Theoretical Tailoring of Perforated Thin Silver Films for Surface Plasmon Resonance Affinity

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THEORETICAL TAILORING OF PERFORATED THIN SILVER FILMS
FOR AFFINITY SURFACE PLASMON RESONANCE BIOSENSOR
APPLICATIONS

by

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A thesis submitted in partial fulfillment of the requirements
for the Honors in the Major Program in Chemistry
in the College of Sciences
and in the Burnett Honors College
at the University of Central Florida
Orlando, Florida

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ABSTRACT

Metallic films, in conjunction with biochemical-targeted probes, are expected to provide early diagnosis, targeted therapy and non-invasive monitoring for epidemiology applications\(^1\)-\(^4\). The resonance wavelength peaks, both plasmonic and Wood-Rayleigh Anomalies (WRAs), in the scattering spectra are affected by the metallic architecture. As of today, much research has been devoted to extinction efficiency in the plasmonic region. However, Wood Rayleigh Anomalies (WRAs) typically occur at wavelengths associated with the periodic distance of the structures. A significant number of papers have already focused on the plasmonic region of the visible spectrum, but a less explored area of research was presented here; the desired resonance wavelength region was 400-500 nm, corresponding to the WRA for the silver film with perforated hole with a periodic distance of 400 nm. Simulations obtained from the discrete dipole approximation (DDA) method, show sharp spectral bands (either high or low scattering efficiencies) in both wavelength regions of the visible spectrum simulated from Ag film with cylindrical hole arrays. In addition, surprising results were obtained in the parallel scattering spectra, where the electric field is contained in the \(XY\) plane, when the angle between the metallic surface and the incident light was adjusted to 14 degrees; a bathochromic shift was observed for the WRA peak suggesting a hybrid resonance mode. Metallic films have the potential to be used in instrumental techniques for use as sensors, i.e. surface plasmon resonance affinity biosensors, but are not limited to such instrumental techniques. Although the research here was aimed towards affinity biosensors, other sensory designs can benefit from the optimized Ag film motifs. The intent of the study was to elucidate metal film motifs, when incorporated into instrumental analysis, allowing the
quantification of genetic material in the visible region. Any research group that routinely benefits from quantification of various analytes in solution matrices will also benefit from this study, as there are a bewildering number of instrumental sensory methods and setups available.
DEDICATIONS

For all future scientists, especially those pursuing careers in the Chemical Sciences

For my mentors, for their guidance and expertise in their subject field

For my family, for their patience and understanding throughout my life
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LIST OF SYMBOLS

Absorption cross section $C_{abs}$
Amplitude of incident light $E_o$
Angle of incidence $\theta_i$
Angle of diffraction $\theta_d$
Extinction cross section $C_{ext}$
Groove periodicity $d$
Incident electromagnetic wave $E_{inc}$
Order of light $n$
Refractive index change $n_b$
Scattering cross section $C_{sca}$
Sensitivity of an SPR biosensor $S_c$
Sensitivity of output $S_{RI}$
Wavelength $\lambda$
LIST OF ABBREVIATIONS

Analytical Figures of Merit (AFOM)
Discrete Dipole Approximation (DDA)
Fast Fourier Transform (FFT)
Limit of Detection (LOD)
Limit of Quantification (LOQ)
SPP Bloch Wave (SPP-BW)
Surface Plasmons (SP)
Surface Plasmon Polaritons (SPPs)
Surface Plasmon Resonance (SPR)
Wood-Rayleigh Anomaly (WRA)
Wood-Rayleigh Anomalies (WRAs)
CHAPTER 1: INTRODUCTION

1.1 Introduction

Metal particle arrays are used in quantification systems and incorporate different scientific disciplines, including surface chemistry/biochemistry, solid-state physics and modern optics. This collective blend of disciplines allows important applications of sensors that reach broader applications in other fields, that include but not limited to, medical diagnostics, therapeutics, miniaturization of optical components, and photonic circuits\(^1\)\(^-\)\(^4\). Recent investigations within photonics have allowed new advances for sensors utilizing optical phenomena. Therefore, sensor design is an attractive area of research. Observing relationships and trends, theoretical research is the preliminary analysis to most fabrication methods. Sensors have been studied with the intent of attaining high analyte selectivity. Either one of the following two classes of sensors are known to provide high selectivity: (1) biosensors, sensors that utilize biologically derived components and typically include complementary binding sites for the analyte of interest or (2) sensors that use selective matrices\(^1\). This study exhausts a variety of periodic nanoscale metallic arrangements in thin films, in order to manipulate the optical spectra and to achieve optimal scattering profile.

1.2 Research Goals

A review of relevant research was included to show that metallic films elucidate biochemical content. These biosensors –the former class of sensors mentioned above in the introduction section– may provide sufficient repeatability after multiple tests. Surface
plasmon resonance (SPR) sensors are alternatives to commonly used electrochemical (E-DNA) sensors and may be more selective or sensitive. Therefore, the ever-increasing demand for precise, sensitive, selective sensors warrants both applied and theoretical solid-state research. The research presented here was aimed at biosensor use in spectrometric techniques. Although three main types of light characteristic modulation exist for sensors, we are concerned only with biosensors that utilize wavelength modulation. Therefore, with respect to the reference optical spectra, either a hypsochromic (blue-shifted) or bathochromic shift (red-shifted) determines the presence of a bound analyte to the perforated Ag film surface. Previous work from our research group in 2009, has allowed an opening for this work to develop surface plasmon resonance (SPR) biosensor design based on the selection of metallic film motif and biorecognition layer. This theoretical study optimizes the narrowest scattering bandwidth, found as a result of the Wood Rayleigh Anomaly (WRA), desirable for precise sensors operating within the wavelength of 400nm-500nm in the visible spectrum. The research presented here is geared toward other upper undergraduates, graduate students within multidisciplinary fields such as materials and computational chemistry, optics, solid-state physics. It would also be of use to experts in the field that are able to contribute to either the theoretical or experimental aspect of SPR sensor design. This study begins with the overview of optical phenomena that allow sensors to operate and proceeds with simulations of optical spectra obtained from the discrete dipole approximation method.
1.3 Significance of Research

It is imperative to understand that theoretical and experimental research have a mutual relationship that depend on one another. Therefore, the advancement in pure theory is needed to systemically pursue experimental areas that will lead to broader impacts in other fields of science. Since it would be costly and time consuming, at best, to explore all areas of experimental perforated Ag film layouts – varying aperture dimensions, spacing, geometry, film thickness, etc. – the research presented here provides a starting point or a platform for future experimental studies. In order to better detect antibodies, toxins, hormones, proteins, bacteria, DNA Strands or other such analytes, scientists must make advancements necessary to develop precise biochemical detection systems utilizing biochemical probes\(^2\). It is expected that the physical layout of Ag film with subwavelength hole arrays will provide not only a precise but also a facile method for analyte identification and/or quantification. This research will demonstrate, with the use of the Discrete Dipole Approximation (DDA) method, the optical spectra of perforated thin silver films. Implementations of such metallic structures are already used in various applications, from stimulated emission to advanced near-field imaging techniques that utilize optical traps and tweezers\(^{4-6}\). Metal films have been extensively studied but fewer authors delve into the applications of thin metallic films with apertures/holes arrays; Ebbesen and co-workers were the first to examine the optical properties of metallic films with periodic subwavelength aperture arrays\(^7\). The majority of previous research in perforated films focuses on the optimal parameters to achieve enhanced transmission not scattering efficiencies. In 2009, our research group published a journal article that revealed extremely low scattering efficiency, less than 1%, for perforated silver films
modified at tunable wavelengths\textsuperscript{8}. Furthermore, this study is aimed toward proving the existence of a hole array, in Ag film, arrangement that lead to strong, sharp, narrow peaks in the scattering spectra in the region corresponding to Wood-Rayleigh Anomalies (WRAs); a first, that our group is aware of, that show WRAs for potential use in surface plasmon resonance (SPR) sensors. Lastly if such arrangement exists, then we shall be concerned primarily with the construction of an ideal arrangement, that is to say, to find the most narrow, sharp, strong peak in the region of the scattering spectra that corresponds to WRAs. Ultimately this research may give the ability to measure the change in bound analyte concentration to provide quick quantitative data.

