e^{i\omega t}]}{dt} + \omega_0^2 \tilde{P}(\omega)e^{i\omega t} \quad \text{(Equation 39)}
\]

\[
\varepsilon_0 \omega_p^2 \tilde{E}(\omega)e^{i\omega t} = (i\omega)^2 \tilde{P}(\omega)e^{i\omega t} + i\omega \gamma_c \tilde{P}(\omega)e^{i\omega t} + \omega_0^2 \tilde{P}(\omega)e^{i\omega t} \quad \text{(Equation 40)}
\]

\[
\tilde{P}(\omega) = \frac{\varepsilon_0 \omega_p^2}{\omega_0^2 - \omega^2 + i\omega \gamma_c} \tilde{E}(\omega) \quad \text{(Equation 41)}
\]

Recalling Equation 21, the permittivity can now be obtained in the Drude-Lorentz form Equation 43. The real and imaginary parts after this full manipulation are shown in Equation 44 and Equation 45.

\[
\tilde{P}(\omega) = \varepsilon_0 \left( \frac{\varepsilon}{\varepsilon_0} - 1 \right) \tilde{E}(\omega) = \frac{\varepsilon_0 \omega_p^2}{\omega_0^2 - \omega^2 + i\omega \gamma_c} \tilde{E}(\omega) \quad \text{(Equation 42)}
\]

\[
\frac{\varepsilon}{\varepsilon_0} = 1 + \frac{\omega_p^2}{\omega_0^2 - \omega^2 + i\omega \gamma_c} \quad \text{(Equation 43)}
\]
\[ \varepsilon' = 1 + \frac{\omega_p^2(\omega_0^2 - \omega^2)}{(\omega_0^2 - \omega^2)^2 + \omega^2 \gamma_c^2} \]  
(Equation 44)

\[ \varepsilon'' = \frac{\omega_p^2 \gamma_p \omega}{(\omega_0^2 - \omega^2)^2 + \omega^2 \gamma_c^2} \]  
(Equation 45)

The material properties now properly account for the plasma frequency of the material, the damping caused by collisions, and the resonance frequency due to the restoring force of the stationary lattice ions. This more accurately models the experimentally measured real and imaginary parts of the dielectric function as plotted over the visible spectrum in Figure 2.3.2. More generally, materials follow a trend by which they are transparent outside of a range of frequencies close to that of the natural resonance. At low frequencies \((\omega \approx 0)\), \(\varepsilon'' \approx 0\), so absorption is negligible. Near the resonance frequency \((\omega \approx \omega_0)\), \(\varepsilon' \approx 1\) and \(\varepsilon'' \approx \frac{\omega_p^2}{\gamma_c \omega_0}\), so a Lorentzian peak appears for \(\varepsilon''(\omega)\) near \(\omega_0\), corresponding to a peak in the absorption over the same frequencies. At high frequencies, \(\omega \to \infty\) and both \(\varepsilon'\) and \(\varepsilon'' \approx 0\), so the material does not exhibit absorption nor reflection.

For dielectric materials, the optical properties depend on the frequency in an order referred to as T.A.R.T. (transmission, absorption, reflection, transmission). They are transmissive for \(0 < \omega < \omega_0 - \gamma_c\), absorptive for \(\omega_0 - \gamma_c < \omega < \omega_0 + \gamma_c\), reflective for \(\omega_0 + \gamma_c < \omega < \omega_0 + \omega_p\), and again transmissive for \(\omega > \omega_p\). The plots in Figure 2.3.3, compiled from MIT open courseware about the Lorentz oscillator and dielectric function, display the real and imaginary parts of the (a) dielectric function and (b) refractive index versus frequency, as well as (c) the reflection spectrum for general insulating materials.

In metals, electrons are free-flowing, not localized to certain atoms. Therefore, the
Lorentz oscillator restoring force is not present, while the damping term remains. The Drude-Lorentz model for metals then takes the form,

$$\frac{\tilde{\varepsilon}}{\varepsilon_0} = 1 - \frac{\omega_p^2}{\omega^2 + i \omega \gamma_c}.$$  
(Equation 46)

Figure 2.3.3. Dielectric function, refractive index, and reflection vs. $\omega$ for insulators.\(^{34}\)

Due to the lack of a lattice-ion-mediated restoring force, metals do not exhibit the low-frequency transmissive region and are instead reflective over this range. Metals are absorptive from $0 < \omega < \gamma_c$, reflective for $\gamma_c < \omega < \omega_p$, and transmissive for $\omega > \omega_p$, thus producing the pneumonic, A.R.T.. This is intuitive if one considers how the electron sea responds to electric field oscillations. At very low frequencies, the electrons can move and change direction at the speed of oscillation, thus preventing transmission of the field into the metal and reflecting the wave. The resonance frequency, which depends on the electron density, amplifies the motion of the charges, thus causing some absorption of the field energy. Transmission occurs when the electrons can no longer respond to the high frequency of oscillation as it exceeds the plasma frequency. Similar plots as shown in Figure 2.3.3 for insulators are shown for metals in Figure 2.3.4 to help the reader visualize the transitions between each optical phenomenon with changing
dielectric function. Again, (a) plots the real and imaginary dielectric function versus frequency, (b) plots complex refractive index components versus frequency, and (c) plots the reflection spectrum.

**Figure 2.3.4.** Dielectric function, refractive index, and reflection vs. $\omega$ for metals.$^{34}$

The plasma wavelength may be used to describe the same phenomena in terms of light wavelength, which is often more familiar over the near-UV – near-IR range in which plasmonics tends to focus. For applications involving visible and near infrared light, noble and other coinage metals (usually Ag and Au) have become the standard. For Au and Ag, the plasma wavelength $\lambda_p$ is approximately 280 nm, in the UV wavelength range, thus making them transparent for shorter wavelengths. The peak in $\varepsilon''$ over the blue and green visible range for Au results in its yellow-red color, while Ag’s lack of absorption peak gives it the familiar grayish color of most metals as it equally reflects most visible wavelengths.

The discrepancy between the absorption of Au and Ag is related to additional contributions from interband electron transitions in the Au band structure. The lower absorptive losses of Ag appear to qualify it as a better choice for plasmonic applications in which the goal is to enhance the local electric field near the metallic structures as much as possible. Ag
nanostructures display a sharper transition between reflection and transmission, which exhibits a sharp enhancement peak. The broader peak of Au, on the other hand, means that it is more difficult to isolate a small wavelength range for enhancement. Other coinage metals, such as Al, typically exhibit much larger $\varepsilon''$ (absorptive losses) than Au or Ag, resulting in resonances that are strongly damped, broader, and weaker. A primary reason for the choice of Au over Ag in many plasmonic applications is due to their surface chemistries, by which Au is more stable than Ag, promoting longer device lifetime. This stability is also related to increased biocompatibility, which is often crucial for biomedical applications. It is also important to remember, however, that for wavelengths greater than 600 nm, $\varepsilon''$ is nearly the same for Au and Ag. In the case of Raman spectroscopy, especially for biomedical applications, laser wavelengths in the NIR are often used. Thus, Au tends to be the metal of choice for many plasmonic applications such as SERS. The remainder of Section 2.3 makes an even more convincing case for the choice of Au over Ag, as geometry-based resonances can push the enhancement peak for Au to 600 nm and longer wavelengths, thus avoiding its absorptive region altogether. For certain structures, this can even produce enhancements exceeding those of Ag.\(^{17,30}\)

Optical techniques that depend on the intensity of light at a point in space depend on the difference between the incident electric field and that resulting near the metal surface due to the presence of the object. The optical enhancement, also referred to as the local field intensity enhancement factor or simply enhancement factor ($EF$), is defined as the square of the local electric field magnitude with respect to that of the incident light (Equation 47). Here, without the complex and vector notation, $E_0$ or $E_i$ is the incident field strength and $E_{loc}$ or simply $E$ refers to the field measured near the metal surface. Values greater than one correspond to enhancement, and those less than one describe a quenching process.
\[ EF(r, \omega) = \frac{|\vec{E}(r, \omega)|^2}{|\vec{E}_0(r, \omega)|^2} \]  

(Equation 47)

A perfect electric conductor (PEC) creates a perfectly reflected field that cancels the incoming field, resulting in \( E_i \approx -E_r \) which corresponds to a low \( EF \). Due to the highly reflective nature of planar metallic surfaces, typically having \( EF < 1 \), it may thus far be difficult to understand their usefulness in optical enhancement applications.

The key benefit of metals for producing enhanced fields becomes more evident for nanostructures with different shapes, specifically those much smaller than the wavelength of the incident light being enhanced. At this scale, the electric field “seen” by the nanostructures is essentially a static electric field at a single point in time, making the corresponding ‘electrostatic approximation’ applicable to analytical solutions for nanoscale optics.\(^{35}\) By this method, Poisson’s equation relating the electrostatic potential to the charge density (see Griffiths)\(^{20}\) is solved versus solving the time-dependent Maxwell’s equations completely. The method still relies on the complex dielectric function \( \tilde{\varepsilon}(\omega) \) when solving the boundary conditions, however. For light in the visible spectrum, \( \sim 500 \) nm, the approximation is valid for objects of \( \sim 10 \) nm or smaller. In this regime, the boundary conditions imposed by metallic nanostructures with different geometries becomes more important in determining the resonance conditions by permitting localized surface plasmon (LSP) modes such as dipolar and quadrupolar modes that oscillate charge back and forth between the edges of a structure. A dipolar charge separation mode is depicted for the electrostatic approximation in Figure 2.3.5.\(^{36}\)

For a 2D cross section of an infinite nanorod surrounded by medium \( \varepsilon_M \), as depicted in Figure 2.3.5, the magnitude of the induced dipole \( p \) which fits the boundary conditions and solves the electrostatic approximation is\(^{35}\)
The same type of dipole mode for a 3D spherical solution is given by

\[ p \propto \frac{\varepsilon(\omega) - \varepsilon_M}{\varepsilon(\omega) + 2\varepsilon_M}. \]  
(Equation 49)

\[ p \propto \frac{\varepsilon(\omega) - \varepsilon_M}{\varepsilon(\omega) + \varepsilon_M}. \]  
(Equation 48)

**Figure 2.3.5.** Metal cylinder/sphere forming a dipole in the presence of an electrostatic field.\textsuperscript{36}

Simply changing the geometry changes the resonance condition which maximizes \( p \) in each case, \( \text{Re}[\varepsilon(\omega)] = -\varepsilon_M \) for the cylinder and \( \text{Re}[\varepsilon(\omega)] = -2\varepsilon_M \) for the sphere. The resonances occurring for structures such as Ag and Au nanospheres may occur at wavelengths for which there are no intrinsic peaks or troughs in the bulk dielectric functions of Ag or Au, respectively. These localized surface plasmon resonance (LSPR) modes are purely geometrical features. Thus, by changing the geometry, metal structures may be made to have resonances over wavelength ranges for which \( \varepsilon''(\omega) \) is low, avoiding losses due to absorption. Again, it is easier to obtain a sharp peak for Ag because it does not have a large \( \varepsilon''(\omega) \) over visible frequencies,
whereas the Au peak is broadened and weakened by absorption. The ability to tune resonance frequencies to increase the $EF$ by changing geometrical parameters is the primary factor that makes plasmon resonances interesting to study and exciting for a wide range of applications. For comparison with the discussion of nanogap structures in Section 2.4, isolated Au and Ag nanospheres have analytically obtained peak $EF$ on the order of 20 and 2000, respectively, for the surface region with the peak field.\cite{17}

Thus, increased control over fabrication of nanoscale geometries in the past few decades has been crucial to the development of novel plasmonic devices and experiments.\cite{17,37–40} This becomes even more crucial when considering different shapes, as sharp corners exhibit higher local field enhancement than rounded edges. Notably, the LSPR redshifts and tends to weaken and broaden with increasing structure size. Also, multipolar resonances add further tunability to certain geometries for plasmonic applications, as these types of modes appear and disappear over different size ranges.

For more advanced geometrical situations, it becomes prohibitively difficult to solve Maxwell’s equations by applying the increasingly complicated boundary conditions, so numerical methods play a very important role in theoretical modeling of plasmonic structures today. See Section 2.7 for more details about computational electromagnetic modeling as relevant to this dissertation work. With infinite possibilities for fabricating geometric combinations of metallic devices to interact with light waves, some considerations are helpful towards developing nanostructures for plasmonic enhancement. There are typically more than one resonance condition associated with a given geometry, as anything but a sphere has multiple dimensions to consider. Different locations on the surface of a shape may have peak enhancement at different wavelengths. Sharp edges, and therefore some cases of rough surfaces,
exhibit the lightning rod effect by which electric fields concentrate at sharp points; this effect may have its own $\lambda$-dependent resonance(s).

The optical enhancement depends very strongly on the polarization direction of the electric field relative to the structure orientation for each mode; the same can be said for the propagation direction. For comparison with spherical structures as previously mentioned, the $EF$ at two corners of an isolated equilateral Ag triangle under polarized incident irradiation are calculated to be on the order of $2 \times 10^4$ and $4.5 \times 10^3$. Bringing together two or more structures within nanoscale distances further complicates the resonance properties, allowing for further tunability to achieve even greater values for $EF$, even to the point that single molecules can be detected. The case of nanogap enhancement is discussed in the following section.

2.4 Nanogap Enhancement

Nanoscale gaps (especially 10 nm and smaller) between plasmonic structures cause hybridization of plasmon modes between the two metallic units, resulting in increased enhancement over that of the isolated structures. Compared to the field enhancement near the same two structures held far apart, there is typically a redshift in the $EF$ resonance peak for small gaps, and the field intensity is mostly concentrated between the structures. Additional resonances may also appear in some cases. Therefore, nanogap structures have often been studied for plasmonic enhancement applications.

The region between structures in which the strongest field is concentrated is often referred to as a hot spot. It is within these hot spots that the greatest $EF$ values occur due to the coupled resonances of the structures on either side.

Computational results for the 2D cross-section of two infinitely long nanowire structures
are shown in Figure 2.4.1. The gap between the structures here was decreased from 50 nm to 1 nm. The plot of optical enhancement \((E/E_0)^2\) versus gap width and the electric field distributions at selected gap widths depict the nearly exponential increase in intensity enhancement as the gap reaches 10 nm and below.

![Figure 2.4.1. Optical enhancement vs. gap width.](image)

An analogy to help explain the phenomenon of hybridized plasmon modes is that of the two-mass spring system. For a single mass oscillating on a spring, it will have a characteristic resonance frequency, given by \(\omega_0 = \sqrt{k/m}\), as shown in Figure 2.4.2(a). When a second spring and second mass are added to the situation, as in (b), there are potentially two coupled resonances that end up affecting one another and cause a hybridized mode.

In this coupled situation, two possible types of oscillation, symmetric and anti-symmetric, may appear. A symmetric mode in which the masses move in the same direction at the same time, as depicted in Figure 2.4.3(a), has a lower resonance frequency, and so can be thought of as
a lower energy hybridized mode. An anti-symmetric mode on the other hand occurs when the masses move in opposite directions at a given time, adding to the restoring force caused by each spring and increasing the resonance frequency and thus, the mode energy (Figure 2.4.3(b)).

![Figure 2.4.2. Depiction of mass-spring systems with (a) one and (b) two oscillators.](image)

![Figure 2.4.3. Coupled oscillators exhibiting (a) symmetric and (b) anti-symmetric modes.](image)

In the case of plasmonic resonances, electrons can oscillate about the surface(s) of a nanostructure in different ways, depending on the light frequency and the proximity and shape of adjacent structure(s). While isolated structures may have specific resonances, such as dipolar modes, at which plasmons typically oscillate, coupled structures may cause the existence of higher order modes or modes that oscillate in different directions. As with the spring system, different modes may have different energies associated with the motion of the electrons, and therefore with the local electric fields produced by the charge density regions. As explained by Prodan et al., the hybridization phenomenon can be used to describe coupled plasmon resonances for more complex systems, at least as a guide to understanding how different modes affect optical responses. An energy schematic as shown in Figure 2.4.4 is often used to describe the
differences between resonances for geometries that may couple two or more types of standard modes. Here, dipolar nanosphere and nanocavity modes are shown to hybridize to one of two possible modes when the two geometries are united to create a nanoshell.

![Diagram showing plasmon mode hybridization energy for different shapes and modes.](image)

**Figure 2.4.4.** Depiction of plasmon mode hybridization energy for different shapes and modes.

In the work by Prodan et al., the anti-symmetric mode increased the overall energy, while it was less than that of the isolated structure types for a symmetric coupled mode. While in some cases, this type of diagram may be more quantitative, this model serves more as a conceptual visualization tool, depicting how different modes may result in higher energy resonances.

Additional considerations of nanogap phenomena and their mathematical treatment for electromagnetic modeling were studied in this dissertation work and are discussed in Section 4.6. This so-called nonlocal model takes into account quantum mechanical effects resulting in an electronic pressure within the metal, but not localized at the surface like most of the simpler classical models tend to assume.
2.5 Raman Spectroscopy & SERS

Optical spectroscopy involves shining light onto a sample and detecting the light after its interaction with the sample, looking at the spectrum of the light’s constituent wavelengths. Peaks and troughs in the spectrum may correspond to different physical or chemical phenomena occurring in the sample, allowing the user to determine various useful properties about the sample or even detect the presence of specific chemicals. Just as there are many types of spectra that can be measured in addition to the electromagnetic variety (mass, auditory, seismographic, electrical, etc.), different optical phenomena can produce different types of light spectra. All optical spectroscopy requires physically spreading out the wavelengths of light in space via a prism or diffraction grating, but the features present in the resultant spectra can have vastly different meanings. For instance, photoluminescence spectroscopy measures how light of a given wavelength can be used to excite atoms of a material such that it later gives off light of a lower energy. Reflection, absorption, or transmission spectroscopy using a broad-spectrum light source measure how efficiently each frequency is reflected, absorbed, or transmitted, respectively. Raman spectroscopy and Fourier transform infrared (FTIR) spectroscopy produce spectra with information about the sample molecules’ vibrations.

Not to be confused with the graduate student dietary staple (ramen noodles), nor Ramin Djawadi, the composer for popular HBO programs, nor Raman as a level in sci-fi author Orson Scott Card’s Hierarchy of Foreignness, the Raman effect refers to the inelastic scattering of incident light upon interaction with molecular vibrational modes. The effect, also known as Raman scattering, was discovered by and named after Sir Chandrasekhar Venkata Raman (1888 – 1970) in 1928, earning him the 1930 Nobel Prize for Physics and India’s highest civilian award, the Bharat Ratna. In the 90 years since his groundbreaking publication titled “A new
radiation”, the optical phenomenon with his name has become increasingly important due to its relation to chemical sensing. In contrast with the elastic Rayleigh scattering responsible for the colors we see in a blue sky or a multi-colored sunset, inelastic Raman scattering involves a shift in energy between the incident and scattered light. Figure 2.5.1 depicts the Raman scattering process, including the spectroscopy aspect. If by any chance the reader were falling asleep by this point, the molecule depicted is that of caffeine.

Figure 2.5.1. Schematic of Raman scattering and spectroscopy.

If a molecular vibration absorbs some energy during the process, the change in energy is referred to as a Stokes’ shift. An anti-Stokes’ shift thus occurs when vibrational modes give up some energy to scattered photons during the process. Each type of vibrational mode such as the stretching, bending, breathing, and rotating of atomic arrangements in molecules will result in one or more peaks in the scattered spectrum. The importance of this optical phenomenon is that each type of molecule produces a unique spectrum, even upon excitation with the same light wavelength. These Raman spectra, with characteristic peak positions, serve as identification fingerprints defined by the unique vibrational modes of each molecule’s different stoichiometry
and structure.

To help visualize the difference between the signatures of two different molecules, Figure 2.5.2 depicts enhanced Raman spectra of (a) trans-1,2-bis(4-pyridyl)-ethylene (BPE) and (b) benzenethiol (BZT, a.k.a. thiophenol), obtained via prior work by Herzog et al. and Fontana et al.42,51 The combined peak profiles of each spectrum is unique to the molecule probed, allowing one to easily determine the difference between two samples using the spectra alone or to detect the presence of a previously unknown material. These organic molecules were also used during the experimental portion of the current work due to their well-known vibrational signatures.

![Figure 2.5.2. SERS spectra for (a) BPE and (b) BZT adapted from work by collaborators.]({})

As shown in the Figure 2.5.1 and Figure 2.5.2 plots, relative wavenumber (cm$^{-1}$) is the standard unit for reporting the shift in light energy compared to the incident wavelength in Raman spectroscopy and the absorption of broadband infrared light in FTIR spectroscopy. Each peak corresponds to a specific vibrational mode dependent on the molecular structure, therefore any type of molecule with a known spectrum can be identified in a sample of otherwise unknown chemical entities.
The primary difference between IR and Raman spectroscopies is that IR light is being absorbed by the molecules as vibrational modes are excited, whereas shorter wavelength light is simply scattered with a change in energy in the case of Raman. Figure 2.5.3 shows a schematic Jablonski diagram for different types of excitation and relaxation processes involving photon-molecule interactions. IR absorption is shown to excite vibrational modes. Rayleigh scattering is shown as an instantaneous process involving a virtual state and a return to the same starting energy. Stokes and anti-Stokes Raman events return to different final energies than the incident light after the virtual state interaction. Resonance Raman occurs when electrons are promoted to an excited state but still scatter light with a different final energy than that of the incident beam.

Figure 2.5.3. Jablonski diagram of optically induced molecular vibrational transitions.

When performing vibrational spectroscopy, one must determine whether it makes more sense to use IR or Raman. The key difference between the two is the type of modes that each can
excite within a molecule; these are known as selection rules. Raman depends on the polarizability of the molecule and therefore can detect modes with no net dipole moment. For IR absorption, the molecular vibration must result in a change in the dipole moment.

To clarify the difference between these types of modes, Figure 2.5.4 depicts the three vibrational modes of CO$_2$. The atoms are represented by spheres with the bonds represented by springs. The symmetrical stretching mode results in an overall change in the polarizability of the molecule, as its length increases and decreases. The other two modes, antisymmetric stretching and bending, on the other hand, do not, but they do cause a dipole moment oscillation. Thus, the stretching mode is Raman active, and the other two modes are more easily detected via IR. Raman is thus more sensitive to homo-nuclear and non-polar bonds such as differentiating between carbon-carbon single, double, and triple bonds. IR is sensitive to hetero-nuclear bonds and polar molecules. While some modes may appear in both types of spectrum, in general, a weakly Raman active mode tends to be strongly IR absorptive and vice versa. The key differentiator is that for molecules with a center of symmetry, no vibrations are both Raman and IR active; the same mode may be active for both types of spectroscopy for molecules with no center of symmetry.$^{52}$ The comparative results for Raman and IR spectra of BPE shown by Zhuang et al. are a great indication of this phenomenon, as BPE has a center of symmetry.$^{53}$

Due to the materials from which they are made (often InGaAs or Ge), IR detectors are still significantly more expensive than detectors in the visible range, in which Raman spectroscopy is typically performed. Spectroscopy in the IR range also typically requires special optics (CaF$_2$ glass, Au mirrors, etc.) that will not absorb IR radiation, as do cuvettes and lenses made of borosilicate or other visibly transparent glasses. Thus, when building a custom setup in a small lab setting, it can often become prohibitively expensive to work with IR optics. The fact
that Raman spectroscopy does not involve absorption is also beneficial, as there is typically less damage to a specimen during testing. The fact that lasers are used also improves the spatial resolution of Raman, versus the typically larger beam spots associated with IR illumination.

Figure 2.5.4. Vibrational modes of CO$_2$ resulting in either Raman scattering or IR absorption.

Laser wavelengths for Raman spectroscopy range all the way from deep UV to near infrared (NIR). While any wavelength may technically be capable of exciting the vibrational modes desired for a specific sample, this does not mean that all will produce the same results. Raman signals are proportional to $1/\lambda_{ex}^4$, where $\lambda_{ex}$ is the excitation wavelength. However, more energetic light is also more efficient at exciting fluorescence in molecules, especially organic substances. Fluorescence from the sample may significantly decrease the signal to noise ratio and therefore the detectability of the Raman signal. Thus, the choice of wavelength for Raman is predicated primarily on two factors: the type of analyte molecule to be detected and the desire to increase the strength of the vibrational scattering signal while minimizing fluorescence from the sample. Spectrometer manufacturers report the following:\textsuperscript{54}

405 and 532 nm are best for inorganic samples and a strong signal (carbon
nanomaterials, semiconductors, metal oxides, minerals, gemstone analysis, resonance Raman experiments, SERS); 633 – 830 nm are best for balancing signal with fluorescence in organics (most chemicals and organics, pharmaceuticals, narcotics, industrial ingredients, biological samples, medical diagnostics, and SERS); 1064 nm is best for fluorescence suppression but provides less signal (edible oils, petrochemicals, polymers, inks, pigments, dyes, varnishes, carbon-based and semiconductor materials, biological samples, and medical diagnostics).

