FABRICATION OF PHOTONIC CRYSTAL TEMPLATES THROUGH HOLOGRAPHIC LITHOGRAPHY
AND STUDY OF THEIR OPTICAL AND PLASMONIC PROPERTIES IN
ALUMINIUM DOPED ZINC OXIDE

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This dissertation focuses on two aspects of integrating near-infrared plasmonics with electronics with the intent of developing the platform for future photonics. The first aspect focuses on fabrication by introducing and developing a simple, single reflective optical element capable of high-throughput, large scale fabrication of micro- and nano-sized structure templates using holographic lithography. This reflective optical element is then utilized to show proof of concept in fabricating three dimensional structures in negative photoresists as well as tuning subwavelength features in two dimensional compound lattices for the fabrication of dimer and trimer antenna templates. The second aspect focuses on the study of aluminum zinc oxide (AZO), which belongs to recently popularized material class of transparent conducting oxides, capable of tunable plasmonic capabilities in the near-IR regime. Holographic lithography is used to pattern an AZO film with a square lattice array that are shown to form standing wave resonances at the interface of the AZO and the substrate. To demonstrate device level integration the final experiment utilizes AZO patterned gratings and measures the variation of diffraction efficiency as a negative bias is applied to change the AZO optical properties. Additionally efforts to understand the behavior of these structures through optical measurements is complemented with finite difference time domain simulations.
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LIST OF ACRONYMS

1D - one dimension(al)
2D - two dimension(al)
3D - three dimension(al)
AFM - Atomic force microscope
AZO - Aluminum doped Zinc Oxide
CAD – Computer Aided Design
CCD - Charge coupled device
CD – Critical distance
CMOS - Complementary metal-oxide semiconductor
CW - Continuous wave
DC - Direct Current
DLW - Direct laser writing
DOE - Diffractive optical element
DPHPA - Dipentaerythritol hexa/penta-acrylate
EBL - Electron beam lithography
EUV- Extreme Ultra-Violet
FDTD - Finite Difference Time Domain
FTIR - Fourier Transformed Infared Spectroscopy
ITO - Indium Tin Oxide
IR- Infared
NPG - N-phenyl glycine
NSOM- Near Field Scanning Microscopy

NVP - N-vinyl pyrrolidinone

PDMS - Polydimethylsiloxane

ROE - Reflective optical element

SEM - Scanning electron microscope

SPP - Surface Plasmon Polariton

SPR - Surface Plasmon Resonance

TCP - Top-cut prism

TE - Transverse electric

TEA - Triethylamine

TM - Transverse magnetic

USPTO – United States Patent and Trademark Office

UV - Ultraviolet
CHAPTER 1

INTRODUCTION

1.1 Motivation

The miniaturization of modern CMOS electronics is approaching its limits. The shift into photonic based technologies is at the precipice of blossoming. The use of plasmonics in modern integrated circuits is the necessary and transitional step in this shift of technologies. This research study focuses on two aspects of integrating near-infrared plasmonics with modern electronics with the intent of developing the platform for future photonics.

The first part of this study introduces and develops a simple, single reflective optical element capable of high-throughput, large scale fabrication of micro- and nano-sized structure templates using holographic lithography. This fabrication method is then used in the second part of this research to fabricate structures utilizing the recently popularized material class of transparent conducting oxides for study of their plasmonic capabilities in the near infrared regime.

Transparent conducting oxides (TCOs) are a material class with metal-like behavior that has attracted a lot of attention due to their promise for low-loss plasmonic applications in the near- and mid-infrared regimes. Because they can be very heavily doped, TCOs exhibit high DC conductivity and their free carrier concentration can be sufficiently high to sustain surface plasmon polaritons in the near-infrared wavelengths. As with conventional metal plasmonics, the optical properties of fabricated TCO structures can be tuned by controlling the size, shape and environment. But what begins to set TCOs apart from metals is their ability to tune the material permittivity via doping or electric field induced carrier accumulation. This along with their lower
intrinsic losses in the infrared regime provide great advantages for designing tunable plasmonic devices.

In the second part of the research, Aluminum Zinc Oxide (AZO) is patterned by holographic lithography in order to exploit its plasmonic properties. Additionally efforts to understand the behavior of these systems through optical measurements complemented with simulations are explored. Together these two research aspects will help further drive the development of future integrated photonics though their enhanced control of sub-wavelength features and their extension into tunable conductive materials.

1.2 Dissertation Outline

Chapter 1 gives the motivation for the research performed. The two primary directions of the research are briefly explained.

Chapter 2 describes why modern electronics is at the precipice of failing to keep up with Moore’s Law and how photonics is one of the prominent solutions for the future of processing. Photonics are then described. Fabrication methods of photonics are introduced and the holographic lithography method and techniques are elaborated on.

Chapter 3 introduces a patented single optical reflective element that uses holographic lithography to produce photonic template patterns using a single incident beam. The construction of the ROE is described. The photo resists used throughout this research are described.
Chapter 4 describes the use of three configurations of the ROE, for the fabrication of woodpile-type photonic crystal templates with 4 and 6 fold symmetry, as well as Penrose quasi-crystal structures.

Chapter 5 uses the ROE to generate four-beam interference patterns for the holographic fabrication of nano-antenna templates.

Chapter 6 introduces plasmonics and the use of alternative materials known as transparent conducting oxides as a way to produce surface plasmon in the near IR regime.

Chapter 7 describes the fabrication of square lattice cylindrical holes on a thin film of aluminum doped zinc oxide and the simulations and optical measurements that show that this particular patterns exhibits resonant standing SP waves.

Chapter 8 describes the diffraction efficiency control of line gratings etched into a thin film of AZO when they are tuned via an applied electrical bias.
CHAPTER 2
PHOTONICS AND HOLOGRAPHIC LITHOGRAPHY

2.1 The Eminent Failure of Modern Electronics

The growth in the capability of semiconductor devices has to a large extent been due to advances in lithography [1]. Miniaturization has enabled both the number of transistors on a chip and the speed of the transistor to be increased by orders of magnitude keeping pace with Moore's law. This law refers to an observation made by Intel co-founder Gordon Moore in 1965 after noticing that the number of transistors per square inch on integrated circuits had doubled every year since their invention. Moore's law predicts that this trend will continue into the foreseeable future. Although the pace has slowed, the number of transistors per square inch has since doubled approximately every 18 months [2]. Unfortunately with the fabrication of smaller and smaller features there arise a slew of issues of which two are so major that they cannot be ignored [1-7].

The first is the resolution of lithography due to the diffraction limit. The minimum feature size possible is given by:

\[ CD = 0.4 \frac{\lambda}{NA} \]  

(2.1)

where \( \lambda \) is the wavelength of light used, NA is the numerical aperture of the lens system used and CD is the critical dimension (smallest feature) possible [2]. The coefficient of 0.4 is commonly referred to as the K1 factor and is denotes processing-related factors. Already the wavelength of light being used is at the DUV range of 193nm [1]. Any further reduction would push further into the UV range requiring the current use of lenses be replaced with specialized non absorbing mirrors and for the whole process to be done in vacuum as air begins to absorb light at 185nm.
Additional efforts to increase NA using high index immersion and off-axis illumination will not be enough [2].

The second problem arising with smaller and smaller features is that the metal interconnects between active regions and transistors are getting smaller too. As the metal interconnect sizes approach the mean free path length of the conducting material, more surface effects appear which are plagued with loss [1]. The solution to this problem either involves replacing the metal interconnects with materials that are not as high in phononic or scattering losses [3-4,6] or to simply retire the use of DC signals between active regions [5]. Additionally problems from overheating with more transistors in a smaller area and quantum tunneling of smaller gap sizes between stacked layers in a transistor are further indication of the future of this technology.

Photonic crystals is one possible solution to these problems as it shifts towards higher frequency communication between active regions in a circuit [7-9]. With higher frequency communication between regions the data processing rate is increased without having to increase the number of active regions [9]. This also solves the diffraction limited resolution issue as the working size for current photonic technology is in the micrometer range. Near IR communication has already been implemented in the macroscale communication between computers and if it were to be applied at the microscale, the whole concept of electronics will be replaced with photonics. Progress in all optical components has already been made in many necessary on-chip components and devices including optical memories [7], inter-connects [9], optical microprocessor [10], waveguides [11-12], power splitters [13], and resonators [14].
For the time being, lithography will move forward using the same imaging tools as today, but with a few new process technologies that have been extending the lifetime of photolithography such as: double patterning, optical proximity correction, phase-shift masks, liquid immersion lithography, and 157nm wavelength[1-2]. All the while photonics is starting to make name for itself as a viable replacement.

2.2 Photonic Crystals

Photonic crystals are composed of periodic dielectric microstructures or nanostructures that affect electromagnetic wave propagation in the same way that the periodic potential in a semiconductor crystal affects electron motion by defining allowed and forbidden electronic energy bands [15-17]. Photonic crystals contain regularly repeating regions of high and low dielectric constant. Photons (behaving as waves) either propagate through this structure or not, depending on their wavelength. Wavelengths that propagate are called modes, and groups of allowed modes form bands. Disallowed bands of wavelengths are called photonic band gaps [15-17]. Three-dimensional (3D) photonic nano/micro-structures have yielded amazing optical functionalities such as negative index meta-materials [18-20], ultra-high Q optical resonators for lasers [21-23], and optical cloaking devices [24-25].

Since photonics crystals affect wave propagation it is essential to study how electromagnetic waves propagate in matter in general [15]. By starting with Maxwells equations we can derive the form of the waves that propagate in photonic crystals. The time domain differential form of Maxwell’s equations in matter are given by

$$\nabla \cdot \mathbf{D}(\mathbf{r}, t) = \rho$$  \hspace{1cm} (2.2)
\[ \nabla \cdot \mathbf{B}(\mathbf{r}, t) = 0 \]  \hspace{1cm} (2.3)

\[ \nabla \times \mathbf{E}(\mathbf{r}, t) + \frac{\partial \mathbf{B}(\mathbf{r}, t)}{\partial t} = 0 \]  \hspace{1cm} (2.4)

\[ \nabla \times \mathbf{H}(\mathbf{r}, t) - \frac{\partial \mathbf{D}(\mathbf{r}, t)}{\partial t} = \mathbf{J}(\mathbf{r}, t) \]  \hspace{1cm} (2.5)

where \( D \) is the displacement field, \( \rho \) is the free charge density, \( B \) is the magnetic induction field, \( E \) is the electric field, \( H \) is the magnetic field, and \( J \) is the current density. Most photonic crystal materials are materials in which there are no sources of charge and no current flowing in the medium (\( \rho = 0 \), \( J = 0 \)). It is also assumed that the medium is dielectric, lossless, and that the dielectric function, \( \varepsilon(\mathbf{r}) \), is real and positive. With these considerations in mind, the relationships between \( E \) and \( D \), and \( B \) and \( H \), can be written as

\[ \mathbf{D}(\mathbf{r}, t) = \varepsilon_0 \varepsilon(\mathbf{r}) \mathbf{E}(\mathbf{r}, t) \]  \hspace{1cm} (2.6)

\[ \mathbf{B}(\mathbf{r}, t) = \mu_0 \mu(\mathbf{r}) \mathbf{H}(\mathbf{r}, t) \]  \hspace{1cm} (2.7)

where \( \varepsilon_0 \) is the permittivity of free space, \( \varepsilon(\mathbf{r}) \) is the dielectric constant, and \( \mu_0 \) is the permeability of free space. The relative permeability factor, \( \mu(\mathbf{r}) \) in Eq. (2.7), is effectively 1, in most materials (non-magnetic). Substituting Equation (2.6) & (2.7) into Equation (2.2)-(2.5), and applying the assumptions of no sources and a lossless, isotropic dielectric with a real and positive dielectric function, Maxwell’s equations become

\[ \nabla \cdot \varepsilon(\mathbf{r}) \mathbf{E}(\mathbf{r}, t) = 0 \]  \hspace{1cm} (2.8)

\[ \nabla \cdot \mathbf{H}(\mathbf{r}, t) = 0 \]  \hspace{1cm} (2.9)

\[ \nabla \times \mathbf{E}(\mathbf{r}, t) + \mu_0 \mu(\mathbf{r}) \frac{\partial \mathbf{H}(\mathbf{r}, t)}{\partial t} = 0 \]  \hspace{1cm} (2.10)

\[ \nabla \times \mathbf{H}(\mathbf{r}, t) - \varepsilon_0 \varepsilon(\mathbf{r}) \frac{\partial \mathbf{E}(\mathbf{r}, t)}{\partial t} = 0 \]  \hspace{1cm} (2.11)
Exploiting the linearity of Maxwell’s equations and assuming that the field pattern changes harmonically with time, the spatial and time dependence can be separated and the equations for the electric and magnetic fields can be written as

\[ E(r, t) = E(r)e^{-i\omega t} \quad (2.12) \]
\[ H(r, t) = H(r)e^{-i\omega t} \quad (2.13) \]

Substituting Equation (2.11)-(2.12) into Equation (2.7)-(2.10) for the electric and magnetic fields, Maxwell’s equations give

\[ \nabla \times E(r) - i\omega \mu_0 \mu(r) H(r) = 0 \quad (2.13) \]
\[ \nabla \times H(r) + i\omega \varepsilon_0 \varepsilon(r) E(r) = 0 \quad (2.14) \]

Since the substitution of Eq. (2.11)-(2.12) into Equation (2.8)-(2.9) returns identical equations reiterating the condition of no sources or sinks, and nothing new is learned from them.

Rearranging Eq. (2.14) as

\[ \frac{1}{\varepsilon(r)} \nabla \times H(r) = -i\omega \varepsilon_0 E(r) \quad (2.15) \]

and taking the curl of both sides gives

\[ \nabla \times \left[ \frac{1}{\varepsilon(r)} \nabla \times H(r) \right] = -i\omega \varepsilon_0 \nabla \times E(r) \quad (2.16) \]

By substituting Eq. (2.13) into Eq. (2.16) and utilizing the relationship, \( \varepsilon_0 \mu_0 = c^{-2} \), where \( c \) is the speed of light, and that \( \mu(r) = 1 \), we note that a vector wave equation presents itself.

\[ \nabla \times \left[ \frac{1}{\varepsilon(r)} \nabla \times H(r) \right] = \left( \frac{\omega}{c} \right)^2 H(r) \quad (2.17) \]

Eq. (2.17) can be rewritten as

\[ \Theta_H H(r) = \left( \frac{\omega}{c} \right)^2 H(r) \quad (2.18) \]
This is an eigenvalue problem with eigenvalues \( \left( \frac{\omega}{c} \right)^2 \), eigenfunctions (or eigenmodes) \( H(r) \), and an operator defined as \( O_H \triangleq \nabla \times \left[ \frac{1}{\varepsilon(r)} \nabla \times \right] \). The operator is linear and Hermitian. For a photonic crystal structure defined by a dielectric function \( \varepsilon(r) \), the eigenvalue equation can be solved to find the eigenvalues and the eigenmodes.

2.3 Fabrication Methods for Photonic Crystals.

Fabrication of photonic crystals in one and two dimensions borrows a lot from conventional lithographic techniques used in today in the fabrication of silicon semiconductor integrated circuits (IC). Current IC fabrication techniques utilize 2D binary facemask and focusing projection system technologies [1]. To fully exploit the use of photonics the fabricated structures should be three dimensional. The only way 3D fabrication is possible with current IC fabrication methods is through stacking multiple layers which suffers from surface / material mismatch.

This section discusses currently available methods of fabricating 3D photonic crystals. And are summarized in Table 2.1. There are three main methods which include colloidal self-assembly, direct writing, and holographic lithography.

<table>
<thead>
<tr>
<th>Method</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct Laser Writing</td>
<td>- High resolution (~ 100’s nm)</td>
<td>- Slow</td>
</tr>
<tr>
<td></td>
<td>- No limit on variety of structures</td>
<td>- Can only fabricate small areas.</td>
</tr>
<tr>
<td>Electron Beam Lithography</td>
<td>- Very high resolution (&gt;10 nm)</td>
<td>- Slow (layer by layer)</td>
</tr>
<tr>
<td></td>
<td>- Wide variety of nanostructures possible</td>
<td>- Expensive</td>
</tr>
<tr>
<td>Colloidal Self-Assembly</td>
<td>- Inexpensive</td>
<td>- Slow process</td>
</tr>
<tr>
<td></td>
<td>- Variety of structures possible (limited by micro- or nanoparticles used for assembly)</td>
<td>- Prone to defects</td>
</tr>
</tbody>
</table>
Holographic Lithography

- Large area fabrication
- Wide variety of structures possible
- Uniform fabricated structures
- Fast process
- Resolution not as high as direct laser writing.

Table 2-1. A comparison of different methods of fabricating photonic crystals [26].

Direct writing is a method that uses a particle or light beam to directly pattern a material. Direct Laser writing and electron beam lithography both fall within this method, which by far has the greatest resolution and capable of producing any type of structure. Unfortunately since the writing occurs at the volume on which the incident beam has greatest density on the surface of the material, the fabrication process occurs at one point in space. To produce patterns in higher dimensions the beam must be moved around to form a raster image (pixilated image) which is a very slow process.

Electron beam lithography (EBL) has been used since the 1990s to fabricate photonic crystals. [27-30] In recent years, it is still used to produce photonic nanostructures on a sub-10 nm scale, which is smaller than other methods are currently capable of. However, the slow, scanning layer-by-layer nature of EBL means that fabrication of large area patterns or 3D structures takes too long for rapid fabrication of photonic structures. [31] While EBL is too slow for large area fabrication, it finds use in fabrication of photomasks, which are used in lithography setups, particularly in the modern IC fabrication.

Direct laser writing (DLW) works via through two-photon absorption in photoresist. Photoresists manufactured for use in lithography, such as SU-8, are sensitive to the ultraviolet (UV) range of light (below 380nm). In a two-photon polymerization process, the photoresist molecule absorbs two photons simultaneously, which behaves like the molecule absorbed a
single photon with half the wavelength of the two photons. For example, two 532nm wavelength photons being absorbed simultaneously will cause the same excitation as a single 266nm wavelength photon. To achieve two-photon absorption, the intensity must be very high in order to have enough photons to have the chance of a two-photon excitation [32]. Typically, this is achieved using a pulsed laser with a high numerical aperture microscope objective lens to tightly focus the light into a very small spot.[32-34] Recently, a continuous wave 532nm laser was used to direct laser write structures in SU-8.[74] Single photon absorption was ruled out in that case, leaving two-photon absorption as the mechanism behind the polymerization of SU8. DLW is a layer-by-layer process, and as such, is very slow to fabricate even small structures.

Colloidal self-assembly was first used for production of inverse opal photonic crystals in 2001 [35] by depositing silica microspheres in suspension onto a silicon substrate. The microspheres form a close-packed FCC lattice on the substrate, and the empty spaces between the spheres were infiltrated with silicon via chemical vapor deposition (CVD). The silica spheres were then removed by etching, leaving behind a Si inverse opal structure. Advances in colloidal self-assembly have led to the incorporation of defects into the structures [36], but the method is prone to assembly defects such as vacancies, disorder, and stacking faults [37].