\textbf{1.4 Organization}

Chapter 1 introduces the topic, sets the expectations of the study, reveals the significance of theoretical exploration within metallic films, and outlines sensor research. Chapter 2 covers background information, advantages and current setbacks related with surface plasmon resonance sensors. Chapter 3 explains the methodology for the discrete dipole approximation and procedure behind tailoring the simulated Ag film architecture. Chapter 4 incorporates and discusses the spectral data obtained throughout the study. Chapter 5 summarizes the key points, evaluates the findings in the study and suggests potential advancements in the integrated field of biosensors and perforated silver films.
CHAPTER 2: LITERATURE REVIEW

2.1 Rayleigh Anomaly

Wood-Rayleigh Anomalies (WRA) can be observed from metal hole arrays and are frequently used in sensory applications\(^9\). To better understand the optical behavior of silver hole arrays, a brief introduction to WRAs was presented here. In 1902, Wood first observed what he deemed as “singular anomalies”\(^{10}\) when he examined a metallic diffraction grating under continuous light. Wood’s observation of this optical phenomenon was useful enough to describe metallic gratings, periodic structures and dielectric layers. His discovery eventually led to the formation of the grating equation, shown in equation 2.1.1, proposed by Rayleigh. Years after Wood’s pioneering research the grating equation allows a more complete characterization of metallic gratings\(^{11}\); pertinent to this study, equation 2.1.1 allows the calculation and therefore prediction of scattered light, of order \(n\), behavior. Where, \(\theta_i\) and \(\theta_d\) are the angle of incidence and the angle of diffraction, respectively; the wavelength \(\lambda\), assumed to be in a vacuum and periodicity of the groove denoted by \(d\).

\[
\sin(\theta_d) = \sin(\theta_i) + \frac{n\lambda}{d} \tag{2.1.1}
\]

Fano proposed two different types of diffraction effects, WRAs\(^{12}\), (1) Rayleigh wavelength an artifact of incident light parallel to the metallic surface and (2) a hybrid resonance mode where the grating sustains complex waves\(^{12,13}\). The hybrid mode between RA and the surface plasmon polariton bloch wave (SPP-BW) was deemed as an RA-SPP mode; although, RA-SPP could be a waveguide mode\(^{13}\). Both types of WRAs are present in the simulated scattering spectra for the Ag film design researched.
2.2 Electromagnetic Theory Behind Surface Plasmon Resonance

Affinity biosensors are made tunable and functional, at desired wavelengths, by surface plasmon resonance (SPR), a phenomenon that occurs from the total oscillation of electrons on a metal surface caused by incident electromagnetic waves. Dielectric and metal arrangement directly affects the observed phenomenon\textsuperscript{14,15}. SPR in turn allows for increased optical efficiencies, such as, attenuation, absorbance and transmission\textsuperscript{16}. A sufficient number of journal articles reveal optical properties of metal nanostructures. In addition, their modification to obtain optical “hot spots” is very attractive for applied areas of research\textsuperscript{17}. Resonance on the metallic surface occurs from one of three typical surface plasmons (SP) excitation methods on the metallic-dielectric interface, including, prism, grating and waveguide coupling\textsuperscript{18}. An observable response can be measured from the change in propagation of the incident light wave\textsuperscript{3}. SPR sensors are devices comprised of metal and dielectric mediums and are classified into two different categories, dependent on what physical quantity the sensors measures. For example, sensors that measure the refractive index are classified as direct sensors. In contrast, indirect sensors are optical devices that quantify the change in analyte concentration opposed to the refractive index\textsuperscript{18}. As explained in the introduction section, the focus is on the latter class of sensors due to the fact that affinity biosensors are a type of indirect SPR sensor. SPR sensors are designed in such a manner that intensity, angular or wavelength characteristics of light can be observed in a typical spectrum\textsuperscript{18}. Overall changes in behavior of light characteristics (wavelength, intensity or angular modulation) will be ultimately observed in simulated spectra. However, formulas were included in the appendix for wavelength modulation spectra only.
2.3 SPR Affinity Biosensors

Biosensors are an example of indirect surface plasmon resonance sensors because the change in bound analyte content can be measured from initial and final states and refractive index changes can be calculated as a result of the difference of bound analyte. At the metallic surface, the concentration of analyte is measured, as shown by the equation (2.3.1), when binding occurs between the immobilized biochemical probe (complementary binding site) and the selected analyte; in turn provides an observable change in light characteristics –either in wavelength, angular or intensity modulation– in the optical spectra as a result of the change (an increase) in the refractive index\(^1\):

\[
\Delta n_b = \left(\frac{dn}{dc}\right)_{vol} \Delta c_b
\]  

(2.3.1)

Equation (2.3.1) shows that the change in refractive index \(\Delta n_b\) can be measured because it is a function of the concentration of the analyte, bound to the complementary chemical probes, and the refractive index increment; where \(\Delta c_b\) denotes the content of the analyte bound to the metal surface and \(\left(\frac{dn}{dc}\right)_{vol}\) denotes the refractive index increment. Analytical figures of merit (AFOM), outside the scope of this thesis, were included in the Appendix A.B. and left for the reader to gain a better quantitative understanding. We expect that a comparison of observable peaks (before and after analyte binding) can be made from the scattering spectra from Ag film presented here. Since the type of chemical probes, mounted on the Ag surface, is dependent on the desired analyte, specific chemical probes were not included but left for future biochemical studies.
CHAPTER 3: NUMERICAL SIMULATION APPROACH

A suitable biosensor must be simulated from silver film with a steep scattering band. We expect this characteristic to aid detection of the bound analyte. The main idea to be addressed is to reveal silver film architectures that will yield narrowest scattering intensity within the wavelength region (400-500nm) of the visible spectra. The optical behavior of light and surface plasmons are directly influenced on the geometry and spacing of the apertures. The simulated silver film may be coated on a material with a high reflectivity, i.e., a glass substrate, to further improve its sensitivity towards the identification of biomolecules at desirable wavelengths\textsuperscript{18,19}. Relevant studies suggest that electrochemical sensors are among the most popular biosensors and despite their widespread use are plagued with electrochemical stability, memory effects and limited use in complex samples, such as blood, urine and crude cellular extracts\textsuperscript{15}. Although current research has improved AFOM\textsuperscript{20} in such matrices, it is hopeful that narrow scattering efficiencies can be obtained by varying the geometry, periodicity spacing, and size of the perforated hole arrays in metallic films, a potential alternative to electrochemical methods. If such narrow bandwidths are observed in our theoretical models, which we expect, then experimental tests can be implemented and various oligonucleotides can be immobilized within the best-suited film. It is expected that both high repeated performance and precision would be obtained from the SPR biosensors. However, only narrow scattering profiles will be examined in these simulations to contribute to the development of SPR biosensors.
3.1 Discrete Dipole Approximation

Discrete Dipole Approximation (DDA) methods were used to calculate scattering efficiencies. Optical efficiencies, such as absorption, extinction/attenuation, and transmittance can be modeled on various target geometries and periodic structures. DDSCAT 7.0, a free software made to implement the DDA method, has already been used to model phenomena within nanostructure arrays, interstellar dust and aerosols\textsuperscript{21-23} which would typically prove difficult for experimental. Perforated thin silver films are represented by periodic structures, ideal for DDSCAT. Since DDA has the capabilities to explore optical spectra of a particle with arbitrary geometry, we were able to theoretically investigate spectral manipulation of scattering profiles of incident light on the metallic film. Approximate solutions to Maxwell’s equations are obtained in DDA from partitioning the cross-sections of each silver film into a finite array of polarizable points/dipole polarizabilities via a hybrid method consisting of Fast Fourier Transform (FFT), convolution and conjugate grading methods\textsuperscript{21,22}.

$$C_{ext} = \frac{4\pi k}{|E_0|^2} \sum_{j=1}^{N} \text{Im}(E^*_{inc} \times P_j)$$  \hspace{1cm} (3.2.1)

$$C_{abs} = \frac{4\pi k}{|E_0|^2} \sum_{j=1}^{N} \left[ \text{Im}(P_j (\alpha_j^{-1}) \times P_j^*) - \frac{2}{3} k^3 |P_j|^2 \right]$$  \hspace{1cm} (3.2.2)

$$C_{sca} = \frac{k^4}{|E_0|^2} \int d\Omega |\sum_{j=1}^{N} [P_j - \hat{n}(\hat{n} \times P_j)] \exp(-ik \hat{n} \times r_j)|^2$$  \hspace{1cm} (3.2.3)