The Raman effect is much less prominent than Rayleigh scattering, and anti-Stokes’ processes occur significantly less often than Stokes’ events. The signal strength of each type of scattering process is dependent on the probability of occurrence. Thus, Raman scattering signals are much weaker and therefore harder to detect than Rayleigh scattered light. Even with the Rayleigh light filtered out of an overall signal, it can be notoriously difficult to detect Raman light from samples, especially those with low concentrations of analyte molecule. Standard spectra display Stokes’ shift peaks due to their higher signal strengths compared to anti-Stokes’. The weak signal strength led to the proposal and development of surface-enhancement for samples that proved difficult to detect otherwise.

Various methods have been developed to improve the sensitivity of Raman spectroscopy systems. In spatially offset Raman, schemes have been implemented to block Rayleigh light and direct only the Raman scattered light to the optical fibers or other collection optics utilized. Methods have also been employed to increase the collection of Raman light from diffuse scattering and other weak signals, which are especially common in standoff measurements as required for safely measuring harmful substances, or as have been implemented in some commercially available handheld systems.

SERS involves adjusting the substrate surface in some way as to enhance the Raman spectroscopy signal strength, increasing the sensitivity of the technique. An interesting feature of SERS is that the enhancing features increase the intensity of both the incident radiation
and the Raman scattered light \((E_{\text{scattered}}/E_{\text{incident}})^2\), resulting in a local field intensity enhancement factor \((EF) = (E_{\text{total}}/E_{\text{incident}})^4\) per molecule. Therefore, in this work, the optical enhancement sometimes references the ratio to the fourth power, depending on the results discussed. This helps to bring the Raman signal from an extremely low and hard to detect scattering cross section (as low as \(10^{-29}\) cm\(^2\)) to levels comparable to and even exceeding fluorescence signals (around \(10^{-16}\) cm\(^2\)). Enhancement factors from \(10^4\) to \(10^7\) are common for plasmonic materials, with single molecule detection possible in some cases that achieve levels up to \(10^8 - 10^{12}\). SERS enhancements are often also attributed to chemical factors, but this effect is typically weaker than electromagnetic enhancement, and is therefore not considered in this work.

SERS often relies on plasmonic structures enhancing the electromagnetic response at the surface of a substrate. Therefore, the enhancement hotspots are fixed for a given substrate, and one must examine the substrate to find molecules of interest located within a hotspot to reap the benefit of the metallic structures. It is beneficial, therefore, to have the highest possible density of hotspots across a substrate. SERS also benefits from surface roughness of plasmonic structures, which are typically made from coinage metals (Cu, Ag, Au) due to their optical responses at visible wavelengths.

Figure 2.5.5 shows a depiction of light scattering from molecules on two substrates, one without (left) and one with plasmonic nanostructures (right). The metallic grating on the substrate to the right is shown to cause enhancement of the light signal scattered from probe molecules due to the plasmonic hotspots in the regions near/between grating structures. Thus, all scattering, including the Rayleigh scattered light, is enhanced by the presence of the metallic grating.
Making use of various nanostructure designs, especially those which make use of tunable parameters, the enhancement of Raman scattered light can be optimized to increase the enhancement factor to levels at which much lower molecular concentrations may be detected. The detection limit for this enhancement is, naturally, obtaining a useful characteristic Raman spectrum when only a single molecule is probed. Single molecule SERS has been demonstrated, though reaching this extreme limit is not the focus of this dissertation work.

Figure 2.5.5. Depiction of Raman scattering (left) compared to plasmonic SERS (right).

2.6 Cathodoluminescence Spectroscopy

Cathodoluminescence (CL) uses an accelerated electron beam, typically within the vacuum chamber of a scanning electron microscope (SEM), impinging on a sample to excite surface electrons, causing emission of light upon their relaxation. CL can also be used to study plasmonic resonance excitability of metallic structures by using the SEM beam to excite plasmons and image the light given off at different locations on the structures.

Figure 2.6.1 depicts the CL process and the setup for obtaining images and spectra. The electron beam is scanned across the sample and at each location of the beam, light is given off depending on the excitability of the structure at that beam position. The light given off by this
resonance is collected via a parabolic mirror inserted into the vacuum chamber along with the sample and the electron optics.

The light can be sent directly to a photomultiplier tube (PMT) for panchromatic imaging, diffracted via a grating and sent to a charge-couple device (CCD) camera to obtain the full spectra, or diffracted and passed through a monochromator slit to the PMT to obtain a “single” wavelength signal. If the diffracted light is collected by the CCD in what is known as parallel mode, hyperspectral images of the sample can be obtained. This data cube is powerful in analyzing plasmonic modes and the locations at which they are most readily excited. CL has been used in the study of plasmon resonances in metallic nanostructures of various sizes under different conditions, as well as for materials characterization studies.

The PMT and CCD can be used to create an excitability map, generated in much the same way as the image obtained via the secondary electron detector in a SEM. The electron beam strikes a specific point on the sample, the location of a single pixel in the CL image. With
the beam focused on a given location, electrons are excited and subsequent photons emitted at nearby sample locations. It is important to note that the total signal is comprised of photons emitted not only from the exact beam position, but from locations all around the sample surface near the beam position. This imaging capability makes CL useful for analyzing plasmonic excitability with high resolution.

Figure 2.6.2 displays a depiction of cathodoluminescence excitation at two different locations on a heptamer structure, each with different excitability. Also shown is a corresponding experimentally obtained panchromatic excitability map containing light of all wavelengths detectable by the PMT. Regions in which the electron beam excites more photons cause a more intense signal at the PMT, colorized here in bright yellow. Less excitable regions produce less signal, colored blue in the excitability map.

![Figure 2.6.2. Schematic of CL excitation with the electron beam directed at (a) the center and (b) the edge of the central structure in a heptamer pattern.](image)

Various applications of CL to the study of plasmonic resonances have been reported within the past decade.\textsuperscript{42,61–64} Coupling CL with other characterization and design techniques has allowed researchers more control over the desired plasmonic resonances in fabricated devices, as
well as aiding in understanding the effects of varying parameters that are able to be controlled. Tuning plasmonic responses via CL has proven useful for plasmonic device design.

2.7 Computational Electromagnetics

When it comes to solving Maxwell’s equations for geometries or situations lacking the symmetry or other simplifying assumptions often made in electromagnetics books and coursework, using a computer is often the only feasible way to solve a problem. Computational electromagnetics typically involves defining a spatial region or multiple regions, each with specific material properties. Regions are then broken up by use of a mesh, which simply produces a high density of calculation points at which the electric and magnetic field can be calculated relative to adjacent points. The material properties and region geometries serve as boundary conditions to predictably alter the field everywhere in the model. By using enough mesh points over the space, a smooth distribution map of electric field amplitude or phase can be obtained.

Using a code-based software such as MATLAB® involves writing a script or function capable of taking inputs related to the physical situation and setting up algorithms to solve the necessary equations for the situational inputs. Ideally, such a code allows for changes to be made to the inputs while still being able to output accurate results. Take, for example, a code designed to calculate and plot the local electric field intensity enhancement everywhere in a two-dimensional space for a given geometry and set of materials. To simulate a geometrical situation in which different regions contain different material parameters, one must utilize a matrix of data values over the geometry as place-holders for these material properties. The matrix is considered as a discretization of the total geometry being modeled, where every matrix position corresponds
to a point in space. The matrix thus contains a user-controlled number of values equal to the total number of desired “mesh points”, as they are often called. The resolution of the resulting plot is dependent on the number of points into which the total space has been discretized, referred to as the coarseness of the mesh. Initial values such as the electric field strength, wavelength, and propagation direction of an electromagnetic wave must be defined for the situation, as well.

When the calculation of the local electric field is performed based on the wave equation, it must be done at every individual matrix coordinate, applying that point’s position information and material properties to the equations. Thus, when the calculation sweeps through all mesh points, there will exist a solution matrix containing the calculated local field values depending on the spatial and material information at each matrix position. The solution can then be further manipulated, such as being divided by the incident field strength and squared. The result can then be plotted to obtain the desired enhancement map image.

An object-oriented programming language or software like MATLAB is well-suited to this type of model, due to its use of matrices and simple recursive functions applied to individual matrix values or entire matrices. The complication with such script-based calculation methods is typically the difficulty of establishing the geometries which will have different material properties than their surroundings. Inputting rectangular, circular, or even elliptical geometries into their mathematical forms to assign certain cells within a matrix to hold the proper material property values is simple enough, but it is difficult to generalize a code for all geometries, especially those for which there is no simple mathematical input by which to define the boundaries of the desired region.

Here is where software packages such as COMSOL Multiphysics® offer significant advantages. Such software typically has a built-in computer-aided design (CAD) type function...
by which more complex geometries can be input into a model. In some cases, integration with another CAD software further increases the user’s control over inputting realistic geometries. Once a geometry is defined, material parameters are input for the desired regions. The user has the freedom to obtain and input material properties based on data from external sources, such as experimentally obtained frequency-dependent complex electric permittivity. This allows for more accurate computational results. In this dissertation work, the optical properties for a given material were set up as interpolation tables such that the simulated incident light frequency could be any value within the range of experimental data. An example geometry for a 3D model is shown in Figure 2.7.1(a) with the corresponding model’s Au regions highlighted in (b). The model is shown after application of the mesh in Figure 2.7.1(c).

**Figure 2.7.1.** Example of computational model geometry, material region selection, and mesh.

Compared to the square mesh into which the geometry is broken up, for example, in a matrix-based simulation as mentioned previously, powerful computational software packages can create meshes broken up into different geometrical segments. A free triangular mesh breaks up the space into many triangles of different sizes and orientations, with each vertex serving as a point of calculation. The mesh can be set to grow at a specific rate so that it is finest near the
geometrical entities of interest or near curved surface, along which the mesh typically needs to be finer to follow the curvature. The mesh points then grow farther apart at distances farther from the points of interest in the model. This variation from fine to coarse meshing helps to reduce computation time while still producing accurate, smooth results.

Technically, once a geometry has been designed and a mesh has been overlain, any physics could be applied to a model such that the desired equations would be solved at each mesh point. In this work, the only physical equations and outputs of interest involved electromagnetics, so the models were set to implement the electromagnetic wave equation, as described in Section 2.2, over the entire space, basing the resulting electric field, charge density, etc. at each mesh point on the incident parameters, geometry, and material properties as inputs.

The models in this work were set up to study the optical responses of periodic geometries; 2D models were established to simulate gratings periodic in one dimension, and 3D models were designed to model plasmonic nanostructures as periodic in two dimensions. While one could simulate many periods of such a repeating structure, the model would be extremely computationally expensive. Here, the model may have a fine enough mesh to cover the many regions of interest with plenty of mesh points, but the model would take a prohibitively long amount of time or use a prohibitive amount of computer memory and processing power. Conversely, the model may be able to compute in a reasonable amount of time with much too low of resolution to be considered useful by significantly increasing the mesh coarseness.

The best strategy, therefore, when modeling periodic structures is often to break down the model into the smallest possible repeating unit cell and simulate this as being periodic using appropriate boundary conditions. For electromagnetic models, this can mean setting up mirror boundary conditions by assigning the proper boundaries as perfect electric conductors (PEC) or
perfect magnetic conductors (PMC). An alternative is to apply periodic boundary conditions, by which the mesh points along one boundary of the model perfectly copy those at the opposite boundary, representing that the geometry perfectly repeats in the chosen direction. In this dissertation work, periodic boundary conditions were applied to the left and right line edges of 2D grating models, and mirror boundary conditions were applied to the appropriate surface edges of 3D models. This allowed for a sufficiently fine mesh to be applied to the models to provide the most accurate computational results without the need to run each iteration of a simulation on one of the University of Arkansas supercomputers.

Another boundary parameter that was established in models included in this work was that of entry and exit ports at the top and bottom of each model, respectively. The use of ports was a convenient way to establish the presence of a plane wave with the desired electric field and frequency as well as providing points of measurement for reflection and transmission of the input wave. The S-parameters provided by the use of ports were used to obtain the value for reflectance ($R$) and transmittance ($T$), and from these, the absorbance could be calculated by the equation $A = 1 - R - T$. This technique was mostly useful when studying a spectrum of incident wavelengths, whereby the reflectance, transmittance, and absorbance spectra could be output.

In addition to ports sandwiching the model in the $z$-direction, perfectly matched layers (PMLs) were applied to thin regions between the outside of the model and the ports. These regions were designed to provide transitions between the model and its top and bottom edges in which any wave components could be absorbed fully. This serves to prevent erroneous “scattering” from the model boundary, which would affect field values in other regions of the model in an unrealistic manner.
The parameters being studied during a simulation test could be swept through a range of values with a controlled step size, allowing for a single run to provide multiple data points. Simultaneous sweeps of multiple variables could be performed as well, resulting in three-dimensional or higher data sets based on all combinations of parameter values. Such sweeps were used in this work to test the responses of structures with a range of incident wavelengths, over a range of widths or diameters for different geometries, or for a range of values of an underlying physics parameter.

The results were obtained in various forms depending on the study. Color maps of electric field intensity distribution over the entire space were valuable visualization tools for observing where the greatest enhancement was occurring for different situations. In many cases, additional mathematics were performed post-computation to obtain additional information from the raw calculated data at all mesh points or over user-defined regions of space. Tables of summed or averaged enhancement values over the swept parameter ranges were used frequently to quantize the results and to produce more informative plots and color maps of the data. The computational results and additional insights obtained from the data are primarily shown and discussed in Chapter 4.
Chapter 3. 
NANOFABRICATION

The ability to create many different possible geometries can result in a wide range of local field enhancement factors across a broad spectrum of incident wavelengths. Therefore, many variations of plasmonic structures and arrays of patterns across substrates have been simulated, fabricated, and characterized experimentally.\textsuperscript{73–76} Fabrication methods today vary widely, with some parameters highly dependent on target applications. Hornyak et al. and review papers over the past two decades describe current top-down and bottom-up methods and their benefits and disadvantages.\textsuperscript{37,38,77–79} Arrays covering entire substrates are useful for enhancing ensemble measurements or sensors in which the inhomogeneous linewidth broadening is not as crucial, since detection may be the primary objective. Colloidal nanoparticles are also commonly used plasmonic structures. These can be self-assembling metal spheres or other geometries, and have been demonstrated in solution or deposited onto a substrate.\textsuperscript{80,81} In solution, biomedical applications become possible, such as \textit{in vivo} single molecule imaging and spectroscopy.\textsuperscript{82,83} Top-down approaches such as various types of lithography are capable of patterning desired geometries at specified locations on a sample, offering a versatility that is not found in the deposition of colloidal nanostructures on a substrate.\textsuperscript{79,84,85} One common drawback of top-down approaches is the cost, both financial and temporal, which is sometimes prohibitive for mass-production of plasmonic nanostructures at scales large enough for useful devices.

Recent developments studying gratings and other periodic metallic substrates include optimization of nanogrooves on Au and Ag surfaces,\textsuperscript{86} two-dimensional square arrays with larger gap widths (~100 nm) patterned via standard electron beam lithography (EBL),\textsuperscript{87} imprinting of
nanoporous square Au gratings to take advantage of surface roughness,\textsuperscript{88,89} large-gap gratings with multiple heights and widths fabricated via traditional EBL,\textsuperscript{90} sinusoidal metal-insulator-metal (MIM) sandwich gratings,\textsuperscript{91} double step gratings,\textsuperscript{92} and circular ring gratings.\textsuperscript{93–95} Optimization of geometric parameters of different grating types for maximum SERS enhancement have also been conducted.

3.1 Fabrication of Nanostructured SERS Substrates

State-of-the-art SERS substrates tend to incorporate some type of nanostructures, whether ordered or disordered.\textsuperscript{96–98} Ordered substrates tend to use top-down methods such as lithography, ion beam milling, stamping/imprinting, or other more unique methods. These allow for strategic design and control over structure geometries, improving plasmonic tunability, often at the expense of fabrication speed and financial cost. Disordered substrates are typically created via drop-casting or spin-coating of colloidally fabricated nanostructures. In these cases, ease and speed of fabrication are gained at the expense of directed structure placement and geometric control.\textsuperscript{97}

In a 2008 review focusing on novel nanostructures for SERS, Tripp et al. have discussed fabrication strategies.\textsuperscript{99} Methods for simply preparing a roughened substrate surface were mentioned, but the paper described EBL, nanosphere lithography, template methods, hybrid methods, and oblique angle vapor deposition as the best options for producing high enhancement, generating reproducible and uniform responses, offering stable shelf lives, and being simple to fabricate.

More recently, Luo et al. compared and contrasted top-down, bottom-up, and combination methods of SERS substrate fabrication, citing work over the past decade.\textsuperscript{100}
Methods discussed include EBL, focused ion beam, nano-indentation, metal-induced chemical etching, ion sputtering, nanoparticle immobilization, oblique angle deposition, galvanic displacement reaction, EBL + Au reduction, EBL + particle binding, and others. Template-assisted techniques making use of ZnO nanowires, nanoimprinted polymers, anodic Al oxide, carbon nanotubes, and colloidal assembly are also described. The primarily used metals in these methods are Au and Ag, and SERS enhancement factors range from $10^6$ to $10^{10}$ for different substrate types.

Wang and Kong reviewed recent progress of plasmonic materials and nanostructures for SERS.\textsuperscript{55} Referenced are bottom-up chemical synthesis techniques including plasmonic and core-shell nanoparticles, nanowires and nanorods, preassembled plasmonic dimers and trimers, nanoprisms, nanocubes, nanostars, and nanosheets. Rationally designed substrates discussed include nanosphere lithography, on-wire lithography, nano-capsules and electric tweezers, nano-antennas by EBL, and nanogaps created by non-traditional techniques, as well as plasmonic gratings and other periodic metallic structures. Hybrid substrates fabricated on photonic crystals and resonant gratings as well as those making use of bio-enabled materials like diatoms, microfluidics, and graphene are discussed as well.

Recent nanogap developments include bowtie structures via combined EBL/electrochemical process by Halas et al.,\textsuperscript{101} femtosecond pulsed laser exposure of photoresists,\textsuperscript{102,103} nanoimprinting to create vertical nanopillars with Au tips,\textsuperscript{104–106} seed growth of plasmonic structures separated by gaps,\textsuperscript{107} creation of gaps during the etching/oxidation of a Si wafer prior to metal deposition,\textsuperscript{108} sacrificial sidewalls via atomic layer deposition,\textsuperscript{47} and other multi-step lithographic procedures including the use of sacrificial layers.\textsuperscript{109} Optimization studies involving nanogap plasmonics have been conducted as well, including some investigation of gap
Related to the current work, the plasmonic activity of a dual-width nanorod with sub-20 nm spacing was recently reported as well, though not specifically for SERS applications.

Self-assembled nanostructure layers or metasurfaces have become a common method of producing large-area SERS substrates, typically with relatively low financial and time requirements compared to top-down methods. Previous work has studied the effect of increasing the diameter of Au nanospheres in self-assembled metasurfaces on the SERS response.\textsuperscript{51} Similarly, tunable gap metasurfaces have been studied in terms of the absorbance peak wavelength over a range of gap widths.\textsuperscript{113,114} These types of tunable gap metasurfaces have yet to be studied as SERS substrates in terms of their effect on the enhancement factor with respect to gap width. Ideally, devices making use of such tunable nanotechnology will take advantage of both the wavelength tunability and the enhancement optimization aspect. Thus, studying the effects of varying geometrical parameters such as the gap width between metasurface structures is crucial to producing optimal nanotechnology-based devices for real world applications. Experimentally verifying computational optimization requires fabrication and optical characterization of tunable devices. The remaining sections in this chapter discuss the fabrication of nanostructures via two tunable methodologies, which are later studied in terms of their potential for optimizing plasmonic electric field enhancement.

\subsection*{3.2 Nanomasking Fabrication Technique}

The initial dissertation work was established around a rational-design lithography technique incorporating a non-traditional method for creating nanogaps with plasmonic gratings. The author previously developed this two-step lithography process, since referred to as
“nanomasking”. The steps of the nanomasking fabrication method are illustrated in Figure 3.2.1, as described in more detail by master’s thesis work and former publications by Bauman et al.\textsuperscript{40,115} Part (i) in (a) – (e) shows a 3D depiction, and (ii) shows a 2D cross sectional view. The basic steps of the method are as follows.

**Figure 3.2.1.** Schematic procedure outline for the nanomasking fabrication technique.\textsuperscript{36,40}

Standard EBL or photolithography patterning is used to control the geometry of primary structures in the chosen photoresist or e-beam resist atop the chosen substrate. After deposition of chosen material(s) and subsequent resist lift-off, the primary patterns remain (Figure 3.2.1(a)). Crucially, during the first material deposition step, the final material (ending up on top of the structure) should be chromium. Upon exposure to oxygen, either in a controlled manner or in ambient conditions, Cr oxidizes to $\text{Cr}_x\text{O}_y$, causing it to expand over the edge of the other materials deposited during the primary step. This oxide layer serves as a “nanomask” during the secondary patterning and deposition steps (b) and (c). Thus, if alignment capabilities allow one to perform a second lithography and deposition process atop the primary structures, a secondary geometry can be overlain with the primary structures (c) and (d). When the materials for the secondary step are deposited, the $\text{Cr}_x\text{O}_y$ serves to prevent deposition in the nanoscale regions beneath the oxide overhang (d). Thus, upon lift-off of the resist and a Cr etch process to remove the $\text{Cr}_x\text{O}_y$ layer, the primary and secondary materials adhered to the substrate are separated by a
nanogap smaller than the lithographic resolution limit, with its width controlled by the thickness of Cr layer deposited during the first step (e).\textsuperscript{36,40}

Nanomasking essentially combines the versatile control of EBL or photolithography with more easily scalable template processes. It allows for many different geometrical designs to be combined as desired, each providing opportunities to tune the structure’s optical response. In addition to being able to fabricate multiple nanogaps and gaps in two dimensions, nanostructures below the electron beam lithography limit can be produced. As outlined by Bauman et al., various devices with sub-20 nm nanostructures and sub-10 nm nanogaps have successfully been fabricated by nanomasking.\textsuperscript{40} Shown in Figure 3.2.2 are colorized SEM images of rectangular secondary structures overlapping with primary square structures at different percentages of overlap. The standard nanomasking gap is visible at each primary edge overlapping a secondary structure, but notable in this case Figure 3.2.2(b) is the resulting 30 nm structure adjacent to the nanogap, which is below the typical resolution limit of the XL30 ESEM used to fabricate the structures.\textsuperscript{36,115,116}

\textbf{Figure 3.2.2.} Sub-lithography resolution nanomasking fabricated structures.\textsuperscript{36,115,116}

With the goal of fabricating SERS substrates in mind, larger area patterns were developed as well. The first that was studied in more detail was a grating structure. As previously
mentioned, many different types of gratings have been fabricated for plasmonic applications, but nanomasking has made possible a dual-width variety which would be difficult to pattern with other standard methods.

