Plasmonic Materials For Use In Alternative Approaches To DUV Nanolithography

Andrew Charles Estroff

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Plasmonic Materials For Use In Alternative
Approaches To DUV Nanolithography

by

Andrew Charles Estroff

A dissertation submitted in partial fulfillment of the requirements
for the degree of Doctorate of Philosophy in Microsystems
Engineering

Microsystems Engineering Program
Kate Gleason College of Engineering

Rochester Institute of Technology
Rochester, New York
March, 2014
Committee Approval:

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ABSTRACT
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**Degree:** Doctor of Philosophy
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**Dissertation Title:** Plasmonic Materials For Use In Alternative Approaches to DUV Nanolithography

Degradation in image contrast becomes a concern at higher numerical apertures (NA) due to mask induced polarization effects. Rigorous coupled-wave analysis (RCWA) was used to simulate the polarization of radiation by the photomask. The results show that higher NA leads to greater polarization effects in all cases. In general, materials with higher refractive indices and lower extinction coefficients tend to pass more of the TM polarization state, whereas materials with lower refractive indices and a relatively wider range of extinction coefficients pass more TE polarized radiation. These properties can provide new design considerations for the development of next generation masking materials.

The unique properties of metamaterials, namely their negative refractive index, permittivity, and permeability, have gained much recent attention. Research into these materials has led to the realization of a host of applications that may be useful to enhance optical nanolithography, such as a high pass pupil filter based on an induced transmission filter design, or an optical superlens. A large selection of materials has been examined both experimentally and theoretically through wavelength to verify their support of surface plasmons, or lack thereof, in the DUV spectrum via the attenuated total reflection (ATR) method using the Kretschmann configuration.

At DUV wavelengths, materials that were previously useful at mid-UV and longer wavelengths no longer act as metamaterials. Composites bound between metallic aluminum and Al$_2$O$_3$ exhibit metamaterial behavior, as do other materials such as tin and indium. This provides for real opportunities to explore the potential of the use of such materials for image enhancement with easily obtainable materials at desirable lithographic wavelengths.
A software program was created to evaluate possible metal-insulator material stack combinations to find materials with a suitable surface plasmon dispersion for the DUV. The resulting materials are comprised of a multilayer Al-Al$_2$O$_3$-Al stack as well as a simple Al-photoresist stack.

These stacks were then fabricated, and used to image the surface plasmons generated by this metamaterial using plasmonic interference lithography, a technique very similar to 2-beam interference lithography used frequently in the Nanolithography Research Labs, with resolution down to an 80nm period.
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<th>Definition</th>
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<td>AFM</td>
<td>Atomic Force Microscope</td>
</tr>
<tr>
<td>APSM</td>
<td>Attenuated Phase Shift Mask</td>
</tr>
<tr>
<td>ATR</td>
<td>Attenuated Total Reflectance</td>
</tr>
<tr>
<td>CD</td>
<td>Critical Dimension</td>
</tr>
<tr>
<td>DOP</td>
<td>Degree of Polarization</td>
</tr>
<tr>
<td>DUV</td>
<td>Deep Ultraviolet</td>
</tr>
<tr>
<td>EUV</td>
<td>Extreme Ultraviolet</td>
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<tr>
<td>FDTD</td>
<td>Finite Difference Time Domain</td>
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<tr>
<td>FTIR</td>
<td>Frustrated Total Internal Reflection</td>
</tr>
<tr>
<td>HMDS</td>
<td>Hexamethyldisilazane</td>
</tr>
<tr>
<td>IC</td>
<td>Integrated Circuit</td>
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<td>ITRS</td>
<td>International Technology Roadmap for Semiconductors</td>
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<tr>
<td>LHM</td>
<td>Left Handed Material</td>
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<tr>
<td>MIM</td>
<td>Metal Insulator Metal</td>
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<tr>
<td>MMC</td>
<td>Matrix Material Calculator</td>
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<td>NA</td>
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<td>Negative Index Material</td>
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<tr>
<td>NPM</td>
<td>Negative Permittivity Material</td>
</tr>
<tr>
<td>OAI</td>
<td>Off Axis Illumination</td>
</tr>
<tr>
<td>OPC</td>
<td>Optical Proximity Correction</td>
</tr>
<tr>
<td>PEB</td>
<td>Post Exposure Bake</td>
</tr>
<tr>
<td>PGMEA</td>
<td>Propylene Glycol Monomethyl Ether Acetate</td>
</tr>
<tr>
<td>PML</td>
<td>Perfectly Matched Layer</td>
</tr>
<tr>
<td>PMMA</td>
<td>Poly(methyl methacrylate)</td>
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</table>
POI  Plane of Incidence
PR  Photoresist
RCWA  Rigorous Coupled Wave Analysis
RET  Resolution Enhancement Technique
RHM  Right Handed Material
SEM  Scanning Electron Microscope
SL  Superlens
SMO  Source Mask Optimization
SP  Surface Plasmon
SPR  Surface Plasmon Resonance
SRR  Split Ring Resonator
TE  Transverse Electric
TIR  Total Internal Reflection
TM  Transverse Magnetic
TMAH  Tetramethylammonium Hydroxide
UV  Ultraviolet
VASE  Variable Angle Spectroscopic Ellipsometry
1. INTRODUCTION

In December of 1947, the vacuum tube era effectively ended with the invention of the transistor by Shockley, Bardeen, and Brattain[1]. Twelve years later, Jack Kilby created the first integrated circuit (IC) on germanium, and within half a year Robert Noyce made the first IC on silicon[2], [3]. These events gave birth to the semiconductor industry.

Gordon Moore, a co-founder of Intel along with Robert Noyce, noticed that the number of transistors on a chip double every 2 years, a trend now termed Moore’s Law and shown in Figure 1.1 [4]. Optical lithography has been one of the most important technologies in enabling the continued scaling of transistors and ICs.

Optical lithography is a method used to transfer the designed IC to the substrate. Typically, a photomask is created to allow electromagnetic radiation to pass through some regions, exposing a photosensitive film known as photoresist (PR) coated atop a silicon wafer. Positive tone PR is removed in exposed regions by an aqueous developer, whereas the opposite occurs for negative tone resist. The underlying layers can then be etched to transfer the desired pattern, the PR is removed, and subsequent processing steps can occur.
Figure 1.1: Moore’s Law showing transistor count of microprocessors versus the year introduced [5].

In the infancy of the semiconductor industry, contact or proximity printing was the main method used for lithography. The photomask was large enough for the entire substrate to be exposed at one time. However, the pattern features on the mask were the same size as those being printed, and the mask has to be brought into near contact with the photoresist. As substrate sizes increased and critical dimensions (CDs) of ICs became smaller, mask contamination from contact with the substrate, production of a defect free mask, and the ultimate resolution of the system rendered contact printing untenable.

To mitigate debris from the substrate impacting imaging performance, unity projection aligners were developed. However, as substrates continued increasing in size, it became increasingly difficult to continue fabricating masks of the same size as the
substrate. To solve this problem, step and repeat systems, known as steppers were developed. These systems incorporated reduction optics, allowing mask CDs to be 4-5x larger than the features printed on the wafer, while exposing one or a few die at a time before ‘stepping’ to the next location on the substrate. Current lithography uses step and scan systems, or scanners, which continue to employ reduction optics and ‘step’ through exposure fields, while also scanning across the mask and wafer through an imaging slit providing better control over aberrations[6].

The resolution limit of these projection optical lithography steppers and scanners is governed by the Rayleigh Criterion, shown in Equation (1.1), where $R$ is the half pitch (CD), $\lambda$ is the wavelength of radiation, $NA$ is the numerical aperture of the system defined as $n \sin \theta$, and a process dependent factor $k_1$ that contains $\sigma$, the partial coherence of the system, a ratio of the source and objective sizes[7].

$$R = k_1 \frac{\lambda}{NA} = \frac{1}{2(\sigma + 1)} \frac{\lambda}{NA}$$  \hspace{1cm} (1.1)

For a fully coherent system $\sigma = 0$, while for a completely incoherent system $\sigma = 1$.

It can be observed from Equation (1.1), that one way to increase the resolution of the projection system is to reduce the wavelength of radiation. The first lithography systems utilized mercury arc lamps filtered for the mid-ultraviolet (UV) spectrum at g-, h-, or i-lines (436nm, 405nm, and 365nm respectively). Wavelength reduction continued with the development of 248nm KrF and 193nm ArF excimer laser sources. Additionally, for the latest 193nm scanners, $NA$ has been increased beyond unity to 1.35 by using water as an immersion medium, which has a refractive index around 1.44 at that wavelength.
Currently, extreme ultraviolet (EUV) systems with a wavelength of 13.5nm are being developed. While this reduction in wavelength provides excellent resolution, it is a somewhat drastic departure from traditional projection lithography. Reflective optics and masks are required due to material absorption at the EUV wavelength, the entire system is under vacuum, radiation scattering and flare from surface roughness becomes a concern, and NA is only around 0.35 for current systems [8]–[17].

Besides wavelength and numerical aperture scaling, there are other resolution enhancement techniques (RETs) that can be used to increase resolution in a system. One such RET is off axis illumination (OAI), which allows diffracted orders from the photomask to be captured by the objective lens that would not be with normally incident radiation. Others RETs include attenuating and alternating phase shifting masks [18], optical proximity correction (OPC) [19], assist features [20], [21], source mask optimization (SMO) [22], polarized illuminators [23], and double- or multiple-patterning [24].

Incorporation of RETs, reduction of wavelength to 193nm, and increasing NA using higher index immersion mediums has allowed optical lithography to create ICs with CDs now at the 22nm node. However, this has not been without its drawbacks. As NA has increased, polarization effects contributed by the photomask have become a concern. These effects will be explored in Chapter 2.

It is not clear what the future of lithography will be. The ITRS roadmap, shown in Figure 1.2, shows that research and innovation are required to continue developing
increasingly smaller devices.

When the process factor, $k_1$, is 0.25, the Rayleigh Criterion is known as the Abbe diffraction limit, defining the smallest printable CDs. Theoretically, this means immersion 193nm lithography should have ended at 33.5nm CDs. By changing the duty ratio of lines and spaces on a photomask, it has been possible to print CDs smaller than 33.5nm, but the pitch cannot be smaller than 67nm without double/multiple patterning and etch steps [26]. Alternative optical lithography techniques that could enable sub-22nm ICs include: interference lithography with trim [27], [28], stimulated emission depletion [29]–[32], solid immersion lithography [33], evanescent wave lithography [34]–[37], and metamaterials and plasmonic lithography [38]–[40].

Evanescent waves, generated by non-radiating diffraction orders from a photomask or by radiation undergoing total internal reflection (TIR), contain all of the
desired image content from the object, but are constrained to the boundary between the object and its bordering medium. A special subset of evanescent waves known as surface plasmons (SPs), electromagnetic waves that travel along the boundary between a conductor and a dielectric, offer the promise of infinite resolution, limited only by the materials used and that they are excited by TM polarized radiation. This dissertation will explore how materials can be tuned to support SPs and used to image at the DUV wavelengths used in current lithography.
2. MASK INDUCED POLARIZATION EFFECTS AT HIGH NUMERICAL APERTURES

2.1 INTRODUCTION

Degradation in image contrast becomes a concern at higher numerical apertures (NA) due to mask induced polarization effects. This section studies how different photomask materials (binary and attenuated phase shift), feature sizes and shapes, pitch values, duty ratios (line to space), and wavelengths effect the polarization of transmitted radiation. Rigorous coupled-wave analysis (RCWA) was used to simulate the polarization of radiation by the photomask. The results will show that higher NA leads to greater polarization effects in all cases. Off-axis illumination increases polarization in one of the first orders, decreasing it in the other. Non-vertical sidewall angles and rounded corners can also impact polarization, but the wavelength of incident radiation has no effect on polarization effects at the same NA values. In general, materials with higher refractive indices and lower extinction coefficients tend to pass more of the TM polarization state, whereas materials with lower refractive indices and a relatively wider range of extinction coefficients pass more TE polarized radiation. These properties can provide new design considerations for the development of next generation masking materials.

Smaller device dimensions and increasing numerical apertures (NA) cause polarization effects at the photomask to become a concern. Minimum pitch values (\( \Lambda \)) on a photomask approach
for a system with \( M = 1/m \), where \( m \) is the magnification of the lens. Assuming \( M = 4 \) \( (m = 0.25) \) for a 4x reduction system, \( NA = 0.85 \), and \( \sigma = 1.0 \) for current generation dry tools, \( \Lambda_{\text{mask}} = 2.35\lambda \). Current generation immersion tools with \( NA = 1.2 \) will result in a minimum mask period of \( 1.67\lambda \), at which point there can be more significant polarization effects contributed by the photomask.

TE polarization is defined as polarization perpendicular to the plane of incidence (POI); additionally, radiation polarized in the POI is referred to as TM polarized. This is shown in Figure 2.1. As \( NA \) increases, the angle of incidence at the wafer’s surface becomes more oblique. For TE polarization, \( NA \) is not a concern since there is no decrease in image contrast due to increased angle of incidence, and image contrast remains 1, as shown by Equations (2.2) and (2.4), where \( \delta = \kappa \chi (\sin \theta) \). However, for TM polarization, as the angle of incidence approaches forty-five degrees, the image contrast decreases until it reaches zero at an angle of forty-five degrees, or ninety degrees between two interfering beams (Equations (2.3) and (2.4)) [41], [42]. Also, TE and TM polarized radiation states do not interfere with one another. This clearly highlights the importance of incorporating polarization into lithography modeling and simulation.

\[
I_{TE} = 2|E_1|^2 (1 + \cos \delta) \\
I_{TM} = 2|E_1|^2 [1 + (\cos \delta)(\cos 2\theta)] \\
\text{Contrast} = \frac{I_{TE} - I_{TM}}{I_{TE} + I_{TM}}
\]
Figure 2.1: Radiation incident upon photomask

Traditional wire grid polarizers allow the attenuation of the TE polarized radiation while allowing the TM state to pass. The electric field of the TE polarized light induces a current in the length of the wires. Forward transmitted radiation is out of phase with the incident TE wave and exhibits greatly reduced intensity. The electric field of the TM polarized light is perpendicular to the wires, a dimension in which the wires are very narrow and restrict the motion of the electrons. Therefore, most of the TM radiation is transmitted unaffected [43].

The parameters which impact the efficiency of a traditional wire grid polarizer include period, duty cycle, thickness, shape, and material. The grating period is the most important of these parameters as it determines the minimum wavelength that can be polarized for a specific diffracted order, as shown in Equation (2.5). As the period decreases, wires become closer together making it easier for TE polarization to induce a current in the wires. Additionally, narrower wires restrict electron motion in the direction perpendicular to the wire even more, lessening the attenuation of the TM mode. Duty cycle is defined as the wire width divided by the period. Assuming a fixed period, if the
duty cycle increases, so does the wire width, attenuating both the TE and TM polarizations more. Again, as in the case for decreasing period, a larger duty cycle will result in a more efficient TM polarizer. As grating thickness increases, the wires are able to generate more current, creating a more efficient polarizer. The shape of the wires also has an effect on the transmission and polarization efficiency. Non-vertical sidewalls and rounded edges cause a decrease in polarization efficiency, a benefit to the lithographer [43].