Holographic lithography makes use of laser beams interfering in the same region to form a periodic intensity distribution of light in photoresist, which is able to form an entire photonic crystal lattice template in a vastly shorter timeframe than the other methods, with the entire exposure process taking seconds. Holographic lithography has been shown to be a versatile, low-cost method of fabrication. While the resolution achieved by this method is not as fine as direct laser writing or electron beam lithography, it is able to pattern much larger areas in a much
shorter time. For these reasons, holographic lithography is used in our research as a simple, versatile, low-cost method of rapidly fabricating photonic crystal templates.

2.4 Holographic Lithography

Multi-beam interference lithography also known as holographic lithography is an excellent optical fabrication techniques which can pattern multi-dimension structures simultaneously. It works on the principle of overlapping multiple beams to form a pattern of constructive and destructive interference that can be recorded into a photo-sensitive material known as a photoresist. This recorded template of the interference pattern can be used to transfer the resulting pattern into the desired material.

Two-beam inference has been successfully used for the fabrication of fiber Bragg gratings widely used in optical telecommunications and sensors [38]. Multi-beam interference has been used in various optical fabrication areas such as nanoelectronics [39-40], nano-antennas [41], metamaterials [42-43], optical trapping [44-45] and various photonic crystals [46-56]. It can produce periodic patterns of all fourteen Bravais lattices [57] and even quasi-periodic patterns [58]. The lattice symmetries and motif in the lattice are controlled by the number of interfering beams, individual beam amplitudes, their respective polarizations, their relative phases, and wave vector configurations [46-59].

2.5 Interference Distribution

Holographic lithography is based on the interference of two or more coherent, monochromatic electromagnetic plane waves (typically collimated laser beams) to produce a
periodic 2D, or 3D intensity pattern that is recorded in photoresist. The electric field of a monochromatic plane wave (laser beam) is given by

$$E(r, t) = E_0 \exp[i(k \cdot r - \omega t + \delta)]$$

(2.19)

where \(E(r, t)\) is the complex electric field, \(E_0\) is the electric field strength constant in the direction of the electric field polarization, \(k\) and \(\omega\) are the wave vector and angular frequency of the plane wave, respectively, and \(\delta\) is the initial phase of the beam. [60] The real part of the electric field, which is the physical solution, is given by

$$E(r, t) = E_0 \cos(k \cdot r - \omega t + \delta)$$

(2.20)

From the superposition principle, the total electric field at a point where the separate electric fields of two or more plane waves overlap is simply the vector sum of the individual fields:

$$E_{\text{total}} = \sum_{i=1}^{N} E_i$$

(2.21)

The intensity of the total electric field is given by

$$I = \langle E_{\text{total}}^2 \rangle = \langle \sum_{i=1}^{N} E_i \cdot \sum_{j=1}^{N} E_j \rangle$$

(2.22)

which is to say that the intensity is the time average of the square of the total electric field. By carrying out the dot product on the right side of Eq. (2.22), the equation becomes

$$I = \langle \sum_{i=1}^{N} E_i^2 \rangle + 2 \langle \sum_{i < j}^{N} E_i \cdot E_j \rangle$$

(2.23)

The real part of the first term on the right side of Eq. (2.23) takes the form

$$\langle E_i^2 \rangle = \langle E_0^2 \cos^2(k_i \cdot r - \omega t + \delta_i) \rangle$$

(2.25)

Utilizing the trigonometric identity for \(\cos(A-B)\), the cosine part of Eq. (2.25) becomes
\[
\cos^2(k_i \cdot r - \omega t + \delta_i) = \left[ \cos(k_i \cdot r + \delta_i) \cos(\omega t) + \sin(k_i \cdot r + \delta_i) \sin(\omega t) \right]^2 \\
= \cos^2(k_i \cdot r + \delta_i) \cos^2(\omega t) + \sin^2(k_i \cdot r + \delta_i) \sin^2(\omega t) \\
+ 2 \cos(k_i \cdot r + \delta_i) \sin(k_i \cdot r + \delta_i) \cos(\omega t) \sin(\omega t)
\]

(2.26)

Given the following time averages of the trigonometric functions,
\[
\langle \cos^2(\omega t) \rangle = \frac{1}{2} \quad \langle \sin^2(\omega t) \rangle = \frac{1}{2} \quad \langle \cos(\omega t) \sin(\omega t) \rangle = 0
\]

(2.27)

and keeping in mind that \( E_{0i}^2 \) is a constant value, we find that
\[
\langle E_{i}^2 \rangle = E_{0i}^2 \left[ \frac{1}{2} (\cos^2(k_i \cdot r + \delta_i) + \sin^2(k_i \cdot r + \delta_i)) \right]
\]

(2.28)

Making use of one more trigonometric identity,
\[
\langle E_{i}^2 \rangle = \frac{E_{0i}^2}{2}
\]

(2.29)

The second term on the right hand side of Eq. (2.23), known as the interference term, and takes the following form,
\[
\langle E_i \cdot E_j \rangle = \langle (E_{0i} \cos(k_i \cdot r - \omega t + \delta_i)) \cdot (E_{0j} \cos(k_j \cdot r - \omega t + \delta_j)) \rangle
\]

(2.30)

Using the same \( \cos(A-B) \) identity as in Eq. (2.25), we find that
\[
\langle E_i \cdot E_j \rangle = E_{0i} \cdot E_{0j} \left[ \cos(k_i \cdot r + \delta_i) \cos(k_j \cdot r + \delta_j) \cos^2(\omega t) \\
+ \sin(k_i \cdot r + \delta_i) \sin(k_j \cdot r + \delta_j) \sin^2(\omega t) + \\
+ \cos(k_i \cdot r + \delta_i) \sin(k_j \cdot r + \delta_j) \cos(\omega t) \sin(\omega t) \\
+ \sin(k_i \cdot r + \delta_i) \cos(k_j \cdot r + \delta_j) \cos(\omega t) \sin(\omega t) \right]
\]

(2.31)

After performing the time average, the two cross terms become zero, and the remaining terms pick up a factor of \( \frac{1}{2} \), resulting in the following equation,
\[
\langle E_i \cdot E_j \rangle = \frac{1}{2} E_{0i} \cdot E_{0j} \cos(k_i \cdot \mathbf{r} + \delta_i) \cos(k_j \cdot \mathbf{r} + \delta_j) \\
+ \sin(k_i \cdot \mathbf{r} + \delta_i) \sin(k_j \cdot \mathbf{r} + \delta_j)
\]  

(2.32)

which leads to

\[
\langle E_i \cdot E_j \rangle = \frac{1}{2} E_{0i} \cdot E_{0j} \cos[(k_i - k_j) \cdot \mathbf{r} + (\delta_i - \delta_j)]
\]  

(2.33)

Taking the results of Eq. (2.29) and Eq. (2.33) and substituting them into Eq. (2.23), we arrive at a general equation for the intensity distribution from the interference of an arbitrary number of monochromatic electromagnetic plane waves (laser beams),

\[
I = \sum_{i=1}^{N} \frac{E_{0i}^2}{2} + \sum_{i<j}^{N} E_{0i} \cdot E_{0j} \cos[(k_i - k_j) \cdot \mathbf{r} + (\delta_i - \delta_j)]
\]  

(2.34)

Eq. (2.34) presents the interference pattern in terms of parameters that can be controlled in interference lithography. The difference between the wave vectors of the different beams, \(k_i - k_j\), determines the reciprocal lattice vectors of the lattice, and subsequently, the lattice vectors of the crystal lattice. The lattice constants of the photonic crystal resulting from the interference of multiple beams are proportional to the wavelength, due to the reciprocal lattice vectors being inversely proportional. Any two beams can produce a line grating interference pattern. If there exists a change in the z component of the wave vector then this line grating periodicity will be in the z direction. This means that with a minimum of three beams a 3D lattice can be formed. The polarization vectors of the laser beams determine the distribution of intensity within the unit cell. [41, 61] The phase difference between the beams, \(\delta_i - \delta_j\), can have a great effect on the interference pattern. By shifting the phase of one or more beams, the resulting interference pattern will shift, and the intensity distribution within the unit cell can change. [41, 62-67]
2-1 shows representative samples of interference distributions that can be accomplished with multiple beams.

![Image showing iso-intensity surfaces for interference patterns from the interference of 3, 4, 5, and 6 beams in an umbrella configuration with and without an additional central beam that introduces a change in wave vector in the z direction that produces a 3D structure. Polar interference angle with optical axis is identical for all side beams in each configuration. Azimuthal angles between side beams are symmetric.](image)

2.6 Holographic Lithography: Fabrication Techniques

Any structure fabricated through holographic lithography must use two or more beams. There are many methods for generating the requisite number of beams needed to produce any desired pattern. Conventional holographic optical setups [41, 64, 68-69] generate the multiple beams using bulk optical elements such as beam splitters, mirrors, and wave plates (for polarization), as seen in an example setup in Figure 2-2. Furthermore, to modify parameters such as phase or polarization of the individual beams, additional optical elements have to be added to the setup. Such complex setups are subject to misalignment, with even small deviations in the
optical path length of the interfering beams introducing phase delays which may not be desirable for fabrication of certain structures.

Figure 2-2 Diagram of an example of a conventional umbrella holographic lithography setup that utilizes multiple bulk optical components which are cumbersome to align and prone to instability [94].

Refractive single optical elements have found much use in the last decade for fabrication of photonic structures. [43,52-54,58,70-73] Typically, a top-cut prism (TCP) is used with an aperture array or top cover to simultaneously generate and interfere the beams together. This approach was used in by Wu et al in 2005 [53] to fabricate 2D hexagonal and 3D FCC-type photonic crystal in SU-8 photoresist. The following year, hexagonal TCPs were used to holographically fabricate 2D honeycomb structures [70]. By using a four-sided, truncated pyramidal prism with wave plates mounted in the aperture above the prism to adjust the polarizations of each beam, Pang et al realized a woodpile photonic structure in SU-8 photoresist [54]. TCPs have also been used to fabricate photonic quasi-crystal structures [73-74] and metamaterial structures [43].
A diagram of a TCP-based setup is shown in figure 2-3. Multiple beams coherent beams are incident on the TCP from top. The beams enter the TCP, whereupon they are refracted into the prism and transmitted to the far side, where they interfere with other beams in a photosensitive film positioned on the opposite side of prism. TCP are usually expensive to have cut and polished and because of the fixed angle for total internal reflection require individual beam phase delays to achieve photonic bandgaps.

Diffractive optical elements (DOE) are typically diffraction gratings or arrangements of diffraction gratings in which the beams diffracted from the gratings are interfered together to produce photonic crystal templates. The diffraction from a grating is given by the grating equation,

\[ a \sin \theta = m \lambda \]  \hspace{1cm} (2.35)
where \( a \) is the period of the grating, \( m \) is the order of the diffracted beam, \( \lambda \) is the wavelength of the incident laser beam, and \( \theta \) is the angle that the diffracted beam of order \( m \) is diffracted into. Gratings can be readily fabricated using holographic lithography, [58] or by using electron beam lithography [75]. The gratings used in holographic lithography typically take the form of phase masks, where the grating consists of a metal or dielectric deposited onto a substrate with a periodic height difference, leading to a periodic difference in the refractive index. This leads to multiple diffracted beams that can be used for fabrication of photonic crystal templates.

Berger et al first used a single DOE, a mask composed of three diffraction gratings rotated 120° relative to each other, to holographically fabricate 2D hexagonal photonic crystals [76]. The three first order beams diffracted from the gratings were interfered in a region below the mask, creating a 2D hexagonal interference pattern in photoresist. More diffraction gratings can be arranged symmetrically about the center of the mask, which generates more first order beams that can be interfered. In a similar fashion, Divliansky et al [77] used a DOE which added a hole in the center of the 3 grating mask to allow a central beam to pass through. The resulting structure was a 3D hexagonal structure. The interference of a central beam along the optical axis of the setup with beams arranged symmetrically from off-axis introduces a periodicity in the interference pattern parallel to the optical axis (typically labeled as the z-axis).

In order to fabricate 3D structures with large band gaps the phase shift between center beam and the symmetric 1\(^{st}\) order side beams must be adjusted. Two groups accomplished this by fabricating 3D photonic crystals using a stack of two orthogonally oriented gratings with a tunable spacer between. In a paper by Ohlinger et al, [51] two orthogonally oriented diffraction gratings were separated by thermally tunable spacer layer. A single circularly polarized laser
beam was incident upon the three-layer DOE. The first grating diffracts an incident, linearly polarized laser beam into two first order beams, (+1, 0) and (-1, 0), and a zero order beam, (0, 0). The second, orthogonally-oriented grating diffracts the (0, 0) beam, producing two new first order beams, (0, +1) and (0, -1), and a zero order beam. But since the (+1, 0) and (-1, 0) beams generated from the first grating have a longer optical path length, they have a phase delay. The DOE was heated so that the spacer layer would expand, tuning the phase delay that was added to the (±1, 0) beams. The expansion of the spacer layer was controlled such that the phase delay for the (±1, 0) beams was adjusted to be $\pi/2$. When the (0, 0), (±1, 0), and (0, ±1) beams are interfered in photoresist thin film positioned beneath the DOE, interconnected woodpile structures were produced. Earlier papers [78-79] reported the use of DOEs consisting of two orthogonally oriented gratings separated by an air gap adjusted to produce a phase delay of $\pi/2$ in the (±1, 0) beams to fabricate diamond-like woodpile photonic lattices. The air gap was tuned using a pressure adjustable mount. Both approaches to the 3-layer phase mask method display the capability to produce a range of structures using four 1st order diffracted beams and a 0th order beam by tuning the phase of two of the beams.
CHAPTER 3
SINGLE BEAM HOLOGRAPHIC BASED REFLECTIVE OPTICAL ELEMENT

3.1 Design and Development of Reflective Optical Element

The Reflective Optical Element (ROE) was developed as a simple more efficient and more economical replacement for the other single optical elements. A drawing of a representative ROE was generated using the 3D CAD software Solid Works, as shown in Figure 3.1(a). It consists of two plastic platforms connected by four pillar supports.

![Figure 3-1 (a)](image)

Figure 3-1 (a) Lab made reflective optical element made of two supporting structures that hold in place multiple reflecting facets used to turn part of one centralized incident beam into multiple side beams for use in holographic lithography. (b) A portion of the single light beam is incident on the facet at an angle of $\beta$ and reflected to interfere with other reflected beams or an unaltered central beam at an interference angle of $\alpha$

The two platforms and the platform supports were drawn in Solid Works and built from white ABS plastic by an UP! 3D printer. The platforms each have cut-outs of regular polygons on which rest the polished reflecting facets. Each facets in the Figure can be setup so that it is some angle $\beta$ relative to the base of the support frame. When the laser beam is incident onto the facet from the top of the support frame, the incident angle on the facet surface is the same as $\beta$. The
reflected beams from multiple facets will be overlapped as shown in Figure 1(b) each with a fixed angle of $\alpha = 180 - 2\beta$ relative to z-direction (this will be used to determine the interfering angle) and their wave vectors are determined by the azimuthal angle that denotes the position of the facet in the cut out and the polar angle $\alpha$. Masks with a determined aperture array (not shown in the Figure 1(a)) were placed on top of the ROE to block unwanted light while allowing only certain beams of the incident light to reflect off the facets. 3D interference structures are formed when the reflected side beams are overlapped with the central beam. Figure 3.1(b) shows how one silicon facet can turn part of the central circular beam into a linearly polarized wave if $\beta$ is chosen to be the Brewster angle. When it overlaps with the unaltered part of the central circular polarized beam, it creates periodic interference in the z direction. Two or more linearly polarized beams reflected form adjacent silicon facets will produce a period interference in the x-y plane. The relative sizes of the polygon cut-outs in each pair of platforms as well as the height of the frame supports determine the angle at which the silicon facet rests and thus the angle of incidence and k vector configuration of the interfering beams.

3.2 Interference of Beams Using Reflective Optical Element

As derived in chapter 2 the interference of multiple beams can be expressed as Equation 2.34. That form is the simplest form to write the resulting interference. But for the purposes of understanding the interference pattern from the Reflective Optical Element (ROE) it is better to keep the expression in its complex form.

$$I = \sum_{i=1}^{N} \frac{E_{0i}^2}{2} + \sum_{i<j}^{N} E_{0i} \cdot E_{0j} e^{-i[(k_i-k_j) \cdot r_+ (\delta_i-\delta_j)]} \quad (3.1)$$
Here the amplitudes $E_{0j,i}$ are complex values that are representative of the complex Fresnel amplitudes of the reflected beams from the ROE. Each complex amplitude can then be separated into $s$ and $p$ polarized components with respect to the facets plane of incidence.

$$E_{0i} = E_{is} r_s + E_{ip} r_p$$  \hspace{1cm} (3.2)

Where $E_i$ is the incident beam into the silicon facet and was usually a circular polarized beam.

$$E_i = \left( E_x e^{-i[kr]} + E_y e^{-i[kr + \frac{\pi}{2}]} \right) \cdot \hat{r} + \left( E_x e^{-i[kr]} + E_y e^{-i[kr + \frac{\pi}{2}]} \right) \cdot \hat{p}$$  \hspace{1cm} (3.3)

Substituting equations 3.3 and 3.2 into 3.1 gives the extended form of the Intensity

$$I = \sum_{i=1}^{N} \frac{E_{0i}^2}{2} + \sum_{i<j}^{N} E_{0i} \cdot E_{0j} e^{-i[(k_i-k_j) r + (\delta_i-\delta_j)]}$$  \hspace{1cm} (3.4)

A Matlab program was written to simulate the intensity distribution using equation 3.4.

The code can be found Appendix A and a variant of this Matlab program was used in all subsequent simulations of intensity distribution from multi-beam interference lithography [80].

### 3.3 Patent

A provisional patent was filed in the United States as a Reflective Optical Element for Holographic Lithography on Aug 1, 2014 and accepted based on the first publication of the ROE in Optical Materials Express [81]. Within the year the patent was re-filed as a Utility Patent and
began USPTO patent review process. The utility patent was issued on Dec 20, 2016 under Patent No. US 9523925 B2.

3.4 Photoresists

Some of the conditions for holographic lithography are not represented in Eq. (2.34). The properties of the exposure process and of the photoresist also have an effect on the structure that develops. Photoresists consist of a monomer that has been sensitized to light of a certain wavelength or range of wavelengths. There are two types of photoresists: positive and negative. In a negative photoresist, the resist that is exposed to the light of the interference pattern is polymerized, and the unexposed resist is removed with a developer. In a positive photoresist, the resist that has been exposed to the interfering beams is removed, while the unexposed regions are allowed to polymerize and remain, leaving the inverse structure of the interference pattern. Negative resists usually suffer from swelling, which limits the resolution of the features possible. The developers used to remove the unexposed resist swell the polymerized chains and help extract the unpolymerized portions, but in the process distort the polymerized regions. For this reason the semiconductor industry has stopped usage of negative resists and have exclusively been using positive resist which do not have this problem [1].