As shown in Figure 3.2.3(a), this type of grating is begun by first patterning a standard single-width grating using normal lithographic definition. In (b), the secondary structures overlap the first such that the primary gaps are mostly filled by secondary metallic structures, besides the small nanomasking gaps resulting between the primary and secondary structures. The final dual-width grating with the Cr layer etched away is shown in (c). Here, each period contains two different grating widths separated by sub-10 nm gaps. This provides additional parameter variation control which can be harnessed to engineer optimal plasmonic responses with more flexibility than what is possible with a standard single-width grating structure.\textsuperscript{36,115,116}

![Figure 3.2.3. Dual-width grating fabrication process.\textsuperscript{36,115,116}](image)

Colorized SEM images of preliminary dual-width grating fabrication structures are shown in Figure 3.2.4. The scale bar in the left panel is 250 nm, and the bar on the right is 500
nm. As shown, the primary and secondary Au structures can be designed with different widths and have sub-10 nm separation. The nanomasking process therefore provides the ability to produce nanostructures and gaps below the resolution limit of the top-down method used by taking advantage of the Cr oxide as a nanoscale mask. Unique geometries and structures can be patterned using this method, which would be otherwise difficult to obtain.\textsuperscript{36,115,116}

![Figure 3.2.4. Colorized SEM images of fabricated dual-width gratings.\textsuperscript{36,115,116}](image)

Two additional examples of unique geometries made possible by this method are shown in Figure 3.2.5. A grid structure is shown in (a) and a concentric circle structure is shown in (b). In both cases, (i) shows the result of the primary fabrication step with the Cr layer shown to have oxidized. Part (ii) displays the resulting structures after the secondary lithography, evaporation, and resist lift-off processes. The circular patterns in (b) show an example of a hybrid structure created by using a different material for the secondary structures than that used for the primary structures. The final resulting patterns are shown in (iii) for each case.\textsuperscript{36,115,116}

The results of a two-step grid fabrication are shown in the colorized SEM image in Figure 3.2.6. In the design shown, different primary and secondary structure widths were shown.
to have been overlapped successfully, resulting in the ability to control multiple parameters including the resultant widths of both structures and the length of each secondary structure parallel to the primary grating structures. The zoomed-in inset displays more clearly the nanogap formed between each overlap of primary and secondary structures. Thus, many nanogaps can be produced over a large area depending on the design of the overlapping patterns. Extrapolation of the grid device shown in Figure 3.2.6 was used to calculate an estimate of the gap density over a macroscale device. The resulting gap density for this non-optimized grid pattern was approximately 500 million gaps/cm².\textsuperscript{36,40}

\textbf{Figure 3.2.5.} Unique nanomasking fabrication capabilities.\textsuperscript{36,115,116}

Additional results for grid pattern designs are shown as colorized SEM images in Figure 3.2.7. As the results demonstrate, it was possible to obtain secondary structures below the lithography resolution limit, here on a larger scale, by varying the spacing/width of the primary patterns. The scale bars may be determined via the labeled widths in parts (a) – (c).\textsuperscript{36,115,117}
Figure 3.2.6. Colorized SEM image of nanomasking-enabled grid pattern.\textsuperscript{36,40}

The nanomasking technique was thus shown, as in previous work, to provide a highly tunable nanogap fabrication method which could be leveraged for nanoscale optical engineering. The high variability of geometric parameters was beneficial to the process of optimizing devices for enhanced local electric fields when coupled with the same variational capability offered by computational electromagnetic modeling.

The lithography and SEM imaging work for this dissertation work was performed using the Electron Optics Facility, part of the Arkansas Nano-Bio Materials Characterization Facility housed in the Nano Building at the University of Arkansas. All electron beam lithography performed in this work was performed using a FEI XL30 Environmental SEM (Field Electron and Ion Company, Hillsboro, Oregon), as outlined by the standard operating procedure developed by the author and outlined in Appendix H.4. During sample analysis, SEM images were obtained via the same tool following the operating procedure outlined in Appendix H.3, and
high-resolution SEM imaging was performed using the FEI Nova Nanolab 600 DualBeam (FIB/SEM) as described in the procedure of Appendix H.1.

Figure 3.2.7. Additional grid pattern results of sub-lithography limited structures.\textsuperscript{36,115,117}

Chemical sample preparation was performed in the shared chemical laboratory in PHYS 104 through the University of Arkansas Department of Physics, specifically using equipment purchased by the Herzog Lab. Resist spin coating was performed using a WS-650-23NPP Modular Spin Processor (Laurell Technologies Corp., North Wales, Pennsylvania), originally a model owned by the Churchill Group, followed by a Herzog Lab purchase. Sample cleaning was enhanced by the use of a PDC-32G Plasma Cleaner (Harrick Plasma, Inc., Ithica, New York). Material deposition was performed using Dr. Omar Manasreh’s electron beam evaporator in his Bell Engineering lab through the Department of Electrical Engineering. Some preparatory and test work was performed using the Nanofabrication Laboratory housed in the Physics Building. Some samples were obtained from and preliminary fabrication work was performed at the High-Density Electronics Center, which is located separate from the main campus at the Arkansas Research and Technology Park. Silicon wafers were diced to more convenient sample sizes (1 cm\textsuperscript{2}) using the K & S 982-6 dicing saw (Kulicke & Soffa Industries, Inc., Singapore).
3.3 Nanoscale Surface Roughness

As discussed in Section 2.4, nanoscale surface roughness, which commonly results from lithography or other nanofabrication processes, can be beneficial to providing additional local electric field enhancement compared to that produced by smooth structures. Thus, studying and understanding the roughness associated with a technique can be important to optimizing it for optical applications. This is especially true for methods resulting in nanogaps, as the roughness of two adjacent structures may greatly affect the gap width or the ability for plasmonic modes to couple across the gap. Therefore, surface roughness studies were performed to measure the gap width over a distance along the gap for fabricated structures. The SEM image in Figure 3.3.1 was used to measure the width \( g \), limited only by pixel density, at each pixel column along the gap length, \( L \).\(^{40}\)

![Figure 3.3.1. Example SEM image used for gap width/roughness analysis.\(^{40}\)](image)

The results obtained via this preliminary gap analysis were plotted as shown in Figure 3.3.2. The plot of \( g \) versus \( L \) shows the amount of width variation caused by the surface roughness on either side of the gap. Over lengths of approximately 25 nm, the gap was decreased or increased depending on the coupled roughness. This variation in either direction resulted in a mean gap width of \( 8.57 \pm 3.03 \text{ nm} \) (8.21 nm median), denoted by the red line in Figure 3.3.2.\(^{40}\)
Figure 3.3.2. Plot of experimentally measured gap width vs. distance along the gap.\textsuperscript{40}

An additional study was performed to characterize multiple gaps for a more accurate representation across nanomasking-produced devices. Here, three gaps were analyzed as described in the following quoted excerpt by Bauman et al.\textsuperscript{115}

The gap widths were determined by measuring the full width at half maximum of the SEM image pixel values along a line drawn perpendicularly across the gap. The location of each edge point was determined in this manner along a gap length, $L$, of 100 nm. From these edge locations, the gap width, average gap width, deviation from the mean, and edge correlation were calculated. The mean value across the three gaps was found to be 7.4 nm with a standard deviation of 2.2 nm. The analyzed gaps are shown in the SEM images at the top of Fig. 5 with the specific locations for each gap measurement length, $L$, labeled. The red plots shown in the middle row of [Figure 3.3.3] display the gap width deviation from the mean, $\Delta g$, versus $L$. The red histogram at the right side of [Figure 3.3.3] plots the number of occurrences, $N$, for gap widths over different $\Delta g$ ranges. The blue plots display the population correlation coefficient, $\rho$, versus $L$, with 1 representing complete correlation and $-1$ representing complete anticorrelation. From these data, it was found that there are ranges in the order of tens of nanometers along each gap over which the secondary structure edge is highly correlated with the edge position of the primary structure. There are also, however, ranges in the same order of length over which the edges are anticorrelated. Considering the total gap lengths studied, there does not appear to be a net correlation among the edge positions across a given gap. Therefore, with the nanomasking fabrication process, an expected gap width can be patterned with a relatively high degree of accuracy, but the roughness of the gap on the secondary structure edge is not necessarily defined by the primary structure surface roughness.
Figure 3.3.3. Gap roughness correlation analysis study results.115

Beyond the fact that this study was useful to further develop and characterize the fabrication process, a key benefit of measuring surface roughness and gap roughness correlation was the potential to incorporate these parameters quantitatively into computational electromagnetic models of nanomasking devices. This helps to more accurately represent the experimentally realized devices.

3.4 Self-Assembled Nanogap Metasurfaces

The goal of the work being to study tunable optical nanostructures for the potential of engineering SERS substrates, it was interesting to study plasmonic substrates created via both top-down and bottom-up synthesis methods. In addition to lithographically defined structures with sub-10 nm gaps and geometries controlled by the nanomasking process, self-assembled Au metasurfaces were studied as part of this work through collaboration with researchers at the United States Naval Research Laboratory (NRL) in Washington, D.C.. The author was able to take part in internship experiences at the NRL, working for one summer in Dr. Jake Fontana’s
physical chemistry lab. The Fontana group has developed a process for developing metasurfaces of Au nanospheres in which the gaps between spheres can be controlled to sub-nm widths. The current section describes the metasurface self-assembly fabrication process as outlined by Fontana et al.\textsuperscript{51,113,114,118}

The directed self-assembly process involves phase separation of nanoparticles from solution and surface tension gradients, which help with the deposition of the metasurface onto a substrate. The fabricated samples in this work used Au nanospheres with diameters of 13.3 ± 0.7 nm (average of TEM measurements), obtained from Ted Pella, Inc. (Redding, California). The Au particles were in an aqueous suspension at an optical density of OD ~ 1 in 1 cm (absorption peak) and stabilized in a sodium citrate solution. A 20 mL scintillation vial was used to mix a solution of 1 mL of tetrahydrofuran (THF) with mono- and dithiol alkane ligands in equal proportions (10 µL of each).\textsuperscript{114}

The author digresses here for a bit of organic chemistry, which may be unfamiliar to the more physics/engineering-oriented reader. Thiols are organosulfur compounds containing a carbon-bonded sulfhydryl group (R-SH), where R represents an organic component, and the SH may also be referred to as a thiol group. Alkanethiols are therefore sulfhydryl groups bonded to alkyl groups where the number of carbons in the molecule determines the prefix (ethanethiol, benzenethiol, etc). These compounds are the sulfur equivalent of alcohol, where sulfur has replaced oxygen in the hydroxyl group of an alcohol; the word mercaptan replaces alcohol in the longer form of the nomenclature as in ethyl alcohol/mercaptan to describe ethanol/ethanethiol. A dithiol contains two SH groups, which can change the way that it bonds to a surface such as that of a Au nanosphere.

The primary driving force for chemisorption of a layer of molecules like thiols on a metal
surface like that of Au is the reduction of excess surface energy. The atoms at the surface of metals like gold have less electrons than those deeper within the bulk lattice of a given structure. Thus, they seek stabilization from other sources, especially elements like sulfur, which is considered to be rich in electrons.\(^7\)

The same type of alkyl group for both the thiol and dithiol were mixed for a given solution, and the volume was doubled to 20 µL for the case of ethanethiols. The Au nanoparticle suspension was mixed into the THF ligand solution. At this stage in the process, the ligands bind to the surfaces of the Au nanospheres, displacing the citrate surfactants and causing the spheres to phase-transfer and become hydrophobic. Because of THF having a lower density than water, the THF and ligand-coated nanospheres phase separate and the spheres rise to the air-fluid interface, forming a layer atop the liquid surface.

While the metasurfaces can be grown along the sides of the vial and removed using a TEM grid or other methods, the convenience of metasurface growth directly onto a substrate was utilized for this work. Once the nanoparticle and THF solutions were mixed, glass or Si/SiO\(_2\) substrates (previously cleaned in potassium hydroxide dissolved in methanol at a concentration of 5% (w/v)) were placed inside each vial for a given synthesis process, and the vial was shaken vigorously. With the substrates and vial walls wetted by the shaking and/or by deliberate pipetting of solution onto the substrates and the substrates repositioned to be nearly vertical, the deposition of metasurfaces onto these surfaces occurs naturally as follows. The different vapor pressures of THF and H\(_2\)O cause the THF to evaporate faster than the water, resulting in a surface tension gradient, which carries the nanoparticles to the vertically oriented surfaces, depositing monolayer films on the substrates and vial walls. The layers formed were macroscopic, substrate-scale metasurfaces of ligand-linked Au nanospheres with interparticle
separation distances controlled by the number of carbons in the alkanethiols. The metasurfaces were left to dry overnight, after which the substrates could be characterized optically. For self-assembly on glass, the regions over which the metasurfaces formed were visibly blue via white light transmission and orange-red via white light reflection. On Si/SiO$_2$ substrates, transmission was not possible, but the film regions were visibly a different color than the naked wafer areas.

The tunability of the metasurfaces comes from the control over the gap size, which is dependent on the choice of alkanethiols used. Previous work has shown that increasing the number of carbons in the ligand molecules results in larger gaps between Au particles throughout the metasurface with a relatively high uniformity.$^{113,119,120}$ In recent work by the Fontana group, the use of both thiols and dithiols in the self-assembly process was determined to improve the uniformity and total area of the resulting metasurfaces, as well as improving their mechanical strength, which made it possible to transfer them to TEM grids. This made it possible to use TEM imaging by which direct nanosphere diameters and gap widths were measured to obtain statistics over large metasurface regions.$^{114}$

The six different gap widths fabricated in this work include C2 (1-ethanethiol/1,2-ethanedithiol), C3 (1-propanethiol/1,3-propanedithiol), C6 (1-hexanethiol/1,6-hexanedithiol), C8 (1-octanethiol/1,8-octanedithiol), C10 (1-decanethiol/1,10-decanedithiol), and C14 (1-tetradecanethiol/1,14-tetradecanedithiol). Colorized TEM images of each ligand length are shown in Figure 3.4.1(a), which has been adapted from Doyle et al., as the same types of metasurfaces were assembled for this work.$^{114}$ Also shown are the interparticle gap distributions (b).

Measuring 1000 gaps for each metasurface, the distribution of gap widths versus ligand length was found as plotted in Figure 3.4.2 with error bars representing the standard deviation at
each number of carbons, $C$. The red solid line corresponds to trends reported in previous self-assembly work by Love et al. and Martin et al., which was explained via the following quote from Doyle et al.\textsuperscript{114,119,120}

The interparticle gap has been shown to increase at $0.12C$ for HCP gold nanospheres coated with alkanethiols.\textsuperscript{119,120} If it is assumed the dithiol ligands set the gap size due to the additional 0.24 nm Au – S bond offset, relative to the monothiol ligand, and are interdigitated, then the gap size is expected to be of the form $0.12C + 0.48$ nm…

…demonstrating the gap size is predominantly set by the length of the dithiol ligands.

**Figure 3.4.1.** Metasurfaces: (a) colorized TEM images and (b) gap width distributions.\textsuperscript{114}

**Figure 3.4.2.** Gap width vs. alkanethiol ligand length in Au metasurface self-assembly.
The black trendline is a linear fit to the data as obtained by TEM imaging with a 0.48 nm shift set due to the same dithiol gap size offset. Both trendlines demonstrate good agreement with the measurements. Thus, it was demonstrated that tunable nanogap metasurfaces can be fabricated with a relatively quick and simple process. Metasurfaces were grown in this way for the aforementioned gap widths to be used in experimental Raman spectroscopy as described in Chapter 5.
Chapter 4.

ENGINEERING NANOSTRUCTURED SERS SUBSTRATES

The goal of this dissertation work was to leverage the types of structures made possible by advanced fabrication capabilities to engineer their optical enhancement for SERS. The geometric control offered by the fabrication techniques described in Chapter 3 was instrumental to this process and motivated the computational modeling of such tunable structures. As described in Section 2.7, FEM models were created using COMSOL Multiphysics so that geometric and physical parameters could be swept, thus providing a theoretical handle by which to engineer the optimal structures for optical enhancement.\textsuperscript{72}

4.1 Dual-Width Gratings

Having demonstrated the capability of fabricating dual-width grating structures with sub-10 nm gaps via the nanomasking technique, the motivation was to use the geometrical tunability of the method to engineer optimized local electric field intensity enhancement. The dual-width grating consists of multiple variable parameters which can be leveraged to optimize the electric field measured in different locations. The first and second structure widths $w_1$ and $w_2$ are controlled by the fabrication designs, and the gap width $g$ and therefore the grating period $P$ are controlled by the Cr oxidation step of the nanomasking process. The thickness of the metal $t$ can be controlled through the evaporation method utilized in practice. These variables are shown in the 3D schematic of a dual-width grating in Figure 4.1.1.\textsuperscript{121}

Computational electromagnetic simulations were designed with $t$, $w_1$, $w_2$, $P$, and $g$ as
possible geometrical variables. Preliminarily, $t$ and $g$ were held constant at 15 nm and 5 nm, respectively, as these values were on the order of standard fabrication results. The models were designed as a 2D cross section (Figure 4.1.2(a)) of the 3D structure shown in Figure 4.1.1. The metallic structures were given experimentally measured complex optical properties of Au ($n(\omega)$ and $\kappa(\omega)$), and the surrounding medium was given a real effective refractive index $n_{eff} = 1.25$ to represent a general case between the values of air and Si.

![Figure 4.1.1. Schematic depiction of the dual-width grating geometrical parameters.](image)

A plane wave with an electric field amplitude $E_0$ polarized perpendicular to the gap as shown in Figure 4.1.2(a) was simulated as incident upon the grating from the top of the model (described by $k$) with the wavelength $\lambda_0$ as a variable. The model was set up with periodic boundary conditions to simulate an infinitely repeating grating in the horizontal dimension. Perfectly matched layers were established at the top and bottom of the model to absorb any field values that may have appeared in these regions to eliminate erroneous calculated scattering from the model boundaries. An example of the resulting electric field intensity enhancement distribution color map from this simulation is shown in Figure 4.1.2(b).
Over all mesh points within the black outlined boxes in Figure 4.1.2(b), the enhancement factor \((EF = (E/E_0)^2)\) values were summed to gather an idea of how light was being enhanced within the gap between structures for different simulation conditions. For widths ranging from 10 to 250 nm in 10 nm steps, the enhancement values were summed over these regions, resulting in the color plots for \(\lambda_0 = 600, 700,\) and \(800\) nm in Figure 4.1.3 (a), (b), and (c), respectively.

**Figure 4.1.2.** Preliminary dual-width model (a) parameters and (b) resulting \(EF\) distribution.\(^{121}\)

**Figure 4.1.3.** Summed \(EF\) in gap regions a range of \(w\) combinations and \(\lambda_0.\)\(^{121}\)

Values on the order of \(10^5\) were obtained for the width combinations producing the largest enhancements. It should be noted that the peak width combination range shifts towards
larger structures with increasing incident wavelength. The diagonal lines with a slope of one in plots (a) – (c) correspond to the standard single-width grating case in which \( w_1 = w_2 \). Thus, the points off this line are for dual-width grating geometry combinations. The reader should note the appearance of twin regions of higher enhancement at the edges of plots (a) and (b), as these regions were found to demonstrate the importance of dual-width geometries after further investigation (Figure 4.1.6).121

From the data plotted along the slope equals one lines in Figure 4.1.3, the three curves in Figure 4.1.4 were obtained. Each curve thus represents a constant wavelength, and enhancement values are for \( w_1 = w_2 \), here swept to 1 \( \mu \text{m} \) to further investigate the situation. The three sets of peaks are labeled \( P_0 \), \( P_2 \), and \( P_4 \), corresponding to information that is clarified in Figure 4.1.6. A redshift can be seen for each set of peaks, though the shift is more prominent for larger structure widths.121

![Figure 4.1.4.](image)

**Figure 4.1.4.** Enhancement vs. single-\( w \) for the \( \lambda_0 \) values shown in Figure 4.1.3.121

From the plots in Figure 4.1.4, the \( w \) values were plotted against the peak \( \lambda_0 \) at which
they occur to better obtain an idea of how each set of peaks was optimized for a specific width depending on the incident wavelength. The results were plotted as shown in Figure 4.1.5. The plot hints that each set of peaks likely relies on a different mechanism, as the optimal structure width varies with different slope for each set when the wavelength is increased.\textsuperscript{121}

**Figure 4.1.5.** Plot of $w$ vs. $\lambda_0$ corresponding to the peaks in Figure 4.1.4.\textsuperscript{121}

The off-diagonal enhancement peaks occurring in Figure 4.1.3 were also of interest, so the range for the sweep of width combinations was increased to 1 $\mu$m to obtain a larger dataset. During this study, the 700 nm wavelength was chosen, as it was this case in which the off-diagonal peaks occurred most prominently. The color plot in Figure 4.1.6 displays a few interesting features.

First, there are indeed regions with peak intensity enhancement values existing for width combinations that make up dual-width gratings. Second, some of these regions produce even greater field enhancement than the strongest single-width values, a testament to the tunability offered by this type of fabrication. Third, the negatively sloped diagonal lines correspond to $w$ combinations with constant $P$ (labeled 0 through 4), along which both the single- and dual-width
peaks occur. These lines of constant period correspond to the labels for each set of peaks in Figure 4.1.4. Interestingly, these lines denoting local enhancement maxima almost appear to occur with some periodicity as well. Note the points of interest labeled $A, i, ii, and iii,$ as they will be referenced in Figure 4.1.10.\textsuperscript{121}

![Figure 4.1.6. Optical enhancement color map for larger dual-$w$ sweep.\textsuperscript{121}](image)

The key finding of this study was that, as can be seen in Figure 4.1.6, the maximum enhancement value occurred for a dual-width geometry, not for a case when $w_1 = w_2$. This result alone motivates further study of new fabrication capabilities offered by the nanomasking technique or other methods. Also interesting here was the way in which the enhancement depends on multiple coupled factors, including $P, w_1, w_2$, and the simultaneous coupling of each
parameter’s effects on the resonance of the system.\textsuperscript{121}

The schematic illustration in Figure 4.1.7 serves to define the parameter $x = w_1 + 2g$, which was used to more concisely describe the variation of one grating width while holding the period constant.\textsuperscript{121}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{schematic.png}
\caption{Schematic of dual-$w$ cross-section depicting the relationship between $x$ and $P$.\textsuperscript{121}}
\end{figure}

The parameter $x$ was swept while keeping the period constant at $P_1 = 430$ nm. This means that $w_1$ was increased while $w_2$ was decreased to maintain a constant period, and $g$ was again held constant at 5 nm. Looking back at Figure 4.1.6 and at the horizontal axis values in Figure 4.1.8(a), this sweep corresponds to width combinations following the black dotted line of constant period $P_1$ from the point of interest labeled $A$ to that labeled $iii$. This view more clearly shows the peak location over the range of $w$ combinations. This peak combination was found to be $w_1 = 60$ nm and $w_2 = 360$ nm. Shown in Figure 4.1.8(b) is a plot of the period width values $P_n$ versus the resonance number $n$ as labeled in Figure 4.1.6. This period-dependent resonance exhibits a nearly linear trend here.\textsuperscript{121}

To gain a better understanding of the effects of varying geometrical parameters, a nonperiod model was designed to study the charge distribution for a relatively large structure. The model consisted of a cross section of a Au slab that was 5 $\mu$m wide, retaining the 15 nm thickness used in previous models for the sake of comparison. The primary goal of this test was to measure the natural plasmon wavelength $\lambda_p$ on the surface of the slab for 700 nm incidence.
zoomed in section of the resulting (normalized) charge distribution map is shown in Figure 4.1.9.

**Figure 4.1.8.** (a) Plot of data along the constant period line \( P_1 \) in Figure 4.1.6. (b) Plot of period width vs. resonance number, as labeled in Figure 4.1.6.\(^\text{121}\)

![Normalized Charge](image)

**Figure 4.1.9.** Charge distribution for a 5 \( \mu \)m long Au slab under 700 nm incidence.\(^\text{121}\)

Periodic regions of positive and negative charge can be seen along the length of the slab, and the wavelength of this periodic distribution was found to be \( \lambda_p = 363 \) nm. Recall that this is very close to the width of \( w_2 \) (360 nm) in the optimized dual-width case measured previously. The following adaption from Darweesh et al. describes the insight offered by the measurement of this plasmon wavelength.\(^\text{121}\)

For the standard single-width grating, when \( w_1 = w_2 = \lambda_p \), the enhancement in the gap is a minimum [see Figure 4.1.4]. Here, when the width of the Au structure matches the resonant plasmonic wavelength, this puts the gap at a plasmon node for all the Au structures and therefore minimizes the charge
fluctuations near the gap and the enhancement in the gap. For the dual-width geometry, when one of the gold widths matches closely with \( \lambda_p \), this gives the greatest enhancement. For this situation, when one width is tuned to \( \lambda_p \), the period of the unit cell also can be adjusted independently to the optimum value for \( P \). This allows for a strong signal in the gap because both \( w \) and \( P \) can be adjusted independently and due to coupling between the two gold structures.

Next, charge distribution maps were measured for dual- and single-width gratings as previously modeled. Shown in Figure 4.1.10(a) and (b) are the resulting electric field intensity and charge distribution maps, respectively, for the regions of interest (i) – (iii) as labeled in Figure 4.1.6. It should be noted that for the single-width grating case (iii), both grating structures were found to exhibit a dipolar resonance along the Au width.

![Figure 4.1.10](image-url). (a) Electric field and (b) charge distributions for regions of interest (i) – (iii).\(^{121}\)

These dipolar resonances have two anti-nodes, one near the gap region on either side of a given structure. For dual-width gratings as in (i) and (ii), the symmetry was broken, and a new coupled mode system was demonstrated. Here, the longer structure can support a quadrupolar mode, while the smaller structure continues to support a dipole resonance. This new hybridized mode couples differently than the all-dipole single-width case, allowing for increased
enhancement to be produced. The difference between the field intensities surrounding the structures in each case is clear.\textsuperscript{121}

To better understand the mechanism behind the dual-width geometry’s greater local field enhancement, a model was produced to study the hybridization of modes to compare isolated structures with the sub-10 nm gap dual-width grating. Recalling the discussion of hybridized plasmon modes in Section 2.4, the energy diagram for grating structures shown in Figure 4.1.11 should be compared to that of Figure 2.4.4. As before, the diagram serves more as a conceptual visualization to explain the possible differences between mode types than as a truly quantitative graph. Here, three geometries are shown: (1) a dual-width structure where $w_1 \neq w_2$, (2) a geometry with the same total $P$ but the larger structure removed, and (3) the opposite case in which the smaller structure has been removed. The hybridization that occurs when bringing the two structures close together is shown to offer two different resonance types which could result in lower or higher resonance energies. The charge distributions found previously provide clues that this type of hybridization may occur.