The transition region of a wire grid polarizer is defined as being between half to twice the wavelength of the incident radiation. Wood noticed a sharp decrease in transmission in this region in 1902; this phenomenon became known as Wood’s Anomalies [44]. In 1907, Lord Rayleigh analyzed Wood’s data and noted that for a specific wavelength ($\lambda$), period ($\Lambda$), material refractive index ($n$), and angle of incidence ($\theta$), a higher diffracted order ($m$) emerges, as [45]:

$$\lambda = \frac{\Lambda \cdot (n \pm \sin \theta)}{m}.$$  \hspace{1cm} (2.5)

Another phenomenon that occurs in the transition region is the transmission of TE polarization as opposed to TM polarization. These have been studied by Honkanen, and will be referred to as inverse wire grid polarizers [46]. The mechanism of action for these polarizers has been attributed to the waveguiding effect of the TM-mode in the grating, and by surface plasmons when the grating material is metallic [47].

The features on the photomask can not be sufficiently approximated by assuming that they are a grating comprised of a thin metal film on a dielectric substrate. For feature sizes greater than twice the wavelength, a diffraction grating results with little to no
polarization effects. For feature sizes less than half of the wavelength, the mask acts as a zero order wire grid polarizer. Between half and twice the wavelength is a transition region where the mask polarizes and diffracts the radiation, and can act as an inverse polarizer for some materials.

2.2 APPROACH

A binary Cr\textsubscript{x}O\textsubscript{y}N\textsubscript{z}-on-glass mask was modeled using an effective media approximation from data collected on materials deposited via magnetron sputtering and characterized by means of ultra-violet variable angle spectroscopy (UV-VASE) [48]. The four layer stack described in Table 2.1 and Table 2.2 represents the graded Cr\textsubscript{x}O\textsubscript{y}N\textsubscript{z} stack.

### Table 2.1: Cr-O-N stack composition. Layer 1 is closest to substrate, layer 4 is furthest.

<table>
<thead>
<tr>
<th>Cr-O-N Stack Composition</th>
<th>Layer 1</th>
<th>Layer 2</th>
<th>Layer 3</th>
<th>Layer 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>90.00%</td>
<td>18.90%</td>
<td>9.45%</td>
<td>0.00%</td>
</tr>
<tr>
<td>CrN</td>
<td>10.00%</td>
<td>2.10%</td>
<td>1.05%</td>
<td>0.00%</td>
</tr>
<tr>
<td>CrOx</td>
<td>0.00%</td>
<td>79.00%</td>
<td>89.50%</td>
<td>100.00%</td>
</tr>
</tbody>
</table>

### Table 2.2: Cr-O-N stack data. Layer 1 is closest to substrate, layer 4 is furthest.

<table>
<thead>
<tr>
<th></th>
<th>Layer 1</th>
<th>Layer 2</th>
<th>Layer 3</th>
<th>Layer 4</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>193nm</td>
<td>248nm</td>
<td>193nm</td>
<td>248nm</td>
</tr>
<tr>
<td>n</td>
<td>0.8209</td>
<td>0.8863</td>
<td>1.5649</td>
<td>1.8142</td>
</tr>
<tr>
<td>k</td>
<td>1.1825</td>
<td>1.8700</td>
<td>0.4121</td>
<td>0.7391</td>
</tr>
<tr>
<td>Thickness (Å)</td>
<td>500</td>
<td>500</td>
<td>133</td>
<td>133</td>
</tr>
</tbody>
</table>

Attenuated Phase Shifting Mask (APSM) materials were also modeled. APSM materials chosen were Tantalum Nitride in a Silicon Nitride host (TaN-Si\textsubscript{3}N\textsubscript{4}), Molybdenum Oxide in a Silicon Dioxide host (MoO\textsubscript{3}-SiO\textsubscript{2}), Silicon in a Silicon Nitride host (Si-Si\textsubscript{3}N\textsubscript{4}), and Tantalum Oxide in a Silicon Dioxide host (TaO\textsubscript{5}-SiO\textsubscript{2}). These materials were also modeled using the effective media approximation described earlier.
All APSM films were designed for a $\pi$ phase shift and 10% transmission. Table 2.3 and Table 2.4 contain the APSM material data [48].

Table 2.3: APSM material composition. Host material in bold and italics.

<table>
<thead>
<tr>
<th></th>
<th>TaN</th>
<th>Si3N4</th>
<th>Si</th>
<th>Si3N4</th>
<th>MoO3</th>
<th>SiO2</th>
<th>Ta2O5</th>
<th>SiO2</th>
</tr>
</thead>
<tbody>
<tr>
<td>157nm</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>10.00%</td>
<td>90.00%</td>
<td>11.50%</td>
<td>88.50%</td>
</tr>
<tr>
<td>193nm</td>
<td>17.00%</td>
<td>83.00%</td>
<td>9.00%</td>
<td>91.00%</td>
<td>30.00%</td>
<td>70.00%</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>248nm</td>
<td>27.00%</td>
<td>73.00%</td>
<td>10.00%</td>
<td>90.00%</td>
<td>27.00%</td>
<td>73.00%</td>
<td>X</td>
<td>X</td>
</tr>
</tbody>
</table>

Table 2.4: APSM material data.

<table>
<thead>
<tr>
<th></th>
<th>TaN-Si3N4</th>
<th>Si-Si3N4</th>
<th>MoO3-SiO2</th>
<th>Ta2O5-SiO2</th>
</tr>
</thead>
<tbody>
<tr>
<td>157nm</td>
<td>2.5626</td>
<td>2.3833</td>
<td>2.4317</td>
<td>2.3482</td>
</tr>
<tr>
<td>193nm</td>
<td>2.889</td>
<td>0.433</td>
<td>0.4462</td>
<td>0.4246</td>
</tr>
<tr>
<td>248nm</td>
<td>3.208</td>
<td>0.223</td>
<td>0.2117</td>
<td>0.2246</td>
</tr>
</tbody>
</table>

Rigorous coupled wave analysis (RCWA) provides an exact solution for Maxwell's equations. GSOLVER, a commercial software program capable of analyzing arbitrary grating thicknesses, numbers of materials, material indices of refraction, buried structures, and varied shapes (represented by stacked layers), was used to perform this experiment.

Unpolarized radiation was modeled by first inputting a 100% TE polarized beam and measuring the transmitted TE intensity in the 0th and 1st diffracted orders and then inputting a 100% TM polarized beam and measuring the transmitted TM intensity in the 0th and 1st diffracted orders.

This was done for 157nm, 193nm, and 248nm radiation depending on the mask material. The mask pitch was varied from 0nm to 1000nm in 10nm increments, and duty ratios examined were 0.2, 0.25, 0.33, and 0.5. Degree of Polarization (defined in
Equation (2.6)) was plotted versus mask pitch for the different materials, feature shapes, duty cycles, and wavelengths.

$$\text{DoP} = \frac{T_{TE} - T_{TM}}{T_{TE} + T_{TM}}$$  \hspace{1cm} (2.6)

By this definition, a degree of polarization of –1 signifies fully TM polarized radiation, +1 signifies fully TE polarization, and 0 means equal TE and TM polarization. The plotted transmission is the average of the transmitted TE and TM polarization states.

The masks were simulated at all of the wavelengths listed for the specific material in Table 2.2 and Table 2.4. All masks were simulated with the light incident at 0 degrees, except for the binary mask, which was also simulated for an off axis illumination of NA = 1.2 and 4x reduction which corresponds to 17.45 degrees in air, 11.5 degrees in quartz. Additionally, all masks were simulated using rectangular features as well as triangular (equilateral) features.

2.3 RESULTS

The Wood’s Anomaly equation can be rearranged to provide the grating pitch at which a particular order emerges. For all on axis cases in this experiment, this corresponds to the first order emerging at \( \Lambda = \lambda \). At this point, the 0-order in all cases experiences a decrease in transmission, and usually is also the mask pitch at which the 0-order experiences the greatest polarization effects. Figure 2.2 through Figure 2.4 show the degree of polarization and transmission data for rectangular shaped APSM and binary mask structures with on-axis illumination and varying duty ratio (TaN-Si\(_3\)N\(_4\) and Si-Si\(_3\)N\(_4\) will be treated together due to similar results). All APSM materials act as traditional wire
grid polarizers for the 0-order, and act as either traditional or inverse wire grid polarizers for the 1\textsuperscript{st}-order depending upon the duty ratio.

For TaN-Si\textsubscript{3}N\textsubscript{4} and Si-Si\textsubscript{3}N\textsubscript{4}, decreasing duty ratio increases the TM polarization efficiency at $\Lambda = \lambda$ for the 0-order, acting as a traditional wire grid polarizer. The 1\textsuperscript{st}-order behavior for these materials acts like a traditional wire grid polarizer for equal lines and spaces, but like an inverse wire grid polarizer for duty ratios less than 0.5. Transmission increases with decreasing duty ratio for the 0-order, but decreases in the 1\textsuperscript{st}-order. This is consistent with basic Fourier-analysis of a square-wave function. For MoO\textsubscript{3}-SiO\textsubscript{2} as the duty ratio decreases, so does the TM polarization efficiency. At $\Lambda = \lambda$ for the 0-order, there is a sharp decrease in polarization efficiency, and at slightly larger mask pitches there is a sharp increase; again the 0-order acts as a traditional wire grid polarizer. The 1\textsuperscript{st}-order acts as a weak traditional wire grid polarizer for a duty ratio of 0.5, but for decreasing duty ratios acts as a stronger inverse wire grid polarizer. Transmission characteristics follow the same trend as in the other APSM case.
Figure 2.2: 0 and 1st order Degree of Polarization and Transmission vs. Mask Pitch for TaN-Si$_3$N$_4$. 
Figure 2.3: 0 and 1st order Degree of Polarization and Transmission vs. Mask Pitch for MoO$_3$-SiO$_2$.

The binary Cr$_x$O$_y$N$_z$ mask acts mainly as a traditional wire grid polarizer for the 0-order. Decreasing duty ratios lead to a decrease in the polarization efficiency of the 0-order. Oppositely, the TE state is passed more than the TM state in the 1$^{st}$-orders, acting more like an inverse wire grid polarizer, and decreasing duty ratio increases the polarization effects. The transmission follows the same trends as previously described.
Similarly to Figures 2.2-2.4, degree of polarization was plotted vs. mask pitch for 157nm and 248nm illumination. This was also performed for off-axis 193nm illumination of the binary mask, and shown in Figure 2.5. The summary of these results for 1.2NA and 0.85NA are shown in Figure 2.6 for APSM and binary mask materials. It is observed that for the same NA, wavelength has no effect on the degree of polarization for APSM materials, but for the binary mask materials, the 0-order experiences a slight increase in DoP with increasing wavelength whereas the 1st-orders experience a slight decrease. Off-axis illumination increases the DoP within one of the 1st-orders while
decreasing the DoP within the other 1\textsuperscript{st} order. A change in wavelength has a similar effect as the on-axis case, however, the 1\textsuperscript{st}-order that experienced a decreased DoP previously experiences an increase in the magnitude of DoP with an increase in wavelength.

![Degree of Polarization vs. Mask Pitch](image1)

**Figure 2.5:** 0 and 1\textsuperscript{st} order Degree of Polarization and Transmission vs. Mask Pitch for OAI of the binary Cr\textsubscript{y}O\textsubscript{z}N\textsubscript{x} mask.

![APSM Material Results](image2)

![Binary Mask Results](image3)

**Figure 2.6:** APSM and binary mask material DoP for different $\lambda$, illumination at different NA.
The simulations that were run to generate Figures 2.2-2.4 were repeated for a 0.5 duty ratio for triangular-shaped features. The results are shown in Figure 2.7. The sloped sidewalls have little effect on the degree of polarization. At higher NAs, the DoP for APSM material features with sloped sidewalls is slightly less than that for the DoP of rectangular features. Sloped sidewalls have an opposite effect on the binary Cr$_x$O$_y$N$_z$ mask - the DoP is slightly greater than in the case of rectangular features. For all mask materials, the 0-order transmission for sloped sidewalls is greater than that for vertical sidewalls; the 1$^{st}$-order transmission remains approximately the same.

![Figure 2.7: APSM and binary mask material DoP for rectangular and pyramidal shapes at different NA.](image)

In addition to the analysis of actual mask materials, simulations were performed to study the degree of polarization as a function of n and k for $\pi$-phase shifting APSM materials. The index of refraction was varied from 0.5 to 3.0 (increments of 0.1) and the extinction coefficient from 0.0 to 1.0 (increments of 0.1). The thickness necessary to obtain a $\pi$-phase shift was calculated for a particular n and k value by first using Equation (2.7) to calculate the interfacial phase jump at the substrate-mask material interface.
(\(\Delta \Phi_{12}\)), the mask material-air interface (\(\Delta \Phi_{23}\)), and the substrate-air interface (\(\Delta \Phi_{13}\)), and using these values in Equation (2.8) to solve for \(d\). A plot of APSM film thickness vs. \(n\) and \(k\) is shown in Figure 2.8. This thickness, \(d\), was then used to calculate transmission as a function of \(n\) and \(k\) using Equation (2.9) [49], [50]. An extinction coefficient was found for a particular transmission and index of refraction, and lines were superimposed on the contour plot for 4% and 15% transmission. Shown in Figure 2.9 is the contour plot of degree of polarization vs. \(n\) and \(k\) with transmission lines overlaid.

\[
\Delta \Phi_{12} = \arg \left( \frac{2n_1^*}{n_1^* + n_2^*} \right) \tag{2.7}
\]

\[
\Delta \Phi = \frac{2\pi}{\lambda} (n_2 - n_3)d + \Delta \Phi_{12} + \Delta \Phi_{23} - \Delta \Phi_{13} \tag{2.8}
\]

\[
T(k) = \frac{(1 - R_{12})(1 - R_{23})}{(1 - R_{13})} e^{-4\pi kd/\lambda} \tag{2.9}
\]

Figure 2.8: Required APSM film thickness for \(\pi\)-phase shift plotted vs. \(n\) and \(k\) (thickness in \(\mu m\)).
It is observed that materials with higher refractive indices and lower extinction coefficients tend to pass more of the TM polarization state. Materials with lower refractive indices and a relatively wider range of extinction coefficients pass more TE polarized radiation. Higher refractive index films are thinner than those with lower refractive indices.