3.2 Solving Maxwell’s Equations with DDSCAT

As mentioned in section 3.1, DDA calculates the cross section of dipole polarizabilities of absorption, scattering and extinction profiles by Ag film and are characterized by the following equations\textsuperscript{23,24}.

$$C_{ext} = \frac{4\pi k}{|E_0|^2} \sum_{j=1}^{N} \text{Im}(E^*_{inc} \times P_j)$$  \hspace{1cm} (3.2.1)

$$C_{abs} = \frac{4\pi k}{|E_0|^2} \sum_{j=1}^{N} \left[ \text{Im}(P_j (\alpha_j^{-1}) \times P_j^*) - \frac{2}{3} k^3 |P_j|^2 \right]$$  \hspace{1cm} (3.2.2)

$$C_{sca} = \frac{k^4}{|E_0|^2} \int d\Omega |\sum_{j=1}^{N} [P_j - \hat{n}(\hat{n} \times P_j)] \exp(-ik \hat{n} \times r_j)|^2$$  \hspace{1cm} (3.2.3)
\[ C_{\text{sca}} = C_{\text{ext}} - C_{\text{abs}} \] (3.2.4)

All spectral cross sections use units of area and are divided by the physical area of the metallic film. The equation most relevant to this study is the scattering cross section and is represented by equation 3.2.3 and 3.2.4. For continuity, equations 3.2.1 and 3.2.2 have been included to show the relationship between all optical properties to obtain equation 3.2.4. Where, \( \Omega \) depicts the integration angle and \( r_j \) represents the coordinate of cube \( j \).

With respect to cube \( j \), the amplitude of the primary beam, incident light, is denoted by \( E_0 \). At the incident wavelength \( \lambda \), let the wave vector be represented by \( k = \frac{2\pi}{\lambda} \), and \( \hat{n} \) is the unit vector, oriented in the same direction as scattering and the incident electric field \( E_{\text{inc}}^j \) at position \( j \) of the cube. The induced dipole is represented by \( P_j \) at position \( j \) of the cube.

### 3.3 Theoretical Methods

It is important to note that the simulations included single unit cells oriented in the \( YZ \) plane, the DDA method was used to model the system shown by the electric field contour in Figure 1 at 300nm, where low scattering was obtained.

![Electric field, \( |E|^2 \) at 300nm, of the hole array system studied. Ag film, thickness of 100 nm, oriented in the \( YZ \) plane containing cylindrical apertures (radii \( r = 50 \) nm) with a distance of 400nm separating each aperture from center to center.](image)
Periodic cylindrical apertures were made inside the metallic layer in the $x$ direction. Unless otherwise noted, a grid length of $\Delta x = \Delta y = \Delta z = 10\text{nm}$ was used in both survey and extensive simulations. Survey calculations were run every 10 nm over the wavelength region of 300-1000 nm; whereas, more extensive calculations were run every 1 nm over the wavelength region of 400-600 nm. To prove validity of the simulation method, scattering spectra was obtained for symmetrical cylindrical apertures with separation distance of 400nm from center to center, and compared to the findings in the H. Wang paper\cite{H.Wang}.

The thickness of silver film was held at 100 nm, and the distance between nearby apertures arranged in a square lattice was set to 400nm, from center to center. The incident light was oriented parallel to the $X$-axis and the perforated Ag film was oriented in the $YZ$ plane. Scattering spectra was modeled for perforated Ag film with cylindrical holes, while varying the radius of the cylindrical apertures ($50$, $100$, and $150$ nm) and depicted in Figure 2 by black, red and violet lines, respectively. The simulated scattering

\textbf{Figure 2. Scattering spectra, between 300 and 1000 nm, for Ag film, thickness of 100nm, containing cylindrical aperture arrays with diameter $d = 100$ nm, 200nm and 300nm, denoted by black, red and violet lines, respectively.}
spectrum shows very good agreement with the scattering spectrum from the Wang paper (not shown); except that the results published by Wang provide a smoother scattering spectrum compared to Figure 2 and is noticeable in the wavelength region above 750nm. Since this region is outside of the desired wavelength range, this survey is acceptable and proves that the DDA method is valid. Observe in Figure 2 that the resonance wavelengths, arising from the WRA, are found between 400 and 500 nm for each of the Ag film designs.

![Graph](image)

**Figure 3.** Scattering spectrum for 100nm thick Ag film with 100nm diameter cylindrical apertures spaced 400nm apart from center to center. 45° angle between incident light and metallic surface.

Since SPR affinity biosensors are typically designed with an angle –between incident light and the metallic surface– not equal to 90°, the angle was changed from 90° to 45°. When this angle modification occurs we must consider both parallel and perpendicular scattering profiles when the electric field is in the XY and XZ planes, respectively. Initial simulations, were evaluated at 45°, as shown in Figure 4 using Ag film with 100nm
cylindrical aperture diameters as an example. Aperture distance was changed thereafter, following the methodology shown in Figures 4 and 5.

![Flowchart](image)

**Figure 4. Main approach for Ag film parameters and adjustments to obtain scattering spectra**

After the simulation of scattering efficiencies were obtained and compared to those of known spectra, the methodology for changing parameters, illustrated in Figure 4, includes (1) surveying a broad wavelength region (300-1000nm), (2) analysis of the spectra—taking note of any signature peaks or peak intensities, (3) comparison of scattering spectra with that of the previous spectra to develop confidence and insight on how to move forward to obtain narrow and strong signals in the desired wavelength region between 400nm and 500nm, (4) careful determination of parameter to change, while holding other parameters constant, and lastly, (5) after changing the desired parameter, simulation of a new spectra in DDA. Part of the art behind the methodology incorporates the correct balance of hypothesis and conclusions to obtain the most sharp and strong signal in the spectra. If weaker or broader peaks were obtained from simulations, the changed parameter was adjusted in an inverse manner. Typical tailoring of parameters
followed the process shown in Figure 5; where once the aperture diameter was selected, the change in distance was attempted prior to the adjustment of the angle between the metallic surface and the incident light and the modification of film thickness.

![Figure 5. Process of Ag film parameters adjustments](image)

### 3.4 Relevant Routines

Since the dipole arrays are dependent on the geometry of the target, routines must be programmed into DDSCAT to fabricate various dipole arrays that correspond to the desired target geometry\textsuperscript{23}. Explored geometries of each of Ag film aperture were cylindrical. All routines correspond to both homogeneous and isotropic targets; routines vary geometries only. Thin silver film was modeled in DDSCAT with rectangular prism and rectangular periodic routines\textsuperscript{23}. Since the silver film consists of homogeneous rectangular targets extended in target \( Y \) and \( Z \) directions, periodic boundary conditions must be used and the “RCTGL_PBC” routine was implemented in DDSCAT on the apertures and the silver film. Dielectric constants for silver and vacuum were used to model the metallic film and environment in DDSCAT, respectively\textsuperscript{25}. The routine “CYLINDER1” which corresponds to a finite cylinder was used to create cylindrical apertures in the Ag film. The repeating unit or unit cell modeled is shown in Fig.1 with thickness and aperture diameter of 100nm.
CHAPTER 4: FINDINGS

4.1 DDA Simulations and Discussion

The narrowest peak, as shown by the violet line in Figure 2, is observed within the desired wavelength region occurs a result of the 300 nm diameter cylindrical apertures (with neighboring distance of 400nm) in the 100nm thick Ag film. This Ag film design appeared to be a promising starting point. The angle between the metallic surface and the incident light was changed from 90º to 45º. After the prescribed adjustment and for any angle not 90º, we must now consider both parallel scattering ($XY$ plane) and perpendicular scattering ($XZ$ plane) – recall that the incident light is parallel to the $X$-axis. Neighboring distance between apertures, center to center, was varied between 340nm and 460nm; the parallel scattering spectra is depicted in Figure 6, with one calculated point per ten wavelengths. An accurate assessment of the peaks in the desired region of the spectra can be made after the removal of 360nm; it appears that there are no attractive spectral bands, corresponding to the WRA, present in the parallel scattering survey with the prescribed parameters, as shown by Figure 6 below. There are, however, strong narrow peaks, orange, violet, blue, green and red lines, in the plasmonic region, with wavelengths longer than 700nm.
Figure 6. Parallel scattering spectra obtained for various cylinder aperture separation distances (340-460nm), from center to center and with radii of 150nm, of perforated silver film, thickness of 100nm, not including 360 nm.