\textbf{Figure 4.1.11.} Depiction of dual-width grating resonance hybridization.\textsuperscript{121}
To test the hybridization concept on the dual-width grating geometry, a model was created in which the local field intensity was again measured in the gap regions between structures, but now for different gap widths. Here, the initial dual-width case which was previously found to produce the optimal field enhancement ($w_1 = 60$ nm and $w_2 = 360$ nm) was selected for $g = 5$ nm. The period for this grating geometry was $P = 430$ nm. This period and $w_1 = 60$ nm were held constant as $g$ was varied, which means that $w_2$ decreased with increasing $g$ ($P = w_1 + w_2 + 2g$). The field was measured over the same integration region for each case.

Additionally, to determine how the coupled structure’s resonances differed from those of isolated nanowires, for each gap value calculated in the dual-width geometry, the same period and gap values were applied to cases in which either $w_1$ or $w_2$ were removed, one at a time. So, for each gap width, three geometries were calculated as those shown in the energy schematic of Figure 4.1.11. The depictions in Figure 4.1.12 also demonstrate the three geometries modeled for a given gap width.\textsuperscript{121}

The electric field intensity distribution plots in Figure 4.1.12 were calculated over a range of gaps. Values of $g = 5$ nm, 20 nm, and 50 nm are shown here, as the intensity enhancement can clearly be seen to increase significantly for the lower gap size. Notably, however, the enhancement near the isolated $w_1$ and $w_2$ structures was not nearly as significant as that for the dual-width grating.\textsuperscript{121}

Also the case for the results shown in Figure 4.1.12, the incident wavelength was swept over a large enough range to obtain spectral peaks for each geometry and gap width. From the dashed boxes, as shown in Figure 4.1.12, which were the same size for each geometry, the intensity enhancement was summed over all mesh points within the box. The distributions shown in Figure 4.1.12 correspond to the incident wavelengths that output the maximum enhancement.
values summed within the gap regions.

**Figure 4.1.12.** Field distributions for single- and dual-width structures at different $g$.  

The waterfall plot in Figure 4.1.13 shows the results of the study as $\sum \left( \frac{E}{E_0} \right)^2$ versus $\lambda_0$ with the same three gap widths as shown before, $g = 5$ nm, 20 nm, and 50 nm. The plot for the case of isolated $w_1$ in each case remains the same, as increasing the gap by decreasing the size of a nonexistent $w_2$ has no effect on the resonance of two 60 nm structures separated by 370 nm. The curves corresponding to isolated $w_2$ structures do change, however, as the value was decreased with each increase in $g$. The $w_2$ curves redshift for longer widths, as one would expect for isolated plasmonic resonances. The intensity distributions associated with the spectral peaks of the dual-width curves (a), (b), and (c) are shown to the right of the plot.  

The dual-width curves offer the greatest insight into the hybridized nature of the resonances. The $g = 5$ nm resonance wavelength has been redshifted from the isolated $w_1$ peak.
by about 100 nm, as well as increasing the peak amplitude by approximately 300 percent. The amplitude increase is ever greater when compared to the $w_2$ resonance. As the gap width increases from 5 to 20 and then to 50 nm, the dual peak can be seen to approach the location and shape of the $w_1$ curve. This is intuitive because as the size of $w_2$ decreases and $g$ increases, the dual-width grating becomes closer and closer to the same situation as the isolated $w_1$ structure. If the gap were increased so much that $w_2 = 60$ nm, then the dual grating would be made up of two 60 nm Au structures, separated by large gaps, which is the same as the $w_1$ isolated structure case. Thus, it was concluded from the data that the combination of both geometries in a dual-width grating structure results in a hybridized plasmonic resonance that differs from the modes associated with either individual structure if the other were removed.\textsuperscript{121}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure4.1.13.png}
\caption{Constant $P = 430$ nm grating spectra with $w_1$ or $w_2$ removed or the full dual-width grating, displaying a hybridization red-shift. (a) $g = 5$ nm, (b) $g = 20$ nm, (c) $g = 50$ nm.\textsuperscript{121}}
\end{figure}

When the structure is designed to have the peak resonance at a specific incident
wavelength, the enhancement can be maximized. The plot of \( \sum \left( \frac{E}{E_0} \right)^2 \) versus \( g \) in Figure 4.1.14 displays the difference between enhancement values at the peak wavelength and at \( \lambda_0 = 700 \) nm, as many of the preliminary results were obtained for this incident wavelength.

![Figure 4.1.14. Plot of summed enhancement vs. \( g \) for \( \lambda_0 = 700 \) and \( \lambda_{peak} \) for four \( g \) values.](image)

Since through the development of this study, the geometry was optimized for 700 nm incidence, the peak value for a gap of 5 nm occurs at 700 nm. As the geometry deviates from this point, however, the optimization shifts from 700 nm to other wavelengths, as shown by the peak positions and color maps in Figure 4.1.13. This serves as a reminder that, while the nanomasking fabrication technique offers versatility in designing structures for optimized resonance at specific light wavelengths, one geometry configuration is not likely to be optimized for two or more different incident frequencies, or therefore two different applications.\(^{121}\)

The development and study of dual-width gratings with sub-10 nm gaps was thus demonstrated, and the potential benefits of such a geometry and a fabrication technique were
illuminated regarding the potential to optimize devices for desired light amplification applications. The theoretical light enhancement increase of approximately 450% should be considered extremely beneficial to device development based on lithographic techniques such as nanomasking for boosting SERS sensitivity.

4.2 Incorporation of Substrate Materials

To further engineer optical enhancement for small gap gratings, models were advanced to incorporate the substrate and other materials, more accurately representing the fabricated devices. First, the Au structures were simulated as being situated atop a layer of SiO$_2$ with air as the surrounding medium above the substrate. Experimental data for the complex refractive index $\tilde{n}(\omega)$ was used for the silicon dioxide region, and a real refractive index of one was applied to the air space. Again, perfectly matched layers were applied to the top and bottom of the model, with periodic boundary conditions applied to the horizontal boundaries. A schematic of the updated model is shown in Figure 4.2.1(a). The results of a single-width sweep were plotted in (b) as the gap region summed enhancement versus $w$, again for 700 nm light incidence. The same type of trend appears as for the model with a surrounding medium, so this was a useful check when advancing the simulation to incorporate the additional material parameters.

The same type of dual-width geometry sweep was conducted for the updated model with air and SiO$_2$ to check for the presence of increased enhancement off the $w_1 = w_2$ diagonal line. The color map in Figure 4.2.2 shows the summed enhancement values in the gap region now for the model incorporating a substrate and air as opposed to an effective surrounding medium. Here, $w_1$ and $w_2$ were swept from 10 to 800 nm. Again, dual-$w$ combinations were found to produce greater enhancement peaks than the single-$w$ peaks overall. This was a promising result
to motivate further advancements to the model which would more accurately represent a physically fabricated sample.\textsuperscript{121}

\textbf{Figure 4.2.1.} Incorporation of surrounding media. (a) Depiction of the updated model. (b) Enhancement results calculated for $w_1 = w_2$.\textsuperscript{121}

The next step in more accurately modeling dual-width gratings was to incorporate the full Si/SiO\textsubscript{2} substrate as well as the Ti adhesion layer used in fabrication to adhere Au to the surface. These additions were important, as the multilayer substrate can have resonance cavity effects of its own, affecting the overall enhancement, and the Ti layer typically damps the plasmon resonances of Au. The damping effect, as discussed in previous work, can be lessened by decreasing the thickness of the Ti layer to be as thin as possible while still providing sufficient adhesion. In practice, a 1 nm layer is typical, and by previous simulations, this reduces the Ti damping to a suitable level.\textsuperscript{122}

In the next advancement of the model, the incident wavelength was also set to 785 nm to begin studying structure optimization for Raman spectroscopy. This wavelength was chosen based on the diode laser implemented in the custom experimental Raman setup, which was designed as described in Section 5.2. Figure 4.2.3 shows a schematic drawing of the model
geometry where the 3D depiction in (a) makes note of the fact that the laser spot was able to cover multiple periods of the grating, depending on the $w$ values, and (b) is a cross section of (a).

Figure 4.2.2. Dual-$w$ enhancement color map incorporating surrounding materials.\textsuperscript{121}

Here, additional variables were established to account for the additional materials. Importantly, the thickness of the silicon dioxide layer is represented by $t_{\text{SiO}_2}$. Now, the gap width was changed to $g = 8$ nm, more closely representing the experimentally realized structures created via nanomasking. The other parameters were kept as described in Section 4.1, and the Ti thickness was held constant at 1 nm. The top and bottom of the model, as previously, were designed to absorb all light coming into contact with the boundaries, so that the air and Si regions were simulated to be infinitely thick.\textsuperscript{123}

With additional design parameters was inevitably coupled additional optimization
capability for the updated model. In addition to seeking the optimal $w$ combinations, $t_{SiO_2}$ was able to be considered in the engineering picture. Now, varying the oxide layer between an air-substrate interface is known to produce thin film interference effects, such as the color variation seen across a puddle of oil on water or a soap bubble. In the same fashion, in fact, the color visible to a person holding a Si wafer with a uniform SiO$_2$ layer is known to be one method for determining the oxide layer thickness. This relates to the way in which a light wave is reflected from the SiO$_2$/air interface and transmitted through the oxide layer while simultaneously being reflected at the Si/SiO$_2$ interface. The reflected waves of a given incident wavelength interfere constructively or deconstructively depending on the oxide layer thickness, thus resulting in only constructively interfered light wavelengths returning to the eye of the person holding the wafer. As this phenomenon depends on incident wavelength, it is periodic with increasing oxide thickness. Therefore, the expected result for optical enhancement in the gap between grating structures atop the substrate was expected to be periodic with increasing $t_{SiO_2}$.$^{25,26}$

Figure 4.2.3. Schematic of full Si/SiO$_2$/Ti/Au/Air system as modeled: (a) 3D (b) cross section.$^{123}$

The simulation was run first for a single-width grating with $w$ swept from 20 to 250 nm,
where 20 nm is already below the fabrication resolution of many techniques, so going smaller than this was deemed unnecessary. Additionally, $t_{SiO_2}$ was swept from 0 to 800 nm. The results of this calculation are shown in Figure 4.2.4. Field intensity distributions are shown in Figure 4.2.4(a) where (i) – (iii) correspond to points of interest on the color map of $t_{SiO_2}$ versus $w$ shown in (b). These distributions thus correspond to specific combinations of $t_{SiO_2}$ and $w$, (i) being the peak enhancement, (iii) one of the lowest, and (ii) falling somewhere in the middle.

![Figure 4.2.4](image_url)

**Figure 4.2.4.** Computational results for sweeping $t_{SiO_2}$ and single-$w$.\(^{123}\)

Note that for this simulation, the results plotted in the color map are for the average field intensity enhancement over the gap region $(E/E_0)^2$ as opposed to the sum of mesh point values, as previously shown. It was deemed that the average over the gap region was more relevant to SERS signal enhancement, as analyte molecules may experience electric field values at different gap regions simultaneously but not as an added field due to all points within the region. The data plotted as a gray sinusoidal line in Figure 4.2.4(c) shows $t_{SiO_2}$ versus $(E/E_0)^2$ for data along the $w = 40$ nm dashed gray line in (b). The dashed blue line in (b) and (c) serves as a guide to note
that the peak along the periodic curve in (c) matches the peak of the color map, which also corresponds to the distribution shown in (i). Thus, varying the oxide thickness gave the expected periodic variation in enhancement.  

The dual-width case was then studied for the updated model. As the oxide thickness of 330 nm was found to produce the largest enhancement, it was chosen to be held constant at this value during the $w_1$ and $w_2$ sweeps. The results of this test are shown in Figure 4.2.5. In (a) are shown intensity enhancement plots corresponding to points (i) – (iv) in part (b). Here, (i) shows the point of least enhancement, (ii) and (iii) show points along the $w_1 = w_2$ line, and (iv) shows the dual-width combination producing the greatest enhancement, that when one structure is 70 nm and the other is 410 nm. This result clearly differs from the previous dual-width model, demonstrating that it is important to incorporate the substrate and all surrounding materials in any attempt to engineer signal enhancement for a given plasmonic device.  

The plots of average gap region intensity enhancement versus $w_1$ in Figure 4.2.5(c) correspond to data taken along the dashed blue diagonal line along single-width combinations and the dashed green line for $w_2 = 70$ nm in part (b). The part (c) $y$-axis is aligned with the color bar for part (b). The comparative plots in (c) demonstrate that once again, with all surrounding materials included, the dual-width grating outperforms the single-width case in terms of maximum gap-region enhancement produced.  

While the dual-$w$ case was found to produce greater optical enhancement than single-$w$ for the constant $t_{SiO_2} = 330$ nm, the true optimization was still needed for $w_1$, $w_2$, and $t_{SiO_2}$ together. Thus, the oxide thickness was swept from 250 to 500 nm, corresponding to the enhancement troughs adjacent to the 330 nm peak in the single-width case. At each thickness, both $w_1$ and $w_2$ were swept as in Figure 4.2.5. The peak enhancement value was obtained for
each \( t_{SiO_2} \) and the corresponding dual-width values were marked as well. First, the peak enhancement values were plotted versus \( t_{SiO_2} \) for each optimized dual- and single-width case. The blue curve in Figure 4.2.6 shows the optimized enhancement values for dual-\( w \) and the red curve shows the results for single-\( w \), for comparison, as in Figure 4.2.4(c). It can be seen that the dual-width optimization produces greater enhancement than single-width optimization for all oxide thicknesses. Important to recognize, as well, is the even larger enhancement increase that was obtained by optimizing \( w_1 \) and \( w_2 \) with a different oxide thickness than the original 330 nm, which appears to only be optimal for the single-width case. Thus, it requires engineering gratings which carefully address all three geometric variables in order to obtain the greatest local field intensity in the nanogaps.¹²³

![Figure 4.2.5](image)

**Figure 4.2.5.** Computational results for optimized \( t_{SiO_2} \) and sweeping dual-\( w \).¹²³

The optimization process revealed the interesting result that for dual-width grating engineering, the optimal \( w_1 \) and \( w_2 \) values remain quite consistent over the full range of oxide
thicknesses. The plot in Figure 4.2.7(a) shows the same data as the blue curve in Figure 4.2.6, but with data points shown at each oxide thickness. Each of these data points corresponds to a pair of points at the same $t_{SiO_2}$ in Figure 4.2.7(b), which describe the values of $w_1$ and $w_2$ for optimal enhancement at each thickness. For average optimal values $w_1 = 72.08$ nm and $w_2 = 409.17$ nm, the standard deviations were 3.80 and 10.96 nm, respectively. Thus, the dual-width combination was able to be determined and then the oxide thickness optimized separately with negligible effect on the best widths.

**Figure 4.2.6.** Peak enhancement values vs. $t_{SiO_2}$ for dual- and single-$w$ optimization.\textsuperscript{123}

**Figure 4.2.7.** Plots of optimized (a) enhancement and (b) widths both vs. $t_{SiO_2}$. 
Thus, by optimizing the plasmonic nanostructures with the substrate, the optical enhancement can be improved by approximately 200 – 300%. This important consideration should not be overlooked when designing devices such as surface-enhanced Raman spectroscopy substrates, as it is a simple, cost-effective way to boost the signal strength without requiring additional lithography steps, etc..\textsuperscript{123}

### 4.3 Additional Grating Considerations

When it comes to simulating SERS substrates, there is some contention as to whether it is sufficient to calculate enhancements based solely on hotspot regions, or if the enhancement values over the entire substrate surface should be averaged to obtain the overall response. In this section, the latter method, surface averaged enhancement, was utilized to produce additional parametric grating studies. The depictions in Figure 4.3.1 demonstrate the different locations over which the enhancement is obtained in each case. Figure 4.3.1(a) shows a dashed red box near the gap region, as summation and average results were obtained in the preceding sections. This is technically considered a volume average or summation, as the model is assumed to extend into and out of the screen/page to a very large relative length. The dashed red contour in (b) demonstrates the path along which all mesh points were averaged to obtain a surface averaged enhancement from such a 2D model.\textsuperscript{124}

The model was designed in the same fashion as previously for studying oxide layer thickness along with other parametric sweeps, as shown with the variables again labeled in Figure 4.3.2(a). The incident wavelength was again held constant at 785 nm, as corresponded to the Raman spectroscopy experimental setup. With the updated surface average method for computing enhancement over the entire structure, single-width sweeps were studied.
Representative resulting intensity enhancement distributions near the gap region are shown in Figure 4.3.2(b) (i) – (iii) for \( w_1 = w_2 \) at 50, 200, and 400 nm.\(^{124}\)

**Figure 4.3.1.** Schematics of (a) volume and (b) surface average data calculation regions along the red dashed lines.

**Figure 4.3.2.** (a) Model schematic and (b) resulting enhancement distributions.\(^{124}\)

One additional study that was conducted involved testing larger gap widths than the sub-10 nm values which had been used up to this point. The data obtained by sweeping \( w_1 = w_2 \) for different gap values, \( g = 10, 50, 100, \) and \( 500 \) nm, was plotted together in Figure 4.3.3(a) as \( \frac{\langle E \rangle^2}{E_0} \).
versus $w = 0$ to 600 nm. Each gap width can be seen to result in a different enhancement peak at a different width, and additional smaller enhancement peaks can be seen at widths greater than 400 nm. Figure 4.3.3(b) shows that for values of $w < 400$ nm, the enhancement is always greater for a given $g$ value if the width is at the optimal value, as opposed to being held constant at $w = 50$ nm, which was only the optimal width for $g = 10$ nm.$^{124}$

![Figure 4.3.3](image.png)

**Figure 4.3.3.** Surface-averaged enhancement vs. (a) $w$ and (b) $g$.\textsuperscript{124}

Next, both $w$ and $g$ were swept from 0 to 600 nm to optimize the parameters with $t_{SiO_2}$, which was swept from 0 to 800 nm. From these calculations, color maps were created for three different oxide thicknesses, $t_{SiO_2} = 330$, 290, and 250 nm, as plotted in Figure 4.3.4 (a), (b), and (c), respectively. The overall enhancement for all $w$-$g$ combinations can be seen to decrease for the thinner oxide layers, as well as the peak value.$^{124}$

The results for the full oxide thickness sweep are shown in Figure 4.3.5. In (a), the color map plots surface averaged enhancement for $w$ vs. $g$ over the simulated range with $t_{SiO_2} = 200$ nm. Here, the dashed white line shows data at constant period $P = w + g = \lambda_0$, along which a
line of slight enhancement can be seen to follow. Points of interest (i) – (iii) correspond to plots of enhancement vs. oxide thickness where the values of \( w \) and \( g \) were selected and held constant based on these regions of (i) maximum, (ii) medium, and (iii) minimum enhancement from part (a). Thus, the curves in (b) correspondingly display periodic trends with different average enhancement values. The values of \((w, g)\) were \((70, 10), (150, 320),\) and \((200, 200)\) for (i), (ii), and (iii), respectively.\(^{124}\)

![Figure 4.3.4](image)

**Figure 4.3.4.** Surface-averaged enhancement for \( t_{SiO_2} \) = (a) 330, (b) 290, and (c) 250 nm.\(^{124}\)

Parts (c) and (d) in Figure 4.3.5 display the same type of study as that in (a) and (b), but for a starting oxide thickness of 330 nm, which was previously demonstrated to be the optimal value in the dual-width study (Section 4.2). First, one should note the increase in maximum enhancement for the optimal region in color map (c) compared to that in (a). This demonstrates that the 330 nm oxide thickness was more optimal for producing enhancement overall compared to \( t_{SiO_2} = 200 \) nm.

One could have determined this as well from the curves in Figure 4.3.5(b), as the periodic curves reach a peak at 330 nm but exhibit troughs at 200 nm. The key in this secondary portion of the study was that \( w \) and \( g \) could now be optimized with the greater enhancement produced.
by utilizing the proper oxide thickness, further increasing the local field strength. The curves plotted in (d) correspond to points of (iii) minimum, (iv) medium, and (v) maximum enhancement as shown in (c). It should be noted that point (iii) holds constant $w = 200$ nm and $g = 200$ nm for all four quadrants in Figure 4.3.5.\cite{124}

**Figure 4.3.5.** Enhancement color maps and plots for varying $w$, $g$, and $t_{SiO_2}$.\cite{124}

One can see that by using the ideal oxide thickness, the medium range enhancement values can be brought close to the maximum values for when a less optimal oxide layer was modeled. Further, the maxima of curve (v) in Figure 4.3.5(d) demonstrate that fully optimizing
the grating (even if just for a single-width, large gap grating) can significantly improve the local field intensity enhancement values. Also, by comparing (b) and (d), it is apparent that the same oxide thicknesses correspond to peaks and troughs in either case. Thus, it can be said that the structure was fully optimized by the sweeps conducted. Interestingly, looking at curve (iv) in (d) in comparison to curve (i) in (b), one may note that even for the much larger $g$ value associated with (iv), the enhancement maxima surpass the minimum values of (i), simply by optimizing the oxide layer. One key development here is that, while sub-10 nm gaps produce the greatest local field enhancements, it can still be possible to take advantage of optimized structures at larger gap values which can typically be more easily fabricated using standard techniques.

4.4 Nanogap Grid Structures

Preliminary design work was undertaken for the type of nanogap grid structures as shown to have been fabricated by nanomasking in prior work and discussed here in Chapter 3. The nanogrid structure was of interest due to its ability to simultaneously produce many nanogaps over a large area. After the benefits of dual-width gratings were determined, it was expected that introducing an additional design parameter, modeling the grids in three dimensions, would be able to provide further optimization of light enhancement. The thought in this case was that introducing additional structure edges into the design would provide additional regions for SERS signals to be enhanced, as well as taking advantage of another directional resonance when optimizing hybridization of modes between structures. Conceptually, the existence of multiple hotspots across the substrate would then look something like the depiction shown in Figure 4.4.1.

The three-dimensional model created to conduct preliminary calculations for this type of structure was set up as a unit cell with mirror boundary conditions, thus containing half widths of
each metal structure, $w_{1x}$ and $w_{2x}$, and the gap between structures $g$. The other structure dimensions, $w_{1y}$ and $w_{2y}$, were also variable. Two-dimensional optimization between the four structure widths became the updated engineering problem. The geometry of the model as created in COMSOL is shown in Figure 4.4.2.

![Figure 4.4.2. Depiction of nanogap grid structure with large area of hotspots.](image)

Again, a Ti adhesion layer was added between the Au and SiO$_2$, which was designed atop an infinitely thick Si substrate, with infinite air space simulated above the structures. Rounded corners with a radius of 4 nm were applied in this model to more accurately represent the fabricated structures. The initial model was set with parameters $w_{1x} = 410$ nm and $w_{2x} = 70$ nm, matching the ideal dual-width combination determined via the two-dimensional results discussed in Section 4.1. Here again, $g$ was set to 8 nm to most closely model the fabricated structures.

The appropriate material properties were applied to the model as described, with frequency dependent optical properties from experimental results used as in the two-dimensional models. The grid structures with Au material properties applied were selected as shown in Figure 4.4.3(a). The mesh was applied using a free tetrahedral arrangement, as was the case for two-
dimensional models as well. A different view is shown in Figure 4.4.3(b) for the model with the mesh applied, and the mesh becomes finer near the metallic structures.

![Figure 4.4.2. Nanogap grid computational model unit cell design.](image)

**Figure 4.4.2.** Nanogap grid computational model unit cell design.

![Figure 4.4.3. Views showing (a) selected Au material regions and (b) mesh applied to the model.](image)

**Figure 4.4.3.** Views showing (a) selected Au material regions and (b) mesh applied to the model.

The preliminary results obtained via this model were obtained by computing a parametric sweep of $w_{2y}$ from 40 to 90 nm with all other parameters held constant at the optimal dual-width geometry combination as mentioned above for the incident light wavelength of 785 nm. As the primary regions of interest were the gaps between structures, electric field enhancement distributions were plotted as $x$-$y$ slices for each value of $w_{2y}$ as shown in Figure 4.4.4.
The areas of greatest enhancement (≈1×10⁴) were found to be mostly concentrated within the gap between structures, but as \( w_{2y} \) increases, more closely representing a dual-width grating, it can be seen in the grid model that the greatest enhancement becomes concentrated near the rounded corner of the secondary structure. As \( w_{2y} \) decreases, the gap region is most filled with enhanced field strengths exceeding the maximum values for the larger \( w_{2y} \) cases. Thus, the preliminary simulation result provides an indication that the ideal structures will likely
incorporate this additional geometrical parameter, so it should be taken into further consideration.