Additionally, the APSM materials with transmission varying from 2-20% (2-70% for MoO$_3$-SiO$_2$) were superimposed on the contour plot to show viable candidates for next generation mask materials. Materials that contribute more TE polarization effects or equal polarization weighting are desirable. From Figure 2.9, materials that meet these criteria with a transmission between 4-15% have an index of refraction between 1.1 and 1.4, and an extinction coefficient between 0.05 and 0.2. None of the materials examined in this paper meet the desired polarization criteria.
2.4 CONCLUSION

Rigorous Coupled Wave Analysis was used to solve Maxwell’s equations for photomasks comprised of APSM materials and \( \text{Cr}_x\text{O}_y\text{N}_z \). Different materials, radiation wavelength, thickness, pitch, duty ratio, feature shape, and incident angle all have an effect on how much a mask will polarize light.

All mask materials act predominantly as traditional wire grid polarizers for the zero order, whereas different materials and duty ratios affect the polarization of the first diffracted orders differently. Off-axis illumination causes an enhancement of the polarization effects in one of the first orders, and a decrease in the other. Sidewall angles other than ninety degrees and rounded corners contribute little to the polarization of the incident radiation. The wavelength has virtually no effect on polarization effects at the same NA values.

Materials inducing a \( \pi \)-phase shift with higher refractive indices and lower extinction coefficients tend to pass more of the TM polarization state, whereas materials inducing a \( \pi \)-phase shift with lower refractive indices and a relatively wider range of extinction coefficients pass more TE polarization.

To reduce polarization effects, greater system reduction, resulting in larger mask feature sizes, could be used. Additionally, new mask materials could be researched.

Given that TM-polarized DUV radiation is the predominant state being passed by photomasks, especially as features on masks become so small that the mask approaches a zero-order grating, it is not hard to be reminded of TM polarized radiation exciting surface plasmons, and the work that others have done in the mid-UV spectrum with
surface plasmons and imaging. Chapter 3 will explore applications for engineered metamaterials that can be used in DUV nanolithography.
3. SURFACE PLASMONS AND APPLICATIONS TO IMAGING

3.1 INTRODUCTION

A surface plasmon is an electromagnetic wave that travels along the boundary between a conductor and a dielectric. Surface plasmons were first noticed experimentally in the early 1900’s by Wood [44] as anomalous drops in the reflected intensity from metal-backed gratings, but it wasn’t until the 1940’s that Fano [51] linked this to earlier theory developed by Sommerfeld [52]. In the late 1950’s, Ritchie [53] performed experiments on electron energy losses in thin foils, and Pines and Bohm [54]–[56] discovered that these losses were due to the excitation of conducting electrons, plasma oscillations they named plasmons [57]. In the 1960’s, Kretschmann and Raether [58], as well as Otto [59], developed techniques to optically excite surface plasmons via attenuated total reflection (ATR). It wasn’t until the early 1990’s that exponential growth in plasmon research began, as the first SP based biosensor was made [60]. Over the next 10 years, SP mediated anomalous transmission was also demonstrated, and the negative index (or permittivity) perfect lens was theorized.
The dispersion relation for surface plasmons can be obtained by solving the wave equation, and will be discussed in more detail later [61]. The resulting surface plasmon dispersion relation for a single interface is

\[ \beta = k_0 \sqrt{\frac{\varepsilon_m \varepsilon_d}{\varepsilon_m + \varepsilon_d}} \]  

(3.1)

where \( \beta \) is the propagation constant, \( k_0 \) is the wave vector of the incident radiation, and \( \varepsilon_m \) and \( \varepsilon_d \) are the dielectric functions of the conductor and dielectric. It should be noted that this dispersion relation is only valid for TM polarization (also known as p polarization) states; surface plasmons are not excited by TE polarization. An example of the dispersion relation for SPs is shown in Figure 3.2.
Equation (3.1) shows that the propagation constant becomes asymptotic when the dielectric functions are equal and opposite in sign. This condition is known as the surface plasmon resonance (SPR). In Figure 3.2, the gray air line represents the dispersion line for radiation in free space, while the SP dispersion curve for the air-metal interface is the gray curve that lies to the right of it (same convention for silica). At frequencies far below the SPR frequency, the SP propagation constant is relatively small, meaning that the SP wavelength, \( \lambda_{sp} = \frac{2\pi}{\text{Real}(\beta)} \), is only slightly smaller than the incident radiation. As the frequency of the incident radiation increases to the surface plasmon resonance frequency, the propagation constant increases and approaches infinity at the SPR frequency, meaning that the SP wavelength becomes infinitesimally small. Real metals are not perfect conductors and exhibit some absorption. This causes the dispersion curves to not become entirely asymptotic, and the dispersion curve sharply moves back to a smaller propagation constant (longer wavelength). Both the bound nature of the surface...
plasmon and its smaller wavelength are the basic mechanisms that allow for the operation of most of the plasmonic applications that will be discussed.

It is apparent from the dispersion curves that a surface plasmon on a simple metal- or NPM-dielectric interface cannot be excited by light due to the SP propagation constant always being larger than the wave vector of light in the dielectric. However, incident light can be phase-matched with the SP by means of prism coupling, a technique referred to as Attenuated Total Reflection (ATR), using either the Otto configuration [59], in which a dielectric prism and metal are separated by an air gap, or the Kretschmann configuration [58], which has the prism and metal film in direct contact. In both configurations, phase matching is accomplished by varying the angle of incidence of the TM polarized radiation, resulting in a sharp decrease in the reflected intensity at some angle beyond the critical angle. The phase matching occurs when the in-plane wave vector of the reflected beam along the metal surface is the same as the propagation constant; this relationship is shown in Equation (3.2).

\[ k_x = \beta = k \sqrt{\varepsilon_d} \sin \theta \]  

(3.2)

The only propagation constants available are those that lie between the air and prism light lines (in Figure 3.2 this would be between air and silica). For ATR to be successful, the NPM film used needs to be sufficiently thin so that the incident radiation can couple from the prism to the SP propagating on the opposite side. ATR profiles are highly dependent upon film thickness and optical properties.
The ATR techniques essentially evolved from early research into total internal reflection (TIR) and frustrated total internal reflection (FTIR) [63]. When radiation is incident on the interface between two media, some is reflected into the first medium, and some is transmitted into the second. If the first medium exhibits a greater index of refraction than the second medium, and the angle of incidence is greater than the critical angle (Equation (3.3)), then all of the incident radiation is reflected.

$$\theta_c = \sin^{-1} \frac{n_2}{n_1}$$  \hspace{1cm} (3.3)

However, some of this incident radiation penetrates into the second medium, and forms an evanescent wave that travels along the boundary of the two media. This was first noticed by Newton [64]. Hall later investigated this, and noticed that by placing a third medium in close proximity (on the order of the wavelength of the incident radiation), light will transmit through the entire structure instead of being totally reflected [65]. Years later, Leurgans and Turner describe the totally internally reflected light as being frustrated [66]. For the special case where the second medium is conducting, like a metal, the evanescent wave is plasmonic in nature, and the term ATR is used instead of FTIR.

First we will consider the response of materials to light, thereby deriving the refractive index. Next, the properties and applications of negative refractive index
materials will be considered. Finally, the role of these materials in lithography is developed via surface plasmon interference.

### 3.2 REFRACTIVE INDEX

Maxwell’s equations are a set of empirically derived equations from which all electric and magnetic laws are derived. Thus, they are essential to deriving the refractive index of a material, and are listed in Equations (3.4-3.7).

\[
\nabla \cdot \vec{E} = \frac{\rho_{\text{tot}}}{\varepsilon_0} \quad (3.4)
\]

\[
\nabla \cdot \vec{B} = 0 \quad (3.5)
\]

\[
\nabla \times \vec{E} = -\frac{\partial \vec{B}}{\partial t} \quad (3.6)
\]

\[
\nabla \times \vec{B} = \mu_0 \vec{J} + \varepsilon_0 \mu_0 \frac{\partial \vec{E}}{\partial t} \quad (3.7)
\]

Equation (3.4) is Gauss’s Law. It was arrived at by applying the divergence theorem to the integral form (Equation (3.8)) and states that the electric flux over a closed surface is proportional to the enclosed charge.

\[
\varphi_E = \oint \vec{E} \cdot d\vec{S} = q_{\text{enc}} \quad (3.8)
\]

Equation (3.5) is Gauss’s Law of Magnetism, requiring that magnetic fields are divergenceless. Physically this means that magnetic monopoles cannot exist.

Faraday’s Law says that changing magnetic fields produce electric fields, and is shown in Equation (3.8).

Lastly, Equation (3.7), is a modification to Ampere’s Law:
\[ \nabla \times \vec{B} = \mu_0 \vec{J}. \]  
\[ (3.9) \]

Maxwell discovered that the displacement current,

\[ \vec{J} = \varepsilon_0 \frac{\partial \vec{E}}{\partial t} \]  
\[ (3.10) \]

needed to be added. This allows for an expression of the conservation of electric charge:

\[ \nabla \cdot \vec{J} + \frac{\partial \rho}{\partial t} = 0. \]  
\[ (3.11) \]

If no charge or current is present, it is implied from Maxwell’s equations that

\[ \nabla^2 \vec{E} - \varepsilon_0 \mu_0 \frac{\partial^2 \vec{E}}{\partial t^2} = \nabla^2 \vec{B} - \varepsilon_0 \mu_0 \frac{\partial^2 \vec{B}}{\partial t^2} = 0 \]  
\[ (3.12) \]

and that waves propagate with velocity

\[ c = \frac{1}{\sqrt{\varepsilon_0 \mu_0}} \]  
\[ (3.13) \]

These equations describe the propagation of electric and magnetic fields in free space. However, modifications need to be made to describe the interaction of these fields with material (i.e. not a vacuum), which eventually result in the definition of refractive index.

To arrive at this definition, it is easiest to consider the interaction of an electric field

\[ \vec{E} = \vec{E}_0 \cos(\omega t) \]  
\[ (3.14) \]

with the atoms of a dilute gas. This electric field excites an electric dipole moment in an atom,

\[ \vec{p} = \alpha(\omega) \vec{E}_0 \cos(\omega t) \]  
\[ (3.15) \]

with the polarizability of the atom, \( \alpha(\omega) \), represented as,
\[
\alpha(\omega) = \frac{q^2/m}{(\omega_0^2 - \omega^2) - i\gamma\omega} \tag{3.16}
\]

where \( \gamma = 1/\tau \). The characteristic collision frequency between the electrons excited by the applied field is \( \gamma \) and the relaxation time of the electrons is \( \tau \). Assuming that there are \( N \) atoms per unit volume, the polarization density is represented as

\[
\vec{P} = N\vec{p} \tag{3.17}
\]

which is associated with the charge density by

\[
\rho_{pot} = -\nabla \cdot \vec{P} \tag{3.18}
\]

Given that the medium is no longer a vacuum, Gauss’s Law (for electricity) becomes:

\[
\nabla \cdot \vec{E} = \frac{1}{\varepsilon_0} (\rho - \nabla \cdot \vec{P}) \tag{3.19}
\]

The displacement field can be represented as

\[
\vec{D} = \varepsilon_0 \vec{E} + \vec{P} \equiv \varepsilon(\omega)\vec{E} \tag{3.20}
\]

which results in Equation (3.19) becoming

\[
\nabla \cdot \vec{D} = \rho \tag{3.21}
\]

The free charge density is represented by \( \rho \), and the permittivity of the medium by \( \varepsilon_0 \):

\[
\varepsilon(\omega) = \varepsilon_0 \left( 1 + \frac{N\alpha(\omega)}{\varepsilon_0} \right) \equiv \varepsilon_0 \left( 1 + \chi(\omega) \right) \equiv \kappa(\omega)\varepsilon_0. \tag{3.22}
\]

\( \kappa \) is the dielectric constant, and \( \chi \) is the electric susceptibility.
Given that the permeability, \( \mu \), is the same as its free-space value at most optical frequencies, it will be ignored (for now). Equations (3.4) and (3.7) are now represented by Equation (3.21) and Equation (3.23).

\[
\nabla \times \overrightarrow{B} = \mu_0 \overrightarrow{J} + \mu_0 \frac{\partial \overrightarrow{D}}{\partial t} \tag{3.23}
\]

Again, if we assume a medium with no charge or current, and with an electric field of \( \overrightarrow{E}_0 e^{-i\omega t} \) and a similar magnetic field, Equation (3.12) can be rewritten with the redefined Maxwell’s equations as

\[
\nabla^2 \overrightarrow{E}_0 + n^2(\omega) \frac{\omega^2}{c^2} \overrightarrow{E}_0 = \nabla^2 \overrightarrow{B}_0 + n^2(\omega) \frac{\omega^2}{c^2} \overrightarrow{B}_0 = 0 \tag{3.24}
\]

providing the expression for refractive index (assuming \( N \frac{\alpha(\omega)}{\varepsilon_0} \ll 1 \)):

\[
n^2(\omega) = \frac{\varepsilon(\omega)}{\varepsilon_0(\omega)} = \kappa(\omega) = 1 + \frac{N}{2\varepsilon_0} \alpha(\omega). \tag{3.25}
\]

If permeability is to be taken into account, Equation (3.25) becomes:

\[
n^2(\omega) = \frac{\varepsilon(\omega)\mu(\omega)}{\varepsilon_0(\omega)\mu_0(\omega)}. \tag{3.26}
\]

This implies that the refractive index, \( n \), can be written simply as:

\[
n = +/\sqrt{\kappa} = +/\sqrt{\frac{\varepsilon\mu}{\varepsilon_0\mu_0}}. \tag{3.27}
\]

Due to Equation (3.16) being complex, the refractive index and permittivity need to be represented as complex quantities,

\[
\tilde{n}(\omega) = n(\omega) + ik(\omega) \tag{3.28}
\]

\[
\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) \tag{3.29}
\]
where \( n \) is the real part of the refractive index, \( k \) is the imaginary part of the refractive index and referred to as the extinction coefficient, \( \varepsilon_1 \) is the real part of the dielectric function, and \( \varepsilon_2 \) is the imaginary part of the dielectric function and is responsible for determining absorption in the material. Inserting Equations (3.28) and (3.29) into yields

\[
\varepsilon_1 = n^2 - k^2
\]  \hspace{1cm} (3.30)

\[
\varepsilon_2 = 2nk. 
\]  \hspace{1cm} (3.31)

Identifying the plasma frequency as \( \omega_p = \sqrt{\frac{Nq^2}{me_0}} \), the refractive index and dielectric functions can be recast as:

\[
\tilde{n} = 1 + \frac{\alpha_p}{4\omega_0^2 - \sigma^2 - i\gamma\sigma} \]  \hspace{1cm} (3.32)

\[
\varepsilon(\omega) = \varepsilon_0 \left( 1 + \frac{\sigma_p^2}{(\omega_0^2 - \sigma^2) - \gamma\sigma} \right)^{-1} \]  \hspace{1cm} (3.33)

For the special case of a free electron gas, as in the case of metals, \( \omega_0 \) becomes very small compared to the optical frequency, the damping term becomes negligible since the electron is free, and the permittivity becomes:

\[
\varepsilon(\omega) = 1 - \frac{\sigma_p^2}{\sigma^2}. \]  \hspace{1cm} (3.34)