More extensive simulations, one calculated point per wavelength, were run in the region of 300-480nm to confirm and ensure that no significant peaks are present in this region. Indeed, both Figures 7 and 8 confirm the initial survey. Figure 7 verifies that both survey and extensive simulations agree; we expected to see extremely low scattering (less than 2.5%) near 320nm and no significant peaks arising from WRA.
Figure 7. Parallel scattering spectra, over the wavelength region of 300-380nm, obtained for various cylinder aperture separation distances (320-460nm), from center to center and with radii of 150nm, of perforated silver film, thickness of 100nm.

The wavelength region between 400-480nm was explored in Figure 8 and shows a broad spectral band represented by the violet line, while all other distances between neighboring apertures do not provide this type of peak. It is noticed, from Figure 8, that the 460nm separation provided the most intense peak, however, the shape and intensity of the peak is not adequate enough to be integrated into sensor design because it is too broad. It is possible that the separations over 460nm may provide a narrower band in the desired region.
Perpendicular scattering survey, for perforated Ag films with cylindrical apertures of 300nm diameters and varying neighboring distances, is shown in Figure 9. Upon inspection of the spectra, there appears to be no significant peaks in the desired region, however, the same checking method was done here, as was done in the parallel scattering. Both Figures 10 and 11 show that there is agreement with the survey and extensive simulations; no significant spectral bands were obtained from the scattering spectra from the prescribed metallic design. We expected to see extremely low scattering (less than 5%) near 320nm and no significant peaks arising from WRA. The wavelength region between 400-480nm was explored in Figure 10 and shows no peaks when the distances between neighboring apertures were varied from 320nm to 460nm. The perpendicular scattering spectra, presented in Figure 10, suggest that the metallic film architectures are not good candidates for the described SPR sensor design.
Figure 9. Perpendicular scattering spectra obtained for various cylinder aperture separation distances (340-460nm), from center to center and with radii of 150nm, of perforated silver film, thickness of 100nm.

Figure 10. Perpendicular scattering spectra, over the wavelength region of 300-380nm, obtained for various cylinder aperture separation distances (320-460nm), from center to center and with radii of 150nm, of perforated silver film, thickness of 100nm.
Since the perpendicular scattering spectra, presented in Figure 11, did not contain desired results, the angle between the incident light and the Ag film surface was varied while holding all other parameters constant. A complete survey was shown by altering the angle from 90 degrees to 60 degrees, as shown in Figure 12, and from 60 degrees to 10 degrees, as shown in Figure 13. The parallel scattering spectra contained in Figure 12 shows that when the incident light is normal to the metallic surface, represented by the blue line segment, we have an intense peak at 450nm. Unexpected results occur at 800nm, when the angle is changed to 80 degrees, that is to say narrow peak with strong intensity can be observed to have extremely low scattering (less than 2.5%) as highlighted by the green line in Figure 12. Although this is not within the desired region, we have discovered a spectral band, possibly a result of a hybridized resonance mode, promising to a different desired wavelength region. To prove exactly how intense this peak is, a more extensive
simulation must include calculations run each nanometer and an adjustment of the grid length from $\Delta x = \Delta y = \Delta z = 10\text{nm}$ to $5\text{nm}$. If we draw attention to the black line in Figure 13, it can be observed that when the angle, between the Ag film and incident light, is changed to 10 degrees there is a significant peak observed in the desired wavelength region corresponding to WRA at approximately 450nm. In any case, when the perforated Ag film design incorporates a 10° angle between the metal surface and the primary beam only one peak is a reasonable candidate in the parallel scattering (Figure 13). To better discern this spectral band, all other lines were omitted from the spectra and both parallel and perpendicular scattering were shown in Figure 14.

![Figure 12. Parallel scattering spectra, over various angles (60-90deg) between incident light and Ag surface, thickness of 100nm, aperture separation distance of 400nm, from center to center, and radii of 150nm.](image-url)
Figure 13. Parallel scattering spectra, over various angles (10-60deg) between incident light and Ag surface, thickness of 100nm, aperture separation distance of 400nm, from center to center, and radii of 150nm.

Figure 14. The comparison of parallel and perpendicular scattering spectra of Ag film, 100nm thickness, and 300 diameter holes in array with spacing of 400nm, between nearest neighbor, with a 10º angle between Ag surface and incident light. Parallel scattering represented in black and perpendicular scattering in red.
Prior to an extensive simulation on the aforementioned Ag film design, more scattering surveys were implemented varying the change in angle by only 1° between the range of 1° and 15°. Figure 15 shows the variation of the scattering spectra when the angle was adjusted between 10° and 15°. It is important to realize the surprising bathochromic shift of signature spectral bands to approximately 510nm from 450nm, of the strong peaks outside of the desired wavelength region; the change in spectral band is most likely due to a hybrid resonance mode, (i.e., SPP-BW) from scattered light of different orders. Simulations shown in Figure 15 provide strong and narrow spectral bands at angles of 12, 13 and 14° at longer wavelength or lower frequency than expected.

Figure 15. Parallel scattering spectra, over various angles (10-15 deg) between incident light and Ag surface, thickness of 100nm, aperture separation distance of 400nm, from center to center, and radii of 150nm.
The parallel scattering spectra obtained from the modification of angles, between the range of 5° and 10°, is shown in Figure 16. Unlike the scattering bands found in Figure 15, no bathochromic shift, outside of the 400-500nm wavelength region, was found and moderately narrow spectral bands were found at a desired wavelength of 450nm. The positions of the spectral bands suggest that the WRA was observed without a hybrid resonance mode. Simulations shown in Figure 16 provide narrow spectral bands with strong intensity for all indicated angles. The spectral band that arises when the angle is adjusted to 9° is the most appealing and denoted by the violet spectral line.

![Figure 16. Parallel scattering spectra, over various angles (5-10 deg) between incident light and Ag surface, thickness of 100nm, aperture separation distance of 400nm, from center to center, and radii of 150nm.](image)

Finally, a survey of the parallel scattering spectra for Ag film with angles between 1° and 5° were simulated and presented in Figure 17; all spectral bands at ≈ 450nm are narrower
than that of the spectral bands contained in Figure 16. By inspection, the most optimal in this region appears to be when the angle between the silver film surface and the incident light is 4º represented by the blue spectral line.

Figure 17. Parallel scattering spectra, over various angles (1-5 deg) between incident light and Ag surface, thickness of 100nm, aperture separation distance of 400nm, from center to center, and radii of 150nm.

More extensive scattering spectra were included in Figure 18 to show optimum peaks for parallel spectra with one calculation per nanometer. The surprising peak outside the WRA region falls very close to 550nm, depicted by the orange line, when the angle between the perforated silver film surface and the primary beam was tailored to 14º and is weaker than the simulated survey over a longer wavelength region. More importantly to this study, we observe that the 100nm thick silver film with 300nm (in diameter), cylindrical holes with a 400nm distance between nearest neighbors give rise to a parallel
scattering bands at the 450nm in wavelength. It can be inferred from the spectra that the 1°, 4° and 9° are possible candidates for SPR biosensor applications, as proven by the black, red and blue lines, respectively.

Figure 18. Parallel scattering spectra, over various angles between surface and primary beam of (1, 4, 9, 14 deg) obtained from 100nm thick Ag film with cylindrical apertures separation distance 400nm, from center to center and with radii of 150nm.

The previous parallel scattering spectra did contain desired results; we focus attention towards the perpendicular scattering profile and continue with the same methodology of varying the angle while holding all other parameters constant to examine if other reasonable attractive results could be obtained in the perpendicular scattering profile. A complete survey was shown by altering the angle from 10 degrees to 60 degrees, as shown in Figure 19, and from 60 degrees to 90 degrees, as shown in Figure 20. As
anticipated, Figure 20 shows that when the incident light is normal to the metallic surface, as shown previously by parallel scattering profile, we have an intense peak at 450nm, indicated by the blue line. The collective spectral results from Figures 19 and 20 suggest that in the desired region the angle change from 90° to 70° show a decay in peak intensity, whereas, the intensity appears to be partially regained when the angle was changed from 60° to 10°.

Figure 19. Perpendicular scattering spectra, over various incident angles (10-60deg) obtained for a fixed cylinder aperture separation distance 400nm, from center to center and with radii of 150nm, of perforated silver film, thickness of 100nm.
Figure 20. Perpendicular scattering spectra, over various incident angles (10-60deg) obtained for a fixed cylinder aperture separation distance 400nm, from center to center and with radii of 150nm, of perforated silver film, thickness of 100nm.