For the model discussed so far, the surface-averaged enhancement to the fourth power was calculated over the Au surfaces not tangent to the model boundaries, the true edges exposed to air for real fabricated structures. The resulting plot of enhancement versus $w_{2y}$ for the optimized dual-width $x$-direction values is shown in Figure 4.4.5.

![Graph](image)

**Figure 4.4.5.** Surface-averaged enhancement versus $w_{2y}$ for the design shown in Figure 4.4.4.

The enhancement values were found to exhibit a nearly exponential increase with decreasing $w_{2y}$, as shown by the field distributions in Figure 4.4.4. Additional preliminary sweeps were run for the 3D grid model to obtain an idea of how changing multiple variables simultaneously affected the local electric field. First, the value of $w_{1x}$ was changed and held constant at 40 nm, on the low end of feasible fabrication resolution for the lithography equipment typically used at the University of Arkansas. Sweeps of $w_{2y}$ were run from 40 to 180 nm for different values of $w_{2x}$ ranging from 50 to 150 nm. This, therefore, modeled a dual-width grid
situation for combinations not previously considered optimal during the 2D grating calculations. Adding in the $y$-direction sweeps provided additional insight.

Figure 4.4.6 displays comparative plots of (a) extinction cross section and (b) surface-averaged enhancement obtained for the grid structures under the simulated geometrical conditions. Interestingly, for both plots there is a notable shift to lower extinction/enhancement with increasing $w_{2x}$, except when it is changed from 50 to 60 nm. Perhaps the results were an indication of an optimal width near 60 nm, as was the case for one of the dual-width structures in the 2D work. Additional studies will be required to further examine these trends and produce results with finer sweep conditions.

![Graph](image)

**Figure 4.4.6.** Plots of (a) extinction and (b) enhancement vs. $w_{2y}$ for various $w_{2x}$; $w_{1x} = 40$ nm.

One final set of preliminary sweeps was performed for the nanogrid model, this time setting $w_{1x} = w_{2x}$ for a range of values from 40 to 150 nm. The results of this study were somewhat less consistent between the extinction trends, shown versus $w_{2y}$ in Figure 4.4.7(a), and the enhancement trends as shown in (b). Here again, it may be noted that there appears to be
an increase in both trends towards $x$-direction widths of 50 or 60 nm, but the extinction plot demonstrates another large increase for the case when both widths equal 150 nm, which was not found for the enhancement results.

It should be noted that sweep errors occurred for the 50 nm and 150 nm cases, causing the data to end abruptly on both plots. Again, additional studies will be required to better understand the optimization problem for these types of nanogrid structures, but these preliminary results demonstrate that the ability to manipulate both $x$ and $y$ dimensions of the nanostructures provides additional enhancement engineering utility to the nanomasking technique. Also, future work with these 3D models will incorporate surface roughness to increase the accuracy of the model.

![Figure 4.4.7. Plots of (a) extinction and (b) enhancement vs. $w_{2y}$ for varying $w_{1x} = w_{2x}$.](image)

4.5 Tunable Nanogap Au Metasurfaces

The Au nanosphere metasurfaces with tunable gaps mentioned in Section 3.4 were simulated in a three-dimensional model by breaking down the close-packed repeating structure
into a hexagonal unit cell. The material properties of the spheres were set to Au with the surrounding material set to an effective lossless refractive index ($n = 1.44$) corresponding to that of the alkanethiol ligand shells connecting each sphere. The metasurface layer was simulated as having air above and a lossless glass or SiO$_2$ substrate layer ($n = 1.53$) below.

Figure 4.5.1 shows a top-down cross-sectional view of the modeled unit cells for a center sphere surrounded by different numbers $N$ of neighboring spheres in the close-packed structure (separated by tunable gap widths). The model was set up with these different unit cells to calculate the difference in absorbance for each case with the hypothesis that a hybridization effect would be noticeable as the hexagonal structure was filled in.

![Metasurface unit cells as modeled for different numbers of removed spheres.](image)

**Figure 4.5.1.** Metasurface unit cells as modeled for different numbers of removed spheres.

Due to the symmetry of the system, the model was established with mirror boundary conditions so that an infinitely periodic metasurface was simulated. The cross-sectional top view depictions in Figure 4.5.2 show multiple periods of the unit cells shown in Figure 4.5.1, mirrored at the boundary of each unit cell. The electric field distributions in each unit cell are mirrored in this same way upon calculation.

The resulting absorbance spectra calculated for each of the unit cells shown above are plotted in Figure 4.5.3. The results are plotted together on the same scale in (a) and split up into a normalized waterfall plot in (b) to illustrate the peak shift. The expected redshift occurs as more nanospheres are added to the model, indicating the type of hybridization of modes that tends to
occur for nanogaps between structures. Interestingly, double peaks were found for some of the spectra, also seemingly blue-shifting out of the simulated range with decreasing nanosphere number.

**Figure 4.5.2.** Mirror boundary conditions visualization of close-packed hexagonal metasurface for different numbers of spheres removed from the unit cell.

The peak absorbance values were obtained and plotted versus wavelength in Figure 4.5.4(a), and these peak wavelengths were plotted versus unit cell nanosphere number in (b). The second plot helps to illustrate the larger peak shift for $N = 0, 1, \text{ and } 2$ and how the shift decreases for greater $N$. Also, this simulation serves as a nice test of the calculation’s accuracy because the absorbance peak $N = 0$ in the unit cell was found to occur at 540 nm, which is in the right range for an isolated Au nanosphere.

Next, all spheres were again present in the unit cell. In fact, since the previous tests were no longer required, the unit cell was reduced to that of two quarter spheres, as shown in Figure
4.5.5 where (a) shows the geometry with the Au material regions highlighted in blue, and (b) shows the model with the mesh applied. The coordinate axis is shown in both images, and as a reminder, \( \vec{k} \) was in the \(-z\)-direction and the incident field \( \vec{E}_0 \) was able to be polarized in either \( x \) or \( y \). With mirror boundary conditions applied, this reduced unit cell still corresponds to the same hexagonally closest-packed metasurface previously modeled by the expanded model.

Figure 4.5.3. Absorbance spectra for different numbers of removed spheres in the unit cell.

Figure 4.5.4. Plots of (a) peak absorbance and (b) the wavelength at which the peaks occur for the data plotted in Figure 4.5.3.
For the next computational results discussed in this work, the Au sphere diameter was set to 15 nm. Because the metasurfaces can be fabricated with a range of gap widths based on the alkanethiols used during self-assembly, the absorbance spectrum was calculated for gaps ranging from 0.3 to 3 nm. The results, plotted in Figure 4.5.6, demonstrate the expected red-shift as the gap width decreases, and an increase in peak absorbance is also visible with decreasing gap, though this effect begins to taper off below 1 nm gap width. The red-shift is expected due to the same hybridization of plasmon modes discussed in Section 4.1 for lithographically defined nanogratings.

The wavelengths at which absorbance peaks were found in Figure 4.5.6 were plotted versus gap width for the same 15 nm diameter metasurface as well as for a diameter of 13.3 nm, which matches the structures fabricated as described in Section 3.4 and characterized optically as described in Section 5.3. The peak wavelength plots are shown in Figure 4.5.7, demonstrating the slight spectral shift caused by varying the Au sphere diameter.

In the interest of SERS signal enhancement across an entire metasurface, the average enhancement factor to the fourth power was calculated over the entire surface of the Au spheres.
within the unit cell, $\left(\frac{E_{\text{surface}}}{E_0}\right)^4$. The surface-averaged enhancement spectra were calculated for each gap width from 0.2 to 3 nm. The results are plotted in Figure 4.5.8 with the directly calculated values shown in (a) and $\log\left(\frac{E_{\text{surface}}}{E_0}\right)^4$ in (b). Again, with decreasing gap, a redshift can be seen in the peak enhancement, with a secondary peak eventually moving into the simulated range.

**Figure 4.5.6.** Absorbance spectra for Au metasurface gap widths from 0.3 to 3 nm.

**Figure 4.5.7.** Peak absorbance wavelength vs. gap width for Au diameters of 15 and 13.3 nm.
The summation was calculated for the enhancement values over each spectrum in Figure 4.5.8, and the resulting $\sum_{\text{spectrum}} (E_{\text{surface}} / E_0)^4$ values were plotted on a log scale versus gap width in Figure 4.5.9. The exponential increase in surface enhancement with decreasing gap width can clearly be seen in this plot. This corresponds well with previous work demonstrating the increased local field enhancement for small gap widths as described in Section 2.4. This was a good indication of the potential enhancement offered by Au metasurfaces for SERS.

**Figure 4.5.8.** (a) Normal and (b) log plots of surface-average enhancement spectra for gap widths from 0.2 to 4 nm.

In the interest of modeling the Raman spectroscopy setup that was built in the Herzog Lab, the incident simulation wavelength was set to 785 nm and the enhancement versus gap width was again analyzed. Here, two models were compared; in one, a finer mesh was used, significantly increasing the computation time. The results of the models were plotted in Figure 4.5.10 with normal y-axis in (a) and log scale in (b). The red curve displays the data calculated via the finer mesh, and the coarse mesh data is in blue. While there is some variation in the overall enhancement values at a given gap width, the overall trends are comparable in either
case. The exponential increase in enhancement can again be seen with decreasing gap width, regardless of the mesh applied to the calculation.

**Figure 4.5.9.** Surface-averaged enhancement summed over Figure 4.5.8 spectra vs. gap width.

**Figure 4.5.10.** (a) Normal and (b) log plots of surface-average enhancement vs. gap width calculated using coarse (blue) and fine (red) mesh for incident wavelength 785 nm.

Enhancement field distributions were obtained using a top-down cross-sectional view, corresponding to a slice in the x-y plane in Figure 4.5.5, of the reduced unit cell model for different gap widths $g$ at the incident wavelength of 785 nm. The plots shown in Figure 4.5.11 display the results for gap widths of 0.2, 0.4, 0.6, 0.8, 1.0, 1.4, 2.0, and 3.0 nm.
Figure 4.5.11. Enhancement $(E/E_0)^4$ distributions for gap widths from 0.2 to 3 nm.
The scale, quantified by the color bar, was the same for all images in the figure. As can be seen in the enhancement distributions, the greatest field strength is localized in the smallest gap regions for all cases. For small gaps, the maximum field region is highly localized in the gap, and the high intensity regions increase in size as $g$ increases. Simultaneously, the enhancement rapidly decreases, becoming barely visible for the 3 nm gap width on this color scale.

These results make sense when considering the exponential plots of enhancement or absorption versus gap width shown previously. The strong hybrid plasmon modes resonant across structures in the metasurface for decreasing gap widths exhibit greatest localized field enhancement by most efficiently absorbing light energy to excite the corresponding modes.

### 4.6 Nonlocal Model for Nanoplasmonics

By the standard model used throughout this section in modeling the optical responses of metasurfaces under different conditions, it has been shown that decreasing the gap between structures results in a seemingly endless increase in the localized and surface-averaged electric field enhancement. One may guess – and experimental results have demonstrated – that this enhancement increase does not continue indefinitely to such small sub-nm scales. In fact, the enhancement curve tends to taper off as the gap width decreases beyond a certain point. The classical Drude model often applied to situations involving plasmonic nanostructures and gaps is considered to be localized at the surface of the metallic structure under study. In this way, the surface charge density is typically pictured, and mathematically treated, as being compressed into an infinitesimally thin layer at the surface. In reality, charge density oscillations are not perfectly confined to the surface as the classical model suggests but take place over some thickness into the material.
As reported by prior theoretical developments, the consideration of electron interactions farther into the material from the surface has the effect of reducing the potential field enhancements.\textsuperscript{125–127} The ‘nonlocal model’ was established as a more accurate description which takes into account electron-electron repulsion resulting from the Pauli exclusion principle by which no two fermions may occupy the same quantum state at a given time. This repulsion and that of the Coulomb force between electrons manifest as a pressure in the sea of electrons, which resists compression in the presence of an incident electromagnetic field. This electron pressure may be described mathematically by a hydrodynamic model, as described by Ciraci et al.\textsuperscript{128} As for the Lorentz oscillator term described mathematically in Section 2.3, this model is implemented as an additional term in the equation describing induced currents $\mathbf{J}$ in a metal under the presence of an electric field $\mathbf{E}$ oscillating at a frequency $\omega$. This additional consideration is shown in Equation 50.

$$\beta^2 \nabla (\nabla \cdot \mathbf{J}) + (\omega^2 + i\gamma_\text{c}\omega)\mathbf{J} = i\omega\omega_p^2\varepsilon_\text{0}\mathbf{E}$$

(Equation 50)

Here, the frequencies $\omega$ and $\omega_p$, damping coefficient $\gamma_\text{c}$, current density, field, and vacuum permittivity are as defined in Chapter 2 and appear in the conventional Drude formula for the complex frequency-dependent permittivity. In this equation, $\beta$ is a term related to the electron pressure. The pressure term is related to the Fermi velocity, $v_F$, where the value of $\beta$ is close to the speed of sound in the Fermi-degenerate plasma of conduction electrons in the metal. The result of including this additional pressure term is that the electric permittivity becomes dependent on the longitudinal depth into the material, now becoming a function of the incident wave propagation vector $\mathbf{k}$. The complex permittivity then takes on separate transverse $\varepsilon_T$ and longitudinal $\varepsilon_L$ forms, where the transverse form is unchanged from the Drude model and $\varepsilon_L$
appears as in Equation 51.

\[
\frac{\tilde{\varepsilon}_L(k, \omega)}{\varepsilon_0(\omega)} = 1 - \frac{\omega_p^2}{\omega^2 + i\omega \gamma_e - \beta^2 |k|^2}
\]  

(Equation 51)

This adjustment to the dielectric function serves to treat the surface charge layer as more of a volume charge density with a thickness into the metal determined by \(\beta / \omega_p \propto \lambda_{TF}\). Here, the Thomas-Fermi screening length \(\lambda_{TF} = v_F / \omega_p\) is on the order of 1 Å. Thus, subnanometer length scales are considered via this additional term within the permittivity. This serves as a semi-empirical model which accounts for quantum mechanical effects. While in some additional semi-empirical treatments tunneling currents between adjacent nanostructures are considered as well, prior reports have demonstrated that experimental results match closely with the hydrodynamic model considered here with no need for the inclusion of tunneling contributions.\(^{114,128–131}\) This suggests that, at least for the length scales considered in the previous work, gap widths of approximately 1 Å to 10 nm, the electronic pressure effect dominates the experimental results over any tunneling effects. It is fair to note, however, that for smaller dimensions or different geometries than considered in these works, tunneling may provide a significant contribution that must therefore be considered.

Equation 51 for the nonlocal model was implemented in electromagnetic models as part of this dissertation work studying the tunable Au metasurfaces described in Sections 3.4 and 4.5. This means that for the metal nanospheres, the electron interactions within a certain radial distance inside the surface of the spheres was considered to affect the results, as opposed to infinitesimally thin charge density layers on the spherical surfaces. Incorporating this theoretical model into the physics of the simulations required an increase in the mesh coarseness of the 3D simulation space to reduce computation time to a reasonable level. Thus, computational results
were obtained for both coarser and finer mesh situations using the local model for comparison with nonlocal results. The resulting data was plotted as surface-averaged enhancement versus gap width as shown in Figure 4.6.1.

A value of $\beta = 1.0 \times 10^6$ is realistic for the nonlocal parameter, demonstrated by prior experiments and theory. The result of the volume charge consideration was a decrease in the local electric field strength within the gap region. Comparing with the local models, the reduction in enhancement for decreasing gap values is visible for the nonlocal consideration, becoming appreciable for gaps less than $\sim 2$ nm. Additional values of $3.0 \times 10^6$ and $5.0 \times 10^6$ m/s were used to further show the decrease in enhancement with increasing nonlocal parameter. Though the coarse model was given the same mesh distribution as that used for the nonlocal calculations, the fine mesh local results were found to provide a better fit overall, as the nonlocal effects become negligible as gap width continues to increase beyond $\sim 2$ nm.

![Figure 4.6.1. Plot of surface averaged enhancement vs. gap width for local and nonlocal models.](image)

Having established the ability of the metasurface models to calculate enhancements while considering nonlocal effects, they were able to be used to engineer optimal enhancement in
devices or to better study and understand gap-dependent enhancement results obtained experimentally. The results of this computational study were compared with experimental SERS data as will be discussed in Section 5.3.
Chapter 5.

OPTICAL CHARACTERIZATION

Experimental characterization of samples was performed using SEM imaging, as described in Chapter 3, as well as CL imaging and spectroscopy and Raman spectroscopy, as described in the current chapter. The goals of the experimental work described in this chapter were to study plasmon resonances qualitatively, develop a custom Raman spectroscopy system, and obtain SERS from fabricated samples to confirm the functionality of the system, compare with computational results, and advance the development of tunable SERS substrate technology.

5.1 Cathodoluminescence Results

Cathodoluminescence imaging and spectroscopy were performed using a Gatan MonoCL4 (Gatan, Inc., Pleasanton, California) system attached to the FEI Nova Nanolab 600 DualBeam (FIB/SEM) in the Electron Optics Facility, part of the Arkansas Nano-Bio Materials Characterization Facility housed in the University of Arkansas Nano Building. Preliminary results from the system after its initial setup are shown in Figure 5.1.1. Here, part (a) displays an SEM image produced with the parabolic mirror inserted into the chamber, which significantly reduces the signal strength and resolution of the scattered electron detector. The image was obtained primarily as a guide prior to collecting the CL panchromatic image shown in part (b). As in Figure 2.6.2, dark blue regions correspond to the weakest cathodoluminescence, as the electron beam caused less excitation at these pixel locations, and the red to bright yellow regions correspond to increasing excitability of electrons on the sample surface. As expected, the Au nanorod shown in the figure was more excitable than the surrounding Si wafer regions, due to
the metal’s greater number of free electrons.

**Figure 5.1.1.** Example of cathodoluminescence imaging results showing an isolated nanorod.60

One key factor in obtaining the best CL results is the thickness of the sample’s metallic structures. The square and circular Au structures shown in Figure 5.1.2 were evaporated with 1 nm of Ti and 15 nm of Au. With metallic layers this thin, the contrast between the CL signal of the Au and the substrate is not as stark as for thicker metal deposition.

**Figure 5.1.2.** CL images of 15 nm thick Au structures with nanogap spacing.

Metallic layers of 80 nm thickness were fabricated for the same types of square and
circular structures as shown in Figure 5.1.2. The resulting CL images for the thicker samples are shown in Figure 5.1.3. Compared to the thinner metal samples, the contrast is much greater between regions of high excitability on the Au and the weak excitability of the substrate on the 80 nm Au samples. The improved contrast for the thicker samples made it easier to see the differences in excitability across points on the sample. As expected, due to plasmonic coupling between adjacent structures, the points of greatest CL excitability were found to occur along the edges of structures that were positioned closest to a neighboring structure.

![CL images of 80 nm thick Au structures with nanogap spacing.](image)

**Figure 5.1.3.** CL images of 80 nm thick Au structures with nanogap spacing.\textsuperscript{60}

The CL system can display hyperspectral images for which every pixel contains a spectrum of the CL signal excited at that point on the sample. Figure 5.1.4 shows such an image for the circular heptamer structure shown in Figure 5.1.3. Here, the spectrum displayed to the right corresponds to a pixel on the Si substrate.

The image in Figure 5.1.5 shows the spectrum at a pixel on the edge of the center Au structure on the same sample as shown in Figure 5.1.4. The signal strength was increased compared to the spectrum at a pixel on the substrate, with the greatest increase occurring for the two broad peaks at approximately 550 and 650 nm. These peaks are associated with the Au
structures, which are coupled to one another and to the substrate, causing the dual-peak structure shown in Figure 5.1.5 as compared to spectra from isolated Au nanodisks as described by Das and Coenen et al.\textsuperscript{64,66,132,133}

**Figure 5.1.4.** CL image and spectrum from a single pixel on the substrate near a Au structure.

**Figure 5.1.5.** CL image and spectrum from a single pixel on one Au heptamer structure edge.

A study of the effect of substrate oxide thickness on the CL response was conducted to corroborate computational $t_{SiO_2}$ variation tests. The CL spectra for nanorods of similar design were tested for two substrate oxide thicknesses, a 100 nm grown SiO$_2$ layer and a native oxide layer of approximately 1 nm. The results are shown in Figure 5.1.6(a) and (b), respectively. Panchromatic CL images are shown in (i), and the spectra taken over the entire regions are
shown in (ii) with the peak regions outlined by the gray dashed lines. Comparing the images in (i) between (a) and (b), the contrast between the substrate and the Au is greater for the 100 nm oxide layer than for the native oxide. Looking at the spectra, the 100 nm oxide resulted in stronger and sharpened peaks compared to the native oxide sample as well as a 50 nm blueshift for the larger Au peak. The outline of the native oxide spectral curve (b-ii) is shown on the same scale as that of the grown oxide layer (a-ii) for comparison.60

Figure 5.1.6. CL panchromatic images and spectra for two substrate oxide thicknesses.60

The schematics and plot in Figure 5.1.7 are shown to clarify the difference between two additional measured samples for the same two oxide thicknesses. The curve outlines as highlighted therein also help to demonstrate the peak shift and sharpening that result from varying the oxide thickness.

The oxide thickness variation calculated via COMSOL was then compared to the
difference between CL spectra as shown in Figure 5.1.8. To the left, the periodic field intensity enhancement variation was plotted with the oxide thicknesses of 1 nm and 100 nm marked by arrows color coded to correspond to the CL curve outlines shown to the right. Interestingly, the 100 nm thickness falls rather near a peak in the periodic trend for the calculated enhancement, and the native oxide thickness appears near a trough. This corresponds well with the experimentally obtained CL images and spectra, for which the 100 nm oxide layer produced a significant signal increase.

**Figure 5.1.7.** Schematics of different oxide thicknesses and corresponding CL spectra.

Additional SiO$_2$ layer thicknesses should be studied via the same method in order to further understand how the experimental results compare to the computational model. This type of study would help to corroborate prior work studying cathodoluminescence signals for plasmonic structures on different dielectric substrates performed by Knight et al..$^{134}$
Figure 5.1.8. Plots comparing computational and experimental oxide thickness variation results.

5.2 Raman Spectrophotometer + Bright-Field Microscope System Design

To experimentally test the potential for fabricated nanostructures to produce strong optical surface enhancement, a Raman spectroscopy setup was devised. While it may have been possible to purchase a commercial Raman spectrophotometer to obtain these results, it was more cost-effective to purchase optical components to construct a custom setup in the lab. The first iteration of the custom setup was designed as a modular system capable of serving as a reflection microscope as well as performing either dark-field, photoluminescence, or Raman spectroscopy.

As an optical bench-top setup incorporating a commercial spectrometer, it was simplest to configure the components in a horizontal fashion so that the light path was always parallel to the table surface. The Raman spectroscopy and reflection microscope portions of this previous setup are outlined as a top-down view in Figure 5.2.1. This optical system was dismantled during lab relocation prior to obtaining most of the experimental results discussed in this work, so it was
not the exact layout used during final experimental data collection, though they were functionally identical.

Building on the initial design, the second iteration of the modular setup was designed to incorporate a reflection/transmission optical brightfield microscope and a Raman spectroscopy system, while the photoluminescence and dark-field portions were moved to a separate setup. The updated design was very similar to the previous system apart from the customized stage and transmission illumination capability.

![Diagram of Raman spectroscopy + microscope hybrid system](image)

**Figure 5.2.1.** Schematic of Raman spectroscopy + microscope hybrid system.\textsuperscript{117}

To make the setup suitable for both modes of operation, the sample stage was designed with a hole so that light might pass through the sample from behind during transmission mode usage. A custom aluminum sample holder and stage attachments were designed to pair a deconstructed OMAX M82ES microscope (OMAX Corp., Kent, Washington) base with two unidirectional Thorlabs PT1 stages (Thorlabs, Newton, New Jersey). These custom parts were fabricated in the UArk Department of Physics machine shop. The microscope slide holder from
the deconstructed OMAX microscope was used to hold an aluminum sample holder piece designed with outer dimensions matching a standard glass microscope slide. This piece allowed for rapid and simple vertical mounting of samples with relatively high positional repeatability. Aluminum feet were fabricated to raise the stage base to the proper height to place the sample into the optical axis of the spectroscopy system. The OMAX focusing knob attached to the base (formerly a vertical z-direction movement) was designed to still be used to focus light onto the sample along the system’s horizontal optical axis (z-direction). The coupled Thorlabs micrometer stages provided sample travel in the x- and y-directions.