### 3.3 Discovery of Negative Refractive Index

Up until recently, refractive index has been thought of as a positive number. However, there is no requirement that the permittivity and/or permeability cannot be negative. For the case when both quantities are negative, the negative root for Equation (3.27) must be chosen. Veselago noted this in 1967 [67].
Light propagation in natural materials forms a right handed-set consisting of the wave vector $\vec{k}$, electric field $\vec{E}$, magnetic vector $\vec{H}$, and the Poynting vector, $\vec{S}$. This is shown in Equations (3.35-3.37) and in Figure 3.4.

$$\vec{k} \times \vec{E} = \omega \mu \vec{H}$$  \hspace{1cm} (3.35)

$$\vec{k} \times \vec{H} = -\omega \varepsilon \vec{E}$$  \hspace{1cm} (3.36)

$$\vec{S} = \vec{E} \times \vec{H}$$  \hspace{1cm} (3.37)

Veselago noticed for negative refractive index materials (NIM) consisting of both a negative permittivity and permeability, the wave vector $\vec{k}$, electric field $\vec{E}$, and magnetic vector $\vec{H}$ form a left handed set, and thus NIMs can be referred to as left handed materials (LHM). This is shown in Figure 3.5. Note that the Poynting vector is in the same direction as in a RHM, whereas the wave vector is now propagating in the opposite direction.
Additionally, Veselago showed that Snell’s Law is still obeyed for NIMs, as shown in Figure 3.6 and Equation (3.38). Note that the reflected wave’s pointing and wave vectors are in the same direction, and are the same for both RHMs and LHMs. However, the transmitted Poynting vector in the LHM refracts on the opposite side of the normal from a wave in an RHM, and that the wave vector is in the direction back towards the interface of material 1 and 2 (opposite direction from the Poynting vector).

\[
\sin \varphi \frac{p_2}{p_1} = n_{2,1} = \left| \frac{\varepsilon_2 H_2}{\varepsilon_1 H_1} \right|
\]

(3.38)
Observing what is occurring in Figure 3.6 leads to the notion that simply a slab of NIM forms a lens (Figure 3.7). Additionally, assuming the material is surrounded by vacuum, and that the NIM has $n = -1$, this is a “perfect” lens; there are no reflections at the interface and all of the radiation is transmitted. Veselago commented on this, but also knew that there are no naturally occurring materials possessing a negative index. Materials, such as metals at optical frequencies, can have a negative permittivity, but exhibit a positive permeability. Pendry, in 2000, showed that a perfect lens can be created out of a slab of negative permittivity material, and that the permeability does not factor into the equation at all [38].
3.4 THE REALIZATION OF NEGATIVE REFRACTIVE INDEX MATERIALS

As previously mentioned, there are no naturally occurring NIMs. There are materials that exhibit either a negative permittivity or permeability, though, and Pendry, Smith, and Shelby realized that by combining these materials, a NIM could be created.

The permittivity of a material can be represented as:

$$\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega(\omega + i\gamma)}.$$  \hfill (3.39)

When the frequency is below the plasma frequency, the damping term often vanishes, and the permittivity becomes negative. Pendry designed a wire structure in 1996 (Figure 3.8) exhibiting a variable plasma frequency, tunable by changing the wire radius and period, as shown in Equation (3.40) [68], [69]. This material has its plasma frequency in the microwave region.
In 1999, Pendry also developed a material, known as a Split Ring Resonator (SRR) with a tunable magnetic plasma frequency [70]. This material is shown in Figure 3.9. The material experiences a negative permeability when frequency of radiation is between the resonant frequency and the plasma frequency, which, for this structure, are defined in Equations (3.41) and (3.42), and are only dependent upon the radius of the outer ring $r$, the period of the rings $a$, and the distance between the inner and outer ring $d$. Similar to the material in Figure 3.8, the material exhibits negative permeability in the microwave region.

\[
\omega_p^2 = \frac{2\pi c^2}{a^2 \ln(a/r)} \tag{3.40}
\]

\[
\mu_{eff} = 1 - \frac{\pi r^2}{a^2} \cdot \frac{2\sigma i}{\omega r \mu_0} - \frac{3d c_0^2}{\pi^2 \omega^2 r^3} \tag{3.41}
\]
\[ \omega_0^2 = \frac{3d c_0^2}{\pi^2 r^3} \quad (3.42) \]

\[ \omega_{mp}^2 = \frac{3d c_0^2}{\pi^2 r^3 \left(1 - \frac{\pi r^2}{a^2}\right)} \quad (3.43) \]

**Figure 3.9: SRR and permeability [70].**

By combining these two materials, D.R. Smith created a NIM in 2000 [71]. This material resembled a SRR with a wire placed in front of the ring (Figure 3.10). This material was tested with only a few of the SRRs in a row.
After testing a stack of SRRs with the wires in front of them, Smith developed what could be considered a “real material” out of SRR-like structures with wires running through the middle of them in 2001. This is shown in Figure 3.11. Shelby then went on to experiment with this material, showing its negative refraction in 2001 as well (Figure 3.12) [72], [73].
Typically, if a dipole of frequency $\omega$ (or radiation propagating through a slit in a photomask) is placed in front of a lens, the lens applies a phase correction to each Fourier component and brings the dipole (or image) to a focus at some distance beyond the lens. However, larger values of the transverse wave vector (higher frequency components), become evanescent, and decay exponentially in the propagating direction (in the case of a photomask the non-propagating orders spread out in the non-propagating direction along the interface between the absorber and glass comprising the mask). These evanescent waves do not contribute to the image, and the resolution of the lens is no greater than

$$\Delta \approx \frac{2\pi}{k_{\text{max}}} = \frac{2\pi c}{\omega} = \lambda. \quad (3.44)$$

Pendry discovers that NIMs cancel the decay of these evanescent waves, and actually amplify them [38]. Resolution for a lens comprised of a NIM includes information from both the propagating waves and the evanescent waves. Milonni shows that minimum resolution becomes

$$\Delta \sim \frac{2\pi d}{|\ln \delta|} \quad (3.45)$$
where $\delta < e^{-2\pi d/\lambda}$ and represents absorption (absorption is now the limiting factor in resolution) [74]. Garcia also shows that absorption introduces aberrations to these “perfect” lenses [75].

Pendry also proves that simultaneously negative permeability and permittivity are not needed [38]. When considering a system in which the components are smaller than the wavelength of light, the electrostatic and magnetostatic fields can be decoupled, and the electrostatic fields are ruled by P- or TM-polarized radiation. In this situation, the permeability is removed from the governing equations, and only the permittivity remains. A material with a negative permittivity will act as a NIM in this case, but only in the near field.

This is a very important discovery, as negative permittivity materials support surface plasmons, and there is a connection between plasmons and the focusing that occurs in a NPM slab lens. Pendry’s note of this occurs at a time just before plasmonics research begins to expand exponentially. Pendry’s research into creating a material with tunable permittivity becomes important with the realization of spoof, or designer, plasmons, which will be discussed in Chapter 4 along with other DUV nanolithographic applications.

### 3.5 REALIZATION OF A NEGATIVE PERMITTIVITY SLAB LENS

Pendry only described how a lens of a slab of NPM could be created. A few years following his description, Fang experimentally demonstrated such a device utilizing Silver at a wavelength of 365nm (Figure 3.13) [39]. 40nm features were etched into a chrome mask, which was separated from the silver superlens using a PMMA spacer layer, with photoresist coated on the bottom surface of the lens. This was then exposed
with 365nm radiation. With the superlens present, ~90nm features were resolved in the photoresist; without the superlens, the resolution was not as fine, and the resolved features were ~320nm (Figure 3.14).

Figure 3.13: Fang’s superlens setup [39].

Figure 3.14: Results from Fang’s superlens. A) Mask. B) AFM of image resolved with superlens. C) AFM of result without superlens. D) Cross section of the letter A in NANO [39].
At nearly the same time, Blaikie and Melville verified this superlensing effect utilizing both single- and double-layer Silver structures (Figure 3.15) [40], [76], [77]. The double-layer configuration was used in an attempt to see if it would improve resolution, as postulated by Ramakrishna, Wood, and Pendry [78], [79].

Figure 3.15: Melville and Blaikie’s superlens stack a) single layer superlens. b) double layer superlens [77].

3.6 PLASMONIC INTERFERENCE LITHOGRAPHY

The NPM slab lenses have certain drawbacks, such as mask features needing to be of the same size as the desired image, and the mask needing to be in contact with the imaging media or spacer layer. In a sense, it could be compared to nanoimprint lithography. Plasmonic interference lithography has been proposed by several researchers as a way to form deep subwavelength images without a mask [80]–[84]. While contact or near-contact between the metal layer and imaging medium are required, it does not require a complex mask.
Plasmonic interference lithography functions similarly to ATR. In ATR, when the phase matching condition is met, the incident radiation is coupled into the surface plasmon at the surface of the metal and air, but this is a traveling wave. Passian shows that if another beam is input into the opposite side of the prism at the resonance angle, a standing wave is formed with the period [85]:

\[ p = \frac{\lambda}{2\sqrt{\varepsilon_d \sin \theta}} \]  

(3.46)

From this equation, it can be observed that the resolution is dependent upon the resonance angle, the refractive index of the prism, and the incident wavelength.

**3.7 STRUCTURED METAMATERIALS WITH A TUNED RESPONSE**
The surface plasmon dispersion relation was discussed in Section 3.1. The surface plasmon frequency is dependent upon the dielectric function of the materials used. It is possible that there is no naturally occurring material that supports the desired surface plasmon dispersion at the excitation wavelength used. At the beginning of Section 3.4 and in Figure 3.8, it is shown that it is possible to create a structured material that can be tuned to provide the desired plasma response. Pendry has recently shown that this structure need not be comprised of wires, but that holes in a thin metal film can be designed to provide surface plasmons with arbitrary dispersion [86]. Others have shown that an even simpler design of a layered metal-dielectric-metal stack can be used to accomplish this [87], [88].

This is of importance in this document, as it will be shown in Chapter 4 that while Aluminum supports surface plasmons in the DUV, it is not ideal. Thus a layered system will be examined to provide the desired plasmon dispersion.

### 3.8 INDUCED TRANSMISSION PUPIL FILTER

A polarization sensitive angular pupil filter can be created by sandwiching a plasmonic material between two dielectrics. Filters of this design were first introduced by Billings, and Berning and Turner, while they were later linked to the field of plasmonics by Otto [89]–[91]. These concepts were then explored further by many others [92]–[103]. These filter shapes approach those proposed by Fukuda, Von Bunau, and Kang and Smith for spatial filtering to increase resolution and depth of focus for projection photolithography [104]–[108].
3.9 CONCLUSION

Victor Veselago discovered in 1967 that negative index materials were theoretically possible, although none existed in nature. Approximately 30 years following his realization, researchers began experimenting with negative permeability and permittivity materials, and shortly thereafter were able to synthesize a material exhibiting simultaneous $\varepsilon$ and $\mu$, thus creating a negative refractive index material useful in the microwave range. Additionally, surface plasmons allow negative permittivity materials to be useful in near-field imaging and optics, negating the need for negative index materials in some applications.
4. PLASMONIC APPROACHES TO DUV NANOLITHOGRAPHY

4.1 SURFACE PLASMONS

Having given an introduction to surface plasmons and their applications in lithography, it is important that we take a more detailed look at their properties. Knowing that a surface plasmon is an electromagnetic wave that travels along a boundary between a conductor and a dielectric, evanescently bound to the direction perpendicular to propagation, we need to apply Maxwell’s equations to this boundary [61]. We will begin with the wave equation assuming no external stimuli:

\[ \nabla^2 \vec{E} - \frac{\varepsilon}{c^2} \frac{\partial^2 \vec{E}}{\partial t^2} = 0. \]  
(4.1)

Assuming a harmonic time dependence of the electric field, \( \vec{E}(\vec{r}, t) = \vec{E}(\vec{r}) e^{-i\omega t} \), and inserting this into Equation 4.1 yields the Helmholtz equation:

\[ \nabla^2 \vec{E} + k_0^2 \varepsilon \vec{E} = 0 \]  
(4.2)

For simplicity, we are assuming a one-dimensional problem. For this case, the dielectric function will only depend on the z-direction, \( \varepsilon(z) \), as based on Figure 4.1, and we consider the wave to be bound along the x-y plane, with the wave propagating along the x-direction; we assume no spatial variation in the y-direction. The propagating waves can be defined as \( \vec{E}(x, y, z) = \vec{E}(z) e^{i\beta x} \), with \( \beta = k_x \). \( \beta \) is the propagation constant of the travelling waves, corresponding to the component of the wave vector in the direction of propagation. Combining this with Equation 4.2 results in
\[
\frac{\partial^2 \bar{E}(z)}{\partial z^2} + (k_0^2 \varepsilon - \beta^2) \bar{E} = 0,
\]

(4.3)

with a similar equation for the magnetic field.

Figure 4.1 Geometry for surface plasmon wave propagation. Gray is metal (z<0), z>0 is dielectric.