Photoresists are made to be sensitive to certain spectra of light, but mixtures of photoresist monomer with various sensitizer chemicals can make the photoresist mixture more sensitive to a particular wavelength. For example, SU-8 photoresist has strong absorption in the UV range, [82] but adding photosensitizers will make SU-8 sensitive to wavelengths in the visible spectrum. [83] Dipentaerythritol hexa-/penta-acrylate (DPHPA) [84], one of the negative resists
used in this work, can be sensitized to light of 532 nm wavelength by adding the photo-initiator Rose Bengal [81]. The amount of photo-initiator (as well as co-initiator and chain extender) varies between setups and applications [85-86]. The positive resist used, S1805 is sensitive to the i-line (365nm) and g-line (436) UV spectra [87]. To maintain the manufacture’s recommended processing this resist’s photosensitive compounds were left unaltered.

The number and intensity of the interfering beams can affect these numbers, as well as the exposure time of the photoresist to the interference pattern. In figure 3-2, two simulations in MATLAB of a five beam interference pattern are shown (4 side beams and a central beam). The interference pattern is calculated, and then a threshold operation is performed, removing the iso-intensity surfaces below that threshold. In figure 3-2(a), the simulated exposure time is longer, resulting in a structure with a higher filling fraction. In figure 3-2(b), the exposure time is less, resulting in a more isolated structure. Ideally, for a 3D photonic crystal template, the structure should be bi-continuous, meaning that the polymerized photoresist structures are interconnected and that the air regions are also interconnected.

Figure 3-2. Simulated effects of exposure threshold in MATLAB. (a) Longer exposure to laser interference pattern leads to higher fill fraction and interconnected structure. (b) Shorter exposure produces lower fill fraction and a lattice of isolated ellipsoids.
A bi-continuous structure allows the undeveloped photoresist to be dissolved and removed from the polymerized photonic crystal template after exposure by allowing the developer to flow freely throughout the template. For an overexposed structure, as in Figure 3-2(a), the undeveloped photoresist will become trapped and irremovable. For an underexposed structure, as in Figure 3-2(b), the exposed regions are isolated, and the entire structure will collapse and wash away with the photoresist in the development process. Bi-continuity is not a necessary condition in 1D or 2D photonic crystal templates, as the developer can wash completely over the entire surface, removing unpolymerized photoresist. To produce the photonic crystal from the template, a silicon double inversion procedure can be used [88]. Although this fabrication step is beyond the scope of this work presented in this research it is possible to convert the fabricated template into a silicon structure with identical patterning. This is done in two infiltration steps. The first infiltration is done with silica via chemical vapor deposition into the inverse structure of a 3D photonic crystal template. The photoresist can be removed after this step using plasma etching or heating to high temperatures. Then the inverse structure is infiltrated with Si, the silica is dissolved, leaving behind a Si replica of the holographically fabricated photonic crystal template.
CHAPTER 4

FABRICATION OF PHOTONIC TEMPLATES USING REFLECTIVE OPTICAL ELEMENT\(^1\)

4.1 Fabrication of Photonic Templates with 4-, 5- and 6-Fold Symmetry

To show the versatility of the ROE we set out to fabricate 3D photonic crystal and quasi-crystal templates with 4, 5, and 6 fold symmetry [89-90]. By using our developed ROE and a single circularly polarized beam, we are able to generate multiple side beams that interfered together with a central circularly polarized beam for the fabrication of photonic templates in SU8 and DPHPA without any other bulk optics. Figure 4-1 shows the beam configurations produced by the ROEs for each symmetry.

![Figure 4-1](image)

Figure 4-1 (a-c) Lab made single exposure, single reflective optical elements with 4, 5, and 6 fold symmetry, respectively. (d) An aperture mask splits the single circular polarized beam into a central and multiple side beams which are incident unto silicon facets that reflect the side beams into s-polarized waves when the incident angle, \(\beta\), is chosen to be the Brewster angle. The unaltered circularly polarized central and the multiple s-polarized side beams then overlap in the wave vector configurations depicted in (e-g) when using the respective 4, 5, and 6 fold symmetric (a-c) ROEs.

The work done and described here is a proof of concept for the use of the ROE for fabrication. For simplicity the experiments chose the incident angle on the ROE to be near the Brewster angle. This choice of angle as will be seen in future subsections of this chapter maximizes the periodicity of the structure in the z direction which make fabrication process easier. This is not ideal for the presence of photonic band gaps but it serves as a proof of concept for the fabrication process and method employed.

4.2 Experimental Setup

Four ROEs have been made and used for the interference holographic fabrication of 3D photonic structures. Table 4-1 lists the exposure laser wavelength, λ (nm), that has been used for the holographic lithography and the refractive index of silicon [91].

<table>
<thead>
<tr>
<th>Beams</th>
<th>λ (nm)</th>
<th>n</th>
<th>Brewster angle (degrees)</th>
<th>α (degrees)</th>
<th>r_p</th>
<th>r_s</th>
</tr>
</thead>
<tbody>
<tr>
<td>4+1</td>
<td>514.5</td>
<td>4.225</td>
<td>76.7</td>
<td>78</td>
<td>24</td>
<td>-0.051</td>
</tr>
<tr>
<td>4+1</td>
<td>532</td>
<td>4.15</td>
<td>76.5</td>
<td>67</td>
<td>46</td>
<td>0.249</td>
</tr>
<tr>
<td>5+1</td>
<td>514.5</td>
<td>4.225</td>
<td>76.7</td>
<td>79</td>
<td>22</td>
<td>-0.102</td>
</tr>
<tr>
<td>6+1</td>
<td>514.5</td>
<td>4.225</td>
<td>76.7</td>
<td>80</td>
<td>20</td>
<td>-0.140</td>
</tr>
</tbody>
</table>

Table 4-1 Exposure laser wavelength, λ (nm), refractive index n of silicon at the exposure wavelength, Brewster angle (degrees) of silicon at the exposure wavelength, incident angle (β) of laser onto silicon surface, interfering angle (α) of the side beam relative to the central beam, and amplitude reflection coefficient r_p, and r_s for p- polarized wave and s polarized wave respectively.

Fresnel equations were used to calculate the amplitude reflection coefficient (r_p, s) for p-wave
and s-wave using the refractive index $n$ of silicon [91] at the exposure wavelength. Three ROEs were designed to have the incident angle, $(\beta)$, of laser onto silicon surface to be close to the Brewster angle (degrees) of silicon at the exposure wavelength. When $\beta=80$ degrees (3.3 degrees away from the Brewster angle), the amplitude reflection coefficients $(r)$ are -0.140 and -0.919 for beams with polarizations parallel with (p-polarized) and normal to (s-polarized) the incident plane, respectively. 97.7% of the reflected beam is s-polarized when the circularly polarized beam is incident onto the silicon. For incident angles of 78, 79 and 80 degrees at the wavelength of 514.5 nm, as well as for incident angle 79 at wavelength of 532 nm, the reflected beams were mainly s-polarized waves. These larger angles were used for the purpose of easy fabrication of 3D photonic crystals. An exposed 3D photonic crystal can be easily developed if the incident angle is large since the periodicity of the photonic crystal in z-direction is relatively larger. In order to get a smaller ratio of lattice constant in z-direction over those in the xy plane, another ROE was designed to have an incident angles away from the Brewster angle for a 4+1 umbrella configuration.

Figure 4-2 Experimental setup used in conjunction with reflective optical element. A single beam is passed through a quarter wave plate and spatial filter, expanded, and collimated for use in the single exposure fabrication of 3D photonic crystals.
An Ar ion laser beam (514.5 nm, Coherent Inc.) was used for the holographic fabrication of photonic structures in SU8. It was passed through a quarter wave plate and spatial filter, then expanded and collimated to a size of 2 inches.

Triethylamine (TEA) was added to a modified SU8 (from MicroChem Corp.) photoresist mixture. In order to accurately control the mol concentration of TEA in the mixture, we firstly prepared a bottle of SU8 mixture with a high concentration of TEA: 20 g of SU8-2035, 0.1 g of 5,7-diiodo-3-butoxy-6-fluorone (H-Nu470), 0.5 g of (4-octyloxphenyl) phenyl iodonium hexafluoroantimonate (OPPI), 0.1 g of TEA and 6 g of propylene carbonate to assist the dissolution. Inside a second bottle, a similar mixture was prepared without TEA. Then a small amount of fully mixed solution with TEA was added to the second bottle to get a mixture with TEA amount being 30 mol % of H-Nu 470. The mixture was spin-coated on a glass slide with a speed of 700 rpm for 30 seconds. The photoresist films were prebaked on a hotplate at a temperature of 65 °C for 90 minutes and exposed to the interference pattern formed through the single beam and the single reflective optical element. For the exposure to 4+1 beams, a laser power of 3 W and a typical exposure time of 10 seconds were used. For the exposure to 5+1 beams, the laser power was 4 W and a typical exposure time was 3.5 seconds. For the exposure to 6+1 beams, the laser power was 4 W and a typical exposure time was 5 seconds. The exposed samples were post-baked at 65 °C for 15-30 minutes. The post-baked samples were developed in PGMEA for 15 minutes, rinsed by isopropanol for one minute and left to dry in air.

For the holography exposure to 532 nm laser (Cobolt Samba), a photoresist mixture was prepared with the following components in the specified weight concentrations: dipentaerythritol penta/hexaacrylate (DPHPA) monomer (Aldrich, 88.83%), a photo initiator rose
bengal (0.11%), co-initiator N-phenyl glycine (NPG, 0.79%), and chain extender N-vinyl pyrrolidinone (NVP, 10.27%). The laser beam was circularly polarized by passing through a quarter wave plate, spatial filtered, expanded and collimated. The mixture was spin-coated on a glass slide with a speed of 2000 rpm for 30 seconds. The photoresist film was exposed to the interference pattern formed through the single beam and the single reflective optical element. The laser power was 150 mW and a typical exposure was 3.2 seconds. The exposed sample was developed in PGMEA for 60 minutes, rinsed by isopropanol for one minute and left to dry in air.

4.3 Lattice Periodicity from Minimized Wave Vector Changes

When multiple beams are overlapped, the intensity distribution of their interference pattern can be determined by equation (2.35) which we iterate here:

\[ I = I_0 + \Delta I(r) = \left\langle \sum_{i=0}^{w} E_i^2 \right\rangle + \sum_{i<j}^{w} E_i \cdot E_j \cos[(k_i - k_j) \cdot r + \Delta \delta_{ij}] \]  

where \( E_i \) and \( \Delta \delta_{ij} \) are the electric field amplitude and initial phase for wave vector \( k_i \) and \( w = 4, 5 \) or 6 for 4+1, 5+1 or 6+1 interferences, respectively. As shown in Figure 1(d), we assume the central beam is propagating in the z-direction. The wave vector \( (k_i) \) in equation (1) for the central \( (k_0) \) and the side beams \( (k_p) \) can be described by:

\[ k_0 = K [0,0,1] \]  

\[ k_p = K \left[ \sin \alpha \cos \frac{2\pi(p-1)}{n}, \sin \alpha \sin \frac{2\pi(p-1)}{n}, \cos \alpha \right] \]

where \( n = 4, 5 \) and 6 for the side beams in the 4+1, 5+1 and 6+1 configurations, respectively and \( p = 1, 2, ..., n \). The magnitude of the wave vector is given by \( K = 2\pi/\lambda \). The wave vector difference
\( \Delta k \) can be considered as reciprocal vectors of structures formed through holoography. The wave-vector difference \( \Delta k_{\text{first}} \) between the neighboring side beams which help determine the \( x-y \) periodicity can be written as

\[
\Delta k_{\text{first}} = k_p - k_{p-1} = 2K \sin \alpha \cos \frac{\pi}{4} \left[ \cos \frac{2\pi}{4} \left( p - \frac{1}{2} \right), \sin \frac{2\pi}{4} \left( p - \frac{1}{2} \right), 0 \right] \quad \text{for } n = 4
\]

\[
\Delta k_{\text{first}} = k_p - k_{p-1} = 2K \sin \alpha \cos \frac{3\pi}{10} \left[ \cos \frac{2\pi}{5} \left( p - \frac{1}{4} \right), \sin \frac{2\pi}{5} \left( p - \frac{1}{4} \right), 0 \right] \quad \text{for } n = 5
\]

\[
\Delta k_{\text{first}} = k_p - k_{p-1} = 2K \sin \alpha \cos \frac{\pi}{3} \left[ \cos \frac{2\pi}{6} (p), \sin \frac{2\pi}{6} (p), 0 \right] \quad \text{for } n = 6
\]

For all interference patterns formed by the 4+1, 5+1, and 6+1 beam configurations, the periodicity in \( z \)-direction is determined from the change in wave vector in the \( z \) direction.

\[
\Delta k_z = k_0 - k_p = (K - K \cos \alpha) = K (1 - \cos \alpha)
\]

### 4.4 Woodpile Structures Using 4+1 Beam Configuration

The argon ion laser of wavelength 514.5 nm at an incident angle of \( \beta=78 \) degrees was initially used for the single beam and single ROE based holographic fabrication of 3D woodpile structures in SU8 photoresist. The 4 side beam’s \( k \) vectors have the same magnitude, same polar angle relative to the central beam, and are equally spaced azimuthally. As shown in Figure 1(e), the central beam (blue) is circularly polarized and the 4 side beams (red) are \( s \)-polarized waves. The central beam can be decomposed into two laser beams: \( k_{0x} \) and \( k_{0y} \), with a phase shift of 0.5\( \pi \) apart and with polarizations perpendicular to each other. By taking advantage of the
intrinsic phase shift of 0.5π in the circularly polarized beam, we eliminate the need for the precise two-layer grating displacement needed in the phase mask fabrication method of woodpile structures. The polarization of k₁ and k₂ are perpendicular to each other but parallel to those of k₃ and k₄ respectively, therefore there is no interference between (k₁ & k₂) and similarly (k₃ & k₄) as can be seen in Figure 1(e). Taking these zero interference terms into consideration in equation (4.1) for the 4+1 beam interference we can simplify the interference as the sum of two sets of interferences: one combination of beams, (k₀ₓ , k₁ , k₃), and the other which is rotated by 90 degrees, (k₀ᵧ , k₂ , k₄). Assuming all side beams have the same initial phase, δ, then these two interference patterns are given by the following equations:

\[
\Delta I_{130x} = E_{0x}E_1 \cos[(k_{0x} - k_1) * r + \delta] + E_{0x}E_3 \cos[(k_{0x} - k_3) * r + \delta] \\
+ E_1E_3 \cos[(k_1 - k_3) * r]
\]  

(4.8)

\[
\Delta I_{240y} = E_{0y}E_2 \cos[(k_{0y} - k_2) * r + \delta + \frac{\pi}{2}] + E_{0y}E_4 \cos[(k_{0y} - k_4) * r + \delta + \frac{\pi}{2}] \\
+ E_2E_4 \cos[(k_2 - k_4) * r]
\]  

(4.9)

Figure 4-3 Composite interference patterns that make up woodpile structure both structures are similar but rotated by 90 degrees in xy plane and offset by ¼ C in the z-direction. Color bar corresponds to an increase in intensity for computer simulations from blue (low intensity) to red (high intensity)
Figure 4-3 shows the composite interference patterns of beams \((k_{0y}, k_2, k_4)\) and \((k_{0x}, k_1, k_3)\) that make up the woodpile structure. The two composite structures can be seen as equal but shifted 90 degrees in the xy plane and with a shift in the z direction due to the phase difference between \(k_{0x}\) and \(k_{0y}\). The phase shift in the z direction between \((k_{0y}, k_2, k_4)\) and \((k_{0x}, k_1, k_3)\) can be written as \((k_i - k_j) \ast r + \Delta \delta = (k_i - k_j) \ast (r + r_d) + \delta\) where \((k_{0y} - k_2) \ast r_d = \frac{\pi}{2}\), \((k_{0y} - k_4) \ast r_d = \frac{\pi}{2}\), and \((k_2 - k_4) \ast r_d = \frac{\pi}{2}\). By simultaneously solving the three equation for \(r_d\) we find that the displacement \(r_d = [0, 0, 0.25 \ast \lambda/(1 - \cos \alpha)]\) is the shift of interference in the z direction of \((k_{0y}, k_2, k_4)\) due to the phase delay, relative to the interference from \((k_{0x}, k_1, k_3)\). From Eq. (4), we can get a structural parameter \(L = 2\pi/|\Delta k_{frst}| = \lambda/(2 \sin \alpha \cos \pi/4)\). Without the shift, \(L\) would have been the lattice periodicity, but due to the shift, we can re-calculate the periodicity in x or y-direction by

\[
\Lambda_{x,y} = 2 \ast L \ast \cos \pi/4 = \lambda/(\sin \alpha)
\] (4.10)

For all interference patterns formed by the 4+1, 5+1, and 6+1 beam configurations, the periodicity in z-direction is,

\[
C = \Lambda_z = 2\pi/(K - K \cos \alpha) = \lambda/(1 - \cos \alpha)
\] (4.11)

Figures 4-4(a) and 4-4(b) show SEMs of the top and cross section of fabricated holographic structures in SU8, respectively. Computer simulations of the top view and cross section of the structure are shown in Figures 4-4(c) and 4-4(d). The SEM looks similar to the simulation. From the SEM, the periodicities in x (or y) and z directions are measured to be 1.15 and 6.50 μm, respectively, compared with theoretical numbers of 1.26 and 5.95 μm based on an incident angle of 78 degrees.
4.5 Fabrication of Quasi-Crystals Using 5+1 Beam Configuration

For the fabrication of 3D quasi-crystals the ROE with an incident angle of $\beta=79$ was initially used. Figure 4-5(a) shows an AFM image of the top view of the fabricated structure in SU8. For eye guidance, five circles were drawn in the Figure around a common pentagon. Five-fold symmetry can be clearly observed from these five circles. Figure 5(b) shows an SEM image of the top view of fabricated 3D structure in SU8. Five circles were also drawn in the Figure around a common pentagon for eye guidance.
Figure 4-5 (a-b) AFM and SEM of fabricated quasi-crystals in SU8 using ROE for 5+1 beam interference lithography. (c) SEM of the cross section view of SU8 quasi-crystal structures fabricated. (d-e) Computer simulated top view and cross section view of 5+1 interference pattern for comparison with SEM images. For eye guidance, five circles were drawn in top view of the SEM, AFM and simulation around common pentagons. Red arrow indicates the air voids and red ellipses indicate the formed structures corresponding to the high intensity ellipse array in the SEM and simulated cross section views. Color bar corresponds to an increase in intensity for computer simulations from blue (low intensity) to red (high intensity).