A broadband halogen source (Fiber Lite MI 150, Dolan-Jenner, Boxborough, Massachussettes) was implemented to provide white light for the reflection/transmission microscope portion of the system. A liquid light guide (Thorlabs OSL2FB) was set up so that it can be switched between two system input ports for either reflection or transmission during imaging/spectroscopy. Lenses were positioned in a Kohler illumination system configuration for both modes, with a 50/50 beam splitter (Thorlabs EBS1) on a magnetic mount required to direct the light to the objective lens turret in reflection mode. The objective lens turret was also repurposed from the OMAX scope, and higher quality 5× and 50× lenses (M Plan, Apo, NIR, Mitutoyo, Sakado, Takatsu-ku, Kawasaki, Kanagawa 213-8533, Japan) were mounted to improve the resolution of the system. Upon reflection from or transmission through the sample, light passed to a tube lens to be refocused. A flip-mounted mirror (Thorlabs ME1-G01) was inserted to then direct the focused image to a CMOS camera (MU300, AmScope, Irvine, California) for computer-monitored imaging via the AmScope software. If the mirror was flipped down out of the light path, the beam entered the slit of the spectrometer (InSight, Princeton Instruments (PI), Trenton, New Jersey), allowing for reflection or transmission spectra to be
obtained. The spectrometer contained a grating turret capable of holding up to four diffraction gratings to provide different spectral resolution options. The CCD camera used was a Pixis InSight 100B, PI. The PI LightField software, version 6.5, was used to control spectroscopy experiments and preliminary data processing.\textsuperscript{135}

The Raman system was designed with a 100 mW continuous wave 785 nm diode laser (RO USB-785-PLR-100-1, Ondax, Monrovia, California) as the excitation source. The beam exited the laser and the first optical element in the path was a bandpass filter to sharpen the linewidth of the laser spectrum (Maxline Laser Line Filter LL01-785-12.5, Semrock, Rochester, New York). The beam then passed through a linear polarizer (Thorlabs LPNIRE100-B) before encountering an optical density filter (OD 3.0, Thorlabs ND30B) on a flip mount and a flip-mounted beam block. The filter reduced the intensity of the beam, which was useful when aligning the beam to the slit and CCD, as the highly sensitive camera became saturated when exposed to even partial laser power. The beam then passed through a half-wave plate (Thorlabs WPH05M-780) on a rotation mount, allowing for control of the polarization angle relative to the initial polarizer direction, and a graded O.D. filter, which allowed for more control of beam attenuation if necessary. A long-pass dichroic beam splitter (RazorEdge\textregistered LPD02-785RU-25, Semrock) then redirected the beam toward the objective lens and sample, bi-directionally reflecting light at 785 nm and shorter wavelengths and passing those longer, with an ultra-steep cutoff near 785 nm. This allowed the laser to illuminate the sample, exciting Raman scattered light which was Stokes shifted to longer wavelengths (increased relative wavenumbers) compared to the laser beam. This Raman light then passed through the dichroic beam splitter while the laser wavelengths themselves were again reflected, this time back toward the laser. An additional long-pass filter (RazorEdge\textregistered LP02-785RU-25, Semrock) further eliminated light at or
below the laser wavelength, helping to clarify the Stokes shifted signal measured by the CCD. The passed Raman scattered light was then focused by a tube lens (Thorlabs TTL200-S8) with a collimation attachment (Thorlabs OSL 2 COL). Provided that the flip-mounted mirror was not directing light to the CMOS camera for imaging at the time, it passed through the slit into the spectrometer where the desired grating spread out the light spatially before directing it to the CCD where a Raman spectrum was measured.

5.3 Surface-Enhanced Raman Spectroscopy Results

This dissertation work was motivated by the desire to engineer plasmonic enhancement via tunable metallic nanostructures. The computational study of Au metasurfaces as discussed in Section 4.5 resulted in the expectation that enhancement increases approximately exponentially with decreasing metasurface gap width down to ~ 1 nm and smaller. The ideal study of the metasurfaces was considered to include a comparison between these computational results and experimental SERS results, which would corroborate the simulations. This section discusses the experimental results obtained for analyte molecules adsorbed onto Au metasurfaces as discussed in Sections 3.4 and 4.5 the Raman spectroscopy system described in Section 5.2.

The first calibration for determination of the successful operation of the Raman system was to attempt to measure a Raman spectrum for a Si substrate. When an entire Si wafer or chip is used for this calibration, the characteristic peak of this thick solid sample is typically easier to detect than that of lower concentration analyte molecules. It was also important to detect a strong, sharp Si peak because it is present as a background signal in all experimental work performed on Si substrates. After aligning as well as possible both the white light spot and laser beam to the same focal point on the sample surface, the two were also simultaneously aligned.
and focused on the CMOS and CCD.

Alignment and focus during this stage were improved by attempting to first detect and then maximize the Si peak appearing at a relative wavenumber of 520 \text{ cm}^{-1}. Preliminary results from this calibration are shown in Figure 5.3.1 with data taken from the primary iteration of the Raman system. On the spectrometer, the center wavelength was set to 2000 \text{ cm}^{-1} using a diffraction grating with 300 grooves/mm to move the laser wavelength peak off of the CCD so as to reduce any camera saturation that might make it difficult to see the Si peak.\textsuperscript{117}

![Figure 5.3.1. Characteristic Stokes Raman peak for Si at relative wavenumber 520 cm\(^{-1}\).\textsuperscript{117}](image)

Preliminary trials were conducted to measure Raman spectra for fabricated nanomasking samples containing different nanogap patterns including the dual-width and grid structures discussed in Chapter 4. The first organic molecule chosen as an analyte for its well-known Raman spectral signature was trans-1,2-bis(4-pyridyl)-ethylene (BPE). An example of the characteristic Stokes Raman spectrum for BPE was shown previously in Figure 2.5.2, along with the molecular structure. Tables describing the characteristic vibrational modes of each molecule can be found in many publications measuring their Raman spectra. This information is not crucial to the enhancement study conducted in the current work, so is not included here.
Samples containing Au metasurfaces were fabricated following the self-assembly procedure in Section 3.4 for different alkanethiols/dithiols, resulting in metasurfaces consisting of Au nanospheres with diameters of 13.3 ± 0.7 nm and varying gap widths between hexagonally close-packed spheres, controlled by the alkyl group used. Solutions of BPE in ethanol were prepared by weighing BPE in powder form and mixing with ~20 mL of ethanol to obtain the desired molarity. Solution molarities from 0.1 mM to 100 mM were prepared. To coat samples in BPE, drop casting and sample soaking were attempted. Soaking the metasurface-containing wafers in the BPE-ethanol solution for at least 45 minutes, removing, and blow drying with N₂ was eventually chosen, as it resulted in better uniformity of coating across the sample surface.

Coating metasurface samples with benzenethiol (BZT) involved a gaseous phase process, due to the highly volatile nature of BZT. The method used in this work involved suspending each sample metasurface side down above an open 20 mL vial containing BZT solution. The high vapor pressure of BZT meant that plenty of molecules were evaporating and contacting the sample, where some were adsorbed on the surface. This was set up by using carbon tape to adhere the sample to the bottom of a small beaker, which was placed upside-down over the open BZT vial, all within a fume hood, as BZT can be an inhalation hazard. Samples were exposed to BZT vapor in this way overnight, though shorter times may have provided sufficient analyte adsorption.

Once samples were prepared with analyte molecules, they were placed in the Raman spectroscopy system for optical characterization. Due to the coating methods, it was assumed that BPE and BZT were distributed over the entire silicon chips containing the Au metasurfaces of different gap width, if not relatively uniformly distributed. Thus, a neat Raman signal could be
measured for each analyte molecule as “on Si” by simply directing the laser spot onto a region of the samples on which there had been no Au metasurface assembly. The SERS measurements then were obtained by moving the laser spot to sample regions containing Au spheres. Conveniently, the difference between regions was visible to the naked eye due to the thin blue film appearance of the metasurfaces on Si. Also making use of the film coloration, attempts were made to take all SERS data from monolayer Au regions vs. potential metasurface multi-layers, which sometimes occur during the self-assembly process.

Maximizing the Raman signal strength from the sample was crucial to the ability to measure sample spectra with the custom setup. For reference, the incident laser power at the sample surface was measured, using a Thorlabs PM160 optical power meter, to be 52.0 mW with no neutral density filter attenuation. Variable parameters of the system were tuned to produce the maximum peak for the bare Si 520 cm\(^{-1}\) peak at the start of experimentation. In order to maximize the peak signal, the 300 grooves/mm diffraction grating was used within the spectrometer, the center wavelength was set to 2000 cm\(^{-1}\), the slit width was set to 10 µm, the exposure time was 30 seconds with five exposures averaged together per output to produce the final measurements, and no laser attenuation was applied during data collection. While the peak resolution was increased when diffraction gratings of 600 and 1200 grooves/mm were used, the signal intensity was significantly reduced to the point that it wasn’t worth the gain in resolution.

A longer exposure, even up to one minute, did not significantly improve the signal intensity beyond that measured with an exposure of 30 seconds. Upon measurement of both a Si background signal from each sample and a SERS signal on each Au monolayer, the Si background was subtracted from the SERS signal for each gap width (\(C\) value) and analyte molecule.
The results were waterfall plotted for each probe molecule. The SERS spectra for samples C2 through C14 (gap widths and alkyl groups discussed in Section 3.4) coated in BPE were plotted as shown in Figure 5.3.2. The peaks occurring in the SERS spectra correspond to the well-characterized BPE Raman spectrum. Here, the SERS signal strength can be seen to increase as the Raman peaks increase in intensity with decreasing gap width (C value), especially for the C6 – C2 metasurfaces.

![Figure 5.3.2. Waterfall plotted BPE SERS spectra for each metasurface C value studied.](image)

The same type of plot was produced for the samples containing BZT, shown in Figure 5.3.3. Again, the SERS signal was enhanced significantly starting around the C6 gap width, and the signal increased with reduced gap width. In this case, the signal increase was not observed to continue from C3 to C2. Instead, a significant decrease in peak enhancement was observed for the BZT SERS spectra produced by the C2 sample. Interestingly, the explanation for this result may correspond to the nonlocal effects that become relevant at such small length scales as the ~0.5 nm gap width of the self-assembled C2 metasurfaces.
Figure 5.3.3. Waterfall plotted BZT SERS spectra for each metasurface $C$ value studied.

The Raman intensities of each characteristic peak were plotted versus gap width for both analyte molecules, with the resulting plot for BPE shown in Figure 5.3.4. A power trend line was fit to the data with reasonable agreement.

The same was done for the BZT SERS peaks, as shown in Figure 5.3.5. Again, a power trend line was fit to the data. Here, the decrease in enhancement from the $C_3$ gap width of 0.55 nm to the $C_2$ width of 0.45 nm is more quantitively illustrated. In both the BPE and BZT plots shown in Figure 5.3.4 and Figure 5.3.5, the gap width error bars were determined via the standard deviations at each carbon chain length as measured by TEM imaging, discussed in Section 3.4. The vertical error bars were based on the noise in the Raman spectra.

An important consideration should be noted regarding the SERS signal increase with decreasing nanogap between Au spheres in the metasurface. In recent work by Doyle et al. which has been referenced throughout this dissertation, the metasurface absorbance was studied versus gap width.\(^{114}\) In the prior work, the absorbance peak was found to redshift with decreasing gap.
width, an expected result which matches the hybridization of plasmonic modes discussed in the computational section of this work as well. Interestingly, the peak absorbance wavelength was found to approach 785 nm, the experimental wavelength used in the current work, for the C3 and especially C2 metasurfaces. Thus, not only were there likely to be gap-induced enhancement effects promoting increased SERS at these smaller gap widths, but there was likely to have been a resonance Raman condition for the same metasurfaces. As discussed in Section 2.5, resonance Raman occurs when the structure being probed absorbs strongly at the same wavelength as the probe laser, or at least within a reasonable spectral range. More studies will be required to determine the exact nature of the SERS results obtained in this work, such as probing the structures with shorter wavelength light to see if stronger SERS signals appear for larger gap widths. This would serve as a clue that the resonance conditions were shifted for larger gap widths, as previously found.

![Figure 5.3.4](image)

**Figure 5.3.4.** SERS peak intensity versus gap width for characteristic BPE Raman peaks.
Finally, these experimental SERS results were compared to the computational results for surface-averaged enhancement versus gap width discussed in Section 4.5. As the primary result of this dissertation work, the plot shown in Figure 5.3.6 combines these computational results with the plots of experimental SERS data for BPE and BZT spectral peak intensities versus gap width, which corresponds to the number of carbons in the metasurface ligands. The BZT and BPE data are shown in blue and red, respectively, and correspond to the left $y$-axis plotting Raman intensity versus gap width. The calculations based on the classical Drude model, referred to as ‘local’, and those based on the modified nonlocal parameter $\beta$ were plotted on the right $y$-axis plotting the surface-averaged enhancement to the fourth power versus gap width. The left $y$-axis was shifted to best fill the plot space with the SERS data, and the right $y$ axis was adjusted to overlap with the experimental data in a reasonably realistic fashion. This was based on prior discussions of the nonlocal model parameter having a realistic value of $\beta \approx 1 \times 10^6$ m/s.
Figure 5.3.6. Plot of signal enhancement versus gap width: comparison between experimental SERS on Au metasurfaces and theoretical surface enhancement in optical metasurface models.

The nonlocal treatment has been developed and applied to different nanogap geometries and situations, as discussed in Section 4.6, including modeling Au metasurfaces as considered in this work. It has been confirmed by comparing model results to experimental absorption and scattering measurements, at least in terms of the reduced red-shift caused by nonlocal effects when gap width decreases. There have yet to be shown experimental results for the increase of a Raman scattering signal with decreasing gap width in consideration of the nonlocal model.

This dissertation work has advanced the study of nanogap plasmonic effects by first modeling nonlocal effects on the field enhancement of tunable gap metasurfaces and secondly by measuring experimental changes in the SERS signal with decreasing gap width. The experimentally obtained data for BZT on C2 metasurfaces were found to demonstrate a slight decrease in Raman intensity compared to that of the C3 data. This decrease corresponds nicely to the enhancement limitation described by the nonlocal electron distribution model as discussed
and modeled in Section 4.6. The plot in Figure 5.3.6 displays the experimental data alongside the computed curves for surface-averaged enhancement to the fourth power versus gap width via the nonlocal model where $\beta = 1.0 \times 10^6$, $3.0 \times 10^6$, and $5.0 \times 10^6$ m/s. It may be deduced from the decrease in experimental signal enhancement from $C3$ to $C2$ that nonlocal effects are likely causing this limitation in the SERS effect at such a small gap width. While the computational curves may be $y$-shifted to change the fit between experimental and theoretical data, the trends match well regardless of the applied $y$-shift. It then becomes a matter of how well the local model is fit to the data versus the nonlocal model, and at what gap widths each model becomes more accurate at modeling the change in SERS intensity.

Although the BPE data does not demonstrate a decrease in signal intensity from $C3$ to $C2$, there is a notable decrease in the rate of change of intensity for this gap width decrease. The difference between the two analyte signal spectra may be due to several factors. Notably, the different molecule deposition methods, soaking in solution versus gas-phase evaporation, may result in different adsorption efficiencies or locations on the metasurfaces. Also, variations between metasurface gap width distributions across samples or even across sample locations may affect these results.

The accuracy with which the models were found to match the SERS data was a positive indication of the benefits of controlling gap width as an effective tool for maximizing Raman signal enhancement. Thus, this dissertation work was successful at providing evidence for the utility of tunable gap plasmonic metasurfaces as realistic surface-enhanced Raman spectroscopy substrates with predictable signal enhancement behavior.
Chapter 6.

CONCLUSION AND FUTURE WORK

The goals of the research work discussed in this dissertation were multifaceted, and throughout this document, evidence has been presented herein to demonstrate their completion. The writing was performed in such a way as to motivate the undertaken research tasks, as well as to give the reader the necessary background knowledge to fully understand the theory, experiments, and results discussed thereafter. The motivation behind the fabrication, computation, and experimental work was to better understand and engineer improvements to the enhancement of light produced by nanostructures with tunable geometries and nanoscale gaps between structures. These types of technological advancements could be applied to many different areas including improving photovoltaic cell absorption, photodetector signals, optical waveguides, and more. This dissertation was focused, however, on engineering improvements to the surface-enhanced Raman scattering signal strength for sensing applications.

Initial goals were the advancement and study of the nanomasking fabrication method developed by Bauman et al.\textsuperscript{36,40} Structures produced by the technique were then also the motivation for computational studies to optimize the optical enhancement produced by tunable nanogap geometries. It was found that for dual-width grating geometries made possible by the advanced fabrication technique, it was feasible to engineer signal enhancements on the order of $10^5$, with a boost of approximately 450 percent over that produced by standard structures created without the use of nanomasking. Also, optimization of the substrate with the metallic structure geometries was found to provide an additional 200 – 300 percent increase in signal enhancement. Cathodoluminescence imaging and spectroscopy results were used to also study the effect of
substrate oxide thickness on optical signal enhancement, matching well with the theoretical model results, which demonstrated that certain periodic oxide layer thicknesses provide strengthened optical signals reradiating from the sample compared with other periodic thicknesses. The study of nanomasking structures was primarily focused on gratings, which were easily simulated via two-dimensional cross-sectional models. The desire to incorporate full nanomasking-enabled dual-width grid structures was the motivation for producing three-dimensional models, for which preliminary calculations were performed as well. These models provided evidence for the high degree of tunability associated with such advanced top down lithography-based methods.

Tunable nanogap metasurfaces were also studied in this work due to their fast, easy, and reliable self-assembly fabrication procedure. These too were simulated to study the effects of gap width on optical enhancement. It was found that the enhancement appears to increase exponentially for decreasing gap width, at least down to approximately 1 nm. The nonlocal theoretical model was applied to the simulations to account for the experimental SERS results obtained for Au metasurface samples of different gap width. These results primarily demonstrated an increase in signal enhancement for decreasing gap width. However, a decrease in SERS signal from 0.3 nm to 0.2 nm gap width for one specific analyte molecule was an indication of nonlocal effects occurring in the experimental measurements, demonstrated by comparing the theory and experiments. This was an exciting contribution to the understanding of experimental SERS in terms of the enhancement produced by small nanogaps between plasmonic structures.

Future work related to this dissertation includes the incorporation of surface roughness into three-dimensional computational models, completion of a motorized stage to improve the
spatial resolution of the experimental Raman system, and using the improved system to experimentally characterize nanomasking substrates.

6.1 Modeling Surface Roughness

A further improvement to the computational modeling of nanomasking self-assembled SERS structures would be the incorporation of surface roughness into the simulations. Nanoscale and sub-nanometer protrusions and depressions appearing over a metallic surface, as in the majority of realistic nanostructure fabrication methods, have been shown beneficial to producing increased local electric field enhancement over that obtained near perfectly smooth structures. Also, when two structures with nanoscale or sub-nanoscale roughness are separated by gap widths on the same order of magnitude, the variation in this width over the length of the separation can become significant to field enhancement. It is therefore important to study these effects via the powerful computational methods employed in this dissertation for optimization of geometrical parameters.

There exist methods to generate semi-random rough surfaces with control over different parameters in COMSOL Multiphysics®, which could be added to three-dimensional models such as the grid structures or spherical metasurfaces discussed in Sections 4.4 and 4.5 in this work. Another possibility would be to upload the experimentally measured gap roughness discussed in Section 3.3 into the models. These methods would serve to increase the accuracy of computational results to improve the engineering of SERS and other devices for future projects.
6.2 Raman Stage Motorization

In the current dissertation work, the primary limitation to obtaining successful SERS measurements from nanomasking structures was expected to be directly related to the limited stage control within the custom Raman spectroscopy setup. A method for adding stepper motors to the \(x\)-\(y\) micrometer stages was investigated, and preliminary work was started towards its implementation. A depiction of the motorized stage addition is shown in Figure 6.2.1. The method involves the use of an Arduino microcontroller (Arduino, Somerville, Massachusetts) to interface between a video game controller (Playstation\textsuperscript{®}, Sony Interactive Entertainment, San Mateo, California) and a stepper motor for each stage, providing stage motion control with resolution on the order of 1 µm in each direction.\textsuperscript{136}

![Figure 6.2.1](image).

**Figure 6.2.1.** Depiction of motorized stage modification for the Raman spectroscopy system.

The necessary components to build this system were obtained, and some setup was performed, but future work will be required to finalize the motorized stage system. This add-on
to the custom Raman spectroscopy/microscope system would benefit further experiments, as spatial scans could be controlled with much greater precision than is currently possible with manual stage adjustment. This would make it much easier to study SERS enhancement across nanomasking device structures.

6.3 Characterization of Nanomasking SERS Substrates

A large part of this dissertation work focused on the fabrication and computational engineering of SERS substrates via nanomasking. This enhancement engineering would ideally be validated via experimental characterization as an iterative process by which the optimal structures would be determined based on similarities and differences between theoretical and experimental results. Thus, future work into the benefits of nanomasking-enabled designs would study the experimental SERS feasibility of such structures and would attempt to produce optimal enhancement via comparison between theory and experiment.
REFERENCES


<www.princetoninstruments.com>

APPENDIX A:

DESCRIPTION OF RESEARCH FOR POPULAR PUBLICATION

Plasmonic Nanostructures: The Optical Engineer’s Modern Toolkit

Creating the next generation of technology for improved solar cells, cameras, displays, computers and sensors will continue to increasingly rely on the ability to controllably create nanoscale patterns and devices from different materials which interact with light in unique and useful ways. Taking some queues from highly periodic nanoscale designs found in nature and adding some homo sapiens ingenuity, we have improved our ability to design, fabricate, simulate, and test nanoscale devices for useful applications. When it comes to optical nanotechnology, tunable shape parameters typically serve as control knobs for how efficiently light will be absorbed, reflected, transmitted, scattered, or otherwise affected by the device, depending on the application.

One light-based sensing technique, known as Raman spectroscopy, can identify the presence of different molecules by measuring the way that they scatter laser light. Due to the unique structure of each molecule, its vibrations are also unique. Therefore, when light interacts with these molecular vibrations of a sample and scatters back to a detector which can measure the light at different wavelengths, the result contains a group of spectral peaks that can be used to identify the molecule’s presence in the sample. In this way, light can be used to detect chemicals of interest in such cases as blood glucose sensors, safety systems in industrial or other settings, and defense/homeland security. The primary difficulty preventing this type of optical device from being used in every day applications is the weakness of the measured signal.
Recent work by researchers at the University of Arkansas has applied advanced tunable nanoscale fabrication methods to create optical devices capable of increasing Raman spectroscopy signals. Two fabrication techniques were studied – one in which the user designs patterns to be created, much like using a stencil to draw a pattern on paper, and the other involves mixing chemicals in a vial and growing a single layer of tightly packed metal nanospheres on a wafer, known as a metasurface. Both techniques offer user control over certain geometrical parameters of the resulting structures, which in turn provide handles for engineering the strongest signal increases when light is shone onto the nanostructures.

Computer models of the different geometrical parameters were used to determine the best theoretical geometries or parameter values. Then, an experimental setup was used to test real structures to see how well the simulations predicted the true behavior of the devices. Raman spectroscopy results using the metasurfaces with different gap widths between adjacent nanospheres were found to match very closely the theoretical calculations, which predicted a strong signal increase as the gap width between spheres was decreased. With this signal enhancement thus demonstrated as a predictable and experimentally realizable phenomenon, it should be feasible to develop real surface-enhanced Raman spectroscopy devices based on this self-assembly technique. These devices, even without extreme improvements, will be capable of boosting weak signals from various samples in applications such as biomedical chemical sensing.

Additional work will continue to improve the understanding of the physics behind this surface enhancement as well as helping to develop devices for use outside of the research lab environment. SERS sensors have taken yet another step toward becoming a useful reality in everyday life, and optical nanostructures have again been demonstrated as priceless for the
optical engineer of 2018 when developing advanced light-based technology.
APPENDIX B:

EXECUTIVE SUMMARY OF NEWLY CREATED INTELLECTUAL PROPERTY

The following list of new intellectual property items were created in the course of this research project and should be considered from both a patent and commercialization perspective.

1. Dual-width plasmonic grating and/or grid structures and the associated fabrication technique for the specific tunable structures.