By applying the curl equations, Equations 3.6 and 3.7, expressions for different components of the electric and magnetic fields can be determined. Again, assuming harmonic time dependence, these expressions are:

\[
\frac{\partial E_x}{\partial y} - \frac{\partial E_y}{\partial z} = i\omega \mu_0 H_x
\]

(4.4a)

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

(4.4b)

\[
\frac{\partial E_y}{\partial x} - \frac{\partial E_x}{\partial y} = i\omega \mu_0 H_z
\]

(4.4c)

\[
\frac{\partial H_z}{\partial y} - \frac{\partial H_y}{\partial z} = -i\omega \varepsilon \varepsilon_0 E_x
\]

(4.4d)

\[
\frac{\partial H_x}{\partial z} - \frac{\partial H_z}{\partial x} = -i\omega \varepsilon \varepsilon_0 E_y
\]

(4.4e)

\[
\frac{\partial H_y}{\partial x} - \frac{\partial H_x}{\partial y} = -i\omega \varepsilon \varepsilon_0 E_z.
\]

(4.4f)

Since propagation is only in the x-direction, and the wave is homogeneous in the y-direction, Equations 4.4a-f simplify to:

\[
\frac{\partial^2 \bar{E}(z)}{\partial z^2} + (k_0^2 \varepsilon - \beta^2) \bar{E} = 0,
\]

(4.3)

with a similar equation for the magnetic field.
Equations 4.5a-f yield two sets of solutions, one for TM polarization, where the solution can have non-zero $E_x$, $E_z$, and $H_y$ components, and the other for TE polarization, which can have non-zero $H_x$, $H_z$, and $E_y$ components. Since for TM polarization the $H_x$, $H_z$, and $E_y$ components are zero, the set of equations reduces to

$$E_x = -i \frac{1}{\omega \varepsilon_0 \varepsilon} \frac{\partial H_y}{\partial z}$$  \hspace{1cm} (4.6a)$$

$$E_z = -i \frac{\beta}{\omega \varepsilon_0 \varepsilon} H_y$$  \hspace{1cm} (4.6b)$$

with the wave equation being

$$\frac{\partial^2 H_y}{\partial z^2} + \left( k_0^2 \varepsilon - \beta^2 \right) H_y = 0.$$  \hspace{1cm} (4.6c)$$

Given that a surface plasmon travels across the interface of a conductor and dielectric, the simplest geometry possible to support SPs is shown in Figure 4.1, where a non-absorbing dielectric occupies the space $z>0$ with a dielectric function $\varepsilon_2 > 0$, and a conductor occupying $z<0$ with a negative dielectric function $\varepsilon_1 < 0$. Examining the TM solutions for Equations 4.6a-c for the dielectric space results in
\[ H_y(z) = A_2 e^{i\beta x} e^{-k_z z} \]  
\[ E_x(z) = iA_2 \frac{k_2}{\omega \varepsilon_2 \varepsilon_0} e^{i\beta x} e^{-k_z z} \]  
\[ E_z(z) = -A_1 \frac{\beta}{\omega \varepsilon_2 \varepsilon_0} e^{i\beta x} e^{-k_z z} , \]  

while for the space occupied by the conductor yields

\[ H_y(z) = A_1 e^{i\beta x} e^{k_1 z} \]  
\[ E_x(z) = -iA_1 \frac{k_1}{\omega \varepsilon_1 \varepsilon_0} e^{i\beta x} e^{k_1 z} \]  
\[ E_z(z) = -A_1 \frac{\beta}{\omega \varepsilon_1 \varepsilon_0} e^{i\beta x} e^{k_1 z} . \]

The component of the wave vector perpendicular to the interface is \( k_z \), which in these equations becomes \( k_2 \) for the dielectric and \( k_1 \) for the conductor. At the interface, \( H_y \) and \( \varepsilon_1 E_z \) must be continuous, thus

\[ A_1 = A_2 \]  
\[ \frac{k_2}{k_1} = -\frac{\varepsilon_2}{\varepsilon_1} . \]

For Equations 4.9a-b to be true, the real part of \( \varepsilon_1 \) must be less than zero, and the real part of \( \varepsilon_2 \) must be greater than zero. This implies that surface plasmons can only exist between the interface of a dielectric and a conductor. Additionally, \( H_y \), Equations 4.7a-b, must still satisfy the wave equation (Equation 4.6c), yielding the wave vectors:

\[ k_1^2 = \beta^2 - k_0^2 \varepsilon_1 \]  
\[ k_2^2 = \beta^2 - k_0^2 \varepsilon_2 . \]
Substituting Equations 4.10a-b into Equation 4.9b provides the dispersion relation for a surface plasmon at the interface:

$$\beta = k_0 \sqrt{\frac{\varepsilon_1 \varepsilon_2}{\varepsilon_1 + \varepsilon_2}}$$  \hspace{1cm} (4.11)

If this analysis is also performed for TE modes, the boundary conditions dictate that $A_1 = A_2 = 0$, resulting in no surface modes for TE polarization.

Remembering that $\beta = k_x$, and that $k_x = \frac{2\pi}{\lambda}$, the surface plasmon wavelength is defined as $\lambda_{sp} = \frac{2\pi}{\text{real}(\beta)}$. Therefore as $\beta$ becomes infinite, the surface plasmon wavelength becomes infinitely small. However, this is not without consequence. Equations 4.7a and 4.8a, representing $H_y$, imply the field decays in the $y$-direction with $e^{-k_2z}$, with $k_2$ being the square root of Equation 4.10b. The larger $\beta$ becomes, the less the surface plasmon penetrates into the dielectric medium. This implies that for lithographic applications, imaging with a very short plasmon wavelength intrinsically means that the penetration of the plasmon into the imaging medium will be quite low.

Figure 3.2 shows a plot of Equation 4.11 for a conductor interfacing with air, $\varepsilon_2 = 1$, and fused silica, $\varepsilon_2 = 2.25$. The wave vector for the surface plasmons lies to the right of the light lines for air and silica, having a $\beta > k$, implying that they cannot be coupled to in the geometry shown in Figure 4.1. Phase matching techniques, such as prism coupling, are required. For the case of prism coupling, phase matching is achieved when the in-plane wave vector, $k_x = k\sqrt{\varepsilon} \sin \theta$, is the same as the propagation constant, $\beta$. This occurs in the realm of total internal reflection, where the $y$-component of the
transmitted propagation vector has become purely imaginary, and only the x-component is real [61], [109].

4.2 MATERIAL CONSIDERATIONS

The surface plasmon dispersion equation shows that a negative permittivity material is needed in conjunction with a dielectric to support surface plasmons. Figure 4.2 shows materials to be explored for use in plasmonic applications at 193nm and 248nm. These materials are represented in both the dielectric function space and optical parameter space. The relationship between these two spaces is shown in Equations 3.28-3.31.

The real part of the dielectric function, $\varepsilon_1$, needs to be negative to support SPs. Materials exhibiting larger negative permittivity values (i.e. a smaller refractive index and a larger extinction coefficient) are more conductive and should exhibit a stronger plasmon resonance with lower damping and absorption because of the small imaginary part of the dielectric function, $\varepsilon_2$. Knowing this, it is observed from Figure 4.2 that material candidates for use in plasmonic applications at 193nm could be Al, Sn, In, W, Si, Mo, Rh, and Cr, while at 248nm the same materials could be useful with the addition of Ni and Pd. Missing from this list are materials such as Au and Ag, which support SPs at mid-UV and longer wavelengths, but exhibit less desirable optical characteristics in the DUV spectrum.

For the perfect lens described by Veselago, the plasmonic superlens described by Pendry, and demonstrated by Fang, it was mentioned that the dielectric medium surrounding the NPM lens should have a permittivity of equal value but opposite in sign to reduce reflections at the interfaces [38], [39], [67]. The plots in Figure 4.2 have a line
in the positive permittivity space where a host of transparent dielectric materials exist, as well as a line in the opposite negative permittivity space where desirable NPM might exist. The material SL denotes the optical parameters for Ag at 365nm, as this material works well as a superlens at that wavelength. At that wavelength it has low absorption, lower than most all materials displayed in Figure 4.2. In superlensing applications, absorption dictates the minimum resolution possible as well as greatly reducing an already small depth of focus [75]. In and Sn are close to this point at 193nm, but exhibit a higher imaginary permittivity component, resulting in more absorption. At 248nm, the only materials close to the desired permittivity space are Pd and Ni, but they exhibit even higher absorption.

It is easily observed that the optical properties of Al and Al$_2$O$_3$ lie on the opposite sides of the desired permittivity space. This fact suggests that a combination of the two materials, when treated as an optically homogeneous new material, may satisfy the requirements for the superlensing material. In the simple case of a planar film stack with all material boundaries parallel to the electric field, the properties of the combined Al/Al$_2$O$_3$ stack would reduce to the spatial average of the constituents, i.e. lie on the line connecting Al and Al$_2$O$_3$ [110]. Such a material could be produced using sputtering techniques. The optical properties of a composite material comprised of ~85% Al and ~15% Al$_2$O$_3$ at 193 nm exhibit similar behavior to those of Ag at 365 nm. It will also be shown in Section 4.5 that e-beam evaporated thin aluminum films exhibit these characteristics as well.
Figure 4.2 Material space to be explored for support of surface plasmons in the DUV spectrum. The legend for the 193nm n vs. k plot applies to the 248nm case as well.

It has also been shown by Ramakrishna and Pendry that the dielectric materials cladding the NPM slab lens do not need to exhibit a permittivity equal but opposite in sign to the NPM, and that this asymmetric lens can help counteract absorption effects from the NPM [111]. This therefore removes some constraints on picking a SP supporting NPM for superlensing, and makes Al a more attractive material to as it is
easily integrated with standard semiconductor processing techniques whereas materials such as Sn or In would be problematic in their unbound states.

4.3 SPECTRAL ANALYSIS OF SURFACE PLASMON SUPPORTING MATERIALS VIA ATTENUATED TOTAL REFLECTION CALCULATIONS

As described previously, surface plasmons are governed by Maxwell’s equations. Standard thin film transmission and reflection matrix calculations are also governed by Maxwell’s equations. This matrix formalization can be used to show the interaction between the incident radiation and SPs. Subsequent modeling was carried out and a simulator was created based on these calculations to examine the SP resonance induced decrease in reflectivity at a certain range of angles and conductor thicknesses. It was also designed to examine the peak angle at which the resonance occurs as well as the resonance’s width at any wavelength.

The matrix methods outlined by Macleod offer an elegant way of calculating reflectance from an ATR setup [112]. Equations 4.12 thru 4.19 were used to calculate reflection for TE and TM polarization states for a given wavelength, varying the incident angle and NPM thickness.

\[
[B]_C = \left\{ \prod_{j=1}^{q} \begin{bmatrix} \cos \delta_j & i \sin \delta_j \\ i \eta_j \sin \delta_j & \eta_j \cos \delta_j \end{bmatrix} \right\} \begin{bmatrix} 1 \\ \eta_{\text{sub}} \end{bmatrix} \tag{4.12}
\]

\[
y_j = n - ik \tag{4.13}
\]

\[
\eta_{js} = \sqrt{n_j^2 - k_j^2 - n_0^2 \sin^2 \theta_0 - 2in_jk_j} \tag{4.14}
\]
\[
\eta_{jp} = \frac{y_j^2}{\eta_{js}}
\]  \hspace{1cm} (4.15)

\[
\delta_j = \frac{2\pi d}{\lambda} \sqrt{n_j^2 - k_j^2 - n_0^2 \sin^2 \theta_0 - 2i n_j k_j}
\]  \hspace{1cm} (4.16)

\[
\rho = \frac{\gamma_0 B - C}{\gamma_0 B + C}
\]  \hspace{1cm} (4.17)

\[
R = \rho \rho^*
\]  \hspace{1cm} (4.18)

\[
T = \frac{4\eta_0 \text{Real}(\eta_{sub})}{(\eta_0 B + C)(\eta_0 B + C)^*}
\]  \hspace{1cm} (4.19)

For the ATR technique there is only one layer, the NPM, so \(q\) and \(j\) are both 1.

The substrate is air, and the initial medium is the quartz prism. The characteristic admittance of the NPM is represented as \(y_j\) and consists of the optical parameters of the NPM. The oblique optical admittance is represented by \(\eta\) and must be calculated for each polarization state. The film phase factor is \(\delta\). The amplitude reflection coefficient \(\rho\) can be calculated from the characteristic matrix of the film stack (Equation 4.12), and from this result, the reflectance can be obtained (shown in Equation 4.18). With oblique incidence and absorbing materials, care must be taken to ensure that the solutions for \(\eta\) for TE polarization states and \(\delta\) are in the fourth quadrant to obtain the correct solution (positive real, negative imaginary).

Figure 4.3 shows the reflectance calculated for an Al film \((n = 0.179, k = 1.95)\) in the Kretschmann configuration at a wavelength of 248nm. As expected, the incident radiation for TM polarization states is largely absorbed into the SP resonance at a range of angles between \(\sim 42-60\) degrees and for a range of film thicknesses to \(\sim 15-50\)nm; no resonance is observed for TE polarization states.
To determine the spectral range over which materials from Figure 4.2 support surface plasmon resonances, an array was setup containing each material and its optical properties at all wavelengths at which data had been collected. For each material at each wavelength, the location of the center of the ATR peak was determined at the optimal thickness. The optimal thickness for each material case varies with wavelength. For more absorbing materials, the reflectance minimum is expected to be shallower and broader. To determine which materials are least absorptive, the filtering criteria were set to only calculate the ATR peak for materials exhibiting reflectance reaching 10% or lower, with a peak breadth at a reflectance value of 10% no greater than 10 degrees.
Figure 4.4 shows the calculated location of the center of the ATR peak and its width for several materials of interest through wavelength. Ag has been used extensively for plasmonic applications in the mid-UV wavelengths and beyond, but these plots clearly show that it is not a useful plasmonic material below ~350nm. Alternatively, Al exhibits plasmonic behavior from the DUV through the end of the visible spectrum. Only below 150nm and above 700nm does its ATR peak begin to broaden. Mo and Rh appear to support SPs at 193nm and 248nm respectively, however, they are highly absorptive and have a very limited useful wavelength range. Sn and In which are of interest for plasmonic applications in the DUV are not shown here for several reasons. Firstly, there was little through wavelength refractive index data in the source used. Additionally, for data that was available, it behaved similarly to Al [113].

While it is clear that these results demonstrate Aluminum supports surface plasmons in the DUV, they need to be considered in conjunction with the plasmon dispersion equation for this ATR setup. Figure 4.5 shows the dispersion curves for an ATR configuration with an Aluminum film and Quartz prism. Incident radiation of 193nm and 248nm correspond to frequencies of ~9.8x10^{15}\text{s}^{-1} and ~7.6x10^{15}\text{s}^{-1}, which means that the accessible surface plasmons are of a wavelength very similar to that of the incident radiation. Most of the applications discussed in Chapter 3 take advantage of the fact that at the surface plasmon resonance, the SP wavelength is much smaller than the exciting wavelength. Therefore, a metamaterial designed to produce a surface plasmon resonance at the desired input frequency needs to be created.
4.4 CREATING A SPOOF PLASMON METAMATERIAL FOR USE AT DUV WAVELENGTHS

According to Equation 3.2, to achieve a large propagation constant the dielectric constant of the prism in an ATR setup needs to be maximized as does the angle at which the reflection minimum occurs. The simulator created in Section 4.3 generated reflection plots through angle and thickness so that different ATR configurations could be analyzed. In Section 3.7, it was discussed that a MIM stack could be used to provide the desired results [87], [88], [114]–[116]. Knowing this, a new simulator was created to generate multilayer alternating metal-dielectric stacks in order to obtain the largest propagation constants possible, resulting in the shortest plasmon wavelength. The largest propagation constants possible at 193nm and 248nm are $5.08 \times 10^7$ m$^{-1}$ and $3.83 \times 10^7$ m$^{-1}$ respectively, and are shown by the arrows in Figure 4.5.
Since aluminum is one of the best plasmonic materials in the DUV, and Al₂O₃ is a relatively high index, absorption-free dielectric, a layered Al-Al₂O₃ system will be examined. A simulator was created to generate and analyze multilayer MIM stacks in order to obtain the largest propagation constants possible, resulting in the shortest plasmon wavelength.

The first module of the simulator is the Layer Maker application (Figure 4.6), which generates the multilayer stacks to be examined. The refractive index and absorption coefficients of the superstrate (prism), metal, dielectric, and substrate can be input, as well as the maximum total stack thickness to be allowed, the maximum dielectric thickness, and the maximum metal thickness allowed (this is the overall maximum metal thickness, not one individual layer thickness, as it is known in the Kretschmann configuration that if the metal is too thick, SPs cannot couple through it). This application then outputs two files containing all layer combinations within the boundary conditions specified. One file is a MySQL table that will be linked to the output of the other applications via an identity string assigned to each MIM stack. The second file contains a machine readable instruction file for the second application. An example of this table is shown in Table 4.1. It should be noted that this application generates stacks comprised of many layers, not simply a 3-layer MIM stack. We are only examining a 3-layer stack here as it is most likely the easiest to fabricate.
Figure 4.6: Layer Maker Application.