These images of fabricated structures in SU8 look similar to the computer simulated top views of the quasi-periodic structure, shown in Figure 4-5(d) where five circles can also be drawn in the simulation around a common pentagon. The circular structures can be considered as the interference pattern due to neighboring side beams. For the structure with five-fold symmetry, it has rotational symmetry but lack of translational symmetry. From equation (4.5), $\Delta k_{first}$ can rotate in a circle with a radius of $2K\sin \alpha \cos (3\pi /10)$. Thus for the holographic structure, we can get a structural parameter $\Lambda = 2\pi /|\Delta k_{first}| = \lambda / (2\sin \alpha \cos (3\pi /10))$ as labeled the radius of one yellow circle in Figure 4-5(d). Theoretically $\Lambda =1.168$ um while $\Lambda =1.108$ um was measured in SEM. Figure 4-5(c) and 4-5(e) show an SEM of cross-section of the fabricated 3D
photonic quasi-crystal and simulated interference pattern. From the simulation, we can see that high intensity elliptical structures were formed in a region separated by sloped low intensity regions as indicated by red arrows in both the SEM and the simulation. For eye guidance, seven ellipses were drawn in the SEM and simulation that correspond to the high intensity ellipses. The distance between the center of the top three-ellipse array and the center of the bottom four-ellipse array equals half of the periodicity in z-direction. The periodicity is measured to be 7.53 um. Theoretically, the periodicity $\lambda/(1 - \cos \alpha) = 7.07$ um.

4.6 Fabrication of Hexagonal Woodpiles Using 6+1 beam Configuration

Ideally we can get more isotropic PhCs with the 6+1 configuration than the 4+1 or 5+1 configuration because of the isotropic motif in the xy-plane of the 6+1 interference. The ROE for 6+1 interference was initially designed with an incident angle of 80 degrees. Figure 4-6(a-b) shows SEMs of top-view of fabricated structure in SU8 at different depths in the z direction, while Figure 4-6(d-e) shows the corresponding computer simulated interference pattern. Because the SU8 thin film surface is not completely flat and perpendicular to the z-axis, the developed structure had different features corresponding to different view depths in the z-direction. Because of this the enlarged view of each splice in the z direction as seen Figure 4-6(a) and 4-6(b) were obtained from the same sample.

In Figure 4-6(a) it is shown that the top’s post-like structures have clearly distinguishable hexagonal symmetry and are weakly linked together. The structures below, which are shown in the splice of 4-6(b), are more distinctly linked together but decreased in intensity. A new post like structure is formed at an orientation rotated by 60 degrees from the top posts’ position.
Figure 4-6 (a-b) SEM of top view of fabricated structures with 6-fold symmetry in SU8. SEM images were taken at different depths in z direction as indicated by the arrows. (c) SEM of cross section of the 6-fold symmetric structure in SU8. (d-e) Computer simulated patterns corresponding to the top view SEM shown in a) and b). (f) Computer simulation of cross section view of structure. A red rectangle was drawn in c) and f) for comparison. Red arrows point from the top view simulations splice to their corresponding height in the 3D cross section simulation. Color bar corresponds to an increase in intensity for computer simulations from blue (low intensity) to red (high intensity).

Figure 4-6(c) shows an SEM, and 4-6(f) shows a computer simulation of the cross section of the 6 fold symmetric 3D structure. Red arrows indicate the top view splice’s z-position in the 3D cross section. Layer-by-layer post-like structures are clearly visible. The supporting posts between layers are not straight but rather, slanted. The skew can be understood from the simulation in Figure 4-6(f) with the red rectangles in Figure 4-6. (c) and (f) drawn for comparison. The curvature...
in the red rectangle of Figure 4-6(c) arises because the supporting post terminates at the center of a layer but the next lower supporting post begins at the right edge of a layer. The lattice constant $\Lambda$ is labeled in Figure 4-6(d) and can be calculated by $\Lambda = 2\pi / |\Delta k_{f_{rst}}| = \lambda / (2\sin \alpha \cos (\pi / 3))$ from Eq. (4.10). For $\beta=80$ degrees, a theoretical value of $\Lambda =1.50$ um is expected while $\Lambda =1.48$ um as measured in the SEM. The periodicity (double of layer distance) of structures is measured to be 8.59 um from the SEM while the theoretical calculation of the periodicity $\lambda / (1 - \cos \alpha) = 8.53$ um.

4.7 Proof of Concept for s-and p- Polarized Reflected Beams

In order to obtain 3D structures with a smaller periodicity, a bigger interference angle and thus a smaller incident angle is needed. If s-polarized waves are required for the side beams, the value of Brewster angle should be smaller. One way to obtain that is to select a material with a smaller refractive index as the surface on which to reflect the circularly polarized laser. The refractive index $n$, that is required for a specific periodicity can then be determined by the Brewster angle. If the surface material is left the same but the angle is moved away from the Brewster angle, we can study the effect of the s- and p- polarization ratio from the side beams on the holographic structure. An ROE with silicon facets was used for the second holographic fabrication using 532 nm laser and an incident angle of 67 degrees. 91.6% of reflected light is s-polarized and 8.4% is p-polarized. Figure 4-7(a-b) shows an atomic force microscope (AFM) image of fabricated structures in DPHPA using a 532 nm laser.
The measured periodicity in x (or y) direction is decreased to 0.675 um close to its theoretical value of .739 um. The AFM shows the structure to be a typical woodpile structure although p-wave was involved in the interference. The β angle range that can be used to form woodpile structures is from 67 to 82 degrees where more than 90% of reflected light is s-polarized. AFM surface profile along two lines in Figure 4-7(a) is shown in Figure 4-7(b). The red line reveals structural parameters of the first layer while the blue line tells us the information on the second layer. Both directions have the same periodicity.

To discuss the robustness and full capability of the ROE more experiments are required at incident angles away from the Brewster angle (where p-polarizations are introduced into the interference). Although not in the scope of this research and will not be fully elaborated on, the idea was explored by other members of the research group in particular to help answer several questions like: (1) how the photonic bandgap is affected if both s- and p-polarized beams are used for the interference, (2) what is the filling fraction of photonic crystals with
maximum bandgap, (3) whether the interference pattern is still bi-continuous so that the un-
polymerized photoresist can still be developed out of the holographic structures, and (4)
whether ROE technique is flexible for the interference lithography with arbitrary angle and
polarization. The results of this work can be found on the published work by Lowell et al [92].

4.8 Laue Diffractions of Fabricated Structures

Laue diffraction patterns [58] from these 3D photonic crystals with 4, 5 or 6-fold
symmetry are shown in Figure 4-8(a-c). The patterns were generated using the 532 nm laser.
These diffraction patterns were formed on a white paper and their digital images were taken
behind the white paper. For the 3D photonic crystals with 4 and 6-fold symmetries, their
corresponding diffraction patterns have 4 and 6-fold symmetries as shown in Figure 4-8(a) and
4-8(c), respectively. The size of diffraction spots is a measure of the diffraction intensity. In Figure
4-8(a) and 4-8(c), the first-order diffractions (as indicated by yellow lines) are stronger than the
second-order diffractions (as indicated by white lines). From the diffraction pattern of the quasi-
crystals in Figure 4-8(b), lots of useful information can be revealed. As indicated by yellow, white,
and red lines for the first, second and third-order diffractions, respectively, ten-fold symmetries
were clearly observed in these diffraction orders, which are typical for Penrose quasicrystals
[27,28]. Similar to the diffraction pattern from Penrose quasi-crystals in reference 27, we
observed pentagon structures (as indicated by light blue lines in Figure 4-8(b)) in the diffraction
pattern and the ratio of radii of the second-order diffraction to the first-order diffraction was
measured to be 1.7, which is close to the golden ratio of 1.618. However, the diffraction pattern
in Figure 4-8(b) is not uniformly distributed in all radial directions. The spot sizes of the second
order diffraction become smaller along the white line as observed in the direction from 1 to 2 and to 3 as labeled in the Figure. However, the spot sizes of the third order diffraction become larger along the red line in the direction from 1 to 2 and to 3. These features might be due to the chiral-type structures [93] as seen in Figure 4-8(c).

Figure 4-8  Laue diffraction patterns from photonic crystals with 4 (a), 5 (b) and 6-fold (c) symmetries, respectively. Yellow, white and red lines were drawn for eye-guidance and grouping the first-, second-, and third-order diffraction spots, respectively. The light-blue lines indicates a pentagon structure in (b).

4.9  Linearly Polarized Incident Light

In order to enrich the application of ROE, we simulate the interference patterns when a linearly polarized light is incident onto silicon facet at the Brewster angle as a function of polarization angle $\alpha$ relative to horizontal direction. The top-view of the interference patterns are shown in Figure 4-9(a2-a4) and 4-9(b2-b4). For both configurations, the motif of the interference pattern is strongly dependent on the angle $\theta$. For example, we can see clearly pentagon structures in Figure 4-9(a2) while the motif is more complicated in Figure 4-13(a4) and pentagon structures are barely visualized.
Figure 4-9  (a1) 5+1 configuration where a linearly polarized light is incident onto silicon surface at the Brewster angle with a polarization angle $\theta$. Top view of interference patterns as a function of polarization angle at 0 (a2), 30 (a3) and 60 (a4) degrees. Five circles are drawn for eye guidance. (b1) 6+1 configuration with a similar condition to (a1). Top view of interference patterns as a function of polarization angle at 0 (b2), 20 (b3) and 40 (b4) degrees. (c1) four silicon facets and one silica facet in a hexagonal arrangement. (c2) top view and (c3) 3D view of the interference pattern. (c4) An enlarged view of the interference pattern.

Combination of different reflective materials inside the ROE can result in some interesting structures. As shown in Figure 4-9(c1) for a hexagonal arrangement, four silicon facets are supported at the Brewster angle of 76.7 degrees for 514.5 nm laser, one fused silica facet is supported at the same angle while the last side is empty (no reflection). Figure 4-9(c2) shows a top view of the interference pattern when a circularly polarized beam at 514.5 nm is incident onto the ROE. Hexagonal structures are still visible. 3D interference pattern is shown in Figure 4-9(c3) and an enlarged view of a small portion is shown in Figure 4-9(c4). Clearly, four silicon facets
and one silica facet in a hexagonal arrangement can be used to generate chiral stair-like 3D structures.
CHAPTER 5

SUBWAVELENGTH CONTROL FOR FABRICATION OF NANOANTENNA TEMPLATES

In this experiment, we use a silicon based reflective optical element consisting of four silicon facets for the control of the polarizations of the interfering beams. Four s-polarized beams are generated for the interference lithography when a single laser beam is incident to four silicon facets at an angle close to the Brewer angle of a silicon surface. By tuning the relative phase delay in one of interfering beams, we are able to fabricate compound photonic crystal structures and tune the relative spacing of the two sub-lattices in the interference pattern of a compound lattice [41-94]. Such an optical setup can be used for the fabrication of nano-antenna templates in both positive and negative resists. We also discuss the control of the nano-gap between the nano-antennas through the laser’s polarization elliptical and the rotation of the ROE [95-96].

5.1 Subwavelength Control of Nano-pattern

Spatially controlling and steering light has been traditionally achieved through conventional optical devices such as lenses and mirrors. These conventional devices suffer from the diffraction limit, and therefore cannot control light on the sub-wavelength scale. Recently, nano-optics research has provided solutions to the aforementioned problem and concurrently has discovered new nano-optical devices. Among these devices are optical nano-antennas, which are very attractive due to their capability to manipulate light at the nano-scale [97-98].

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antennas have varied applications including: single molecule detection, enhanced solar cells, near-field scanning optical microscopy, and parallel nano-lithography [99-103].

The nano-antenna can be fabricated by electron beam lithography (EBL) or focused ion beam (FIB) lithography. But, due to their serial manners, both EBL and FIB fabrication processes are slow and expensive. Hsu et al. [104] have reported a parallel method of direct metal patterning using electrochemical etching with a superionic conductor stamp. Etching of the metal film at the contact region resulted in a metal pattern complimentary to the original stamp.

Nanostencil lithography (NSL) has also been reported for nano-antenna fabrication [105]. NSL is a shadow-mask patterning technique and relies on a direct deposition of materials through a pre-patterned mask which acts as a stencil. The stencils contained large numbers of nanoapertures/nanoslits with a variety of shapes, sizes, and arrangements that were used as a shadow-mask for direct deposition of materials [105].

Another prominent nanofabrication approach is achieved through laser holographic lithography [89,106] which is considered as one of the most attractive techniques for its controllability and flexibility. This method has already been applied for the fabrication of nano-antennas using four-beam interference [41,94,96]. This was achieved by controlling phase, polarization, and laser beam intensity in order to tune the relative spacing of the two sub-lattices in the interference pattern of a compound lattice. However the use of bulk optical components for the interference resulted in a complicated optical set-up. This prompts the use of the Reflective Optical element.
5.2 Experimental Setup

As shown in Figure 5-1, the ROE used a four-beam interference that has 6-fold symmetry. The ROE platforms each have cut-outs of regular hexagons on which rest the reflective Silicon (Si) or Gallium Arsenide (GaAs) wafers. A mask with a determined aperture array, was fabricated in similar fashion to the platforms and placed in front of the ROE to block unwanted light while allowing only certain beams of the incident light to reflect off the Si or GaAs wafers and be redirected as the necessary multiple interfering beams in holographic lithography. The relative sizes of the polygon cut-outs in the platforms as well as the height of the supports determine the angle at which the Si or GaAs wafer rests and thus the angle of laser incidence and k-vector configuration of the reflected beams. The phase delay can be introduced by a liquid crystal retarder (Thorlabs) as shown in magnified view of the ROE in Figure 5-1(a) or by inserting a glass cover slip that will introduce a change in optical path length for that beam.

This ROE approach can achieve control of phase, polarization, and intensity of the interfering laser beams. Rotations of both the quarter wave plate and the ROE can select laser intensity for beams reflected from an incident circularly (or elliptically) polarized laser beam. The phase delay is controlled by the liquid crystal retarder.

This particular pattern was chosen because in order to see the effect of changing the initial phase of one beam it is required to isolate its contribution. This configuration of four beams can generate an interference pattern which can be considered as compound photonic crystal lattices formed by combining the cross terms of any three beam interference [59,107]. In this manner, when one beam is modified with a phase shift it affects only one of the two sub lattices.
that make up the compound photonic crystal. This technique is analogous to the IC fabrication
technique known as double patterning that allows circumvention of the diffraction limit.

Figure 5-1 (a) Schematic of experimental optics setup using the quarter wave plate for
polarization control, liquid crystal retarder for phase delay, ROE for polarization selection and
beam overlapping, and rotation of ROE for intensity control of individual reflected beam. (b) Solid
Works model of the ROE that can be fabricated by a 3D printer. (c) Top view schematic of ROE
orientation.

Four reflective Si or GaAs wafers were put on four sides of the hexagon. These four
surfaces can reflect the incident laser beam with an orientation and beam configuration as shown
in Figure 5-1(c). The Si or GaAs wafer surface forms an angle of 76 or 78 degrees (close to the
respective Brewster angles of Si or GaAs) relative to the bottom platform surface. The ROE was
mounted in a lens mount (Thorlabs) and illuminated by the laser beam as shown in the magnified portion of Figure 5-1(a). The ROE can be rotated to adjust laser intensity of individual reflected beams when an elliptically polarized laser beam is incident onto the ROE. The laser was circularly (or elliptically) polarized by a quarter wave plate, spatially filtered, expanded and collimated. The spatial filter used a 10x objective lens and a 35 mm aperture while the collimating lens had a 300mm focal point as depicted in the schematic of the experimental set up in Figure 1 (a). A CCD camera (Edmund Optics USB 2.0 CCD Machine Vision Cameras) together with an objective lens (100×) was used to monitor the interference pattern.

For the orientation in Figure 5-1(c), the wave propagation vectors of the s-polarized reflected beams have azimuthal angles of 0, 60, 120, and 240 degrees. Wave vectors of these four reflected beams can be written as

\[ k_1 = \frac{2\pi}{\lambda} [-\sin \Theta, 0, \cos \Theta, ] \]

\[ k_2 = \frac{2\pi}{\lambda} [\sin \Theta \cos(-60), \sin \Theta \cos(-60), \cos \Theta, ] \]

\[ k_3 = \frac{2\pi}{\lambda} [\sin \Theta \cos(60), \sin \Theta \cos(60), \cos \Theta, ] \]

\[ k_4 = \frac{2\pi}{\lambda} [\sin \Theta, 0, \cos \Theta, ] \]

where \( \lambda \) is the wavelength of the laser and \( \Theta \) is the angle of the interfering beam relative to the vertical direction. These four reflected beams form an interference pattern where the beam intensity \( I(r) \) is determined by Eq. 2.34 which we rewrite here

\[ I = I_0 + \Delta I(r) = \sum_{i=1}^{N} \frac{E_{0i}^2}{2} + \sum_{i<j}^{N} E_{0i} \cdot E_{0j} \cos[(k_i - k_j) \cdot r + (\delta_i - \delta_j)] \]
where \( k \) is a wave vector, \( \delta \) the initial phase, \( E \) and \( e \) the constant of electric field strength and electrical field polarization direction, respectively. The interference cross term can be expanded for this configuration as

\[
\Delta I(r) = Q_{1,2} \cos \left[ 2\pi \left( \frac{3}{a} \hat{i} - \left( \frac{1}{b} \right) \hat{j} \right) \cdot (x + y) + (\delta_2 - \delta_1) \right] \\
+ Q_{1,3} \cos \left[ 2\pi \left( \frac{3}{a} \hat{i} + \left( \frac{1}{b} \right) \hat{j} \right) \cdot (x + y) + (\delta_3 - \delta_1) \right] \\
+ Q_{1,4} \cos \left[ 2\pi \left( \frac{4}{a} \hat{i} + (0) \hat{j} \right) \cdot (x + y) + (\delta_4 - \delta_1) \right] \\
+ Q_{2,3} \cos \left[ 2\pi \left( 0 \hat{i} + \frac{2}{b} \hat{j} \right) \cdot (x + y) + (\delta_3 - \delta_2) \right] \\
+ Q_{2,4} \cos \left[ 2\pi \left( \frac{1}{a} \hat{i} + \left( \frac{1}{b} \right) \hat{j} \right) \cdot (x + y) + (\delta_4 - \delta_2) \right] \\
+ Q_{3,4} \cos \left[ 2\pi \left( \frac{1}{a} \hat{i} - \left( \frac{1}{b} \right) \hat{j} \right) \cdot (x + y) + (\delta_4 - \delta_3) \right]
\]

(5.3)

Where \( Q_{i,j} = E_i E_j e_i e_j \), \( a = \lambda / (\sin \theta \cos 60) \), \( b = \lambda / (\sin \theta \sin 60) \), \( \lambda \) is the laser wavelength. These four beams can generate an interference pattern which can be considered as compound photonic crystal lattices formed by combining any three beam interference [59-107].