2. Tunable plasmonic metasurfaces and the associated self-assembly fabrication technique.

3. The use of engineered nanostructures for optimized surface-enhanced Raman spectroscopy at specific incident wavelengths.
APPENDIX C:

POTENTIAL PATENT AND COMMERCIALIZATION ASPECTS OF LISTED INTELLECTUAL PROPERTY ITEMS

The current chapter discusses the potential likelihood or value of pursuing a patent for any aspects of the dissertation work which may have commercial value.

C.1 Patentability of Intellectual Property (Could Each Item be Patented)

The three items listed were considered first from the perspective of whether or not the item could be patented.

1. As mentioned in the author’s master’s thesis work, the nanomasking technique can be patented, as it is novel, unique, and non-obvious. The specific structures made possible via the technique offer unique benefit and therefore could be pursued as patentable technology. In addition to this dissertation work, prior disclosure of the technique and resulting structures would prevent patenting the technology, however.

2. The same could be said for the Au metasurfaces discussed in this dissertation work. While the self-assembly technique offers unique benefits for producing tunable metasurfaces, this dissertation and other prior publication of the technique and resulting structures would prevent patenting of the method and/or technology.

3. It is possible that a complete SERS substrate device could be patented based on the fabrication techniques and resulting structures discussed herein, but additional novel, unique, and non-obvious combinations of the nanoscale structures would have to be implemented to increase the likelihood of a successful patent application.
C.2 Commercialization Prospects (Should Each Item Be Patented)

The three items listed were then considered from the perspective of whether or not the item should be patented.

1. The dual-width gratings and associated fabrication technique should not be patented, as prior publication of the technique and resulting devices prevents patenting them.

2. The same prior publication of Au nanosphere metasurfaces with tunable gaps prevents either the technique or the resulting devices from being patented.

3. Further development of a self-contained SERS system should be patented if it were to be developed as a commercially viable product.
C.3 Possible Prior Disclosure of IP

The following items were discussed in a public forum or have published information that could impact the patentability of the listed IP. The devices and the technique have been discussed thoroughly in multiple conference settings, conference proceedings articles, news releases, grant applications, peer-reviewed journal articles, and the current dissertation work. No intellectual property non-disclosure forms were involved, and many of these sources of documentation are now within the public domain. Therefore, it would not be possible to patent any of the technology that has resulted from the current dissertation work. Further novelty, uniqueness, and non-obvious technology would need to be developed in order to obtain a patent related to the work and/or related technology/devices/processes. Specifically, the first mention of each potentially patentable technology appeared as follows:

1. One would have to consider the paper which lays out the nanomasking process as prohibitive for future patentability of the technique:


2. An earlier and primary paper regarding the SERS metasurface fabrication should be considered as prior disclosure of the method which could reduce the patentability of the technique:


3. The same publication should potentially be considered, even in the case of trying
to patent a system-level device/technique/process, incorporating the SERS metasurfaces into a more fully-integrated SERS sensing system:

APPENDIX D:

BROADER IMPACT OF RESEARCH

The current appendix discusses the applicability of research methods used in this dissertation work to other problems facing humanity, the impact of the results on the United States and the world societies, and the impact of the results on the environment.

D.1 Applicability of Research Methods to Other Problems

The fabrication methods implemented in this dissertation work could certainly be utilized for different types of technology outside of SERS sensing, especially optical, electronic, or of course optoelectronic devices. The geometrical tunability offered by the methods could just as well be used to engineer enhanced absorption, reflection, transmission, or electrical conduction in other devices such as solar cells, photodetectors, thermoplasmonic heating devices, display technology, or other areas. The same type of optimization study for different light wavelengths or spectral ranges would aid in the design of similar nanostructure-based devices for these various applications. The custom Raman spectroscopy system used in this work was developed so that it might easily be modified to provide additional capabilities, such as introducing a secondary laser for measurement of different Raman samples or a completely different type of spectroscopy entirely. The computational models can certainly be modified or used in their current form to calculate additional parameters and gain new insights for a variety of applications.
D.2 Impact of Research Results on U.S. and Global Society

The potential impacts of the dissertation work on the U.S. and global society are many. Optical enhancement produced by designing nanostructures as in this work may be able to benefit sensors, detectors, solar cells, optical computers, communications, displays, and more. With such a wide range of applications for plasmonic light enhancement optimization, it is difficult to think of an area of the world that will not one day be affected by this area of research and development.

Sensing technology primarily holds the key benefit of providing safety from dangerous chemicals, either in one’s environment or inside of one’s own body. Thus, improvements to SERS sensing as demonstrated here may make it easier to produce cheaper, more portable sensing technology capable of saving lives around the globe. It may also help protect international borders from threats carried out by dangerous or illegal weapons. If medical professionals in third world countries were able to take advantage of cheap, handheld sensors that can detect the presence of specific chemicals in real-time, many disease diagnoses may be made, chemical balances such as glucose levels in diabetics may be more easily monitored, and other biomedical processes may be simplified.

Improved light-enhancement at the nanoscale can be harnessed for photodetection to improve camera technology, communications systems, and optical computing. Solar cell efficiency may be improved, as will continue to be critical to reducing carbon emissions across the planet. Plasmonic pixels may help improve display technology by improving the efficiency of computer, television, and smart phone screens. Energy savings enabled by such improvements typically translate to economic benefits for the localities in which they are implemented.

The fabrication techniques discussed are capable of producing a range of nanoscale
device geometries, limited primarily by the imagination of the user. Thus, the potential applications vary greatly beyond optical sensor devices. The primary benefits of this work, however, will stem from the development of optical technology which requires engineering the ideal nanoscale features for localized electric field enhancement.

D.3 Impact of Research Results on the Environment

In general, plasmonic nanotechnology has held promise for improving solar cell technology by providing increased thin-film solar cell absorption efficiency, which helps to reduce cost. Cheaper solar cells increase use demand, which is crucial to increasing their success and ubiquity across the globe. Until renewable energy sources produce the clear majority of energy used by homo sapiens on planet Earth, any step toward this end must be considered beneficial. Thus, the ability to design and create nanostructures with any degree of engineering capability for optical applications must be considered as an option to improve solar cell technology, which must start to become more common if global climate change is to be combated.

Specifically related to the SERS sensor portion of the current work, the ability to detect harmful substances will be beneficial to the environment in terms of waste management and control of pollutants/emissions. Any improvements to systems which can efficiently detect chemicals in liquid and gas phases, as can Raman spectroscopy, must be considered for their potential environmental benefits.
APPENDIX E:

MICROSOFT PROJECT FOR PHD MICROEP DEGREE PLAN
<table>
<thead>
<tr>
<th>Task Name</th>
<th>Qtr 3, 2018</th>
<th>Qtr 4, 2018</th>
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</thead>
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<tr>
<td>END GAME</td>
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<tr>
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<td>Start of final corrections</td>
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<td>Last Day to Send Title, Abstract &amp; Scheduling Information to Micro</td>
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<tr>
<td>Finish Powerhouse Hall of Foam Beer Challenge</td>
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APPENDIX F:
IDENTIFICATION OF ALL SOFTWARE USED IN RESEARCH AND DISSERTATION GENERATION

Computer #1:
Model Number: Toshiba Satellite P55t-A5116
Serial Number: 2E062215S
Location: N/A
Owner: Stephen Bauman

Software #1:
Name: Microsoft Office 2013
Owner: University of Arkansas Fulbright College of Arts and Sciences

Software #2:
Name: Nanopattern Generation System (NPGS) v9 Office Installation
Owner: University of Arkansas Institute for Nanoscience and Engineering

Software #3:
Name: DesignCAD 2000LT with NPGS
Owner: University of Arkansas Institute for Nanoscience and Engineering

Software #4:
Name: Adobe Reader XI v11.0.01
Owner: Stephen Bauman (freeware)

Software #5:
Name: Google SketchUp 8
Owner: Stephen Bauman (freeware)

Software #6:
Name: GNU Image Manipulation Program (GIMP) 2.8.14
Owner: Stephen Bauman (freeware)

Software #7:
Name: Zotero 4.0.21.2
Owner: Stephen Bauman (freeware)

Computer #2:
Model Number: ASUS Essentio Series X18-82071
Serial Number: 150290C00700
Location: PHYS 109
Owner: Herzog Lab
Software #1:
Name: COMSOL Multiphysics
Owner: Herzog Lab (individual computer license)

Software #2:
Name: COMSOL Multiphysics
Owner: University of Arkansas Microelectronics-Photonics Graduate Program

Software #3:
Name: Nanopattern Generation System (NPGS) v9 Office Installation
Owner: University of Arkansas Institute for Nanoscience and Engineering

Software #4:
Name: DesignCAD 2000LT with NPGS
Owner: University of Arkansas Institute for Nanoscience and Engineering

Software #5:
Name: Microsoft Office 2013
Owner: University of Arkansas Fulbright College of Arts and Sciences

Software #6:
Name: MATLAB R2014a (Version 8.3)
Owner: University of Arkansas Department of Physics

Computer #3:
Model Number: N/A (Custom built)
Serial Number: N/A (Custom built)
Location: PHYS 109
Owner: Herzog Lab

Software #1:
Name: COMSOL Multiphysics
Owner: Herzog Lab (individual computer license)

Software #2:
Name: COMSOL Multiphysics
Owner: University of Arkansas Microelectronics-Photonics Graduate Program

Software #3:
Name: Nanopattern Generation System (NPGS) v9 Office Installation
Owner: University of Arkansas Institute for Nanoscience and Engineering

Software #4:
Name: DesignCAD 2000LT with NPGS
Owner: University of Arkansas Institute for Nanoscience and Engineering
Software #5:
Name: Microsoft Office 2013
Owner: University of Arkansas Fulbright College of Arts and Sciences

Software #6:
Name: MATLAB R2014a (Version 8.3)
Owner: University of Arkansas Department of Physics

Computer #4:
Model Number: Dell 3615KL – 04W – B86
Serial Number: 8XRZL51
Location: Nano Room 125
Owner: University of Arkansas Institute for Nanoscience and Engineering

Software #1:
Name: Nanopattern Generation System (NPGS) v9 Microscope Installation
Owner: University of Arkansas Institute for Nanoscience and Engineering

Software #2:
Name: DesignCAD 2000LT with NPGS
Owner: University of Arkansas Institute for Nanoscience and Engineering

Computer #5: Accessed University of Arkansas VLab General Access Computing Lab
Model Number: N/A
Serial Number: N/A
Location: VLab General Access Computing Lab
Owner: University of Arkansas IT Services

Software #1:
Name: Adobe Photoshop v?
Owner: University of Arkansas IT Services

Computer #6:
Model Number: ASUSTek Computer Inc. K501UW-NB72
Serial Number: G3N0CX062849119
Location: N/A
Owner: Stephen Bauman

Software #1:
Name: Microsoft Office 2016
Owner: University of Arkansas Fulbright College of Arts and Sciences

Software #2:
Name: TeamViewer 13
Owner: Stephen Bauman (freeware)
Software #3:
Name: ImageJ
Owner: Stephen Bauman (freeware)

Software #4:
Name: Adobe Reader XI v11.0.01
Owner: Stephen Bauman (freeware)

Software #5:
Name: Arduino GUI
Owner: Stephen Bauman (freeware)

Software #6:
Name: GNU Image Manipulation Program (GIMP) 2.8.14
Owner: Stephen Bauman (freeware)

Software #7:
Name: Zotero 4.0.21.2
Owner: Stephen Bauman (freeware)

Software #8:
Name: Skype
Owner: Stephen Bauman (freeware)

Software #9:
Name: MATLAB 2018a
Owner: Stephen Bauman (purchased student license)

Computer #7:
Model Number: Dell Precision T5610
Serial Number: BJKQM02
Location: N/A
Owner: Herzog Lab

Software #1:
Name: Microsoft Office 2016
Owner: University of Arkansas Fulbright College of Arts and Sciences

Software #2:
Name: TeamViewer 13
Owner: Stephen Bauman (freeware)

Software #3:
Name: Skype
Owner: Stephen Bauman (freeware)

Software #4:
Name: MATLAB 2018a
Owner: Stephen Bauman (purchased student license)

Software #5:
Name: COMSOL Multiphysics 5.3a
Owner: Herzog Lab (purchased individual computer license)

Computer #8:
Model Number: HP OMEN 870-224
Serial Number: 4CE709190Q
Location: PHYS 106
Owner: Herzog Lab

Software #1:
Name: LightField version 5 (Princeton Instruments)
Owner: Herzog Lab

Software #2:
Name: AmScope camera software
Owner: Herzog Lab

Software #3:
Name: Arduino GUI
Owner: Herzog Lab (freeware)

Software #4:
Name: DesignCAD 2000LT with NPGS
Owner: University of Arkansas Institute for Nanoscience and Engineering

Software #5:
Name: Microsoft Office 2016
Owner: University of Arkansas Fulbright College of Arts and Sciences

Software #6:
Name: MATLAB R2014a (Version 8.3)
Owner: University of Arkansas Department of Physics
APPENDIX G:
ALL PUBLICATIONS PUBLISHED, SUBMITTED, AND PLANNED

JOURNAL ARTICLES:
First-Author Peer-reviewed Publications:


Peer-reviewed Publications:


In Preparation & Planned:


CONFERENCE PUBLICATIONS:


APPENDIX H:
MANUALS AND DIRECTION SHEETS DEVELOPED

The following sections have been included for the sake of future users of the equipment and/or software described herein. Some modifications have been made to the versions included in Bauman et al.\textsuperscript{36}

H.1 Hi-Res SEM Imaging with the FEI Nova Nanolab 600 DualBeam (FIB/SEM)

********** The procedure for just imaging is different from the electron beam lithography procedure. One can safely turn on the beam without fear of resist exposure in the case of imaging.**********

- *Gloves!* must be worn whenever the sample or chuck is handled!
- Sign into the logbook.

Keyboard shortcuts:
- +/- to zoom in/out
- Center Click = drag around movement, Double Click = jump to click location
- Beam Shift knobs are easier at higher magnifications
- Shit + mouse clicks to do stigmation, etc.
- Shift + Ctrl you can drag screen around
- F5 goes full screen and back
- There’s a way to do the small focus box and other things via keyboard, somehow...

1. Starting up the FEI System Control Software
   a. Username: user     Password: user
   b. Double click the gray box to expand it and move it to the top right of the screen
      i. Click START
      ii. Username: user     Password: user
         **What is blue is selected! The FIB and SEM both use the same control panel!**
      **Never click WAKE UP!**
   c. Check CCD screen
      i. Make sure no one has left a sample inside the chamber (contact Mourad if so)
   d. Check for green symbol for ion, electron, and vacuum chambers
   e. Click VENT
- The chamber part turns orange while venting. Black means that it is fully vented.
2. Sample Loading
   a. *Gloves!* for touching the sample/chuck
   b. Insert the chuck into the pin slot in the chamber (may need to loosen the screw slightly)
   c. Align the sample with the door in such a way that you can remember, and such that the Faraday cup is opposite the chamber door.
   d. Use the allen wrench to tighten the screw slightly so that the chuck is held in place
   e. Close the door gently and hold it in place while clicking PUMP to evacuate the chamber
   **Be careful with fingers near the door, as it pull the door closed once pumping begins**
   f. Wait for the Black, Orange, Green chamber icon sequence

3. Exploring the Sample Orientation
   a. The beam can be turned on (Beam On → Play/Pause) without fear of messing up the sample
   b. It is a good idea to find and focus on the Faraday Cup and confirm that the X and Y directions are as expected and draw a picture of the sample’s orientation with X and Y directions labeled.
      • Center Click = drag around movement, Double Click = jump to click location
      • Beam Shift knobs are easier at higher magnifications
      • Shift + Ctrl you can drag screen around
      • F5 goes full screen and back

4. Finding the Eucentric Height for Imaging
   ***Notes***
   • The eucentric height is the distance between the beam column and the sample at which the best focus can supposedly be obtained for a given machine.
     a. Beam Control → Navigation
     b. Use small particles on the sample surface - not down in a scratch - with easily visible contrast to focus the beam at at least 1000X magnification.
     c. After the sample is in focus, the Z FWD icon will measure the true distance of the sample from the bottom of the electron column.
     d. Look at CCD and enter 5 mm as the Z value. This moves the sample up.
   ***Be ready to hit Escape and/or click cancel if the sample comes too close to the column!***
     e. Continue focusing, using Z FWD, and moving the sample to 5 mm up to at least 8000X magnification.
     f. For high resolution focus, the stigmator will need to be adjusted as well.

5. High Resolution (Immersion) Mode Imaging
   • Must be at the eucentric height and at least 1200X magnification in order to use hi-res mode.
     o Don’t leave the scope in immersion mode when you zoom back out.
   *****Hi-Res mode uses a strong magnet close to the sample, so no ferrous materials (like stainless steel) or liquid should be used without discussing it with Mourad!*****

6. Shared Computer Network
• There is a switch that changes between the Nova computer and the computer with the shared hard drive space. SEM taken via the Nova should be saved onto the one whose screen is on the left and tower is on the right on the floor, where they can be saved onto a USB drive.
  o Take an image and Save As .tif16 normally. Use .jpg to save the colored measurements.
  o Path: sdb-d000 (C: Shared Folder/sjbauman)

7. Checkout procedure
a. Bring the stage height Z to ~28 mm, set x=0 and y=0.
b. Zoom out SEM and go to standard voltage, spot size, and scan speed
c. Turn off the beam (Pause and then Beam Off).
d. Press Vent and wait until the stage door opens with a gentle pull.
e. Remove the sample. Hold the door closed and press Pump button. Wait until the vacuum indicator is Green.
f. Sign out of the logbook.
g. Don’t forget your USB drive!
Cathodoluminescence Imaging/Spectroscopy with the FEI Nova Nanolab 200 + Gatan Mono CL4:

Cathodoluminescence with the FEI Nova Nanolab 200 + Gatan Mono CL4:

****************
- **Gloves!** must be worn whenever the sample or chuck is handled!
- Always be careful with the mirror and its separation distance from the sample.
- Always make sure to pause the Nova CCD screen when trying to take CL measurements so that the infrared light inside the chamber turns off and does not interfere with the CL signal.
- Aperture 7 is used for normal SEM imaging (smaller aperture, less signal, better resolution).
- Aperture 3 is a larger aperture so provides more signal for CL at the expense of SEM resolution.
  - Can play with the x and y aperture knobs while doing lens modulator to improve more.
- SEM scan can be controlled via Nova or CL computer, not both simultaneously.
- Centering the optical hotspot on the CL signal/Pulse screen is crucial to obtain optimal results. The beam shift should be zeroed, and the mirror physically moved in order to center this.
- If the contrast is turned all the way up on the PMT controller, some interference noise in the CL signal will be amplified to the point of dominating the signal.
- If the PMT counts do not appear correct, turning on/off the CCD power/chiller (black box on the ground behind the CL computer table) seems to fix this issue.

****************

Keyboard shortcuts:
- +/- to zoom in/out
- Center Click = drag around movement, Double Click = jump to click location
- Beam Shift knobs are easier at higher magnifications
- Shift + mouse clicks to do stigmation, etc.
- Shift + Ctrl you can drag screen around
- F5 goes full screen and back
- There’s a way to do the small focus box and other things via keyboard, somehow...

1. Starting up the FEI System Control Software
   a. Username: user  Password: user
   b. Double click the gray box to expand it and move it to the top right of the screen
      i. Click START
         ii. Username: user  Password: user
            **What is blue is selected! The FIB and SEM both use the same control panel!**
            **Never click WAKE UP!**
   c. Check CCD screen
      i. Make sure no one has left a sample inside the chamber (contact Mourad if so)
   d. Check for green symbol for ion, electron, and vacuum chambers
2. Sample Loading
   a. *Gloves!* for touching the sample/chuck
   b. Insert the chuck into the pin slot in the chamber (may need to loosen the screw slightly)
   c. Align the sample with the door in such a way that you can remember, and such that the Faraday cup is opposite the chamber door.
   d. Use the allen wrench to tighten the screw slightly so that the chuck is held in place
   e. Close the door gently and hold it in place while clicking PUMP to evacuate the chamber
      **Be careful with fingers near the door, as it pull the door closed once pumping begins**
   f. Wait for the Black, Orange, Green chamber icon sequence

3. Exploring the Sample Orientation
   a. The beam can be turned on (Beam On → Play/Pause) without fear of messing up the sample
   b. It is a good idea to find and focus on the Faraday Cup and confirm that the X and Y directions are as expected and draw a picture of the sample’s orientation with X and Y directions labeled.

4. Finding the Eucentric Height for Imaging
   ***Notes***
   - The eucentric height is the distance between the beam column and the sample at which the best focus can supposedly be obtained for a given machine.
   a. Beam Control → Navigation
   b. Use small particles on the sample surface - not down in a scratch - with easily visible contrast to focus the beam at at least 1000X magnification.
   c. After the sample is in focus, the Z FWD icon will measure the true distance of the sample from the bottom of the electron column.
   d. Look at CCD and enter 10 mm as the Z value. This moves the sample up.
   ***Be ready to hit Escape and/or click cancel if the sample comes too close to the column!***
   e. Continue focusing, using Z FWD, and moving the sample to ~7 mm up to at least 8000X magnification.
   f. For high resolution focus, the stigmator will need to be adjusted as well.

5. Inserting the Gatan system parabolic mirror
   *****
   - Must be slightly farther away than the normal working distance (use ~6 or 7 mm WD to be safe).
   - This mirror costs ~$10,000 with all of the connections etc! Don’t crash it into the sample!
   *****
   a. Zoom out SEM to relatively low magnification.
   b. Turn screen to be visible from the Gatan mirror insertion point.
c. Slowly push the mirror into the system by hand until the hole is centered on the SEM screen.

6. Starting up the CL System
a. Start the Gatan software.
b. Turn on the PMT controller and temperature regulator if it is off (small round black button).
c. Make sure that the PMT voltage is at least less than ~600 V (signal usually starts to appear around 1000) and that the software shows essentially zero counts.
d. Turn on the CCD power source/temperature regulator (black box on the ground behind the desk) only when you are going to use Parallel mode as it causes noise in the Panchromatic image signal, which only uses the PMT.

7. Setting up for CL Measurements
a. Select Zero Beam Shift from the Stage menu on the Nova.
b. Zoom the SEM scan to where the mirror hole fully fits in the image.
c. Pause the SEM scan on the Nova.
d. Select Search on the Gatan software to view the live SEM scan, CL image (after brightness/contrast adjustments), and Pulse image (raw PMT data).
e. Adjust the sample height manually via the micrometer on the Nova so that the hotspot on the CL screen is focused as well as possible.
i. A good working height is most likely somewhere around 5.5 - 6.0 mm.
f. Move the mirror (and rotate the MonoCL system, if allowed) as necessary to bring the hotspot as close to the center of the CL image as possible. Playing with the beam shift does move the hotspot, but according to Dr. Knight, this isn’t the best way to do it? Qigeng says it works.
   **** Make sure to turn off the beam when rotating the system, in case it would lose vacuum and could potentially harm the gun.****

8. Taking CL Measurements
a. Focus the SEM on the desired structure.
b. Using Search, Preview, or Report on the Gatan software will show CL and Pulse results if the system is set to Panchromatic mode.
c. The modes work as follows:
   Panchromatic - sends all light from each electron beam location (each pixel) directly to the PMT.
   Monochromatic - sends all light through a slit and onto a grating (there are 3 different grating options). From here it either goes to the CCD (Parallel mode) or through another slit to the PMT (Serial mode).
   1. Parallel - wavelengths that have been spread out by the grating impinge on the CCD directly, creating a spectrum. Builds the hyperspectral image data cube more quickly, but has less sensitivity than the PMT.
   2. Serial - light goes through a second slit, passing only this small wavelength band to the PMT. Takes longer to build up the hyperspectral image data cube, but gives greater sensitivity than the CCD.
d. Need to make sure that the PMT voltage is sufficiently high to produce counts on the Gatan software screen.
e. If a spectral image is taken via Parallel or Serial mode, each image pixel contains a spectrum, and thus the spectra can be viewed all around the sample as desired. Use the Slice window to view the entire image for a single wavelength. (Window/Floating Window/Slice).
   - Drift correction - Under the Spectral Imaging menu (also may provide a checkbox option when setting up a spectral imaging run). This does a check of the provided SEM image with the current scan to make sure that the scan is not drifting away from the desired structure during the imaging process.
   - Sub-pixel Fuzzing/Scanning - Helps improve a signal with low counts by essentially averaging multiple pixels. You don’t technically lose resolution, the image just looks like you have?
   - Picker Tool - Use this to get a spectrum for the selected box on a spectral image.