Layer Maker, computes possible MIM stack combinations

Figure 4.7: Diagram representing Layer Maker application output.
Table 4.1: Output from Layer Maker application.

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The second application is the Matrix Material Calculator (MMC), and is written in MATLAB. It reads the instruction file from the Layer Maker application and calculates reflection profiles through angle for each generated stack. These calculations are performed using matrix methods described by Macleod, shown in Equations 4.12 through 4.19.

The third application is the Beta Profiler. It analyzes the reflection profiles, and calculates the angle at which the reflection minimum occurs, the reflectance value, and the value of the propagation constant (from Equation 3.2). This data is also stored in a MySQL table. By itself, this data is not inherently useful. However, using join statements in MySQL, this data can be merged with the table from the Layer Maker application, and sorted to display results that are useful. Since output of the MMC and the Beta Profiler are stored in a MySQL database it possible to quickly sort though the data to find optimal cases and analyze the results. An example of a joined output from the Layer Maker and Beta Profiler are shown in Figure 4.9.
Figure 4.9: Beta Profiler application.

Table 4.2: Joined data in MySQL.
The fourth application is the RT Profiler, which is uses the Layer ID to test cases that appear promising. The results shown in Figure 4.10 are the output of the RT Profiler application. They show that a 3 layer stack comprised of 7nm-27nm-7nm of Al-Al₂O₃-Al (LayerID 19856 in Table 4.2) yields a metamaterial with a shorter plasmon wavelength than is capable with just aluminum (124nm compared to 171nm).

![Figure 4.10: ATR results for single 20nm Al layer (left), 7nm Al, 27nm Al₂O₃, 7nm Al stack (right).](image)

Since the final layer of the tunable metamaterial proposed is Al, it is understood that it will oxidize. The Layer Maker application has been modified to allow an asymmetric stack to be simulated (modified examples of Tables 4.1 and 4.2 shown in Appendix B). This makes it possible to simulate our metamaterial stack with a surface oxide layer present, or with a capping material comprised of some other element that may offer more desirable optical properties than an aluminum oxide.
There are several benefits of this simulation approach. Firstly, this matrix method of calculation provides fast results. Simulations of 1 single-layer ATR stack in FDTD software took on the order of a minute to complete. Using this matrix method based simulator, 50,000 different thin film stack combinations completed in approximately 90-120 minutes. Secondly, it is quite flexible. Any optical constants desired can be input, and it has been modified further to allow for an asymmetric stack to be input. It has also been modified to allow the optical parameters and thicknesses to vary in order to help model errors that will be seen during fabrication. The joined output data allows one to see the fabrication tolerances allowed to achieve an acceptable result.

The thin film matrix calculations used throughout this document can also be used to calculate the electric field intensity below the stack, which would be representative of
imaging possible for plasmonic interference nanolithography (calculations based on work by Fan [42] and Flagello [117]). Results for the configurations in Figure 4.10 are shown in Figure 4.12. The resulting pitches of 62nm and 84nm are similar to those calculated using Equation 3.46.

![Figure 4.12 Electric field intensity profiles below a 7nm-27nm-7nm Al-Al₂O₃-Al stack (left) and 20nm Al film (right) deposited on a quartz prism.](image)

If a higher index prism is used, an even smaller plasmon wavelength can be achieved. Figure 4.13 shows the electric field intensity for a 7nm-34nm-7nm Al-Al₂O₃-Al stack using a sapphire prism ($n = 1.92$), resulting in a 50nm pitch (the ATR profile is nearly identical to that for the quartz prism example shown in Figure 4.12). The resulting pitch for the 20nm Al film with the sapphire prism is still nearly identical to that with the quartz prism, due to the fact that the higher index of the prism is offset by a 10° shift, from ~46° down to ~36°, in the resonance angle.

![Figure 4.13: Electric field intensity profiles below 7nm-34nm-7nm Al-Al₂O₃-Al stack (left) and 20nm Al film (right) deposited on a sapphire prism.](image)
4.5 DETERMINATION OF OPTICAL CONSTANTS VIA ATR

Attenuated total reflectance experiments were performed on e-beam evaporated Al films deposited directly onto an equilateral fused silica prism \((n_{193} = 1.56, n_{248} = 1.51)\). The Al film was deposited using the CHA e-beam evaporator at the RIT SMFL, utilizing a pure Al wire as the deposition source and a carbon FABMATE crucible. For all experiments, the base pressure of the system was \(\sim 3.5 \times 10^{-7}\) Torr, with a deposition rate between \(0.5 - 1.0\) Å/s. This was the lowest base pressure achievable by this system, and was chosen to prevent incorporation of oxygen in the films [118]. To prevent sputtering of the material within the chamber, and to prevent as many contaminants as possible from being incorporated into the deposited film, the Al in the crucible was melted at a very slow rate, slowly ramping the deposition current up to 40mA over the course of 20 minutes. The material was allowed to pre-deposit with the shutter closed until the glass cover slide protecting the viewing port became opaque. The prism was placed in a jig hanging from a planetary (non-rotating) near the Inficon deposition monitor, to ensure that the thickness on the monitor and prism were as close as possible. The deposition setup is shown in Figure 4.14.
Figure 4.14: CHA E-beam evaporator used for deposition (left). The other two images show how the prism was mounted in the system for deposition.

A Coherent OptexPro ArF laser was used for the 193nm ATR measurements, while a Cymer ELS 4600D-1 KrF laser was used for the 248nm measurements.

Originally, all of this work was to be performed at 193nm, but the OptexPro laser stopped functioning.

Intensity measurements were taken with a Coherent J5-09-0A0-5M detector. To gather the ATR data, the prism was placed on a goniometric stage, which was aligned using retro-reflectance, and measurements were taken every 1 degree, from an external angle of -40 to +55 degrees measured from the normal to the external prism face (85.19-27.15 degrees inside the quartz prism). Laser power increased during operating time, so laser power was measured throughout the experiment so that it could be corrected in the final data.
After performing the ATR experiments, a nonlinear least-squares optimization, $\min_x \sum_i (\text{experimental}_i - R_i(\text{parameters}))^2$, was used to fit the calculated ATR data from the thin film matrix formalization to the experimental results. The parameters allowed to vary to fit the data were refractive index, absorption coefficient, and film thickness. Other parameters initially allowed to vary were experimental angular error (a global lateral shift in the data), detector offset (a global vertical shift in the data), and a scaling factor to match the two datasets. After becoming more familiar with the measurements, accounting for the rise in laser power with temperature over time, and correcting the data for reflectance at the prism interfaces not involved in exciting the surface plasmon, the only non-optical variable allowed to vary was the angular offset. This optimization routine is quite useful, as it is capable of providing the optical constants for a single thin conducting film. If there are multiple films involved, an effective index and thickness for the entire stack can be arrived at, but not the properties of the individual films [119]–[124]. Additionally, it will be shown that for these thin aluminum films variable angle spectroscopic ellipsometry (VASE) does not provide
dependable optical constant and thickness results [125], [126]. VASE measurements are still useful for dielectric films at the thicknesses used.

Before proceeding with the results from deposition and the ATR measurements, we should first discuss the properties of aluminum. At the wavelengths used, the published optical constants of aluminum are $n_{193} = 0.1149$, $k_{193} = 2.234$, $n_{248} = 0.1856$, and $k_{248} = 2.904$. It is expected that our thin aluminum films will differ from these values, perhaps significantly. Aluminum develops a native oxide when exposed to atmosphere of about 5nm in thickness [127]. Given that our Al films need to be sufficiently thin (less than 50nm, and more typically below 20nm) to allow coupling of the incident radiation to the surface plasmon, this oxide could comprise a significant portion of the film. For reference, Figure 4.16 shows the ATR profiles for the published aluminum optical constants at the two wavelengths of interest.
Based on the ATR results shown in Figure 4.16 for published bulk Al optical constants, the first Al films were deposited to a thickness near 20nm (in-situ measurement). The 193nm ATR measurement and fitted results are shown in Figure 4.17. Comparing these results to those in Figure 4.16, it is observed that these films are vastly different from what was expected. The reflectance minimum in both cases is much higher than expected, and is shifted almost 15 degrees higher than expected. It was determined through discussions with other users of the evaporator that the incorrect deposition material was placed in the tool. Most likely, 99% Al, 1% Si wire was used. Additionally, the evaporator was not cleaned prior to deposition, which most likely contributed to the poor results.
Following these depositions, the evaporator was thoroughly cleaned, and it was ensured that the deposition material was 100% Al wire. Again, ~20nm Al films were deposited. The ATR measurements and fits are shown in Figure 4.18.

During deposition of the Al films, a sample piece was included to be measured by ellipsometry. Two different types of fitting were attempted. One case was deposited on a fused silica slide, the other case on a silicon wafer with 1000nm oxide grown on the surface. For the latter case, the addition of a thick dielectric between the Al film and Si substrate enhances the information content of multiple angle measurements by varying the path length for different incident angles. For the former case, the combination of
VASE and transmitted intensity also to produces a unique result for the Al film on the fused silica substrate [125]. Multisample analysis can also aid in these measurements, but the optical constants for the material in the samples must not change. Given that we know the optical constants of aluminum vary with thickness, and that our evaporated results are not constant across depositions, it is not possible to perform an accurate multisample analysis [128]. Figure 4.19 shows the VASE results for 10nm and 20nm thick Al films deposited on an oxide coated silicon wafer, with Figure 4.20 showing the VASE results from a 20nm Al film deposited on a fused silica slide. The optical constants and thicknesses determined from the ATR and VASE measurements are shown in Table 4.3.

Figure 4.19: VASE model fits for a 10nm (left) and 20nm (right) Al film coated on a 1000nm silicon dioxide layer thermally grown on a silicon wafer.

Figure 4.20: VASE model fit for a 20nm Al film coated on a fused silica slide.
Case | n | k | Thickness (nm)
--- | --- | --- | ---
10nm 100% Al, VASE interference | 0.24 | 1.67 | 10.76
20nm 100% Al, VASE interference | 0.08 | 1.74 | 20.14
20nm 100% Al VASE transmission | 0.20 | 1.73 | 21.3
21nm 99% Al, 1% Si, ATR | 0.24 | 1.58 | 32.4
23nm 99% Al, 1% Si, ATR | 0.31 | 1.34 | 27.8
20nm 100% Al, ATR | **0.27** | **1.32** | **21.2**
22nm 100% Al, ATR | **0.28** | **1.32** | **20.9**

Table 4.3 Aluminum optical constants and thicknesses determined by VASE and ATR.

It is clear from the results in Table 4.3 that the ATR and VASE results do not agree with each other (compare bold and italicized results, respectively). Based on the literature, the VASE results may not be accurate, and thus ATR will be used to determine the optical constants for the thin aluminum films used [126].

The optical constants for our ~20nm aluminum film at 193nm are $n_{193\text{nm}} = 0.28$ and $k_{193\text{nm}} = 1.32$. These are the values that will be inputted into the simulator to calculate the desired material stack to provide an ATR profile with the desired response for imaging at 193nm. Recalling that bulk Al has $n_{193\text{nm}} = 0.11$ and $n_{193\text{nm}} = 0.22$, it is clear that a 20nm film exhibits different characteristics. Referring back to Figure 4.2, according to the effective media approximation (EMA), our Al film is similar to a homogeneous Al-O composite material comprised of 85% Al and 15% Al$_2$O$_3$ [129]. The difference in refractive index can be attributed to the fact that a surface oxide forms, which can be up to 7nm thick, which is not an insignificant amount in a 20nm thick film [127].
ATR measurements were also performed on aluminum films at 248nm. Referring to Figure 4.16, the thickness range for minimum reflectance is similar, and films were deposited with target thicknesses of 10nm, 15nm, and 20nm. Results for the first set of deposited films are shown in Figure 4.21.

![Figure 4.21: ATR measurements for 20nm (left) and 15nm (right) Al films at 248nm.](image)

The optical constants, especially the refractive index, appear to be slightly higher than expected, possibly owing to not cleaning the evaporator prior to deposition. The thicknesses are also in disagreement with the in-situ thickness monitor by up to 60%. At first, the fitting routine was called into question. Some of the literature recommends performing ATR measurements at a second wavelength, which will provide different optical constants, but the same thickness. Therefore, a second ATR measurement of the 15nm film was performed, and is shown in Figure 4.22. This measurement at a different wavelength confirmed that the thickness measured via ATR at 248nm was correct. A summary of the results of these measurements are shown in Table 4.4.
Figure 4.22: ATR measurement for the 15nm Al film in Figure 4.21 (right) at 405nm.

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Table 4.4: Optical constants and thicknesses determined by ATR for Figures 4.21, 4.22, 4.23, 4.24.

After these first depositions, while cleaning the system, a leak was found in the cooling water line to the in-situ thickness monitor, as well as a short in the cable to the monitor. These tool errors accounted for the thickness discrepancies. After fixing the problems with the evaporator’s in-situ thickness monitor, a test run was performed. This is shown in Figure 4.23 with the results in Table 4.4. Observing the plot of reflectance vs. angle, the plot appears overly broad, while the minimum reflectance angle is shifted far to the right, farther than is possible for a single aluminum film of this thickness. It was noted during deposition that the tool was dirty, so the tool was cleaned. The depositions post-cleaning are shown in Figure 4.24, with the results also summarized in Table 4.4.
After the evaporator was cleaned, the profiles shown in Figure 4.24 are closer to the expected result, especially the 15nm case, when compared to Figure 4.16. The evaporator’s in-situ thickness monitor is now off by approximately 30%, but after fixing the cooling line and ground cable, the thickness offset is consistent. The resulting optical constants for the 20nm film are $n_{248\text{nm}} = 0.318$ and $k_{248\text{nm}} = 1.95$, and $n_{248\text{nm}} = 0.226$ and $k_{248\text{nm}} = 1.81$ for the 10nm film. These are the values that will be inputted into the simulator to calculate the desired material stack to provide an ATR profile with the desired response for imaging at 248nm.
Knowing the optical constants for the aluminum to be used in creating a tuned metamaterial stack for imaging in the DUV spectrum, we must now determine the optical constants for the dielectrics to be used in the material stack. The dielectric materials that will be used are aluminum oxide (Al$_2$O$_3$) and photoresist (PR), specifically JSR 2928-JN7, which is supposed to provide a thickness of 70nm at a spin speed of 2500RPM. Dielectrics can still be measured accurately by VASE at the thicknesses we will be examining.

Aluminum oxide was deposited by the same method as the aluminum films used in the ATR examples. The only difference is that Al$_2$O$_3$ requires a higher deposition current, around 150mA, to achieve the same 0.5 – 1.0Å/s deposition rate. VASE measurements for 10nm and 20nm thick Al$_2$O$_3$ films are shown in Figure 4.25, with optical constants and thickness results shown in Table 4.5.