5.3 Tuning Phases for Control of Lattice Compound Structure

Figure 5-2(a) shows the interference pattern assuming the initial phase for all four beams to be zero or \( 2n\pi \) (\( n \) is an integral number). The lattice symmetry is hexagonal, and lattice constants in \( x \) or \( y \) direction are \( a \) and \( b \), respectively, as labeled in the Figure 5-2(a). The distance between the closest neighbors is also \( b \). A relatively weak pattern appears among the high intensity patterns.
5.3.1 Phase Tuning \( K_2 \)

We begin by changing the phase of wave vector \( K_2 \) when we tune the phase of beam 2 by a phase delay, the relative intensity strength will change as shown in the Figure 5-2. When the phase delay is \( \pi/2 \) or \( 2n\pi + \pi/2 \), the weak pattern picks up intensity and has almost the same intensity as the others (see Figure 5-2(b)). As shown in Figure 5-2(c), the weak intensity pattern and the strong intensity pattern switch their intensity distribution when the phase delay is \( \pi \) or \( 2n\pi + \pi \). We can understand the interference pattern shifting through the following explanations [108-109]. The interference pattern can be assumed to be formed by combining the simple lattice formed without beam 2 (i.e. beams 1, 3 and 4) with simple lattices formed with beam 2 (i.e. beams (2, 3, 4), or beams (2, 1, 4), or beams 2, 1, 3)) [26]. By adding the phase delay to beam 2, the interference cross terms of equation 5.3 that involve beam 2 can be expressed as

\[
Q_{1,2} \cos \left[ 2\pi \left( \frac{3}{a} \hat{i} - \frac{1}{b} \hat{j} \right) \cdot (x + y) - \pi \right] \tag{5.4}
\]
\[
Q_{2,3} \cos \left[ 2\pi \left( (0)i + \left( \frac{2}{b} \right)j \right) \cdot (x + y) + \pi \right]
\]

\[
Q_{2,4} \cos \left[ 2\pi \left( \left( \frac{1}{a} \right)i + \left( \frac{1}{b} \right)j \right) \cdot (x + y) + \pi \right]
\]

\[
Q_{1,2} \cos \left[ 2\pi \left( \left( \frac{3}{a} \right)i - \frac{1}{b}j \right) \cdot (x + y + \frac{a}{4}i + \frac{b}{4}j) \right]
\]

\[
Q_{2,3} \cos \left[ 2\pi \left( \left( \frac{0}{i} \right)i + \left( \frac{2}{b} \right)j \right) \cdot (x + y + \frac{a}{4}i + \frac{b}{4}j) \right]
\]

\[
Q_{2,4} \cos \left[ 2\pi \left( \left( \frac{1}{a} \right)i + \frac{1}{b}j \right) \cdot (x + y + \frac{a}{4}i + \frac{b}{4}j) \right]
\]

In above expressions, the phase delay is transferred to the lattice shifting \( r_s \) through \(( k_i - k_j ) \cdot r \pm \pi = ( k_i - k_j ) \cdot ( r + r_s ) \), where \( r_s = (0.25a, 0.25b) \) or \( r_s = (0.25a, 1.25b) \) (\( a \) and \( b \) are the lattice constants in \( x \) and \( y \) directions, respectively). (0.25\( a \), 1.25\( b \)) is equivalent to (0.25\( a \), 0.25\( b \)) in the periodic lattice. Thus, part of the interference pattern is shifted to the (1, 1) direction and thus the intensity is added to the weak intensity part of dumbbell shape pattern. The shift of pattern also switches the intensity distribution in Figure 2(c) as compared with Figure 1(a). If the phase delay is 0.5\( \pi \), \(( k_i - k_j ) \cdot r \pm 0.5 \pi = ( k_i - k_j ) \cdot ( r + r_s ) \) gives \( r_s = (0.125a, 0.125b) \) or \( r_s = (-0.125a, -0.125b) \). The shifts of patterns in (1, 1) and (-1, -1) directions split the overall pattern into dipole structures as shown in Figure 5-2(b).

Experimentally, it is hard to insert the liquid crystal device in the path of beam 2 because of the limited space between beams 2 and 4. We performed the phase tuning by inserting a glass cover slip into beam 2. By the rotating the cover slip, the beam travels a different optical path.
distance, thus introducing a phase delay in the beam. The introduced phase delay $\Delta \delta$ as a function of the glass cover slip rotation angle $\beta$ can be described as [53],

$$
\Delta \delta(\beta) = \frac{2\pi}{\lambda} \left\{ \frac{d}{\cos \alpha} [n_{\text{glass}} - n_{\text{air}} \cos(\beta - \alpha)] - (n_{\text{glass}} - n_{\text{air}})d \right\}
$$

(5.6)

Where $\alpha$ is the refraction angle in glass, $n$ is the refractive index, $\lambda$ is the incident wavelength and $d$ is the glass thickness which is 130 microns. Figure 5-3(a) shows the AFM topography of the fabricated interference structures when the rotation angle is zero. The pattern can be described as two sets of 2D hexagonal photonic crystals (or compound photonic crystal [24-26]). Inset is a simulated pattern which is generated by assuming a phase delay of $0.25 \pi \text{ in beam 2}$. The agreement between the simulation and the AFM is very good. The increasing intensity in the middle part of the weak dumbbell shape pattern can also be verified in the surface profile of the AFM as shown in Figure 5-3(b). Although the rotation angle is zero, the thickness of the slide itself has introduced $0.25 \pi$ or $2n\pi + 0.25 \pi$ phase delay in the beam 2. From the Figure 5-3(b), the periodicity $q$ is measured to 1.42 microns. Theoretically, $b = \lambda / (\sin \theta \sin 60) = 1.51$ microns, when the incident angle is 78 degrees thus the interfering angle relative to z-axis is 24 degrees. The discrepancy between theoretical and measured periodicity might be due to angle accuracy. Figure 5-3(c) shows the 3D view of the measured AFM. It clearly shows the two sets of lattices with different heights.

When the rotation angle of the cover slip is increased to 3 degrees, approximately $0.25 \pi$ phase delay is added into beam 2 relative to the case with zero rotation angle. Thus, a total of $2n\pi + 0.25 \pi + 0.25 \pi$ phase delay is added to beam 2. Figure 5-4(a) shows the AFM topography
of the fabricated interference pattern structures. Dipole structures are clearly shown. Figure 5-4(b) shows the surface profiles along the red and blue lines in (a). The red curve in the figure 5-4(b) indicates an equal height for the dipole in (a). The measured periodicity is 1.43 micron, very close to the value measured in Figure 5-3(b). Figure 5-4(c) shows 3D view of the AFM image. Nano-dipole structures are observed but the non-uniformity is also observed. It is caused by the non-uniform thickness of the glass slide cover slip and dust on the glass surface. In the next section, sample uniformity is greatly improved when using a commercial liquid crystal phase retarder for the phase tuning.

Figure 5-3 (a) AFM topography of the fabricated 2D compound photonic crystal structures in DPHPA when the rotation angle is zero degree. Inset is a simulated pattern for comparison. (b) A surface profile measured along the lines in the AFM image. (c) 3D view of the AFM as in (a).

Figure 5-4 (a) AFM topography of the fabricated 2D compound photonic crystal structures in DPHPA when the rotation angle is 3 degrees. (b) A surface profile measured along the lines in the AFM image. (c) 3D view of the AFM in (a).
5.3.2 Phase Tuning $K_1$

When the initial phase of beam 1 is delayed by $\pi$ or $2n\pi+\pi$ related to other beams, the interference will have a dual-basis hexagonal lattice pattern [51-52]. Because the beam 1 is isolated from other three beams by two empty spots (without silicon chips) in the hexagonal optical element, we are able to insert a commercial liquid crystal variable phase retarder (LCR-1-vis, Thorlabs) into beam 1 so that the phase delay will be accurately controlled by changing the voltage across the liquid crystal. As it will be seen, the pattern shift caused by the phase delay of $\pi$ in beam 1 is similar to the one caused by phase delay of $\pi/2$ in beam 2. The shift is determined by the interference cross terms from equation 5.3 that involve beam with wave vector $k_1$: 

$$Q_{1,2} \cos \left[ 2\pi \left( \frac{3}{a} \hat{i} - \frac{1}{b} \hat{j} \right) \cdot (x + y) + \pi \right] \quad (5.4)$$

$$Q_{1,3} \cos \left[ 2\pi \left( \frac{3}{a} \hat{i} + \frac{1}{b} \hat{j} \right) \cdot (x + y) + \pi \right]$$

$$Q_{1,4} \cos \left[ 2\pi \left( \frac{4}{a} \hat{i} + (0) \hat{j} \right) \cdot (x + y) + \pi \right]$$

$$Q_{1,2} \cos \left[ 2\pi \left( \frac{3}{a} \hat{i} - \frac{1}{b} \hat{j} \right) \cdot (x + y + \frac{a}{8} \hat{i} - \frac{b}{8} \hat{j}) \right] \quad (5.5)$$

$$Q_{1,3} \cos \left[ 2\pi \left( \frac{3}{a} \hat{i} + \frac{1}{b} \hat{j} \right) \cdot (x + y + \frac{a}{8} \hat{i} + \frac{b}{8} \hat{j}) \right]$$

$$Q_{1,4} \cos \left[ 2\pi \left( \frac{4}{a} \hat{i} + (0) \hat{j} \right) \cdot (x + y + \frac{a}{8} \hat{i} \pm \frac{b}{8} \hat{j}) \right]$$

From these equations, the shift occurs in (1, 1) and (1 -1) directions. Figure 5-5(a, b) shows the simulated interference pattern for phase delay of zero and $1\pi$ in beams. A shift of pattern in y direction is noticeable by comparing Figure 5(a) with (b). By tuning the phase of beam 1, the
holographic pattern will repeat itself after $2\pi$ phase delay relative to other, as shown in Figure 5-5(c).

![Four beam interference pattern with beam 1 phase delayed by 0 $\pi$ (a), 1 $\pi$ (b), and 2 $\pi$ (c). Color bar indicates intensity decreases from the top color to the bottom color.](image)

Figure 5-5 Four beam interference pattern with beam 1 phase delayed by 0 $\pi$ (a), 1 $\pi$ (b), and 2 $\pi$ (c). Color bar indicates intensity decreases from the top color to the bottom color.

Figure 5-6(a) and (b) show the AFM images of fabricated structures when beam-1’s phase shift is zero and 2.286V voltage is applied on the liquid crystal, respectively. The 2.286V voltage across the liquid crystal can introduce approximate 0.8 $\pi$ phase shift for the laser beam. In both Figures, the same sample surface area of 14x14 $\mu$m² is scanned for the AFM images. Single motif in a hexagonal lattice is observed in Figure 6(a) while dual motifs in a hexagonal lattice are obvious in Figure 5-6(b). From these images, we are confident that the current single reflective optical element has the ability to define a compound lattice with local twin motifs at each site of the hexagonal lattice.

![AFM topography of the fabricated 2D photonic crystal structures in DPHPA with single motif in a hexagonal lattice. (b) AFM topography of the fabricated 2D compound photonic crystal structures in DPHPA.](image)

Figure 5-6 (a) AFM topography of the fabricated 2D photonic crystal structures in DPHPA with single motif in a hexagonal lattice. (b) AFM topography of the fabricated 2D compound photonic crystal structures in DPHPA.
5.4 Holographic Fabrication of Nano-Antenna Templates

In previous sections, choosing to pattern the interference in a negative resist has the compound photonic crystals are formed at interference intensity maxima regions. In this section, we study nano-antenna templates appeared at the intensity minima regions of the laser interference pattern.

If we used a positive resist the intensity minima regions would remain and leave isolated nano-antenna templates.

5.4.1 Holographic Fabrication in Negative Resist

A 532 nm laser (Cobalt Samba) was used for the laser exposure on the negative photoresist. It was incident onto silicon surface at 76 degrees, close to the Brewster angle of 76.5 degrees. The photoresist was a mixture of the following components in the specified weight concentrations: dipentaerythritol penta/hexaacrylate (DPHPA) monomer (Aldrich, 88.46%), a photo initiator rose bengal (0.2%), co-initiator N-phenyl glycine (NPG, 0.8%), and chain extender N-vinyl pyrrolidinone (NVP, 10.54%) [10]. The mixture was spin-coated on a glass slide with a speed of 3000 rpm for 30 seconds. The photoresist film was exposed to the interference pattern formed from the reflected beams from the silicon ROE. The laser power was 150mW, and a typical exposure time was 4 seconds. The exposed sample was developed in PGMEA for 3 minute, rinsed by isopropanol for one minute and left to dry in air.
Figure 5-7 Simulated four beam interference patterns when the phase delay of beam-1 is 0 \( \pi \) (a) and 1\( \pi \) (b) relative to the other three beams. Color bar indicates the intensity drops from top to the bottom. (c-d) SEM images of fabricated nano-antenna templates in DPHPA corresponding to the simulated patterns in (a-b), respectively. The white ellipses in the Figures are for the eye-guidance.

Figure 5-7 (a-b) shows simulated four beam interference patterns when the phase delay of beam-1 is 0 \( \pi \) (a) and 1\( \pi \) (b) relative to the other three beams. (The dark red color is for high intensity region while the dark blue color is low intensity region). The intensity of four beams was set to be equal by selecting an incident beam with circular polarization. The simulations forms dual-lattice structure in Figure 5-7(b) and single-lattice structures in Figure5-7(a), both of which are in agreement with the results from spatial light modulator based interference patterns [67,110]. Figure 5-7(e-f) shows SEM images of fabricated structures in DPHPA corresponding to the beam-1’s phase delay of 0 \( \pi \) (e) and 1\( \pi \) (f) relative to the other three beams. Figure 5-7 (c-d) shows simulated four beam interference patterns when the phase delay of beam-1 is 0 \( \pi \) (c) and 1\( \pi \) (d) relative to the other three beams. The intensity of four of the four beams was not equal . This was accomplished by using an elliptically polarized incident beam. As will be explained in
section 5.5 the gap size is able to be increased by using an elliptical polarization that results in the reflected beam with intensity ratios of ratio \((I_1 \times I_4)/(I_2 \times I_3) = 5.1\) where \(I_1:I_2:I_3:I_4 = 2.5:1:1:2.5\). In a negative resist a longer development and shorter exposure time will remove more of this larger nanogap leaving behind only a thin separator between the low intensity regions. Figure 5-7(g-h) shows SEM images of fabricated structures in DPHPA corresponding to the beam-1’s phase delay of \(0 \pi\) (g) and \(1\pi\) (h) relative to the other three beams. As this intensity ratio predicts the centers of the weakest intensity are further apart than if circularly polarized light would be. To diminish the nanogap size the exposed structure required longer development and shorter exposure times.

5.4.2 Holographic Fabrication in Positive Resist

GaAs was used in the ROE to reflect the laser beam and select the polarization of the reflected beam for the fabrication in positive resist. 457.9 nm with a power of 1.35 W from an Innova Sabre Ar ion laser (Coherent Inc.) was incident onto GaAs surface at 78 degrees. At the laser wavelength of 457.9 nm, the GaAs refractive index is 4.71 and the Brewster angle for GaAs is 78 degrees. Thus the reflected beams are mainly s-polarized.

A modified photoresist was prepared by mixing equal parts of positive resist S-1805 (Shipley) and PGMEA (Microposit: SU8 developer) and stirred with a magnetic stir bar at 90-120 rpm for 24 hrs. Before spin-coating the resist, PGMEA was spin-coated on glass-slide substrate at 6000rpm for 30s. Then the diluted positive photoresist was spin-coated onto the glass-slide at 6000rpm for 30s. The sample was then prebaked on a hotplate at 120C for 90s then allowed to cool slowly to room temperature.
Figure 5-8 Simulations of inverted four beam interference patterns when the phase delay of beam-1 is 0 \( \pi \) (a) and 1\( \pi \) (b) relative to other three beams. (c, d) SEM images of fabricated nano-antenna templates in positive resist corresponding to the simulated patterns in (a, b), respectively. The red and white ellipses in the figures are for eye-guidance.

To reduce backscattering the samples were placed on a glass cube and index matching oil (glycerol) was used during exposures. Most successful samples had typical exposure times of 2.45-2.65 seconds. Before development, the index matching oil was wiped away using paper towels soaked with isopropyl alcohol.

Exposed samples were then developed via submersion in 2 separate concentrations of diluted MF-319 (Microposit) developer. The developer was diluted using deionized water and concentrations are written as ratio (MF: H\(_2\)O). Exposed samples were developed for 20 seconds in (1:0) concentration of developer then immediately moved to a concentration of (3:1) and allowed to develop an additional 60 seconds. The samples were then rinsed by submerging them in deionized water for 60s. The samples were then dried using a nitrogen gun.

As discussed later, the nano-gap size between bow-tie of the di-pole can be controlled by the intensity ratio of \((I_1\times I_4)\) over \((I_2\times I_3)\). To demonstrate the effectiveness of ROE approach, the elliptically polarized laser was incident onto the ROE. By rotating the ROE and monitoring the
interference pattern in CCD camera, an intensity ratio \(\frac{I_1 \times I_4}{I_2 \times I_3} = 2.15\) was selected and used for holographic lithography. Figures 5-8(a,b) show the simulations of inverted interference pattern (i.e. 1 minus the normalized interference intensity) when the phase delay of beam-1 is 0 \(\pi\) and 1\(\pi\) relative to other three beams, respectively. The patterns shown in the figures are actually low-intensity regions where positive resist will remain after receiving laser exposure. Dipole patterns are expected in Figure 5-8(a) while tri-pole patterns in Figure 8(b).

![Figure 5-9 (a) Atomic force microscope (AFM) images of fabricated nano-antenna templates in positive resist. (b) AFM profile measured along the red line in (a).](image)

Figures 5-8(c,d) show SEM images of fabricated di-pole and tri-pole structures corresponding to the simulated patterns in Figure 5-8(a,b), respectively. The red and white ellipses were drawn as eye-guidance for di-pole and tri-pole structures. The SEM images look the same as the simulated structures, indicating the effectiveness of ROE approach. Figure 5-9(a) shows an atomic force microscope (AFM) image of the fabricated di-pole nano-antenna template in positive resist and Figure 5-9(b) shows AFM profile measured along the red line in (a). As seen from Figure 5-9(b), the thickness of one arm of the dipole is higher than the other, indicating that the phase shift of beam-1 relative to other beams is not exactly 0 \(\pi\) (or 2\(n\pi\)). Distance between
two dipoles along the red was measured by AFM to be 2.26 µm, compared with 2.21 µm measured by SEM and theoretical value of 2.25 µm. The dipole size measured by AFM is 740 nm, compared with 730 nm measured by SEM. The gap between bow-tie of the dipole is measured to 218 nm by AFM, compared with 220 nm measured by SEM.

5.5 Tuning the Nanogap through an Elliptically Polarized Incident Beam

As shown in Figure 5-10(a), the polarization of incident laser onto the ROE can be linearly, circularly or elliptically polarized by controlling the rotation of quarter wave-plate. Figure 5-10(a) shows the orientation of an elliptical laser where the endpoint of the electrical field vector traces an ellipse as it is rotated around. The major axis of the ellipse forms an angle of β relative to the line linking beam 1 and beam 4 as shown in Figure 510(b).