Next, a survey of the perpendicular scattering spectra for Ag film with angles between 10º and 15º were simulated and presented in Figure 21. Unlike the parallel spectra, for the same variation in angles shown in Figure 15, no bathochromic shifts (outside of the region of the visible spectrum for WRAs) were noticed in the perpendicular spectra; this suggests that there is no hybrid resonance mode, i.e, SPP-BW. However, there are attractive narrow peaks with moderate band intensity apparent near 450nm.
The perpendicular scattering spectra obtained from the modification of angles, between the range of 5° and 10°, is shown in Figure 22; scattering bands in this spectra, appear to be narrower than those in Figure 21, and are observed at 450nm. The positions of the spectral bands suggest that the WRA was observed and simulations provide the most desirable spectral bands with strong intensity when the angle is adjusted to 5°, depicted by the black spectral line.
Figure 22. Perpendicular scattering spectra, over various angles (5-10 deg) between incident light and Ag surface, thickness of 100nm, aperture separation distance of 400nm, from center to center, and radii of 150nm.

The perpendicular scattering spectra obtained from the modification of angles, between the range of 1º and 5º, is shown in Figure 23; scattering bands in this spectra, appear to be narrower than those in Figure 22 and as a consequence narrower than those spectral lines in Figure 21; these peaks are observed at 450nm. The positions of the spectral bands suggest that the WRA was observed and simulations provide the most desirable spectral bands with strong intensity when the angle is adjusted to 1º, depicted by the black spectral line.
Figure 23. Perpendicular scattering spectra, over various incident angles (1-5deg) obtained for a fixed cylinder aperture separation distance 400nm, from center to center and with radii of 150nm, of perforated silver film, thickness of 100nm.

More extensive scattering spectra were included in Figure 24 to show optimum peaks for perpendicular spectra with one calculation per nanometer and to compare the same silver architecture that lead to optimum peaks in the parallel scattering. As it was expected, there were no surprising peaks outside the WRA region and every peak was observed near 450nm. Black and red spectral lines prove that 1° and 4° angles are the desirable in the perpendicular scattering spectra; in addition, this result implies that both 1° and 4° angles lead to narrow perpendicular and parallel scattering profiles, shown by Figures 24 and 18, respectively, in the region between 400-500nm. If we further compare Figures 18 and 24, the 9° provided a strong peak in the parallel profile but provided a much weaker peak in the perpendicular scattering profile. When the angle between the perforated silver
film surface and the primary beam was tailored to 14° and we find a very weak band in the perpendicular and compared to a hybrid resonance peak in the parallel scattering spectrum.

Figure 24. Perpendicular scattering spectra, over various angles (10-60deg) obtained for a fixed cylinder aperture separation distance 400nm, from center to center and with radii of 150nm, of perforated silver film, thickness of 100nm.

Next, the scattering spectra, shown in Figure 25, was acquired when the thickness Ag layer was variable and the incident light was held constant –normal to that of the perforated film surface; this survey was simulated by altering the thickness from 50 nm to 120nm. It should be observed that from 100nm to 120nm there was a decrease in spectral band intensity. On the other hand, we demonstrate that the reduced thickness –from 100nm to 90nm, 90nm to 80nm and from 80nm to 70nm –provides a narrow increase in peak strength. The most optimum in this survey appear to be 70nm, 80nm, and 90nm
depicted by the green, blue and violet segments, respectively. By inspection, we see that after the film reaches a thickness of 60nm the peak becomes less prominent and by time the film is 50nm the band is starting to more closely resemble the 120nm segment.

![Figure 25. Scattering spectra when incident light is normal to metallic surface, over various film thickness (50-120nm) obtained for a cylindrical aperture separation distances of 400nm, from center to center and with radii of 150nm.](image)

More extensive scattering spectra were included in Figure 26 and 27 to show optimum peaks when the thickness is 90nm and 80nm, respectively. Calculations for both figures were simulated with one calculation per nanometer and the grid length was changed from 10nm to 5nm and show the same relative location in the spectra, with a wavelength slightly shorter than 450nm, intensity (near 10% scattering) and width.
Figure 26. Scattering spectra, for the incident light normal to the silver surface cylinder aperture separation distance of 400nm, from center to center and with radii of 150nm, of perforated silver film, thickness of 90nm.

Figure 27. Scattering spectra, for the incident light normal to the silver surface cylinder aperture separation distance of 400nm, from center to center and with radii of 150nm, of perforated silver film, thickness of 80nm.
Since the above scattering spectra, presented in Figure 26 and 27, did contain desired results, the angle between the incident light and the Ag film surface was varied while holding all other parameters constant for each one of these architectures (where the thickness of the perforated layer was either 80nm or 90nm). First, the study of the Ag film with thickness of 80nm was explored, followed by the simulations when thickness was 90nm. A complete survey was shown by altering the angle from 90 degrees to 50 degrees, as shown in Figure 28, and from 50 degrees to 10 degrees, as shown in Figure 29. The parallel scattering spectra contained in Figure 28 shows that when the incident light is normal to the metallic surface, represented by the orange segment, we have an intense peak at 450nm. Unexpected results occur at 800nm, when the angle is changed to 80 degrees, that is to say narrow peak with strong intensity can be observed to have extremely low scattering (less than 2.5%) as highlighted by the blue line in Figure 28. It should also be noted that when the angle reaches 50 degrees, as shown with the black segment, we observe an intense peak near 710nm. Although these two peaks are not within the desired range, we have discovered (1) a spectral band, possibly a result of a hybridized resonance mode, and (2) very strong and narrow peaks that are promising to a different desired wavelength region. Furthermore, the simulated the region in between 10° and 50° shows that when the angle is at 40° we notice an unexpected peak. The blue line in Figure 29 shows an extremely narrow peak, strongest in this study, that starts from approximately 60% scattering, drops to approximately 5% at 670nm, and then returns to over 50% scattering in a range of only 25nm.
Figure 28. Parallel scattering spectra, over various incident angles (50-90deg) obtained for a fixed cylinder aperture separation distance 400nm, from center to center and with radii of 150nm, of perforated silver film, thickness of 80nm.

Figure 29. Parallel scattering spectra, over various incident angles (10-50deg) obtained for a fixed cylinder aperture separation distance 400nm, from center to center and with radii of 150nm, of perforated silver film, thickness of 80nm.
The perpendicular scattering spectra obtained from the modification of angles, between the range of 90° and 50°, is shown in Figure 30; there are no new attractive scattering bands in these spectra, not including when the incident light is normal to the metal surface represented by the orange line segment.

**Figure 30.** Perpendicular scattering spectra, over various incident angles (50-90deg) obtained for a fixed cylinder aperture separation distance 400nm, from center to center and with radii of 150nm, of perforated silver film, thickness of 80nm.

Figure 31 shows the perpendicular scattering profile when the angle is adjusted between 10° and 50°. Unlike the previous spectra, we simulated a desirable spectral band, the black line segment, close to 450nm when the angle was adjusted to 10°, a product of WRA. In conjunctive, spectral results from Figures 30 and 31 suggest that in the desired region that changing from 90° to 70° the peaks decay (loose intensity) and from 60° to 10° the peaks are regained (become more prominent).
Since the above scattering spectra, presented in Figure 31 and 32, did not contain attractive results in the desired region, the angle between the incident light and the Ag film surface was varied for the perforated silver layer with thickness of 90nm. Complete survey simulations was shown by altering the angle from 90 degrees to 50 degrees, as shown in Figure 32, and from 50 degrees to 10 degrees, as shown in Figure 33. As expected, the parallel scattering spectra contained in Figure 32 shows that when the incident light is normal to the metallic surface, represented by the orange segment, we have an intense peak at 450nm. However, unexpected results occur at 800nm, when the angle is changed to 80 degrees, that is to say narrow peak with strong intensity can be observed to have extremely low scattering (less than 2.5%) as highlighted by the blue line in Figure 32. Consider the comparison of spectra when the angle is 50º in Figure 28 with
Figure 32, the observed peak at 710nm, as shown with the black segment, becomes less prominent when the thickness increases by 10nm.