![Figure 4.25: VASE model fits for targeted 10nm (left) and 20nm (right) aluminum oxide films deposited on a silicon wafer.](image-url)
Table 4.5: Optical constants and thicknesses determined by VASE for evaporated aluminum oxide films.

The optical properties for aluminum oxide at both wavelengths of interest are $n_{193\text{nm}} = 1.82$ and $n_{248\text{nm}} = 1.71$. The refractive index at 248nm is the same as the value published on RIT’s material database, while the value at 193nm is close to the published value of $n_{193\text{nm}} = 1.79$. Unlike aluminum, aluminum oxide’s optical properties do not vary with thickness. Similarly to the deposition of aluminum for the ATR experiments, the actual thickness still differs from the evaporator thickness reading by ~30%.

The photoresist (JSR 2928-JN7) was coated at 3000RPM, soft baked at 110°C for 90 seconds, and measured using VASE, shown in Figure 4.26. The thickness at 3000RPM was 53.9nm, with optical constants of $n_{193} = 1.69$, $k_{193} = 0.04$, $n_{248} = 1.61$, and $k_{248} = 0.01$. Diluting the PR with propylene glycol monomethyl ether acetate (PGMEA) at a ratio of 1:2 PR:PGMEA, a thickness of 28nm was achieved at a spin speed of 2500RPM. This thickness will be used in the imaging experiments in Section 4.7.

<table>
<thead>
<tr>
<th>Target Thick (nm)</th>
<th>Wavelength (nm)</th>
<th>n</th>
<th>k</th>
<th>Thickness (nm)</th>
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<tr>
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<td>193</td>
<td>1.82</td>
<td>0</td>
<td>13.8</td>
</tr>
<tr>
<td>10</td>
<td>248</td>
<td>1.71</td>
<td>0</td>
<td>13.8</td>
</tr>
<tr>
<td>20</td>
<td>193</td>
<td>1.82</td>
<td>0</td>
<td>26.1</td>
</tr>
<tr>
<td>20</td>
<td>248</td>
<td>1.71</td>
<td>0</td>
<td>26.1</td>
</tr>
</tbody>
</table>
Attenuated total internal reflection experiments and variable angle spectroscopic ellipsometry have provided us with the optical constants of the materials we wish to use to create metamaterial stacks to perform lithography in the DUV spectrum. Knowing these values, we can now input them into the simulator demonstrated in Section 4.4.

### 4.6 FABRICATION AND TESTING OF TUNED METAMATERIAL STACKS

To create a 3-layer MIM stack of aluminum and aluminum oxide at 193nm, the optical constants for the materials are entered into the simulator, with ranges for the thicknesses being 1-20nm for the Al and 1-60nm for the Al_2O_3, resulting in 24,000 total stacks to be examined. After this finished running, the data was sorted, limiting the results to reflectance minimum values below 0.1 and at angles of 70 degrees or greater, resulting in 857 stacks that may be of use.

Since the maximum angle that can be measured via ATR with our setup is ~85 degrees, and therefore also the largest angle we can use for imaging, we are interested in cases around 80 degrees. Also, given our deposition process, we should look at layer
thicknesses no thinner than 5nm. Imposing these additional constraints, the number of stacks of interest are reduced to 107. For these tolerances, the top Al layer (closest to the prism) has a range of thicknesses from 5-7nm, the bottom Al layer can range from 5-14nm, and the aluminum oxide layer sandwiched in between the two Al layers can range from 9-20nm. If we choose a 5nm-15nm-5nm Al-Al₂O₃-Al stack as the center point, and allow a 30% tolerance in thickness for each layer, since that is our evaporator tool offset, the resulting film stack combinations and their minimum reflectance angle are shown in Table 4.6.

<table>
<thead>
<tr>
<th>Top Al (nm)</th>
<th>Aluminum Oxide (nm)</th>
<th>Bottom Al (nm)</th>
<th>Angle (degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>15</td>
<td>5</td>
<td>77.34</td>
</tr>
<tr>
<td>5</td>
<td>15</td>
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<td>76.43</td>
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<td>5</td>
<td>15</td>
<td>7</td>
<td>75.08</td>
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<td>75.98</td>
</tr>
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<td>5</td>
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<td>7</td>
<td>74.62</td>
</tr>
<tr>
<td>6</td>
<td>15</td>
<td>7</td>
<td>73.72</td>
</tr>
</tbody>
</table>

Table 4.6: Possible film stack combinations for a 5nm-15nm-5nm Al-Al₂O₃-Al MIM stack with a 30% tolerance allowed in thickness greater than the chosen values.

This 5nm-15nm-5nm Al-Al₂O₃-Al stack was then fabricated. The deposition parameters were the same as outlined previously. The films were deposited sequentially in the evaporator without breaking vacuum, as the CHA e-beam evaporator is capable of holding up to 8 target deposition materials. The first material was deposited, the crucible
containing the target material was allowed to cool, the second material was then selected and deposited, allowed to cool, and finally the third material was deposited. The experimental results were confirmed via the ATR setup used previously, and are shown in Figure 4.27, plotted alongside the theoretical results for that stack.

![ATR measurement of 193nm metamaterial stack](image)

**Figure 4.27: Experimental results for a 5nm-15nm-5nm Al-Al₂O₃-Al MIM stack at a wavelength of 193nm.**

The experimental and theoretical results look quite similar, with the resonance angle and reflectance minimum matching well. This is of interest, as all of the incident radiation is coupled into the surface plasmon. There is, however, a discrepancy between the two closer to the critical angle. All of the ATR results have the largest error between theory and experimental around the critical angle, but this case is larger than the rest. Given that vacuum wasn’t broken between depositing materials, it could be that the
optical constants of the Al layer closest to the prism didn’t oxidize at all, and has substantially different optical properties than the final layer. None of the stacks listed in Table 4.6 exhibit a reflectance value as low as the experimental results near the critical angle. This is not of extreme importance to us though, as we do not plan on imaging anywhere near the critical angle.

Similarly, this work was also performed at 248nm. The optical constants for the two materials were inputted into the simulator, with ranges for the thicknesses being 1-20nm for the Al and 1-60nm for the Al₂O₃, resulting in 24,000 total stacks to be examined. After this finished running, the data was sorted, limiting the results to reflectance minimum values below 0.1 and at angles of 70 degrees or greater, resulting in 1171 stacks that may be of use. Due to the shift to a larger wavelength, most thicknesses have increased as well, with the center point for the first aluminum layer being around 9nm. Examining the data, a 9nm-30nm-9nm Al-Al₂O₃-Al stack appears to be a good midpoint, and applying the same criteria as for the 193nm case, the resulting 78 stacks of interest are shown in Table 4.7. Due to the larger number of possible stacks, the table is grouped by the top aluminum layer, with thickness ranges listed for the dielectric and bottom aluminum layers corresponding to a range of resonance angles greater than 70 degrees (see Appendix for full table).
<table>
<thead>
<tr>
<th>Top Al (nm)</th>
<th>Aluminum Oxide (nm)</th>
<th>Bottom Al (nm)</th>
<th>Angle (degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>30 to 36</td>
<td>9 to 12</td>
<td>70.55 to 79.6</td>
</tr>
<tr>
<td>9</td>
<td>37</td>
<td>10 to 12</td>
<td>77.79 to 79.15</td>
</tr>
<tr>
<td>9</td>
<td>38</td>
<td>11 to 12</td>
<td>78.24 to 78.69</td>
</tr>
<tr>
<td>9</td>
<td>39</td>
<td>12</td>
<td>78.24</td>
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</tr>
<tr>
<td>10</td>
<td>34</td>
<td>10 to 12</td>
<td>75.52 to 77.79</td>
</tr>
<tr>
<td>10</td>
<td>35 to 36</td>
<td>11 to 12</td>
<td>76.43 to 77.34</td>
</tr>
<tr>
<td>10</td>
<td>37</td>
<td>12</td>
<td>76.88</td>
</tr>
<tr>
<td>11</td>
<td>30 to 31</td>
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</tr>
<tr>
<td>12</td>
<td>32</td>
<td>12</td>
<td>73.72</td>
</tr>
</tbody>
</table>

**Table 4.7: Possible film stack combinations for a 9nm-30nm-9nm Al-Al$_2$O$_3$-Al MIM stack with a 30% tolerance allowed in thickness greater than the chosen values.**

These results can also be examined graphically, and are plotted in Figure 4.28. These plots are generated by first choosing a resonance angle of interest, and then choosing the desired stack based on those results. Shown in this Figure 4.28 are two cases, one for a resonance angle of ~76 degrees for the 20nm Al optical constants at 248nm, with the other case being at an angle of 80 degrees, using the 10nm Al optical constants. Given the 3-D nature of these plots, they are not the easiest to read; the author finds it easier to look at the data as a list.
Figure 4.28: Scatter plots of material thicknesses for a given resonance angle. 76.4 degree angle (left) for optical constants of the 20nm Al film at 248nm, 80 degree resonance angle (right) for the optical constants of the 10nm Al film at 248nm. Colored axis is the reflectance value at the ATR minimum.

This 9nm-30nm-9nm Al-Al$_2$O$_3$-Al stack was then fabricated in the same manner as the 5nm-15nm-5nm Al-Al$_2$O$_3$-Al stack measured at 193nm. The experimental results were confirmed via the ATR setup used previously, and are shown in Figure 4.29, plotted alongside the theoretical results for that stack.
Figure 4.29: Experimental results for a 9nm-30nm-9nm Al-Al₂O₃-Al MIM stack at a wavelength of 248nm.

Again, the experimental and theoretical results look quite similar, with the resonance angle and reflectance minimum near the expected values, and within the values of the angles listed in Table 4.7. As in the previous case at 193nm, the plot is compressed in the y-direction. As per our previous results, as well as Raether, a higher index of refraction of the metallic layer generally leads to compression in the y-direction, while a lower absorption coefficient leads to a broadening of the ATR peak and a shift of the resonance to the left [62].

4.7 IMAGING WITH TUNED METAMATERIAL STACKS

Now that these stacks have been created, their imaging properties need to be examined. Figure 4.30 was created from the stacks in Figures 4.27 and 4.29 using the part.
of the simulator that calculates the electric field intensity below the stack for two interfering beams, shown in Section 4.4 for the theoretical values. As expected, the profiles are nearly identical, as the resonance angle for the 193nm 5nm-15nm-5nm Al-Al₂O₃-Al and 248nm 9nm-30nm-9nm Al-Al₂O₃-Al stacks are almost the same as the theoretical cases in Figure 4.12.

For the 193nm case, the resulting pitch and penetration depth are 69nm (0.36λ) and 29nm (0.15λ), while the pitch and penetration depth for the 248nm case are 91nm (0.37λ) and 50nm (0.2λ). While calculating the electric field intensity under the stack via this method is useful to get an estimate of the pitch and depth of focus, the intensity is normalized, and it does not fully represent what is occurring throughout the entire stack. To observe this, we will use Lumerical, a commercial-grade simulator based on the finite-difference time-domain (FDTD) method [130].

To setup our plasmonic interference lithography cases in Lumerical, the y boundary conditions are set to perfectly match layer (PML) on top and bottom to prevent reflections, whereas the x boundary conditions are set to periodic, so that the structure
continues infinitely in that direction. The mesh grid was set to 1nm, and TM-polarized radiation was input for two beams at equal but opposite angles to create the interference pattern; the angles are chosen based on the ATR response of the structure. Figure 4.31 shows the FDTD simulation of the 7nm-27nm-7nm Al-Al$_2$O$_3$-Al stack from Figure 4.10.

![Figure 4.31: FDTD simulation showing electric field intensity for 7nm-27nm-7nm Al-Al$_2$O$_3$-Al stack.](image)

The electric field does couple through to the bottom of the structure, but most of the radiation is absorbed in the middle dielectric layer. Although much of the radiation is absorbed in the region occupied by the aluminum oxide, the coupling of the plasmon is asymmetric throughout the depth of the material, resulting in a reversed image at the bottom compared to the top. The period of the oscillation is still the same as in Figure 4.12. This is unfortunate, as this represents what is occurring for the MIM stacks we have created.

To see if a better solution is available, the 248nm stack was re-simulated, including photoresist on the bottom of the stack, to find a case with a thin Al$_2$O$_3$ region.
The best case found was 6nm-8nm-5nm-30nm Al-$\text{Al}_2\text{O}_3$-Al-PR stack, exhibiting a resonance angle at 79 degrees. Figure 4.32 shows the ATR and electric field profiles.

![Figure 4.32: ATR profile (left) and electric field profile (right) for a 6nm-8nm-5nm-30nm Al-$\text{Al}_2\text{O}_3$-Al-PR at 248nm wavelength.]

If the same search criteria were used to find the 9nm-30nm-9nm Al-$\text{Al}_2\text{O}_3$-Al stack to find this stack, it wouldn’t have been found. The ATR minimum is not very strong, but the resonance angle is large at 79 degrees, resulting in a pitch of 84nm. It appears as though a large amount of the radiation is absorbed below the stack into the photoresist, but a lot is also captured by the middle layer, similar to the example shown in Figure 4.31. Therefore, it would behoove us to look at a case where the middle aluminum oxide layer is replaced with photoresist.

Figure 4.33 shows the electric field profile of a 6nm-36nm-72nm Al-PR-Al stack at 193nm illumination. While the results look interesting, yielding a pitch of ~54nm, there are a few problems. The exposure at the top of the structure, which when developed is actually the bottom, is blurred together. When developed, all of the photoresist would likely wash away. Additionally, fabricating a structure like this would require Al to be
deposited on top of the PR. The deposition method we have been using emits radiation, and would likely expose the photoresist. This is obviously undesirable.

Based on the literature that had been researched, we initially believed we need to create this multilayer stacks to shift the dispersion curve lower to provide a shorter plasmon wavelength for better resolution [61], [86], [87]. However, knowing that for ATR to occur we need to be operating in the total internal reflection regime, if the index of photoresist coated on the bottom of the aluminum film is of a lower index than the prism, a single layer of aluminum with photoresist as the substrate could be used. While photoresist at 193nm and 248nm illumination exhibits a higher index of refraction than fused silica, sapphire has a higher index of refraction than photoresist at both wavelengths ($n_{193nm} = 1.92$ and $n_{248nm} = 1.85$). Figure 4.34 shows the ATR profile with varying aluminum thickness for a sapphire prism-Al-PR stack.
These results are intriguing. Since the prism is of a higher index than fused silica, and the resonance angle is pushed out to 83 degrees, the resulting pitch from Equation (3.46) is 68nm. However, since this case assumes that the substrate is the photoresist, the PR must be coated very thick. Knowing that the penetration depth is only a fraction of the wavelength (~50nm), this would only work with a negative tone photoresist. An FDTD simulation of this stack is shown in Figure 4.35 for both TM and TE polarization. Note that there is very little coupling into the photoresist for the TE case, as expected.