Figure 5-10 (a) Illustration of ellipse traced out by the rotating endpoint of the electrical field vector of the incident laser. (b) The orientation of the ROE relative to the major axis of the ellipse in (a) makes an angle of β. (c) Simulated interference patterns when circularly polarized laser is incident onto the ROE. The white rectangle indicates the location of intensity modulation related to the gap-size. Color bar indicates an intensity drop from top to bottom. Simulated four-beam interference patterns when the orientation angle β of the ROE relative to the major axis of the ellipse is 90 (d), 0 (e) and 45 degrees (f).
The nano-gap size between two arms (bow-tie) of the nano-antenna dipole can be controlled by the ellipticity and rotation angle $\beta$ as explained below. When circularly polarized laser is incident onto the ROE with an orientation in Figure 5-10(b) all side arm amplitudes are equal (i.e. $E_1 = E_2 = E_3 = E_4$). The intensity ratio for this case is $(I_1 \times I_4)/ (I_2 \times I_3) = 1.0$. The nano-gap size between two arms (paired white dots in Figure 5-10(c)) is determined by the intensity modulation inside the white rectangle. Intensity modulation in the horizontal direction of the interference pattern (Figure 5-10(c)) is determined by the ratio of $E_1E_4$ over total intensity. When the major axis forms an angle of 90 degrees, $E_1$ and $E_4$ have strengths smaller than $E_2$ and $E_3$. For example, Figure 5-10(d) shows an interference pattern for intensities $I_1:I_2:I_3:I_4=1:2.5:2.5:1$. The intensity ratio $(I_1 \times I_4)/(I_2 \times I_3)=0.16$. As seen in the simulation, the two arms of dipole are linked together and the nano-gap is closed. When the major axis forms an angle of 0 degrees, $E_1$ and $E_4$ have strengths larger than $E_2$ and $E_3$. Figure 5-10(e) shows a simulation for four beam interference pattern when $I_1:I_2:I_3:I_4=2.5:1:1:2.5$. The intensity ratio $(I_1 \times I_4)/(I_2 \times I_3)=6.25$. The nano-gap opens up in Figure 5-10(e) more than that in Figure 5-10(c), as judged with the help of color bar. When the rotation angle $\beta=45$ degrees, $E_1$ and $E_4$ have strengths larger than $E_2$ but smaller than $E_3$. For the case of $I_1:I_2:I_3:I_4=1:0.75:1.5:1$, the interference pattern is shown in Figure 5-10(f). The intensity ratio for this case is $(I_1 \times I_4)/ (I_2 \times I_3) = .89$. The nano-gap size is smaller than that of the $\beta=0$ intensity pattern of Figure 5 (e) but larger than that of the $\beta=90$ figure 5-10(d) intensity pattern that completely closes the gap. As can be seen by comparing with Figure 5-10(c) whose intensity ratio is 1.0, the smaller intensity ratio of 0.89 produces a smaller gap size as judged with the help of color bar.
CHAPTER 6
FUNDAMENTALS OF PLASMONICS

Surface plasmon polaritons (SPPs) are coupled photon and electron oscillations that exist at the interface between dielectrics and metals. SPP-based plasmonics has emerged recently as a promising and fast-moving research area for applications in broad areas from surface enhanced Raman sensing [111] to energy harvesting (e.g. solar cells) [112], and plasmonic waveguides [113], plasmon lasers [114] and modulators [115].

6.1 Surface Plasmon Polaritons

To gain some insight into surface plasmon polaritons, we first consider the general dispersion relation of a single interface between two media with permittivity and permeability given by $\varepsilon_{1,2}$ and $\mu_{1,2}$ that gives bound modes (surface electromagnetic waves).

Figure 6-1 Light incident, reflected and transmitted at the interface of two materials
The scattering matrix relates the amplitude of the forward going and backward going incident and scattered fields of a system[116-117]. For the system comprising a single interface between two media, as shown in figure 6-1, the scattering matrices can be written as

\[
\begin{pmatrix}
E_{1(s,p)}^- \\
E_{2(s,p)}^+
\end{pmatrix} = S
\begin{pmatrix}
E_{1(s,p)}^+ \\
E_{2(s,p)}^-
\end{pmatrix} = \begin{pmatrix} r_{s,p} & t_{s,p} \end{pmatrix}
\begin{pmatrix}
E_{1(s,p)}^+ \\
E_{2(s,p)}^-
\end{pmatrix}
\]

(6.1)

where \(E_{i(s,p)}^+\) & \(E_{i(s,p)}^-\) are the forward and backward going (in the z-direction) electric field amplitudes for s- or p-polarized (TE- or TM-polarized) light in the \(i\)th medium respectively, \(S\) is the scattering matrix, and \(r_{s,p}\) and \(t_{s,p}\) are the Fresnel reflection and transmission amplitudes for a single interface.

We write the Fresnel coefficients in terms of the normal component of the wave vector in the \(i\)th medium \(k_{zi}\)

\[
\begin{align*}
  r_p &= \frac{k_{z2} - k_{z1}}{k_{z2} + k_{z1}} \frac{\varepsilon_2}{\varepsilon_1} \\
  t_p &= \frac{2k_{z2}}{k_{z2} + k_{z1}} \frac{\varepsilon_2}{\varepsilon_1} \quad (p\text{ polararization})
\end{align*}
\]

(6.2)

\[
\begin{align*}
  r_s &= \frac{\mu_2}{k_{z2} + \mu_1} \frac{k_{z1}}{k_{z2}} \\
  t_s &= \frac{2\mu_2}{k_{z2} + \mu_1} \frac{k_{z2}}{k_{z1}} \quad (s\text{ polararization})
\end{align*}
\]

(6.3)

where

\[
k_{zi} = \sqrt{n_i^2 k_0^2 - k_x^2}
\]

(6.4)

and \(k_0\) is the free space wave vector, \(k_x\) is the in plane wave vector and \(n_i = \sqrt{\varepsilon_i\mu_i}\) is the index of refraction for the \(i\)th layer.
For bound modes, we note that the poles of the scattering matrix occur when the
determinant of its inverse is zero. Therefore, for this scenario it requires that the denominator of
the reflection and transmission coefficients to vanish giving the dispersion relations for the bound
modes of the system to be,

\[
\frac{k_{z2}}{\varepsilon_2} = \frac{k_{z1}}{\varepsilon_1} \quad p \text{ polarization} \tag{6.5}
\]

\[
\frac{\mu_2}{k_{z2}} = -\frac{\mu_1}{k_{z1}} \quad s \text{ polarization} \tag{6.6}
\]

Substituting equation 6.4 into equation 6.5 and 6.6 allows the dispersion relation to be
written as

\[
k_x = k_0 \sqrt{\frac{\varepsilon_1 \varepsilon_2 (\varepsilon_1 \mu_2 - \varepsilon_2 \mu_1)}{\varepsilon_1^2 - \varepsilon_2^2}} \quad p \text{ polarized} \tag{6.7}
\]

\[
k_x = k_0 \sqrt{\frac{\mu_1 \mu_2 (\mu_1 \varepsilon_2 - \mu_2 \varepsilon_1)}{\mu_1^2 - \mu_2^2}} \quad s \text{ polarized} \tag{6.8}
\]

If the bounding media are both nonmagnetic ($\mu_1 = \mu_2 = 1$) then equation 6.7 simplifies
further to the more common form of the dispersion relation of p- polarized surface
electromagnetic waves.

\[
k_x = k_0 \sqrt{\frac{\varepsilon_1 \varepsilon_2}{\varepsilon_1 + \varepsilon_2}} \tag{6.9}
\]

It is worthwhile to note there is no equivalent solution to Eq. (2.8) for materials with no
magnetic response, indicating that only p-polarized surface waves can exist on such surfaces. The
opposite is true for interfaces between materials with no electric response, which support only s-polarized surface waves.

Also, in order for the mode to be bound to the surface the normal component of the wave vector in each medium equation 6-4 must be imaginary (otherwise power would propagate away from the surface), requiring \( k_x > n_i k_0 \) and only an interface bounded by media with combinations of \( \varepsilon_{1,2} \) and \( \mu_{1,2} \) that satisfy this condition can support surface electromagnetic waves. For example, a p-polarized surface wave excited at the interface between non-magnetic media requires \( \varepsilon_1 \) and \( \varepsilon_2 \) to have opposite signs. Also note that, since \( \varepsilon_{1,2} \) and \( \mu_{1,2} \) are in general complex, the resulting in-plane wave vector will also be complex \( k_x = k'_x + ik''_x \).

Having now determined the dispersion relation for surface electromagnetic waves we are in a position to understand their character. From Maxwell’s equations we can simply determine the electric and magnetic field profiles in each half space, and these are given by:

\[
E_1 = E_x \left[ 1, 0, \frac{k_x}{k_{z1}} \right] e^{i(k_x x + k_{z1} z - \omega t)}
\]

(6.10)

\[
E_2 = E_x \left[ 1, 0, \frac{k_x}{k_{z2}} \right] e^{i(k_x x - k_{z2} z - \omega t)}
\]

(6.11)

\[
H_1 = E_x \left[ 1, \frac{\omega \varepsilon_1}{k_{z1}}, 0 \right] e^{i(k_x x + k_{z1} z - \omega t)}
\]

(6.12)

\[
H_2 = E_x \left[ 1, -\frac{\omega \varepsilon_2}{k_{z2}}, 0 \right] e^{i(k_x x - k_{z2} z - \omega t)}
\]

(6.13)

where \( E_i \) & \( H_i \) are the electric and magnetic fields in the \( i \)th medium, \( \omega \) is the angular frequency, and \( E_x \) is the tangential electric field strength at the interface. Since, in general, both \( k_x \) & \( k_z \) are complex, these equations describe the fields of an inhomogeneous plane wave of mixed transverse and longitudinal character. In other words, surface electromagnetic waves consist of
field components both in the direction of the propagating wave vector (longitudinal) and
perpendicular to the propagating wave vector (transverse), and have planes of constant phase
and amplitude that are no longer co-planar and therefore the fields are inhomogeneous.

From the electric and magnetic fields we can define the decay length in the direction of
propagation as the distance over which the field intensity decays to 1/e of its original value ($L_x$),
while the decay lengths normal to the interface are defined as the distance over which the field
amplitude decays to 1/e of its maximum value (at the interface) in the $i$th medium ($L_{zi}$). From
the magnitudes of equations 6.1-6.13 get their values to be,

$$L_x = \frac{1}{2k_x''}$$  \hspace{1cm} (6.14)

$$L_z = \frac{1}{k_{zi}'}$$  \hspace{1cm} (6.15)

When we specify the two materials that satisfy the surface electromagnetic wave (SEW)
conditions as a dielectric and a metal, the SEW takes the more common known Surface Plasmon
Polariton (SPP) as a free photon in the dielectric couples with the metal bulk plasmons to form
a polariton. This wave was type of wave that was first observed and recorded by Wood in 1902
[118] to describe the

By plotting in Figure 6-2 the dispersion relation of equation 6.9 we are able to see the
conditions for the types of modes that exist. We plot the dispersion relation in the manner in
which it is frequently presented—by describing the frequency dependent permittivity of the
metal with a Drude model with no dampening term. (which will be fully explained in the
subsequent subsection of this chapter). For $\omega < \omega_{sp}$ the dispersion relation of the SPP closely
follows the light-line (the maximum in-plane wave vector available to a freely propagating photon of frequency $\omega$ which very similar the dispersion relation for a weakly bound photon grazing the surface). As the frequency of the SPP approaches the surface plasma frequency ($\omega_{sp} = \frac{\omega_p}{\sqrt{1 + \varepsilon_d}}$) [119] the dispersion relation of the SPP moves further away from the light-line; the mode becomes more tightly bound to the surface, and the longitudinal character of the mode begins to dominate such that the mode more closely resembles a “pure” surface plasmon. Above this frequency there is a gap in the solution to Eq. (6.9) (between $\omega_{sp}$ and $\omega_p$), before the upper branch, which corresponds to the Brewster angle, and is not a bound surface wave, begins. This simplified model ignores losses which are important to fully understand the physical components to SPP.

![Surface plasmon dispersion relation](image)

Figure 6-2 Plot of frequency vs Real in plane wave vector of a surface plasmon [120]
6.2  Excitation of Surface Plasmon Polaritons

Because the surface plasmon dispersion is below the photon dispersion (Figure. 6-2) for all energies, it is clear that surface plasmon cannot be excited by plane waves incident on the interface from the dielectric side because regardless of the angle of incidence, the surface plasmon modes of the same frequency have a larger momentum. In order to excite surface plasmon, additional momentum has to be somehow provided. In practice, this is usually done either by placing a regular grating structure at the interface (which also disturbs the plasmon mode) [120] or by letting the excitation light pass through a medium with a high refractive index (e.g. a prism).

For a grating coupled SPP at the interface of a metal and dielectric surface the dispersion relation is given by

$$k_{SPP} = \frac{\omega}{c} \sqrt{\frac{\varepsilon_m \varepsilon_d}{\varepsilon_m + \varepsilon_d}} \pm \frac{2\pi}{\Lambda}$$

(6.16)

In the high refractive index case, the excitation light can either come from the side of the dielectric (so-called Otto-configuration [121]) or from the metal side (Kretschmann configuration [122]) as seen in Figure 6-3. In the Otto configuration, there has to be a small gap between the dielectric and the metal surface, because otherwise the surface plasmon dispersion would also be altered. In the Kretschmann configuration the metal film has to be very thin in order to allow the light field to reach through the film. Near Field Scanning Microscopy (NSOM) excites the SPP in at the near field regime [123]. Excitation is also possible from scattering of the local field by surface features.
Figure 6-3 Methods of SPP excitation: (a) Kretschmann configuration, (b) two-layer Kretschmann configuration, (c) Otto configuration, (d) excitation by a SNOM tip, (e) diffraction on a grating, (f) diffraction on surface features, (g) diffraction on the edge [120].

To finally determine the SPP waveform it is required that we define the dielectric and metal on which this wave occupies at their interface. To do so the majority of material characterization done was done by utilizing the Drude-Lorentz models.

6.3 Lorentz Model for Dielectrics

For dielectric media the Lorentz oscillator model is used to describe the optical properties. The Lorentz oscillator model is used to describe the interaction between atoms and electric fields in classical terms, Lorentz proposed that the electron is bound to the nucleus of the atom by a force that behaves according to Hooke’s Law. An applied electric field would then interact with
the charge of the electron, causing “stretching” or “compression” of the spring, which would set
the electron into oscillating motion. [124].

The bound electron can be considered to have the equation of motion

\[ m \frac{d^2 \vec{r}}{dt^2} + m \Gamma_o \frac{d\vec{r}}{dt} + m\omega^2 \vec{r} = -e\vec{E} \]  

(6.17)

where \( m \) is the mass of the electron, \( \Gamma_o \) is the dampening factor, \( \vec{E} \) is the localized driving field.

\( m \frac{d^2 \vec{r}}{dt^2} \) is the acceleration force, \( m \Gamma_o \frac{d\vec{r}}{dt} \) is the dampening force, and \( m\omega^2 \vec{r} \) is the restoring force, with resonant frequency of \( \omega_i \). The solution to this equation yields the expression for the amplitude of the oscillations in terms of the photon energy \( \omega \).

\[ \vec{r}(\omega) = \frac{1}{m} \left( \frac{-e\vec{E}}{(\omega^2_i - \omega^2) + i\Gamma_o \omega} \right) \]  

(6.18)

The induced dipole moment is related to \( \vec{r}(\omega) \) by the relation

\[ \vec{\mu}(\omega) = -e \cdot \vec{r}(\omega) = \frac{1}{m} \left( \frac{-e^2\vec{E}}{(\omega^2_i - \omega^2) + i\Gamma_o \omega} \right) \]  

(6.19)

And the polarizability \( \alpha(\omega) \) is given by \( \vec{\mu}(\omega) = \alpha(\omega)\vec{E} \) thus

\[ \alpha(\omega) = \frac{1}{m} \left( \frac{-e^2}{(\omega^2_i - \omega^2) + i\Gamma_o \omega} \right) \]  

(6.20)

Taking the sum of the single atom dipole moment over all atoms in a volume, it comes out that

the polarization per unit volume is given by

\[ P(\omega) = N \cdot \alpha(\omega) \cdot E(\omega) = \varepsilon_0 \cdot \chi(\omega) \cdot E(\omega) = \varepsilon_0 \cdot (\varepsilon(\omega) - 1)E(\omega) \]  

(6.21)

With the resulting expression for the dielectric permittivity as,

\[ \varepsilon(\omega) = 1 - \left( \frac{Ne^2}{\varepsilon_0 m} \right) \left( \frac{1}{(\omega^2_i - \omega^2) + i\Gamma_o \omega} \right) = 1 - \left( \frac{\omega_p^2}{(\omega^2_i - \omega^2) + i\Gamma_o \omega} \right) \]  

(6.22)

Here the factor inside the first parenthesis is the plasma frequency squared.
6.4 Drude-Sommerfeld Model for Metals

A simple model for metals was developed by Drude [125] based on the kinetic gas theory. It assumes independent and free electrons with a common relaxation time. Sommerfeld incorporated corrections originating from the Pauli-exclusion principle (Fermi-Dirac velocity distribution). This so-called free-electron model was later modified to include minor corrections from the band-structure of matter (effective mass) and termed quasi-free-electron model. This Drude-Sommerfeld model describes very successfully many properties of metals despite its drastic assumptions. At optical frequencies it often fails due to the presence of interband transitions which must be accounted for in a separate “background permittivity” term.

The basic picture of the properties of metals in the framework of this theory is a gas of independent, point-like electrons. These electrons move freely in between independent collisions with unspecified collision centers (lattice ions, other electrons, defects, phonons, etc.), which occur with an average rate of \( \Gamma_0 = \frac{1}{\tau} \) with \( \tau \) being the so-called electron relaxation time. Each collision leads to a complete loss of directional information and results in a random orientation of the electron velocity afterwards.

In a similar manner that the Lorenz oscillator was derived we can derive the Drude-Sommerfeld model, the only notable difference is that there is no restoring force in this model. The complex dielectric function given by the Drude–Sommerfeld oscillator model is.

\[
\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\Gamma_0 \omega}
\]

with \( \omega_p \) plasma frequency and \( \Gamma_0 \) the electron relaxation rate. \( \varepsilon_\infty \) includes the contribution of the bound electrons to the polarizability and should have the value of 1 if only the conduction band electrons contribute to the dielectric function. The plasma frequency is given by
\[ \omega_p = \sqrt{\frac{e^2 N_e}{\varepsilon_0 m^*}} \]  

(6.24)

where \( e \) is the electron charge, \( m^* \) the effective mass and \( \varepsilon_0 \) dielectric permittivity of vacuum.

The electron relaxation time can be calculated from the DC conductivity \( \sigma \) by \( \Gamma = \sigma m_e / N e^2 \).

The optical properties of metals can be determined experimentally by reflection and transmission measurements on clean surfaces under ultrahigh vacuum conditions. They show a somewhat ambiguous behavior: whereas the low energy values are well described by the Drude-Sommerfeld model, additional contributions are present at higher energies. The reason is the excitation of electrons from deeper bands into the conduction band (interband excitations). In noble metals the electrons originate from completely filled d-bands, which are relatively close to the Fermi-energy. An additional reason for the derivation from the Drude-Sommerfeld behavior is that the conduction band is increasingly non-parabolic for higher energies.