The simulated parallel scattering, in the region between 10º and 50º, shows that when the angle is set to 10º we observe a broad spectral band just above 450nm, however, due to the broad characteristic of the spectral band we do not expect the Ag film design to be very useful for SPR applications. Comparing the 80nm and 90nm thickness when the angle is set to 40º (Figures 29 and 33, respectively), we do not notice a significant peak (due to the survey simulated one point per ten wavelengths) in the 90nm motif at 670nm, represented by the blue line in Figure 33, whereas, the 80nm motif exhibits an extremely narrow peak at this wavelength region.
The perpendicular scattering spectra obtained from the modification of angles, between the range of 90° and 50°, is shown in Figure 34; there are no new attractive scattering bands in these spectra, not including when the incident light is normal to the metal surface represented by the orange line segment. Figure 35 shows the perpendicular scattering profile when the angle is adjusted between 10° and 50°. At 450nm, we notice a desirable spectral band, the black line segment, close to 450nm when the angle was adjusted to 10°, a product of WRA. Similar to that of the 80nm and 100nm thickness, the conjunctive spectral results from Figures 34 and 35 suggest that in the desired region that changing from 90° to 70° the peaks decay (loose intensity) and from 60° to 10° the peaks are regained (become more prominent).
Next, we consider the spectra when the cylindrical aperture diameter was adjusted from 300nm to 200nm and the Ag film thickness is restored to 100nm. Figure 36 presents the parallel scattering spectra when the variation of the neighboring distance was varied after
the removal (360nm) to obtain a more accurate assessment of the peaks in the desired wavelength region.

Figure 36. Parallel scattering spectra obtained for various cylinder aperture separation distances (340-460nm), from center to center and with radii of 100nm, of perforated silver film, thickness of 100nm, not including 360 nm.

It appears that there are no attractive spectral bands, corresponding to the WRA, present in the parallel scattering survey with the prescribed parameters, as shown by Figure 36 above. We may observe that all peaks in Figure 36 exhibit strong narrow spectral bands, ranging from 610nm to 800nm as a result of an increase in separation. With respect to peak intensity, as the separation distance increases the intensity is compromised. Next, we consider the perpendicular spectra for the prescribed silver motif containing cylindrical apertures of diameter 200nm. All peaks do not exhibit desirable spectral bands in any region of the perpendicular spectra shown in Figure 37 when the neighboring distance is changed between 340-460nm.
Relevant to the initial goal of this work, Tables 1 and 3 include reasonable spectral bands (corresponding to possible Ag candidates to be integrated into SPR affinity biosensors) simulated by DDA methods. These tables include the dimensions for the Ag layer and the angle at which the primary beam must be adjusted to the surface. During this study a number of unexpected but very attractive bands for sensory applications were noticed (due to some other resonance mode); the dimensions and angle for such bands were included in Table 2 and 4. There were no significant peaks in the perpendicular scattering profile outside the range of 400-500nm (occurring from non-WRAs); thus, a table could not be fabricated for these Ag film designs.
### Table 1

<table>
<thead>
<tr>
<th>Wavelength of Peak (nm)</th>
<th>Description (Strength/Width)</th>
<th>Angle Between Incident Light and Ag Surface</th>
<th>Film Thickness (nm)</th>
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<tbody>
<tr>
<td>445</td>
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<td>450</td>
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<td>9º</td>
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Table 1. A table of Ag film designs that produce narrow parallel scattering bands inside the 400-500nm range occurring from WRAs for Ag film containing cylindrical apertures with diameter of 300nm and with nearest neighboring distance of 400nm.

### Table 2

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<th>Wavelength of Peak (nm)</th>
<th>Description (Strength/Width)</th>
<th>Angle Between Incident Light and Ag Surface</th>
<th>Film Thickness (nm)</th>
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Table 2. A table of Ag film designs that produce narrow parallel scattering bands outside the 400-500nm range occurring from non-WRAs for Ag film containing cylindrical apertures with diameter of 300nm and with nearest neighboring distance of 400nm.
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<thead>
<tr>
<th>Wavelength of Peak (nm)</th>
<th>Description (Strength/Width)</th>
<th>Angle Between Incident Light and Ag Surface</th>
<th>Film Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>445</td>
<td>Strong/Narrow</td>
<td>90°</td>
<td>100</td>
</tr>
<tr>
<td>440</td>
<td>Moderate/Narrow</td>
<td>15°</td>
<td>100</td>
</tr>
<tr>
<td>440</td>
<td>Moderate/Narrow</td>
<td>14°</td>
<td>100</td>
</tr>
<tr>
<td>440</td>
<td>Moderate/Narrow</td>
<td>13°</td>
<td>100</td>
</tr>
<tr>
<td>440</td>
<td>Moderate/Narrow</td>
<td>12°</td>
<td>100</td>
</tr>
<tr>
<td>440</td>
<td>Moderate/Narrow</td>
<td>11°</td>
<td>100</td>
</tr>
<tr>
<td>445</td>
<td>Moderate/Narrow</td>
<td>10°</td>
<td>100</td>
</tr>
<tr>
<td>440</td>
<td>Strong/Narrow</td>
<td>9°</td>
<td>100</td>
</tr>
<tr>
<td>440</td>
<td>Strong/Narrow</td>
<td>8°</td>
<td>100</td>
</tr>
<tr>
<td>440</td>
<td>Strong/Narrow</td>
<td>7°</td>
<td>100</td>
</tr>
<tr>
<td>440</td>
<td>Strong/Narrow</td>
<td>6°</td>
<td>100</td>
</tr>
<tr>
<td>440</td>
<td>Strong/Narrow</td>
<td>5°</td>
<td>100</td>
</tr>
<tr>
<td>440</td>
<td>Strong/Narrow</td>
<td>4°</td>
<td>100</td>
</tr>
<tr>
<td>440</td>
<td>Strong/Narrow</td>
<td>3°</td>
<td>100</td>
</tr>
<tr>
<td>440</td>
<td>Strong/Narrow</td>
<td>2°</td>
<td>100</td>
</tr>
<tr>
<td>440</td>
<td>Strong/Narrow</td>
<td>1°</td>
<td>100</td>
</tr>
<tr>
<td>445</td>
<td>Moderate/Broad</td>
<td>10°</td>
<td>80</td>
</tr>
<tr>
<td>445</td>
<td>Moderate/Broad</td>
<td>10°</td>
<td>90</td>
</tr>
</tbody>
</table>

Table 3. A table of Ag film designs that produce narrow perpendicular scattering bands inside the 400-500nm range occurring from WRAs for Ag film containing cylindrical apertures with diameter of 300nm and with nearest neighboring distance of 400nm.

<table>
<thead>
<tr>
<th>Wavelength of Peak (nm)</th>
<th>Description (Strength/Width)</th>
<th>Angle Between Incident Light and Ag Surface</th>
<th>Distance Between Nearest Neighbor (nm)</th>
<th>Film Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>620</td>
<td>Strong/Narrow</td>
<td>45°</td>
<td>340</td>
<td>100</td>
</tr>
<tr>
<td>680</td>
<td>Strong/Narrow</td>
<td>45°</td>
<td>380</td>
<td>100</td>
</tr>
<tr>
<td>710</td>
<td>Strong/Narrow</td>
<td>45°</td>
<td>400</td>
<td>100</td>
</tr>
<tr>
<td>740</td>
<td>Strong/Narrow</td>
<td>45°</td>
<td>420</td>
<td>100</td>
</tr>
<tr>
<td>760</td>
<td>Strong/Narrow</td>
<td>45°</td>
<td>440</td>
<td>100</td>
</tr>
<tr>
<td>800</td>
<td>Strong/Narrow</td>
<td>45°</td>
<td>460</td>
<td>100</td>
</tr>
</tbody>
</table>

Table 4. A table of Ag film designs that produce narrow parallel scattering bands outside the 400-500nm range occurring from non-WRAs for Ag film containing cylindrical apertures with diameter of 200nm.
CHAPTER 5: CONCLUSION

5.1 Summary

This thesis highlighted the preliminary framework for the integration of Ag film into SPR biosensors that have advantages when quantification of analytes, such as genetic material, is desired. A number of perforated Ag film motifs were simulated based on tailoring of cylindrical diameters, separation distance between nearest apertures, film thickness and modification of the angle between the incident light and the metallic surface. In summary, we demonstrated that scattering spectra is to a large extent determined by both the Ag film architecture and angle at which the primary beam strikes the Ag surface. The preliminary test results shown in the introduction, parallel with previous published scattering spectra for symmetrical (cylindrical) aperture geometries, allowed us to conduct an expansion study to focus solely on optimizing the scattering spectra within the resonance wavelength region of 400-500nm. Narrow scattering spectra were simulated and compiled in this investigation from the modification of cylindrical apertures diameter sizes, distance between single unit cells of apertures, thickness of the metallic film, and the angle in which the incident beam contacts with the surface of the silver grating. Fine-tuning of the scattering spectra was implemented by adjusting the distance of the spacing between nearest neighbors. Perforated silver film with thickness of 100nm, cylindrical aperture diameters of 300nm with neighboring distance of 400nm, and an angle between 1° and 15° exhibited reasonable overall scattering profiles (both perpendicular and parallel) within the resonance wavelength between 400-500nm suggesting that these Ag films are reasonable candidates for SPR biosensors. As shown by the tables of compiled data, we have theoretically modeled variations of Ag nanostructures for synthetic
frameworks. Most ideal spectroscopic setups can be designed dependent on the more restrictive choice of the optimal operating wavelength for either the biorecognition layer or the perforated Ag layer. In addition, there were surprising results found when an 80º angle was set between the incident light and perforated Ag film (thickness of 80nm, 90nm, and 100nm) with cylindrical hole array diameters of 300nm and a separation distance of 400nm.