9. Shared Computer Network
   - There is a switch that changes between the Nova computer and the computer with the shared hard drive space. Images/data taken via the CL computer should be saved onto the one whose screen is on the left and tower is on the right on the floor, where they can be saved onto a USB drive.
     o Path: Network/sdb-d000/C:/Shared Folder/sjbauman

10. Checkout procedure
   a. Turn off PMT and CCD power/controllers.
   b. Exit Gatan software if finished saving images/data.
   c. Bring the stage height Z to ~28 mm, set x=0 and y=0.
   d. Carefully remove parabolic mirror from the chamber.
   e. Zoom out SEM and go to standard voltage, spot size, and scan speed
   f. Turn off the beam (Pause and then Beam Off).
   g. Press Vent and wait until the stage door opens with a gentle pull.
   h. Remove the sample. Hold the door closed and press Pump button. Wait until the vacuum indicator is Green.
   i. Sign out of the logbook.
   j. Don’t forget your USB drive!

Additional Considerations:
   - CL measures the excitability of the sample, not actually where the light is coming from. The image location information comes from the beam scan’s current position, just like the SEM image. The brightness is from how much light comes out of the entire sample. The image, therefore, only shows where the sample was most strongly or weakly excited and thus caused more or less light to be emitted (from somewhere). For some samples such as metasurfaces or gratings, light could even be emitted from so far away that it is out of the detection range.
   - Al crystal calibration for transition radiation
   - Carbon luminescence and plasma cleaning to fix it
   - Perceptually uniform color scales
   - Better mirror position control and larger mirror are improvements in the other company’s system
• Abajo group’s transition radiation widget online and the review paper. We will need to do these corrections in order to get publication quality results
H.3 SEM Imaging with the FEI XL30 ESEM

Scanning Electron Microscopy with the FEI XL30 ESEM:

*********** The procedure for just imaging is different from the electron beam lithography procedure. One can safely turn on the beam without fear of resist exposure in the case of imaging.***********
- *Gloves!* must be worn whenever the sample or chuck is handled!
- Sign into the logbook.

1. Starting up the Computer
   a. Username: guest Password: esemuser1
   b. ESEM control interface is located in C: → xl → mc → mctrl
   i. Username: students Password: esemuser1
   c. Check for “Vac OK” (10⁻⁶ up to 10⁻⁴)
   d. Click VENT
   e. Click CCD in Detectors to see inside the chamber
      *Make sure no one has left a sample inside the chamber (contact Mourad if so)*
   f. Boot the NPGS computer to get its calibration started
      Username: ebluser Password: ebluser1
      *Minimize the window that pops up. It is initializing the software that controls the ESEM*

2. Sample Loading
   a. *Gloves!* for touching the sample/chuck
   b. Be sure that the stage is not screwed down all the way so that the working distance can be made to be 7 mm without exceeding the stage limits.
   c. Insert the chuck into the pin slot in the chamber (may need to loosen the screw slightly)
   d. Align the sample with the door in such a way that you can remember, and such that the Faraday cup is opposite the chamber door.
   e. Use the allen wrench to tighten the screw slightly so that the chuck is held in place
   f. Close the door gently and hold it in place while clicking PUMP to evacuate the chamber
      **Be careful with fingers near the door, as it will pull the door tightly closed once pumping begins**
   g. While waiting for the vacuum to pump down to “Vac OK”, begin working with NPGS

3. Nano Pattern Generation System (NPGS) Software
   a. Computer should be performing calibration - minimize this window.
   b. Open NPGS from the desktop
      Select desired Project folder
   **Note** The A/B switch can always be set to B with no repercussions. This is the only way to use NPGS for lithography or digital imaging. When set to B, the NPGS main menu can be used to go between SEM and NPGS control. Via the Digital Imaging menu, NPGS can be used to obtain slow-scan SEM images that can be saved via USB instead of saving images and burning CDs via the ESEM computer.
4. **Exploring the Sample Orientation**
   a. The beam can be turned on (10.0 kV button) without fear of messing up the sample
   b. It is a good idea to find and focus on the Faraday Cup and confirm that the X and Y directions are as expected and draw a picture of the sample’s orientation with X and Y directions labeled.
   - There are two beam control modes using the mouse. The crosshair centers on a double-clicked location. The target moves in the direction of the cursor during a left click held down. Use them interchangeably for efficiency

5. **Finding the Eucentric Height for Lithography**
   ***Notes***
   - The eucentric height is the distance between the beam column and the sample at which the best focus can supposedly be obtained for a given machine.
   a. The sample should be at a distance of ~20-28 mm from the electron column, as the previous user should have moved the stage to this height.
   b. Use small particles on the sample surface - not down in a scratch - with easily visible contrast to focus the beam at at least 1000X magnification.
   c. After the sample is in focus, the Z FWD button will measure the true distance of the sample from the bottom of the electron column using the height at which you have focused the beam.
   d. Switch the detector to CCD and enter 10 mm as the Z stage value. This moves the sample up.
   ***Be ready to hit Escape and/or click cancel if the sample comes too close to the column!***
   e. Continue focusing and moving the sample to 10 mm up to at least 8000X magnification.
   f. For high resolution focus, the stigmator will need to be adjusted as well.

6. **Saving Images**
   - **Black Desktop with NPGS software:**
     a. From the NPGS menu, go to the Digital Imaging window
     b. With the ESEM under NPGS control, take a new image using the desired parameters
     c. Save the image to the appropriate desktop folder
     d. Save the image to your USB drive
   - **White Desktop with MCtrl software:**
     a. Using the In/Out → Image menu option, give the image an appropriate title
     b. Save the image to the appropriate desktop location
     c. Use Nero to burn the saved images to a CD

7. **Checkout procedure**
   a. Set magnification to minimum
   b. Bring the stage height Z to 28mm, set x=0 and y=0
   c. Set Voltage to 10.0 kV and Spot Size to 3
   d. Turn off the beam (HV) and switch to CCD detector
   e. Press Vent and wait until the stage door opens with a gentle pull.
   f. Remove the sample. Hold the door closed and press Pump button. Wait until the vacuum indicator is “Vac OK”
g. Close the microscope user interface
h. Log off and turn off ESEM screen monitor. Turn off the NPGS computer
i. Sign out of the logbook.
j. Don’t forget your USB drive or CD!
H.4 EBL with the FEI XL30 ESEM

Electron Beam Lithography with the FEI XL30 ESEM:

********** The procedure for just imaging is different than the electron beam lithography procedure. One must be careful during the lithography procedure not to treat the sample the same as if he/she was viewing the sample. **Shooting a beam of electrons at the sample to view it will expose the resist**, so one must be aware of the location of the beam on the sample surface at all times!**********

- *Gloves!* must be worn whenever the sample or chuck is handled!
- Sign into the logbook.

1. Starting up the Computer
   a. Username: guest     Password: esemuser1
   b. ESEM control interface is located in C: → xl → mc → mctrl
   i. Username: students     Password: esemuser1
   c. Check for “Vac OK” (~10⁻⁶ up to 10⁻⁴)
   d. Click VENT
   e. Click CCD in Detectors to see inside the chamber
   .Make sure no one has left a sample inside the chamber (contact Mourad if so)
   f. Boot the NPGS computer to get its calibration started
   .Username: ebluser   Password: ebluser1
   i. Minimize the window that pops up. It is initializing the software that controls the ESEM.

2. Sample Loading
   a. *Gloves!* for touching the sample/chuck
   b. Be sure that the stage is not screwed down too far so that the working distance can be made to be 10 mm without exceeding the stage limits.
   c. Insert the chuck into the pin slot in the chamber and make sure it lowers all the way.
   d. Align the sample with the door in such a way that you know how it will move in x and y based on the door being parallel to y, opening and closing along x.
   e. Close the door gently and hold it in place while clicking PUMP to evacuate the chamber.
      **Be careful with fingers near the door, as it will pull the door tightly closed once pumping begins**
   f. While waiting for the vacuum to pump down to “Vac OK”, begin working with NPGS (checking patterns and run files)

3. Nano Pattern Generation System (NPGS) Software
   ****For issues with NPGS and/or DesignCAD, see the troubleshooting Google Doc in the folder SJBauman/Labs and Procedures/NPGS.****
   a. Black computer should be performing calibration - minimize this window.
   b. Open NPGS from the desktop
   i. Select desired Project folder
   c. **DesignCAD Software**
      **All commands must be done with the NPGS dropdown menu (even SAVE)**
      - Layers and Line Styles are important.
o Dashed lines will be “area-dose” filled polygons. Solid lines will be single passes of the beam.
  - NPGS can do different doses or spot sizes depending on colors and layers in the design.
  - See additional documentation for NPGS and DesignCAD tips/troubleshooting.

**Note** The A/B switch can always be set to B with no repercussions. It must be set to B to use NPGS for lithography or digital imaging. When set to B, the NPGS main menu can be used to go between SEM and NPGS control. Via the Digital Imaging menu, NPGS can be used to obtain slow-scan SEM images that can be saved via USB instead of saving images and burning CDs via the white ESEM computer.

4. Exploring the Sample Orientation

***Viewing the sample exposes it!!!***
- The beam should not be turned on until you are confident that the sample is out of the way. It is good to move the stage so that the beam will be off the chuck on the side of the Faraday Cup, because it is a useful point of reference to find the samples once the beam is on.

a. Go to the CCD screen.

b. Start at \((x, y) = (0, 0)\). Moving to \((-12,000,0)\) µm will bring the edge of the sample near the beam column for our SEM mounts.

c. The beam can be turned on (10.0 kV button) when you’re confident the beam won’t hit your sample and the resist will therefore not be accidentally exposed.

d. It is a good idea to find and focus on the Faraday Cup and then carefully explore the edges of the sample. Confirm that the X and Y directions are as expected by your pattern designs and run file. The NPGS software run files will move in the same \((x, y)\) directions as the SE view in the ESEM control software.

e. Draw a picture of the sample’s orientation on the mount (also draw the Faraday cup) with \(x, y\), and positive rotation directions labeled.

5. Finding the Eucentric Height for Lithography

***Notes***
- The eucentric height is the distance between the beam column and the sample at which the best focus can supposedly be obtained for a given machine.
- Accelerating Voltage 30 kV will be used for lithography, as it gives the best depth of focus, so any focusing should be done at this voltage, not 10 or 15 kV.
- You’ll want to end up at Spot Size 1 for the final and highest resolution focusing, because that’s what you’ll use to pattern the small important features and you’ll pattern those first in the run file. It can be easier, however, to first find areas containing small particles using Spot Size 3 and then switch once you’re ready to try to optimize the resolution of imaging small particles using Spot Size 1.

a. The sample should be at a distance of ~20-28 mm from the electron column, as the previous user should have moved the stage to this height. We need to determine the exact distance by focusing and letting the machine determine the distance by using this focal length.

b. Use small particles on the sample surface with easily visible contrast to focus the beam at least 1000× magnification.
c. Once the sample is in focus, the Z FWD button will measure the true distance of the sample from the bottom of the electron column using the height at which you have focused the beam.
d. Switch the detector to CCD and enter 10 mm as the Z stage value. This moves the sample up.
   ***Be ready to hit Escape and/or click cancel if the sample comes too close to the column!***
  c. Continue focusing and moving the sample to 10 mm up to at least 8000X magnification, making sure the sample doesn’t crash via the CCD screen if you need to move the stage towards the beam column.
f. For high resolution focus, the stigmator may need to be adjusted as well.
a. To do this, play with the x and y stigmator knobs, focusing between adjustments to see if the image stays relatively stationary on the screen when it goes out of focus.

6. Checking the Beam Current
   • Spot size and accelerating voltage affect the beam current. This then affects the dose.
     Spot size may vary depending on the aperture adjustments and the filament condition.
     The spot size numbers do not actually mean anything about the size of the beam. From most recent measurements, one can expect values approximately as follows:
       o Spot 1: 9.5 pA
       o Spot 2: 142 pA
       o Spot 3: 676 pA
       o Spot 4: 237 pA
       o Spot 5: 308 pA
       o Spot 6: 243 pA
       o Spot 7: 207 pA
     • Thus, we use Spot 1 for the small important patterns and switch to others with higher beam currents when writing larger, less detailed patterns.
  a. Go to maximum magnification at the hole in the center of the Faraday Cup.
  b. Replace the Sample Crash Detector BNC cable with the Ammeter BNC.
  a. A warning will pop up saying that you’ve crashed the sample, which you have not done. Click OK
  c. Turn on the picoammeter and push ZCHK.
  d. Record beam current value. (Should be ~10 pA for Spot Size 1).
  e. Zoom back out to find the marked sample corner and center the beam on the corner.
  f. If possible, rotation alignment will help to make sure that the screen x and y align with the sample edges.

7. NPGS Run Files
   ****For issues with NPGS and/or DesignCAD, see the troubleshooting Google Doc in the folder SJBauman/Labs and Procedures/NPGS.****
   • Run files move in the same x,y directions as the SE screen when imaging
  a. Need the first step (Entity 1) to turn the ESEM to External Mode
  b. Need a secondary step (Entity 2) to bring up the comment window before movement/writing steps. Here, you can write whatever notes and reminders you would like.
  c. Based on the known orientation of the sample, a move step will bring the beam away from the corner of the sample to the desired writing location prior to writing the pattern.
a. For our small chips, we move 5000 µm in both the negative x- and y-directions. This puts the beam near the center of the chip.

- The dose is a measure of current per unit area (A/m²), and when you input a desired dose for a pattern at a specific Spot Size and its corresponding measured beam current, NPGS calculates and adjusts one/all of the following:
  - Dwell Time: how much time the beam to spends at each spot along the path of writing.
  - Center-to-Center Distance: how far the beam is moved between adjacent spots along the path of writing.
  - Line Spacing: most likely similar to center-to-center distance, but one being a horizontal and one being a vertical measurement. I tend to set them as the same value.
- NPGS can be made to write patterns in an array, varying the dose for each step by controllable percentage amounts if desired (used for dose tests).
  - The dose percentage can be controlled, and entering the beam current value in the main NPGS window calibrates based on the measured current and the desired run file current to get the correct dose.
- NPGS moves back to the center of the array (where it started the array from) afterwards.
- Make another move at the end of the write to bring the beam back to the sample corner.
- Command → Calibrate DACS can often fix an NPGS run error

8. Checkout procedure
a. Set magnification to minimum
b. Bring the stage height Z to ~28 mm, set x=0 and y=0
c. Set Voltage to 10.0 kV and Spot Size to 3
d. Turn off the beam (HV) and switch to CCD detector
e. Press Vent and wait until the stage door opens with a gentle pull.
f. Remove the sample. Hold the door closed and press Pump button. Wait until the vacuum indicator says “Vac OK”
g. Close the microscope user interface
h. Log off and turn off ESEM screen monitor. Turn off the NPGS computer
i. Sign out of the logbook.
j. Don’t forget your USB drive or CD!
H.5  EBL with the JEOL JBX 5500

This section was authored primarily by Ahmad Darweesh, but the work includes edits and collaboration by the author.

SOFTWARE
This step can be divided into 3 sub-steps
A- Pattern Designer
B- Calibration
C- Exposure

At the beginning go to “EOS mode” at the top and hit “Select” then hit “Select” again and find your file from “calibration name list”. Then choose “Mode 4” then hit “OK” and hit “OK” again. Make sure that you are using the right aperture. In our case “Apu1” look at the machine.

A- Pattern Designer
Hit the home button to return the stage to the home position

1- Plugin the flash disk
2- Copy gds file from usb and paste it into “c/Documents sitting/eb/My document/patterns/Herzog lab/xxxxx”
3- Hit “Pattern Designer”
4- Hit “option” then hit “convert gds file”
5- Hit “open” and go to the “xxxxx Folder” and choose the gds file.
6- Hit “select all” layers then “OK”
7- Put 100 in “Field Size” (If you are using lens5)
8- Keep the input and output files in the same names.
9- “Shot Modulation” (using different doses) we do not use it if we have one dose.
10- Choose “NONE”
11- Hit “Start to Convert”
12- Hit “File”, then Hit “Import” and choose the file that you converted with v30 extension.
13- Hit “Runout” then “Yes”.

B- Calibration
Make sure the pressure in CH1 = 1.5e-4. If not just wait. We have manual and automatic calibrations.
a- Manual Calibration
Four main buttons appear in this step: FC, AE, BE, and AU. The order of the buttons is FC, BE, AE and AU in case of doing “WOB” or FC, AE, BE, and AU in case of not doing “WOB”. If you change the current or lens, you need doing WOB. Let us suppose we need to do “wobb”
   • FC Step
1- Hit “FC” then “MOVE”. (If you get an error like ‘stage momentum’ just wait for a minute then redo 1
2- Hit “Beam On”
3- Adjust the current by playing with “LENS2/3” to get the desire current (100 pA=0.100nA).
4- Hit “Beam Off”.
5- Since we changed the current, we need to go to “BE” to make “WOBB” before going to AE.

· BE step
6- Hit “BE” then hit “MOVE”
7- Hit “Display” and choose “SE Image” (the beam automatically being ON)
8- Use the arrows to make the BE mark (cross) in the middle.
9- Change the “Unit Step” to move smoother.
   10- Put 10,000 into “Scan width” and 2,000 into “Scan Clock”
   11- Hit “entry” then “BE”
   12- Hit the first box next to ‘SE Image’ to get “Rapid Scan”
   13- Put 500 into “Scan Clock”
   14- Hit “WOBB” choose “LENS2/3” then hit “WOBB” button.
   15- Try to stop Wobbling (as much as possible) by using the knobs in the machine.
   16- Hit “WOBB” to stop wobbling.
Note: if you are going to use the same aperture and file, you do not need to do wobbling.
17- Hit “SEI Setting” and put 2,000 in “Scan Clock”
18- Hit “Rapid Scan” to stop it.
19- Bring the cross in the middle (using the arrows)
20- Hit “entry” then “BE”
21- Hit “Beam Off”.
Note: Try to setup BE and AE very fast
22- Go to “FC” and hit “MOVE” to check the current.

· AE Step
23- Hit “AE” then “MOVE”
24- Hit “BEAM ON”
25- Make it (the pic) in the middle.
26- Hit “entry” then “AE”
27- Hit “BE” then “MOVE” to check it

· Au step
1- Hit “AU” then “MOVE”
2- In “SEI Setting” put 1,000 into “Scan width”
3- Play with “contrast” and “Brightness” to see the GNPs.
4- Put 500 into “Scan Clock” after finishing return it back to 2,000
5- On the top right there is “FOCUS”, play with that to get a good pic of GNPs.
6- Put 10,000 into “Scan width”
7- Hit “Beam Off”
8- Go to Home Position (optional)
Note: To finish AU step quickly, you can use auto calibration. To do that, hit calibration, hit Focus Square after finish save it (hit “main” and “save”)
b- Auto Calibration
1- Hit “Calibration”
2- Choose the first four squares (make sure of “calibration condition name”)
3- Choose “load” and pick the calibration file from the drop-down menu. Click “Execute” to load the file
4- Hit “Execute calibration”
5- After finishing hit “Deselect”
6- Hit “main” then hit “save” put the date or any comments you want.
7- Hit “OK” then “close”

C- EXPOSURE
1- Hit “Exposure”
2- Hit “Type” then choose the last option (BX…) Not using Wafer.
3- Put 1,000 into the “Line”
4- Put 400 into the “Plane”
5- Hit “Chip a” and choose v30 file (the desire file)
6- Drag a and put it in the big square. And right click on it.
7- Choose “Properties”
8- Put the numbers of X and Y that you calculated into “Position” (in microns)
9- Hit “OK”
10- Go the right side and choose “EOS Mode” and make sure it is “EOS Mode 4”
11- Hit “properties” of “Job1”
12- Put “2,4,8,16,32, or 64” depending on the Excel file sheet “JBX-5500 scan speed calculation”
13- Hit “OK”
14- Hit “RUN” . If it asks you to save it as another name, say “Yes” and choose a name.
H.6 COMSOL Multiphysics Helpful User Information

Computer/File Maintenance:
- Recovery files
  - If hard drive space is being rapidly depleted due to COMSOL files, delete unneeded recovery files in C:\Users\comsol\v53 (or current version)\recoveries
  - It is possible to change the default COMSOL settings to not save these if desired.
  - For help, see the following video link on the recovery file location: https://www.comsol.com/blogs/how-and-when-to-open-recovery-files-in-comsol-multiphysics/

- Running COMSOL via comsol.bat built-in batch file
  - This handy technique allows users to queue up multiple files to run serially without opening the COMSOL user interface. Each file can be saved with a chosen filename when running has completed, and a .txt logfile can be output during running in order to check progress.
  - This method also automatically saves recovery files into the working folder.
  - The file must be added to the Path environment variable in the advanced settings of the PC properties. For detailed information on this process, see the following: https://www.comsol.com/blogs/how-to-run-simulations-in-batch-mode-from-the-command-line/
  - Syntax: comsolbatch -inputfile Model1.mph -outputfile Model1_solved.mph -batchlog Model1_solved.txt
  - To edit, simply edit the text file in Notepad and save. To run via Command Prompt, open this file.

Geometry, Units, Materials, Defining Parameters:
- The best practice is to input units any time values that ought to have units are used.

- Geometrical units must be defined for all entities for them to be properly built.

- When sweeping geometrical parameters, units must also be input in the parametric sweep “Units” section.

- Ideally, physics parameters such as wavelength are defined initially and other physics variables such as frequency are calculated from these. (Same for input electric field strength being used to derive input power, irradiance, etc)

- Interpolation tables are handy for taking data from a source such as refractiveindex.info and using it to, for example, apply material property values over a range of wavelengths that may not be directly reported in the original table.
  - Very useful for complex refractive index/dielectric permittivity
  - Be careful to check and input the correct units for each table column here.

- Electrical conductivity $\sigma$
  - Use actual experimental value in the material parameters table
Set sigma to zero in the Wave Equation settings (only necessary when using permittivity ($\varepsilon'$ and $\varepsilon''$) instead of refractive index ($n$ and $k$)).

Current density calculations need the correct $\sigma$ value, but optical calculations do not because the ‘lossiness’ of the material is already contained in the imaginary part of the refractive index/permittivity. If you put both a complex optical value and a conductivity value, it counts the lossiness twice, giving incorrect results.

**Meshing:**
- Mapped mesh for PML
  - Use a Distribution across edges to get the desired number of mapped points at these boundary domains.

- Free tetrahedral everywhere else
  - Put a Convert mesh entity at the boundary between Mapped and other types
  - Allow for quick growth so that mesh becomes coarser in non-critical regions to save computation time.
  - May need to control the finesse/coarseness in important regions to balance between high resolution results and fast computation time.

- Typically, it is a good idea to run a convergence test to determine how coarse a mesh may be while still producing the proper results. This requires running a base simulation for which an expected calculation result exists. The mesh should be started at a finer value to obtain the expected results, and the coarseness should then be increased until the results deviate significantly from those expected. This defines the optimal coarseness for the model, at which point the calculation speed will be the fastest and the model will still produce accurate results.

**Physics:**
- Check the units of the frequency/wavelength in Wave Equation settings.

- Periodic boundary conditions require matching mesh edges at opposite boundaries.

- Mirror boundary conditions
  - Perfect Electric Conductor applied to opposing boundaries in direction perpendicular to the E-field polarization.
  - Perfect Magnetic Conductor applied to the other opposing boundaries that aren’t pierced by the wave propagation direction.

- Perfectly Matched Layers should be applied to absorb scattered waves at boundaries. The regions must be defined in the Definitions tree.

- Ports may be used to input the propagating electric field equation into the model vs. inputting it as a Background Field. Inputting the same field in both places doubles the field strength, as it is input twice into the model.
• Ports are useful for calculating Transmission and Reflection via the S-parameters that they provide in the model. It is possible that T and R may be calculated via other line or surface integrals, however.
  o Use the expression abs(emw.S11)^2 to calculate Reflection using Port 1
  o Use the expression abs(emw.S21)^2 to calculate Transmission using Port 2
  o Use 1 = T + R + A to calculate the Absorption using the calculated Transmission and Reflection values.

• Unless calculating things like diffraction patterns for a grating, we don’t need the higher Diffraction Order modes (1, 2, etc). These can safely be disabled if they are left over from the plasmonic wire grating model etc.

• If the geometry is being swept such that the model width changes, the input power should be a function of the surface area seen by the incoming wave so that the power is constant across all model dimensions through the parametric sweep.

**Results:**
• Derived Values
  o There may be some differences between Average: Summation, Average: Integration, and other options. Check the values to be sure the desired outcome is being calculated.

• Absorption and Scattering Cross Sections can be calculated by defining the proper equations (see models)

• Surface average enhancement can be used in place of a region average near a nanogap, for example, to obtain the average E^2 over any surface(s).