Combining the complex dielectric function given by the Drude and Lorentz models gives us a way to calculate a material that is both conducting and dielectric over the spread of wavelengths from the UV into the near-IR. Throughout this research, the frequencies \( (\omega=2\pi f) \) are converted to energies by the Planck relation \( E = hf \) and given in units of electron volts (eV).

\[ \varepsilon(\omega) = \varepsilon_b - \frac{\omega_p^2}{\omega^2 + i\Gamma_p \omega} + \frac{f_1 \omega_1^2}{\omega_1^2 - \omega^2 - i\Gamma_1 \omega} \]  

(6.25)

The model parameters in Eq. (1) obtained for the AZO film are as follows: \( \varepsilon_b \) is the background permittivity related to the bound inner electrons, \( \omega_p \) is the unscreened plasma frequency, \( \Gamma_p \) is the carrier relaxation rate, and \( f_1 \) is the strength of the Lorentz oscillator with center frequency \( \omega_1 \) and relaxation \( \Gamma_1 \). Here \( f_1 \omega_1^2 \) is the Lorentz unscreened plasma frequency for bound modes.
6.5 Alternative Plasmonic Materials

Typically noble metals such as gold and silver have been used in plasmonic devices, but recently new plasmonic materials with metal-like behavior have attracted a lot of attention due to their promise for low-loss plasmonic applications in the near- and mid-infrared regimes. Transparent conducting oxides (TCOs) [126-127], like indium tin oxide [115,128-130], gallium-doped zinc oxide [131], and aluminum-doped zinc oxide (AZO) [132-133], are a group of alternative plasmonic materials. Because they can be very heavily doped, TCOs exhibit high DC conductivity [126,127]. The free carrier concentration in TCOs can be high enough so that TCOs exhibit metal-like behavior in the near-infrared and mid-infrared ranges [115-137].

In addition to the methods employed to tune the optical properties of noble metals, which include controlling the size, shape and environment [138], the permittivity of TCOs can also be adjusted via doping or electric field induced carrier accumulation, providing great advantages for designing tunable plasmonic devices over conventional metals through electrical tuning [115,128-133,137,139].

Furthermore, TCO based technologies enable low-cost, CMOS-compatible fabrication and integration procedures for plasmonics.
CHAPTER 7
SURFACE PLASMON RESONANCES IN AZO STRUCTURED FILM

In this experiment we studied the surface plasmon resonance (SPR) in hole arrays in transparent conducting aluminum-doped zinc oxide (AZO). CMOS-compatible fabrication process was demonstrated for the AZO devices. The localized SPP resonance was observed and confirmed by electromagnetic simulations. Using a standing wave model, the observed SPP was dominated by the standing-wave resonance along (1,1) direction in square lattices[141-142]. This research lays the groundwork for a fabrication technique that can contribute to the core technology of future integrated photonics through its extension into tunable conductive materials.

7.1 Atomic Layer Deposition of Al Doped Zinc Oxide Film and Characterization

The hole array structure in AZO film began with the deposition of the Al-doped ZnO (AZO) films on glass slides by atomic layer deposition (ALD) using an Ensure Scientific 9200 ALD system. Reaction precursors Trimethylaluminum [(CH₃)₃Al, TMA] and Diethylzinc [(C₂H₅)₂Zn, DEZ] were used respectively as the Al and Zn sources, while H₂O vapor was used as the oxidant. Ultrahigh purity nitrogen was used as the purging gas with a flow rate of 20 sccm. The process pressure was about 10⁻¹ Torr and the substrate temperature was maintained constant at 250 °C during deposition.

The glass substrates were cleaned using standard cleaning procedures prior to being

---

loaded into ALD chamber for deposition, which included cleaning with acetone and alcohol, rinsed by DI water, dried with flowing nitrogen gas, and finally immersed in room temperature plasma for 10 s. In this study, a 4% Al-doped ZnO film was achieved by separating one TMA-water cycle with 24 DEZ-water cycles.

In order to characterize the film, the dielectric function was obtained by spectroscopic ellipsometry (V-VASE, J. A. Woollam). The permittivity of the AZO was measured from an area of un-patterned film near an area of patterned film to take into account changes brought about from wet etching and photoresist prebaking, which will be described in the next section. Since both areas underwent the same lithographic processing they can be expected to have the same optical properties. The complex dielectric function given by Equation 7.1 of the film was obtained by fitting a Drude–Lorentz oscillator model to the ellipsometry data [19].

\[
\varepsilon(\omega) = \varepsilon_b - \frac{\omega_p^2}{\omega^2 + i\Gamma_p \omega} + \frac{f_1 \omega_1^2}{\omega_1^2 - \omega^2 - i\Gamma_1 \omega}
\]  

(7.1)

The model parameters in Eq. (1) obtained for the AZO film are as follows: \( \varepsilon_b = 3.358 \) is the background permittivity, \( \omega_p = 1.450 \text{ eV} \) is the unscreened plasma frequency, \( \Gamma_p = 0.139 \text{ eV} \) is the carrier relaxation rate, and \( f_1 = 0.701 \) is the strength of the Lorentz oscillator with center frequency \( \omega_1 = 2.253 \text{ eV} \) and relaxation \( \Gamma_1 = 0.688 \text{ eV} \).

7.2 Lithographic Fabrication of Array Structure on AZO Film

Two-beam holographic lithography was used to form the patterned array of cylindrical holes on a positive resist which is later used as a template for wet etching the holographic pattern into the deposited AZO film. A laser beam of wavelength 457.9 nm and a power of 1.0 W from
an Innova Sabre Ar ion laser (Coherent Inc.) was passed through a $\lambda/2$ wave plate, spatially filtered and collimated. This linearly polarized beam was then passed through a beam splitter and the two resulting beams were redirected with mirrors to overlap with an angle of $2\theta=17.5^\circ$ between them at the sample’s surface. After the first exposure, the sample was rotated 90 degrees for a second exposure. Each exposure of this two beam configuration produces a sinusoidal line grating, and when orientated perpendicular to each other, produce a square lattice of cylindrical holes.

Figure 7-1  (a) Wet etching depth into AZO as a function of etching time. b) Laser diffraction from the AZO structures using 532nm laser and c) AFM images of fabricated hole arrays on AZO thin film.

A modified photoresist was prepared by mixing equal parts of positive resist S-1805 (Shipley) and propylene glycol monomethyl ether acetate (PGMEA) (Microposit) and stirred with a magnetic stir bar at 100 rpm for 24 hrs. Before spin-coating the resist, PGMEA was spin-coated on glass-slide substrate at 6000 rpm for 30s. Then the modified positive photoresist was spin-coated onto the glass-slide at 6000 rpm for 30s. The sample was then prebaked on a hotplate at 120 °C for 90s and allowed to cool slowly to room temperature. Most successful samples had typical exposure times of 3.45-3.50 seconds.
Exposed samples were then developed via submersion in 2 separate concentrations of diluted MF-319 (Microposit) developer. The developer was diluted using deionized water and concentrations are written as ratio (MF: H₂O). Exposed samples were developed for 45 seconds in (1:0) concentration of developer then immediately moved to a concentration of (3:1) and allowed to develop an additional 60 seconds. The samples were then rinsed by submerging them in deionized water for 120s. The samples were then dried using flowing nitrogen gas.

Wet etching of the holographically patterned AZO was accomplished via submersion of sample in a 4% wt/wt solution of diluted acetic acid, CH₃COOH (distilled white vinegar) and rinsing with deionized water. After certain etching times, the hole depth in the structured AZO was measured by atomic force microscope (AFM) using the contact mode. If necessary after each AFM measurement, the sample was re-submerged in acetic acid for additional etching. Figure 7-1(a) shows the hole depth as a function of etching time. The etching rate was found to be about 80 nm per minute. After a total etching time of 68s, no further increase of depth was observed due to complete etching to the bottom. The transmission spectra between the samples partially etched and completed etched are completely different to each other. The transmission features of the partially etched sample are most similar to that of bare AZO film. Then the positive resist was removed by submersion in ethanol for five hours, and dried using flowing nitrogen gas.

Figure 7-1(b) shows laser diffraction pattern of the holographic structures in AZO using a 532 nm laser. The observation of diffraction orders of (1,0), (1,1), (2,0) and (2,1) as labeled in Figure 7-1(b) indicates a large-area uniformity in the structured AZO. From the diffraction measurement, the period of square lattice was calculated to be 1528 nm. Figure 7-1(c) shows the AFM image of the fabricated structure with hole diameter of 889 nm and thickness of 92 nm. The side wall of
the holes is not vertical due sidewall etching. The 889 nm was obtained using the diameter measured at the bottom of the hole because the SPP happened at the interface between the AZO and the glass substrate as shown later by the simulations. The average period measured by AFM is also near 1528 nm.

7.3 Measured FTIR and FDTD Simulations

FTIR transmission spectrum through the holographically structured AZO, bare AZO film and glass substrate was measured using a Nicolet 6700 spectrometer from Thermo Electron. The results are shown in Figure 7-2(a). The measured FTIR spectra were in units of wave number (cm$^{-1}$) but were converted to wavelength (nm) in order to compare FTIR data with simulation results in Figure 7-2(b) and 7-2(c). The transmission of bare AZO film in the inset in Figure 7-1(a) shows a decreased transmission with increasing wavelength between 2900 nm and 4000 nm, in agreement with the simulation in dark gold in Figure 7-2(c). We did not observe the O-H stretching mode in 3430 cm$^{-1}$ (2915 nm) in the transmission spectrum of bare AZO film. The appearance of the mode at 2915 nm might be caused by the hydrothermal method [143]. For the structured AZO, the transmission in Figure 7-1(a) is increased with increasing wavelength after a dip, similar to the simulations in Figure 7-2(b) and 7-2(c). A 12.6% transmission dip (relative to the value at 3070 nm) centered at 3467 nm is observed for the structured AZO due to the localized SPP resonance as explained below.

In order to understand the transmission spectrum, simulations were performed with the finite-difference time-domain (FDTD) method, using an MIT open source software package MEEP [144]. Accuracy of the simulation was verified by reproducing the spectra of Figure 2 in reference
by L. Wu et al [145]. For the simulation in AZO structures, we used normal incident Gaussian wave propagating in the –z direction with the electric field polarized in the (0,1) direction or in (1,1) direction.

Figure 7-2  (a) FTIR spectra of fabricated hole arrays in AZO at normal incidence. Inset are transmission spectra for bare AZO film and glass substrate. Simulated transmission spectra for fabricated hole arrays with incident light polarized along the (0,1) (b) and (1,1) (c) directions. Simulated transmission for bare AZO film on 200 nm glass substrate is also shown for a comparison.

With the above parameters for the 92 nm AZO layer and structural parameters of 1528 nm periodicity and 889 nm hole diameter for the hole array as input into the FDTD program, MEEP, transmission spectra were obtained. For the best explanation of the FTIR data which was taken with unpolarized light at normal incidence, the average of the simulations with incident light polarized in (0,1) and (1,1) directions can be displayed. But we chose to display them separately due to the different SPP resonance pathways. Figure 2(b) shows the result for the incident light polarized in (0,1) direction. In experiments, the glass substrate has a thickness of 1 mm.
Such large substrate thickness cannot be simulated due to required resolution and resulting increased computing time. However, because the SPP occurs along the interface of AZO and glass substrate, a thin glass thickness can be used. Black solid dots in Figure 2(b) is the transmission spectrum for a glass thickness of 200 nm. A transmission dip centered at 3263 nm appears, away from the experimental location 3487 nm. If the glass thickness is increased from
200 nm, the dip is expected to be red-shifted with an increase of the effective refractive index, $n_{\text{eff}}$, which is given by:

$$
\frac{\varepsilon_{\text{AZO}}\varepsilon_d}{\varepsilon_{\text{AZO}} + \varepsilon_d}
$$

If a thickness of 1000 nm is used, the transmission as represented by red circles in Figure 2(b) shows a 13.8% dip (relative to the data point at 3061 nm) centered at 3412 nm, very close to the experimental location. Additionally, as a quick test for validity, if the plasma frequency is increased to 1.6 eV from 1.45 eV, the effective refractive index $n_{\text{eff}}$ is decreased as expected from Eq. (3) thus the transmission dip is blue-shifted. This is shown in Figure 2(b) by the green dot simulation for hole array structures in AZO with the plasma frequency of 1.6 eV, a glass thickness of 1000 nm, hole diameter of 889 nm and periodicity of 1528 nm.

Figure 2(c) shows the transmission for the incident light polarized in (1,1) direction for a glass thickness of 1000 nm and 200 nm but with the same hole diameter of 889 nm, periodicity of 1528 nm and the plasma frequency of 1.45 eV. Simulated transmission of bare AZO film with the same permittivity on 200 nm glass substrate is also shown for a comparison. In contrast to the results in Figure 2(b), the transmission dip for glass thickness of 200 and 1000 nm is at the same wavelength of 3336 nm. As explained below, the SPP resonance occurs in (1,1) direction and is highly confined in the AZO/glass interface so differences in the glass thickness barely changes the SPP location.

In order to properly understand the SPP resonance, we studied the electric field intensity at different locations for both (0-1) and (1-1) polarizations in Figure 3. The unit cell of hole arrays in AZO generated by MEEP is shown in Figure 3(a) and the labels the periodicity of hole arrays and the hole diameter, P and D, respectively Figures 7-3(b) and 7-3(e) show the E-field intensity
at the location just below the AZO layer in the xy plane near the glass/AZO interface, for incident light polarized in (0,1) and (1,1) directions, respectively. Additionally the red dashed lines numbered #1-#5 and #1-#6 respectively in 7-3(b) and 7-3(e) indicate the location for cross-section views in yz plane which the remaining subfigures represent. Figure 7-3(c) is the yz cross section along line #5 in Figure 7-3(b), representing the simulations’ permittivity and therefore structure, where the green, red and blue regions represent glass, AZO, and air respectively. Figures 7-3(d1-d5) show the E-field intensity in yz plane viewed along the red dashed lines (#1-#5), respectively, of Figure 3(b). Additionally, Figure 7-3(f1-f6) show the E-field intensity in yz plane viewed along the red dashed lines (#1-#6), respectively, of Figure 7-3(e). The white dashed lines in Figure 7-3(d) and 7-3(f) indicate the boundary of the AZO layer.

The SPP resonances occur at the AZO/air interface, around the hole, and AZO/glass interface [146]. Figure 7-3(d3-d5) and 7-3(f3-f6) confirm the electric field enhancement around the hole. Other than the SPP around the hole, only Figure 7-3(d1) shows an E-field confinement in AZO/glass interface for (0,1) polarization. However, for (1,1) polarization, all Figure7-3 (f1-f4) show a strong E-field confinement in AZO/glass interfaces.

7.5 Standing Wave Model

For the AZO and glass (or air) interface, surface plasmon is a wave propagating in the interface with a dispersion relation given by equation (6.16) and rewritten here as

\[ k_{SPR} = \frac{\omega}{c} \sqrt{\frac{\varepsilon_{AZO} \varepsilon_d}{\varepsilon_{AZO} + \varepsilon_d}} + \frac{2\pi}{\Lambda} \quad (7.3) \]
where \( c \) is speed of light, \( \varepsilon_d \) and \( \varepsilon_{AZO} \) are the permittivity of dielectric materials and AZO, respectively. In our periodic holographic structure in AZO, a normal incident light can be coupled with a surface plasmon to form a SPP under the condition of momentum conservation. With above information of E-field intensity distribution, we can identify the region of E-field confinement to be in AZO/glass interface. Figure 7-4(a) and 7-4(b) show the four unit cells of E-field intensity as displayed in Figure 7-3(e) and 7-3(b), respectively with a rectangle drawn in (1,1) direction. The transmission dips can be understood by a mechanism of SPP resonance in the form of standing wave in the pathway and region indicated by the rectangles in (1,1) or (-1,1) directions. The standing wave needs to meet the following equation [147]:

\[
W \frac{2\pi}{\lambda} n_{eff} = m \pi + \phi
\]  

(7.4)

where \( n_{eff} \) is the effective index for the SPP, \( W \) is the propagating length as indicated by the rectangle length in Figure 7-4(a) and 7-4(b), \( m \) is an integer number and \( \phi \) is the phase shift due to the SPP mode reflection. Figure 7-4(c) and 4(d) shows the cross-section view of E-field intensity in yz plane along the (1,0) direction of the unit cell for the incident light with (1,1) polarization and with incident light of (0,1) polarization respectively. Figure 7-4(e) and 4(f) shows the cross-section view of E-field intensity along the diagonal direction of the unit cell for the incident light with (1,1) polarization and with incident light of (0,1) polarization respectively. Based on the E-field intensity in yz planes of Figure 7-3(f4) and Figure 7-4(e), the anti-node of the standing-wave is away from the hole edge by \( W \times 11.7\% \) which corresponds to a phase shift close to \((-3/4)\pi\). The same amount of phase shift was shown for SPPs in graphene[148]. Using Eq. (5), \( m=2, \phi = (-3/4)\pi \), dielectric function obtained from ellipsometry data and \( W = \sqrt{2}P - D \) (where \( P \) and \( D \) are the periodicity of hole arrays and the hole diameter, as labeled in Figure 7-3(a)), our
calculation finds a SPP resonance wavelength at 3458 nm along (1,1) direction as labeled by the
white rectangle in Figure 7-4(a,b) for the hole array structure with P=1528 nm and D=889 nm.
This value of 3458 nm is very close to the transmission dip at 3336 nm at the simulated spectrum
with (1,1) polarization (red circles in Figure 7-4(g)) for AZO structures with P=1528 nm and D=889
nm.

Figure 7-4 Four unit-cells depicting the E-field intensity for incident light polarized in (1,1) (a)
and (0,1) (b) direction on the xy plane. (c-d) show the cross-section of E-field intensity along the
y direction of the unit cell along gray and with yellow lines in (a) and (b) respectively. (e-f) show
the cross-section of E-field intensity along the diagonal direction of the unit cell along red and
with purple lines in (a) and (b) respectively. (g) Simulated transmission spectra with the incident
light in (1,1) polarization with P=1528 nm and D=889 nm (red circles), P=1600 nm and D=889
(blue triangles) and P=1528 nm and D=1100 nm (green squares).

To further test Eq. (5), we calculate the SPP resonance wavelength for hole arrays with different
structural parameters. If P=1600 nm and D=889, the calculated resonance SPP wavelength is
3669 nm, versus the transmission dip at 3576 nm in simulated spectrum (blue triangles) with
(1,1) polarization. For P=1528 nm and D=1100 nm, the calculated resonance along (1,1) direction is 3056 nm, compared with the dip at 2941 nm on the simulated transmission spectrum (green squares) with the incident light in (1,1) polarization. There is very good agreement between calculated and simulated transmission dips due to the SPP standing wave. We can conclude that the localized SPP resonance in (1,1) dominates the transmission dip of the spectrum in Figure 7-4(g).

Knowing now the SPR wavelength both experimentally and theoretically, we can now justify the use of small glass substrate in the simulations. The penetration depth of the SPR field into the dielectric is given by [25]

\[
\delta_d = \frac{\lambda_{SPP}}{2\pi} \sqrt{\frac{\varepsilon'_m + \varepsilon'_d}{(\varepsilon'_d)^2}}
\]

(7.5)

where \(\varepsilon'_m\) is the real permittivity of is conducting film, \(\varepsilon'_d\) is the real permittivity of the dielectric and \(\lambda_{SPP}\) is the wavelength of the SPR [116]. For a SPR plasma wavelength of 3467 nm the penetration depth is calculated to be 692 nm, indicating the glass simulation thickness is large enough and that the SPR is highly is confined to the AZO/glass interface. Only glass thicknesses below this value could affect the value of \(n_{eff}\) and alter the SPR wavelength.