5.2 Outlook

Extensions could be investigated by implementing smaller grid lengths and more calculations per nanometer to obtain the best peak characteristic for any of the spectra survey presented here. Furthermore, other investigations may involve examining the perforated Ag motifs with distance greater than 460nm with cylindrical hole diameters of 300nm. Desirable results may be obtained in the parallel or perpendicular scattering (when the angle of incidence is 45º) because the peaks become less prominent as the distance between neighbors decreases. Further investigation could be warranted in when the cylindrical hole diameter was 200nm, since most of the work presented here was on the 300nm diameter. Other explorations should include the study of the unexpected results around 800nm to the corresponding Ag film designs. There may exist significant or reasonable candidates for such SPR sensors with smaller aperture diameters but were not explored in this study. As routinely practiced, a series of experimental studies must be performed to show good agreement with the data presented here and to discern how close these simulations coincide with simulations. Before these metallic film designs can contribute to SPR applications in the quantification of biomolecular analytes (i.e.,
hormones, proteins, bacteria, DNA strands, etc.) more simulations and experimental data must be collected and other film designs must be investigated further.
APPENDIX A: SYSTEM MODEL
APPENDIX A: SYSTEM MODEL

Code input for the directory ddscat.par
'================================ Parameter file ======================='

**** PRELIMINARIES ****

'NOTORQ' = CMTORQ*6 (DOTORQ, NOTORQ) -- either do or skip torque calculations

'PBCGS2' = CMDSOL*6 (PBCGS2, PBCGST, PETRKP) -- select solution method

'GPFAFT' = CMETHD*6 (GPFAFT, FFTMKL)

'GKDLDR' = CALPHA*6 (GKDLDR, LATTD)

'NOTBIN' = CBINFLAG (NOTBIN, ORIBIN, ALLBIN)

**** Initial Memory Allocation ****

100 100 100 = dimensioning allowance for target generation

**** read dipole source ****

0               ! number of dipole source (if >0, followed by the relative wavelength, position, and magnitude)

**** Target Geometry and Composition ****

3               ! part of the target

0 0 0 0         ! orientation : flip or not along X, Y, Z

0 0 0           ! shift along x, y, z/grid

'RCTG1PRSM' = CSHAPE*9 shape directive

10.0 26.0 26.0 = shape parameters PAR1, PAR2, PAR3,...

0 0 0 0         ! orientation : flip or not along X, Y, Z

0 -7 -7         ! shift along x, y, z/grid

'RCTG1PRSM' = CSHAPE*9 shape directive

10.0 40.0 40.0 = shape parameters PAR1, PAR2, PAR3,...

0 0 0 0         ! orientation : flip or not along X, Y, Z

0 -7 -7         ! shift along x, y, z/grid

'RCTG1PRSM' = CSHAPE*9 shape directive

-10.0 40.0 40.0 40 = shape parameters PAR1, PAR2, PAR3,...

***** index of refraction of the medium ***************

(1.00, 0.0) = index of refraction of the medium (real)

3 = NCOMP = number of dielectric materials

'dielvac.tab' = name of file containing dielectric function

'deelag.tab' = name of file containing dielectric function

'dielvac.tab' = name of file containing dielectric function

***** square: 0 or hexagonal: 1 (Z shift by half, Y sqrt(3)/2) array ****

0               ! array arrangement; 0: square, 1: hexagonal

***** remove some components ****

1               ! how many components are removed

1               ! components removed

****** how many components in the dark ****

0               ! how many components are in the dark

0               ! components in the dark

***** near efield spectrum calculation ****

0               ! how many (<20) points (distinguished by composite) will be calculated
1 ! component number of the point

'***** CONJUGATE GRADIENT DEFINITIONS *****'
1.00e-4 2000 = TOL = MAX ALLOWED (NORM OF |G|=|E>-AC|E|)/(|AC|E|) and loop

'***** Interaction cutoff parameter for PBC calculations *****'
1.00e-2 = GAMMA (1e-2 is normal, 3e-3 for greater accuracy)

'***** Angular resolution for calculation of <cos>, etc. *****'
0.5 = ETASCA (number of angles is proportional to [(3+x)/ETASCA]<88>2)

'***** Wavelengths (micron) *****'
.3 1. 71 'LIN' = wavelengths (first,last,how many,how=LIN,INV,LOG)

'***** Effective Radii (micron) *****'
.130105 .130175 1 'LIN' = eff. radii (cylinder diameter 20, 63, 100 nm)

'***** Define Incident Polarizations *****'
(0,0) (1.,0.) (0.,0.) = Polarization state e01 (k along x axis)
2 = IORTH (=1 to do only pol. state e01; =2 to also do orth. pol. state)

'***** Specify which output files to write *****'
1 = IWRKSC (=0 to suppress, =1 to write '.sca' file for each target orient.
0 = IWRPOL (=0 to suppress, =1 to write '.pol' file for each (BETA,THETA)

'***** Prescribe Target Rotations *****'
0. 0. 1 = BETAMI, BETAMX, NBETA (beta=rotation around a1)
0 0 1 = THETMI, THETMX, NTHETA (theta=angle between a1 and k)
0. 0. 1 = PHIMIN, PHIMAX, NPHI (phi=rotation angle of a1 around k)

'***** Specify first IWAV, IRAD, IORI (normally 0 0 0) *****'
0 0 0 = first IWAV, first IRAD, first IORI (0 0 0 to begin fresh)

'***** Select Elements of S_ij Matrix to Print *****'
16 = NSMELTS = number of elements of S_ij to print
11 12 13 14 21 22 23 24 31 32 33 34 41 42 43 44 = indices ij of elements to print

'***** Specify Scattered Directions *****'
'TFRAME' = CMDFRM (LFRAME, TFRAME for Lab Frame or Target Frame)
1 = NPLANES = number of scattering planes
0. 0. 180. 10 = phi, thetan_min, thetan_max, dtheta (in deg) for plane 1
**Code input for calscanew.f**

**DDSCAT --- DDSCAT 7.0.7 [08.08.31]**

**TARGET --- Rectangular prism; NX, NY, NZ = -9 40 40**

**GPFAFT --- method of solution**

**GKDLDLDR --- prescription for polarizabilities**

**RCTGL_PBC --- shape**

9240 = NAT0 = number of dipoles

0.07681963 = d/aeff for this target [d=dipole spacing]

0.010000 = d (physical units)

----- physical extent of target volume in Target Frame -----

-0.055000 0.045000 = xmin,xmax (physical units)
-0.205000 0.195000 = ymin,ymax (physical units)
-0.205000 0.195000 = zmin,zmax (physical units)

AEFF = 0.130175 = effective radius (physical units)

WAVE = 0.300000 = wavelength (physical units)