Figure 4.35: FDTD simulation of plasmonic interference lithography for a sapphire prism coated with 8nm Al and photoresist as a substrate, TM polarization (left), TE polarization (right). Note there is almost no absorption in the photoresist for the TE case, and a large reflected component.
Raether offers a much more elegant solution [62]. Simply coating the metal with a thin dielectric causes the ATR minimum to shift to higher angles! This means that there could be a solution where a thin positive photoresist could be coated on the metal surface to image the surface plasmon wave. To test this idea, the optical constants for the quartz prism, aluminum, and JSR 2928 JN-7 photoresist at 248nm were input into the layer maker simulator. Similar search criteria to the 3-layer MIM stacks were used. The simulator yielded an answer of 10nm Al, 28nm PR. There are many other solutions, with the Al thickness ranging from 5-20nm, and the PR thickness being as high as 40nm for thinner Al layers, but limited to a thickness of 12nm for a 20nm thick Al layer. This stack was fabricated, and the measured ATR profile along with the theoretical profiles for a few varying Al thicknesses are shown in Figure 4.36.
Figure 4.36: ATR profile for experimental 10nm-28nm Al-PR stack at 248nm, with additional theoretical ATR profiles for slightly varying Al thickness.

Again, similar to the MIM stacks, there is some compression of the ATR profile in the y-direction, but the ATR minimum is below 0.1 and located near where it should be at 81 degrees. Based on Equation (3.46), this should result in an 83nm period. Electric field profiles calculated by our simulator and Lumerical are shown in Figure 4.37, confirming the 83nm period. Penetration depth from our simulator is around 12-38nm, depending on what intensity level is taken as the cutoff. Lumerical shows that the field does not completely penetrate the PR, but it will be shown via experiment that the plasmon does couple through the depth of the photoresist.
With simulations have demonstrating that plasmonic interference imaging is possible with this fabricated double layer aluminum-photoresist stack, it was verified experimentally. To verify that the interference imaging setup and photoresist processing functioned properly, some low angle, large pitch imaging was performed.

The interference setup is shown in Figure 4.38. To test this, a fused silica slide was dehydrate baked at 200°C for 120 seconds, coated with HMDS at 3000RPM for 60 seconds, and baked at 120°C for 60 seconds. It was then coated with JSR 2928 JN-7 resist (thinned 1:2 PR:PGMEA) at 2500RPM for 60 seconds and soft baked at 110°C for 90 seconds. Following coating, it was exposed at 248nm using the Cymer ELS 4600D-1 KrF laser for 60 seconds, post exposure baked (PEB) for 60 seconds at 110°C, and then developed in tetramethylammonium hydroxide (TMAH) for 60 seconds. The interference angle used was 15 degrees in air, resulting in a ~400nm pitch.
Imaging in photoresist on a silicon wafer or quartz slide is relatively common, but the material stack proposed here requires that imaging directly on the surface of a prism. The photoresist process must first be verified on the prism. A special chuck was created to hold the prism in the spin coater, and is shown in Figure 4.39.

It was first verified by coating silicon wafers that diluting the JSR 2928 JN-7 1:2 PR:PGMEA results consistently in a PR film thickness of 28nm at a spin speed of
2500RPM. All soft bakes and post exposure bakes were performed in proximity mode, with the very edge of the coated prism face resting on a wafer piece on the hot plate. Initial exposures resulted in no exposure fields. A thermocouple was placed on a wafer on the hotplate, and it was determined that although the hotplate was set to 110C for the softbake and PEB, the surface of the wafer was only reaching 98C. With the thermocouple attached to a prism, it was determined that the surface of the prism only reached a temperature of 81C after 5 minutes. For the initial test exposures, the softbake was performed for 10 minutes, and the PEB for 7 minutes. It is possible that the PEB temperature was not high enough to catalyze the resist for development. The hotplate temperature was raised to 125C, resulting in the prism reaching a stable temperature of 98C after 5 minutes. With a 10 minute softbake and 7 minute PEB, exposure and develop times were reasonable at about 1 minute each.

To additionally test the system, a pitch of 136nm was imaged in PR coated on the prism, corresponding to 37 degrees inside the prism (or 65.75 degrees in air, if this were to be imaged on a wafer). The prism was coated with what is now the standard prism coating process: spin coat diluted JSR 2928 JN-7 at 2500RPM, proximity bake at 125C for 10 minutes, expose, PEB at 125C for 7 minutes, develop for 1 minute. The 136nm pitch exposure is shown in Figure 4.40. While not the best looking image, TM polarized radiation results in degraded imaging performance as angle increases in interference imaging.
Figure 4.40: Low contrast ~136nm pitch imaged into photoresist with TM polarized 248nm interference lithography.

Knowing that the prism coating process works, test exposures on the 10nm-28nm Al-PR stack began. It was noticed on some of the first stacks coated, that after a 1 minute develop in TMAH, there was no photoresist or aluminum remaining; the prism was stripped bare. It is known that aluminum is dissolvable in strong bases, as the Al gets converted into aluminum hydroxide ($\text{Al(OH)}_4$) [131]. TMAH, ($\text{CH}_3)_4\text{NOH}$, is a strong base. Previous work with plasmonic superlenses done in the mid-UV spectrum never ran into this problem as they were working with solvent developable PRs, as well as using silver as their metal.
To ensure the process succeeded, etch tests of 10nm films on fused silica were performed with varying concentrations of developer, as well as time to clear exposed resist and aluminum. The results are summarized in Table 4.8. Based on these results, a dilution ratio of 1:40 TMAH:water was chosen. It should be noted that the TMAH based developer used is CD-26, which begins at 0.26N. 1:40 dilution results in 0.00634N.

<table>
<thead>
<tr>
<th>Developer (mL)</th>
<th>Water (mL)</th>
<th>Normality (N)</th>
<th>Time to clear Al (s)</th>
<th>Time to clear Al+exposed PR (s)</th>
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<td>0</td>
<td>0.26</td>
<td>25</td>
<td>NA</td>
</tr>
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<td>0.13</td>
<td>25</td>
<td>NA</td>
</tr>
<tr>
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<td>40</td>
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</tr>
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<td>4</td>
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<td>40</td>
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<td>No change</td>
<td>No change</td>
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</table>

Table 4.8: Dissolution rates of aluminum in different strengths of developer. For times to clear with a range, first number is when thickness changed was first observed, second number was the time when fully cleared.

The interferometer was setup to provide an angle of 81 degrees inside the prism, the resonance angle for the 10nm-28nm Al-PR stack. The prism was coated with the standard process (JSR 2928 JN-7 diluted 1:2 spin coated at 2500RPM, proximity baked at 125C for 10 minutes), exposed for 1 minute with the laser set to 8000uJ and 100Hz, post exposure baked for 7 minutes at 125C, and after cooling, developed for one minute in 0.006N developer and rinsed. The sample was prepared by first hard baking the resist, then sputtering with gold for 30s.

Upon examination in the SEM, at first, no images were seen. However, while focusing on debris around scratches that were made in the films to help find the location being studied, line/space patterns were observed, of a pitch similar to that expected for this stack. It is theorized that due to the height of the prism in the gold sputterer, that the
normal deposition time yields a gold film that is far too thick to see topography in a 28nm thick PR film underneath (sputter deposition rate generally squares with distance from target). When the sample was scratched, the PR appears to have adhered well to the gold, and SEM images demonstrating this are shown in Figure 4.41.

![SEM images of ~80nm period line/space pairs in photoresist from plasmonic interference nanolithography at 248nm with a 10nm-28nm Al-PR material stack. Image on the right is a higher resolution image of the photoresist features on the “fingers” of the debris in the image on the left.](image)

Investigating the sample further showed that more examples of this were evident on the sample, and are shown in Figure 4.42.
To confirm these results, the prisms were stripped, cleaned, and recoated. Since there are three prisms to work with, and can perform two exposures per prism, an exposure matrix was performed, with exposures ranging from 30s to 105s. This was done due to the fact that the output power from the laser is known to vary from day to day, resulting in a differing exposure time for the desired feature size. The coating process and bake temperatures remained the same as before, but the development time was changed based on visual observation; development time was between 30-45s. After development,
the prisms were dried, hardbaked at 125C for 10 minutes, and mounted for inspection. Samples were not coated with gold.

Figure 4.43 shows images closer to the edge of the field, where a lower exposure dose was received than near the field center, due to the Gaussian distribution of the beam. The pitch is ~80nm, as expected, but the duty ratio is not 1:1, with the photoresist lines being larger than the spaces.

![SEM images of ~80nm period line/space pairs in photoresist from plasmonic interference nanolithography at 248nm with a 10nm-28nm Al-PR material stack. 1 minute exposure time, 40s develop. The lines and spaces observed in photoresist are not entirely consistent across the exposure field. It can be seen in the bottom right of Figure 4.43-left that the image begins to deteriorate. As shown in Figure 4.36, a 2nm shift in thickness of the Al film from 8-10nm results in a 20% change in the amount of radiation absorbed. Typically in lithography, a 10% exposure latitude window is desired so that small changes in exposure dose result in acceptable photoresist imaging. While the dose from the laser over our short exposure times is relatively consistent, the amount absorbed into the photoresist may not be for these plasmonic stacks. Some AFM scans were performed when first studying the film properties in Section 4.5, and showed that over a small scan range (~1]
micron), the film thickness varied by 1-2nm. Knowing that this could lead to a 20% shift in exposure, thickness variations in the aluminum film could certainly lead to loss of image fidelity.

Towards the center of the exposure field, line/space pairs with a duty ratio closer to 1:1 were observed. This is shown in Figure 4.44.

![SEM image](image)

**Figure 4.44:** SEM images from the field center of a ~80nm period, 1:1 duty ratio line/space pairs in photoresist from plasmonic interference nanolithography at 248nm with a 10nm-28nm Al-PR material stack. 1 minute exposure time, 40s develop.

Figures 4.43 and 4.44 demonstrate that this 2-layer metamaterial stack is capable of deep subwavelength imaging at an input wavelength of 248nm, corresponding to \(0.5\lambda/NA\). By changing to a shorter wavelength of 193nm, and using a sapphire prism with a refractive index of 1.92, a similar metamaterial stack is capable of imaging down to a period of 50nm.

This is a significant result. It is the first time plasmonic imaging has been achieved using wavelengths in the DUV spectrum. These stacks, when tested via ATR,
exhibited no transmission beyond the critical angle. All imaging was performed at the optimal plasmon resonance angle, an angle at which all incident radiation is coupled into the surface plasmon, resulting in very little reflection, and no transmission. This is evidenced by the reflection minimums near zero in Figures 4.27, 4.29, and 4.36, as well as noting the exposure times in the plasmonic setup are near those for the interference images created in photoresist on a bare silicon wafer.

Despite the fact that surface plasmons offer the promise of infinite resolution, real-world materials limit performance. In this configuration, the propagation constant can not exceed that of the prism (see Figure 4.5), thus limiting resolution to \(0.5\lambda/NA\), which is a resolution achievable by immersion or solid immersion lithography. The benefit to the configurations shown in Chapter 4 is that the surface plasmon propagation constant has been increased to its largest attainable values in this setup, resulting in the smallest imageable surface plasmon wave. Also beneficial is that most all of the incident radiation is coupled into the surface plasmon at the interface of the aluminum and photoresist. Additionally, these, or similar, metamaterial stacks could be used in superlensing or mask-generated plasmon interference lithography, potentially reducing the achievable resolution even further.
5. CONCLUSION

It has been shown that as photolithography reaches its resolution limits, polarization effects induced by photomasks are becoming a concern. Features approaching the wavelength of light begin to pass predominantly TM polarized radiation, detrimental to projection lithography, but useful for plasmonic imaging applications, as plasmons are only excited by TM polarized radiation.

A selection of materials has been examined both experimentally and theoretically through wavelength to verify their support of surface plasmons, or lack thereof, in the DUV spectrum via the attenuated total reflection method using the Kretschmann configuration. At DUV wavelengths, materials, such as silver, that were previously useful at mid-UV and longer wavelengths no longer act as metamaterials. Structured materials comprised of alternating layers of aluminum and aluminum oxide, or photoresist, exhibit metamaterial behavior, as do some elemental materials such as aluminum, tin, and indium. These elemental and structured materials exhibit the best properties for use in plasmonic lithographic applications, as shown here.

It was shown that variable angle spectroscopic ellipsometry is not accurate for measuring very thin absorbing films. Performing attenuated total reflectance measurements in the Kretschmann configuration and using thin film matrix calculations to fit reflectance data for varying optical properties and thickness to the measured reflectance data, it is possible to obtain accurate refractive index and thickness information for the deposited films.
Elemental aluminum yields a plasmonic response in the DUV spectrum, but the in-plane wave vector of the surface plasmon is of a similar wavelength to the exciting radiation. A systematic approach was taken to create a simulator to examine material and thickness combinations to generate useful tunable metamaterials for use in the DUV. The simulator is based on the thin film matrix formalization, and has the ability to accept any number of materials consisting of any desired optical properties. The simulator then calculates the propagation constant for each combination, as well as the reflection and transmission from the film stacks, since it is known that the surface plasmon induced reflectance minimum correlates to the plasmon wavelength. When the reflectance minimum is at larger angles, the propagation constant reaches its largest values, implying the smallest plasmon wavelengths.

The advantage to this thin film matrix method approach is speed. FDTD methods are time consuming, with a single Kretschmann configuration ATR measurement taking 10 minutes to an hour, depending on the accuracy level chosen. A simple 3-layer metal-insulator-metal metamaterial stack approaches tens of thousands of different material combinations with the material thicknesses limited to a maximum of 20-40nm each. The created simulator is capable of analyzing one material combination through angle in a fraction of a second, while analyzing the full suite of thousands of stack combinations in 30-120 minutes.

Using this simulator, metamaterials comprised of a 3-layer alternating aluminum-aluminum oxide-aluminum stack were generated, and then validated via ATR. 5nm-15nm-5nm and 9nm-30nm-9nm Al-Al₂O₃-Al stacks were shown to provide desirable
results at 193nm and 248nm respectively. It was demonstrated via simulation, however, that these may prove difficult to perform plasmonic interference lithography with.

A more simple double-layer aluminum-photoresist stack was created, verified via ATR, and proven to be as capable as the 3-layer stack. A stack comprised of 10nm Al coated with 28nm of photoresist provided a resonance angle of 81 degrees, similar to the 3-layer stacks examined. It was then demonstrated that this metamaterial stack is capable of plasmonic interference nanolithography at a resolution of 80nm at an input wavelength of 248nm. By moving to a higher index prism and a shorter wavelength, imaging down to a 50nm period is achievable with a similar configuration.
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Table A-1: Full expansion of Table 4.7.
### 7. APPENDIX B – MODIFIED SIMULATOR EXAMPLE

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Table B-2: Modified asymmetric layer maker output. t-vals are layer thicknesses generated by inputs from Table B-1.
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<th>theta</th>
<th>min_r</th>
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</table>

Table B-3: Joined layer maker and beta profiler results for modified asymmetric simulator
8. REFERENCES