K*AEFF = 2.726379 = 2*pi*aeff/lambda

n = (1.0000, 0.0000), eps. = (1.0000, 0.0000) |m|kd = 0.2094 for subs. 1

n = (1.5166, 0.9552), eps. = (1.3878, 2.8974) |m|kd = 0.3754 for subs. 2

n = (1.0000, 0.0000), eps. = (1.0000, 0.0000) |m|kd = 0.2094 for subs. 3

TOL = 1.000E-04 = error tolerance for CCG method

(1.0000 0.0000 0.0000) = target axis A1 in Target Frame

(0.0000 1.0000 0.0000) = target axis A2 in Target Frame

(0.20944 0.0000 0.0000) = k vector (latt. units) in TF

(0.0000, 0.0000)(1.0000, 0.0000)(0.0000, 0.0000) = inc.pol.vec. 1 in TF

(0.0000, 0.0000)(0.0000, 0.0000)(1.0000, 0.0000) = inc.pol.vec. 2 in TF

(1.0000 0.0000 0.0000) = target axis A1 in Lab Frame

(0.0000 1.0000 0.0000) = target axis A2 in Lab Frame

(0.20944 0.0000 0.0000) = k vector (latt. units) in Lab Frame

(0.0000, 0.0000)(1.0000, 0.0000)(0.0000, 0.0000) = inc.pol.vec. 1 in LF

(0.0000, 0.0000)(0.0000, 0.0000)(1.0000, 0.0000) = inc.pol.vec. 2 in LF

BETA = 0.000 = rotation of target around A1

THETA = 0.000 = angle between A1 and k

PHI = 0.000 = rotation of A1 around k

absorption coeff. iter mxiter

JO=1: 6.5158E-01 8 33
JO=2: 6.5158E-01 8 33
mean: 6.5158E-01

Mueller matrix elements for selected scattering directions in Target Frame

| theta | phi | Pol. | S_11 | S_12 | S_13 | S_14 | S_21 | S_22 | S_23 | S_24 | S_31 | S_32 | S_33 | S_34 | S_41 | S_42 | S_43 | S_44 |
|-------|-----|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| 0.00  | 0.00 | 0.0000 | 1.6901E-01 | 9.1721E-08 | 8.991E-08 | 4.264E-09 | 9.172E-08 | 1.690E-01 | 2.601E-08 | 4.551E-08 | -8.991E-08 | 2.601E-08 | -1.690E-01 | -5.350E-08 | -4.264E-09 | 4.551E-08 | 5.350E-08 | -1.690E-01 |

52
<p>| | | | | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
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<tr>
<td>180.00</td>
<td>0.00</td>
<td>0.0001</td>
<td>4.1772E-02</td>
<td>2.1210E-07</td>
<td>-2.611E-08</td>
<td>1.172E-08</td>
<td>2.121E-07</td>
<td>4.177E-02</td>
</tr>
<tr>
<td>4.177E-02</td>
<td>-3.024E-09</td>
<td>4.232E-08</td>
<td>-2.611E-08</td>
<td>3.024E-09</td>
<td>4.177E-02</td>
<td>-6.258E-08</td>
<td>1.172E-08</td>
<td>-4.232E-08</td>
</tr>
<tr>
<td>1.172E-08</td>
<td>-4.232E-08</td>
<td>6.258E-08</td>
<td>4.177E-02</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Code input for w000r000k000.sca

!!!!!!
! sz: 2008.09.08  calculate the reflectance of a thin film from the
! output of DDA program
!!!!!!!!!!!!

implicit none
integer i,j
real wave,s11f,s12f,s11b,s12b,temp,absp,absv
real s41f,s42f,s41b,s42b
character*100 ctemp

open (file="absp.dat",unit=40)
open(file="absv.dat",unit=42)

open (file="scap.dat",unit=60)
open(file="scav.dat",unit=62)

open (file="scaplc.dat",unit=64)
open(file="scaprc.dat",unit=65)

open (file="scavlc.dat",unit=66)
open(file="scavrc.dat",unit=67)

open (file="transp.dat",unit=70)
open(file="transv.dat",unit=72)

open (file="transplc.dat",unit=74)
open(file="transprc.dat",unit=75)

open (file="transvlc.dat",unit=76)
open(file="transvrc.dat",unit=77)

open (file="extp.dat",unit=80)
open(file="extv.dat",unit=82)

open(file='extavg.dat',unit=90)
open(file='norm.dat',unit=92)
do i=0,80
  open(unit=30,file=
    "w"//char(i/100+48)//char(mod(i/10,10)+48)
& //char(mod(i,10)+48)//"r000k000.sca")
do j=1,13
   read(30,*)
enddo
read(30,*) ctemp,wave
do j=15,33
   read(30,*)
enddo
read(30,*) ctemp,absp
read(30,*) ctemp,absv
write (40,*) 1000*wave,absp
write (42,*) 1000*wave,absv

do j=36,38
   read(30,*)
enddo
read(30,*)temp,temp,temp,s11f,s12f
& .temp,temp,temp,temp,temp,temp,temp,temp,temp,temp,temp
& .s41f,s42f
write (70,*) 1000*wave,s11f+s12f
write (72,*) 1000*wave,s11f-s12f
write (74,*) 1000*wave,0.5*((s11f+s12f)+(s41f+s42f))
write (75,*) 1000*wave,0.5*((s11f+s12f)-(s41f+s42f))

write (76,*) 1000*wave,0.5*((s11f-s12f)+(s41f-s42f))
write (77,*) 1000*wave,0.5*((s11f-s12f)-(s41f-s42f))

read(30,*)temp,temp,temp,s11b,s12b
& .temp,temp,temp,temp,temp,temp,temp,temp,temp,temp,temp
& .s41b,s42b
write (60,*) 1000*wave,s11b+s12b
write (62,*) 1000*wave,s11b-s12b
write (64,*) 1000*wave,0.5*((s11b+s12b)+(s41b+s42b))
write (65,*) 1000*wave,0.5*((s11b+s12b)-(s41b+s42b))

write (66,*) 1000*wave,0.5*((s11b-s12b)+(s41b-s42b))
write (67,*) 1000*wave,0.5*((s11b-s12b)-(s41b-s42b))
write (80,*), 1000*wave,s11b+s12b+absp
write (82,*), 1000*wave,s11b-s12b+absv

write (90,*), 1000*wave,.5*(s11b+s12b+absv+s11b-s12b+absp)
write (92,*), 1000*wave,absp+s11b+s12b+s11f+s12f &
   , absv+s11b-s12b+s11f-s12f

   close(30)
   enddo
   close(40)
   close(42)
   close(60)
   close(62)
   close(80)
   close(90)
end
APPENDIX B: PERFORMANCE CHARACTERISTICS BASED ON ANALYTICAL FIGURES OF MERIT
APPENDIX B: PERFORMANCE CHARACTERISTICS BASED ON ANALYTICAL FIGURES OF MERIT

The equations that best characterize AFOM and affect affinity SPR biosensor performance have been included in this section. If the reader is interested in prism coupling, either Kretschmann or Otto, the sensitivity, resolution, limits of quantitation, limit of detection and the dynamic range equations can be quickly accessed below\textsuperscript{18}

**Sensitivity**

\[ S_c = \frac{\partial Y}{\partial c} = \frac{\partial Y}{\partial n_b} = \frac{dn_b(c)}{dc} = S_{RI}S_{nc} \]  \hspace{1cm} (A.B.1)

\[ \left( \frac{\delta \lambda_r}{\delta n_{ef}} \right)_{prism} = \frac{1}{\left( \frac{dn_p}{d\lambda} \right) \left( \frac{dn_{ef}}{dn_p} \right) - \frac{dn_{ef}}{d\lambda}} \]  \hspace{1cm} (A.B.2)

\[ (S_{\lambda})_{prism} = \frac{\varepsilon_m^2}{-\frac{n^2 d\varepsilon_m}{d\lambda} + \varepsilon_m' (n^2 + \varepsilon_m') n \frac{dn_p}{d\lambda}} \]  \hspace{1cm} (A.B.3)

**Resolution**

\[ \sigma_1(I) = \sqrt{I^2 \left( \sigma_{I_{rel}}^L \right)^2 + I \left( \sigma_{I_{rel}}^S \right)^2 + \sigma_D^2} \]  \hspace{1cm} (A.B.4)

**Limit of quantification (LOQ)**

\[ c_{LOD} = \frac{10}{S_c(c=0)} m\sigma_{blank} \]  \hspace{1cm} (A.B.5)

**Limit of detection (LOD)**

\[ Y_{LOD} = Y_{blank} + m\sigma_{blank} \]  \hspace{1cm} (A.B.6)

\[ c_{LOD} = \frac{1}{S_c(c=0)} m\sigma_{blank} \]  \hspace{1cm} (A.B.7)
REFERENCES