7.4 SPR Limitations

So far we reported surface plasmon resonance around 3467 nm. The resonance wavelength is related to the plasma frequency of the AZO film. The square of the plasma frequency scales directly with the imaginary part of the permittivity in Eq. (3). Our simulations show that increasing plasma frequency by 0.1 eV blue-shifts SPP resonance wavelength by 76 nm. The SPP resonance wavelength does not scale linearly with the periodicity of the hole arrays.
because of the effective refractive index change with the wavelength in Eq. (4) and (5). Our simulation shows that the SPP resonance wavelength redshifts by 555 nm when the period of the hole array is increased from 1000 nm to 1900 nm. The blue shift of resonance wavelength is limited by the crossover frequency (the frequency at which the real part of the permittivity of the material crosses zero). The redshift of the resonance is limited by the optical loss which is related to the imaginary part of the permittivity.

Our data show that our AZO film has the lowest optical loss around 1000 nm and increases with the increasing wavelength. Because of the high optical loss, the contrast of the observed resonance is not very high (both experimental and simulation results). Besides the plasma frequency, the carrier relaxation rate $\Gamma_p$ in Drude model in Eq. (3) is related to the optical loss. Our simulations show that the resonance dip still appears for $\Gamma_p = 0.2 \, eV$ but disappears for $\Gamma_p = 0.3 \, eV$ ($\Gamma_p = 0.139 \, eV$ is our measured relaxation rate).

Because the crossover frequency of AZO is in the infrared range and it has a low optical loss relative to the noble metals in the infrared range, it motivates further studies of the complete absorption through SPP resonance for detector applications in the mid-infrared regime by integrating the AZO with semiconductors.

7.5 SPR with Incident Polarization In (1,0) direction

To further test the resonance mechanism, simulations were done introducing another set of small holes into the larger hole (size=889 nm) arrays to form a super-lattice as shown in the insets of Figure 7-5(a) and 7-5(b). If the holes are small, namely 100nm, there is minimal change when comparing the (1,0) or the (0,1) polarizations to the structure pattern with no superlattice
holes. This resonance dip position and depth remain unchanged because the small hole is at the
nodes of the resonance. As the hole size is increased to 350nm, the resonance dip becomes
smaller as shown in Figure 7-5(a) and 7-5(b).

Figure 7-5 Simulations of superlattice structure, that introduce smaller holes between the square
array pattern. With increasing hole size in both a) with (0,1) and b) with (1,1) polarizations it is
seen that the dip in transmission disappears corresponding to a loss of SPR as the AZO pathway
is removed [149].

As the hole size is increased to 250 nm, the resonance dip becomes smaller as shown in
Figure 7-5(a) and 7-5b). When the hole size is increased to 350 or 400 nm, the resonance path is
blocked and the dip at 3400 nm disappears while a weak dip around 2900 nm becomes visible
corresponding to a resonance in the (0,1) direction [149].

Figure 7-6 Computed E-field intensities at two wavelengths of 2881 nm (a) and 3400 nm (b) with
a polarization in (1,0). (c) Computed E-field intensity in the dual hole structure with a polarization
in (1,0) [149].
This mode assignment can be confirmed by the computed electric-field (E-field) intensities at the AZO/glass interface at the wavelength of 2881 nm in figure 7-6(a) and 3400 nm in figure 7-6(b) for source polarization in (1,0) for structures without the small holes. The E-field intensity for 3400 nm has a distribution along the diagonal direction (in (1,1) direction) while E-field intensity has a distribution in (1,0) direction for 2881 nm. When small holes with a size of 400 nm are incorporated in the structure, and a Gaussian beam is used the E-field intensity does not have a distribution along the (1,1) direction indicated the presence of the holes strongly favors the 2881 mode figure 7-6 (c).

7.6 Design Engineering the Structure Parameters for SPR Tuning

Up to this point, we have focused on the results for the particular hole array that was fabricated. However, a resonant wavelength in the wavelength range of 1350-1750 nm is desired for application in plasmonic/photonics integrations with communication technologies. In order achieve this coveted regime, the resonant wavelength of the nanohole array structure should be tuned by carefully choosing period Λ, hole diameter d, and hole depth t, and carrier concentration. For this reason, the general trends of varying the period, the hole diameter, and the hole depth should be provided. These general trends will also be useful if other regimes than the communications wavelengths are desired.

FDTD simulation were performed using (1,1) polarized light normally incident on the structure with a negligible (10nm) glass substrate. It should be noted that the set of parameters Λ= 1500 nm, d =900 nm, and t = 100 nm and \(\omega_p = 2.5 \text{ eV}\) in the following simulations have been chosen based on their proximity to the lithographically fabricated
structure and maximizing plasma frequency to blue shift the SPR. It is important to note that each time only one of the four parameters will be varied, while the others are kept unchanged.

7.6.1 Varying Plasma Frequency

Oxide semiconductors such as zinc oxide, cadmium oxide, and indium oxide can be highly doped to make them conducting films.[150,151]. Since these semiconductors have a large bandgap, they are transparent in the visible range. Like any other semiconductor, the optical properties of TCOs can be tuned by changing the carrier concentration and annealing process. The optical response of free carriers as described by the Drude model can be used to estimate carrier concentration where the plasma frequency is directly proportional to the square root of the carrier concentration.

\[
\omega_p = \frac{e^2 N_e}{\sqrt{\varepsilon_0 m^*}}
\]  

(7.6)

In this model, \(e\) is the electron charge, \(m^*\) is the effective electron mass, \(\varepsilon_0\) is the permittivity of free space, and \(N\) is the density of free charges. In the simulation we vary the value of plasma frequency between the values of 1.74 eV and 2.5 eV. A value of 1.74 eV for the frequency is a nominal value reported to have been achieved via pulsed laser deposition [134] while the value of 2.5 eV would represent a very high doping capable of placing the SPR within the optical communications regime.
Figure 7-7 Calculated spectra of transmission at normal incidence for the arrays of cylindrical holes ($\Lambda=1500$, $d=900$ nm, $t=100$ nm) for a range of plasma frequencies ranging from 1.74 eV-2.5 eV. Trend indicates a blue shift of the position of the SPR by 76 nm for every 0.1 eV increase in plasma frequency. AZO was previously reported to be incapable of supporting SPPs at $1.55 \mu m$ because of its smaller plasma frequency. However better deposition techniques have recently shown that AZO films [134,140] can optimized for large plasma frequencies at $1.55 \mu m$. Figure 7-7 shows the transmission spectra of the cylindrical array as plasma frequency is varied. The simulations show that increasing Plasma frequency by 0.1 eV blue shifts SPR by 76 nm. Not shown is the Drude relaxation dependence which was also simulated and resulted in a nonlinear relationship that was best modeled by an exponential rate of change of $(\Delta \Gamma )^{-0.029}$. The base simulation had a Drude dampening factor of 0.044.

7.6.2 Varying Periodicity

From equation 2 we expect to see that an increase in $\Lambda$ will result in an increase in wavelength of SPR. Figure 7-8 shows the simulated spectra of the transmission of the hole array for periods $\Lambda$, between 1000 and 1900 nm, where the holes have a diameter of $d=900$ nm and a depth of $t=100$ nm. The key finding is that as the period increases 100nm, the peak of the SPR redshifts by 61 nm Figure.
7.6.3 Varying Hole Diameter

Figure 7-9 shows the simulated spectra of the transmission of the hole array for a variety of hole diameters, d, between 600nm to 1300nm. It is notable that the SPR is redshifted by 9.1nm for every 100nm increase in hole diameter. This parameter has a significantly smaller contribution to SPR when compared to that of period variation. As expected when hole diameter increases less AZO is present to absorb incident light so transmission intensity increases. As the hole diameter increases, the resonance red shifts and becomes weaker. However, the transmission peak broadens as the disk diameter decreases. This is due to the fact that the remaining portion of the film begins to support higher order plasmonic modes that start to overlap as the hole size decreases [152,153].

![Transmission Varying Periodicity](image)

Figure 7-8 Calculated spectra of transmission at normal incidence for the arrays of cylindrical holes (\(\omega_p=2.5\), d =900 nm, t = 100 nm) for a range of periodicities ranging from 1.0 -1.9 um. Simulation trend redshifts the position of the SPR of 61nm for every 100nm increase in periodicity.
Figure 7-9 Calculated spectra of transmission at normal incidence for the arrays of cylindrical holes ($\omega_p=1.74$, $\Lambda=1500$ nm, $t=100$ nm) for a range of hole diameters ranging from 800-1600 nm. Inset shows linear trend that redshifts the position of the SPR of 10nm for every 100nm increase in hole diameter.

7.6.4 Varying AZO Thickness

Figure 7-10 shows the simulated spectra of the transmission of the hole array for varying AZO film thickness, $t$, ranging from 50-300nm. Within the small range between 50-200nm the relationship between SPR and AZO thickness is linear. The SPR is blue shifted by 36nm for every 10nm increase in AZO thickness. The experimental observation of broad SPP resonances in ITO films was previously reported in [154,155]. Those reports demonstrated a thickness-dependent SPP on ITO thin films. Not shown is the glass thickness dependence which was also simulated and resulted in a nonlinear relationship that was best modeled by an exponential rate of change of glass thickness of $(\Delta t_{glass})^{0.029}$. The base simulation had a glass thickness of 10nm.
Figure 7-10 Calculated spectra of transmission at normal incidence for the arrays of cylindrical holes ($\omega_p=2.5$, $\Lambda=1500$ nm, $d=900$ nm) for a range of AZO thicknesses that range 50-300 nm. Simulation shows trend that redshifts the position of the SPR of 10 nm for every 100 nm increase in hole diameter.

7.6.5 Design Engineering the SPR

By combining all the parameter trends used to fabricate a square lattice cylindrical hole array we can outline a general design guideline for fine-tuning the SPR wavelengths using this configuration. By comparing to parameters of an initially simulated structure we can approximate the value of the SPR for a structure with arbitrary parameters using the following:

$$
\lambda_{SPR} = \lambda_{SPR_0} + \left[.6163(p-p_0)\right] + \left[.0935(d-d_0)\right] + \left[2271 \ast (I^{-0.027} - I_0^{-0.027})\right] \\
+ \left[2005(t_g^{0.029} - t_g^{0.029})\right] + \left[-760.1(\omega-\omega_0)\right] + \left[-.366(t-t_0)\right]
$$

(7.7)

where, $\lambda_{SPR_0}=1903$ nm which is the wavelength of resonance for a structure with $p_0=1500$ nm period and $d_0=900$ nm hole diameter in an AZO thin film of $t_0=100$ nm thickness whose
permittivity is modeled with a plasma frequency of $\omega_0=2.5\text{eV}$ with Drude dampening of $\Gamma_0=0.044\text{eV}$ situated above a glass substrate of thickness $t_{g0}=1000\text{nm}$. These values are a comparative guide only and do not fully explain the mechanism behind the effect of each of the parameters on the SPR and are valid only within the range of simulated parameter values.

To test the accurateness of this design engineering we consider the fabricated array structured thin film which has experimental parameters of $p=1528\text{ nm}$ period with $d=889\text{ nm}$ hole diameter on AZO with thickness of $t=114\text{ nm}$ of $\omega_0=1.45\text{eV}$ plasma frequency with $\Gamma=0.139\text{eV}$ Drude dampening on a glass substrate of thickness $t_{g}=1\times10^6\text{ nm}$. This results in a design SPR at 3485 nm which is very close to the experimental value of $\lambda_{SPP}=3487\text{ nm}$. 
CHAPTER 8

ELECTRICALLY TUNED CARRIER CONCENTRATION IN AZO

The optical performance (such as the working frequency) of plasmonic devices is usually fixed after their fabrication. Progress has been achieved in the tunability of plasmonic devices using liquid crystal or ionic liquids [156], graphene[157], VO₂[158], Perovskites [159], and other phase-changing materials, that owe their large electrical and optical tunability as either a function of voltage or temperature. Transparent conducting oxides (TCO) have been used to tune the optical properties of plasmonic and optical devices by altering their carrier concentration through voltages. Because TCOs have a low optical loss relative to the noble metals in the infrared range [141], they can be excellent candidates for active plasmonics in the near-infrared and mid-infrared spectral range with applications in infrared sensing, thermal manipulation, telecommunication, and nano-antennas. Very recently, indium tin oxide (ITO) has been studied for its applications in tunable plasmonic devices by several groups[160-164] and only a few groups have studied optical and plasmonic tunability in Al-doped ZnO (AZO) [133].

In this experiment, we report on the holographic fabrication and wet etching of gratings in AZO which was prepared by atomic layer deposition (ALD). Diffractions from the AZO grating were observed to change in efficiency when a negative bias was applied to the AZO. The electrical tuning of diffraction efficiency can be explained by the complex refractive index changes due to the carrier concentration changes under various bias voltages.

8.1 Fabrication of AZO Gratings

Fabrication of the AZO grating began with preparation of a 100 nm AZO and 5 nm Al₂O₃ film that were grown by ALD [141,165] on commercial ITO coated glass slides (1×1 inch²) to form an AZO/Al₂O₃/ITO/glass multi-layer film. Two-beam interference lithography fabrication techniques on a positive resist similar to the successful 2D pattern reported in chapter 7 [141] was used to fabricate gratings in the resist spin-coated above the AZO film. Four laser exposures produced four gratings in the 1×1 inch² slide. The enlarged view of two gratings is shown in Figure 8-1(a). After etching and development, the grating is transferred to the AZO layer as shown in Figure 8-1(b). The average grating period, depth and AZO width are 915 nm, 87.5 nm and 400 nm, respectively, as measured by AFM. Using silver paste and gold wires for bonding as shown in figure 8-1(a), the grating was connected to an Agilent B1500A Semiconductor Device Analyzer and a negative bias was applied to AZO, as illustrated in Figure 8-1(c), for current and capacitance measurements.

Under a negative bias, we expect a carrier accumulation in AZO near the AZO/Al₂O₃ interface, which will in turn change the plasma frequency \( \omega_p \) of the AZO film due to the carrier concentration (N) change through Equation 7.16 which is rewritten here [166].

\[
\omega_p = \frac{e^2 N_e}{\sqrt{\varepsilon_0 m^*}}
\]  

(8.1)

where \( e \) is the electron charge, \( m^* \) the effective mass and \( \varepsilon_0 \) dielectric permittivity of vacuum. In this paper, \( m^*=0.38m_e \) is used [127].
A change of plasma frequency will result in a change of complex permittivity in the carrier accumulation region and their relations can be understood through both Drude and Lorentz oscillator models:

\[
\varepsilon(\omega) = \varepsilon' + i\varepsilon'' \tag{8.2}
\]

\[
\varepsilon(\omega) = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\Gamma_0 \omega} + \frac{f_1 \omega_1^2}{\omega_1^2 - \omega^2 - i\Gamma_1 \omega} \tag{8.3}
\]

where \(\varepsilon_\infty\) is the high frequency permittivity, \(\Gamma_0\) the carrier relaxation rate, and \(f_1\) the strength of the Lorentz oscillator with center frequency \(\omega_1\) and relaxation \(\Gamma_1\). The Lorentz oscillator model cannot be ignored in this work because the measurement wavelength is in the visible spectrum.

A change of complex permittivity will result in a change in complex refractive index. The change of complex refractive index \((\Delta n)\) will create an optical path difference \((\Delta n \times d)\) between the light that passes a thickness \(d\), of AZO and air in Figure 8-1(c) and also generates an absorption change related to the imaginary part of the complex refractive index.

Figure 8-1 (a) Enlarged view of two out of four gratings fabricated on 1×1 inch2 substrate. The device is connected to a power supply through a silver paste and gold wires. Dashed line indicates the edge of AZO. AFM of grating pattern in AZO (b). (c) Schematic of grating device. A voltage is applied to the grating between AZO and ITO.
The use of AZO and ITO in the device was chosen because it has potential applications in tunable transmissive devices such as phase masks [167] for holographic lithography [49]. Because the grating was not formed in the ITO layer as seen in Figure 8-1(c), the change of optical properties in ITO will not contribute to the optical path difference from the grating.

8.2 Tunable Diffraction Efficiency

To detect the change of complex refractive index brought about by the carrier concentration change, a 532 nm green laser was used for the measurement of the 1st order diffraction efficiency. The laser polarization was set to be either parallel to or perpendicular to the grating groove direction and the results are summarized in Figure 8-2(a) for run-1, run-2 & run-3 and in 2(b) for run-4, run-5 & run-6, respectively. The diffraction efficiency measured using light perpendicular to the grating is 74% of that using parallel light, compared to the ratio of 76% using a commercial phase mask.

Diffraction efficiency was measured when a negative voltage was applied on the AZO side as shown in Figure 8-1(c). After each run with the grating parallel to the incident light polarization, the device was discharged for several seconds before the next run was started. For the runs with the grating perpendicular to the incident, the device was discharged for 4 minutes between runs.

The experimental data shows that run-6 can almost repeat run-5, possibly due to the longer time discharging between run-5 and run-6. The bias voltage to the device was usually kept on when adjusting the voltage for the next measurement and switched off only between runs when a large change in voltage was expected to be applied, i.e. from -4V to 0V. The exception is the last data point at v=-1.1 V in the run-6, by accident. The voltage was seen to jump to v=-8 V
after the accident. After that, the device was permanently damaged due to the breakdown of Al₂O₃ spacer. This unplanned incident prevented the completion of run-6 however gives insight into the breakdown voltage of the device.

Figure 8-2 Voltage dependent diffraction efficiencies of AZO grating structure in Figure 1 from 532 nm laser for the laser polarization parallel to the grating groove (a) and perpendicular to the grating groove (b) when the AZO is under negative voltage.

When the bias was swept from 0 to -1 V, only a small fluctuation of diffraction efficiency was observed, indicating that a minimum or threshold voltage is needed to change the diffraction efficiency. A threshold voltage was also observed for an ITO based modulator by Shi et al [163].

For the bias variation from -1 to -3.5 V, the diffraction efficiency continuously decreased from around 2.0% to 1.6% for laser polarization parallel to the grating, Figure 8-2(a). For laser polarization perpendicular to the grating, the efficiency was decreased from 1.45% to 0.90%, Figure 8-2(b).

A depletion layer is formed on the ITO when the positive bias is applied to the AZO as shown in Figure 8-1(c). If the electrical permittivity values of Al₂O₃ and ITO are assumed to be εₐl₂o₃=9ε₀ and ε_{ITO}=9.3ε₀ (ε₀ is the permittivity in free space) and the carrier concentration of the
ITO is assumed to be $N_d = 6.6 \times 10^{20}$ cm$^{-3}$ then the depletion width and voltage drop can be calculated [163-164]. At 1V positive bias on ITO, the depletion width is calculated to be 0.15 nm and a voltage of 0.015 V is dropped due to the depletion. So, the carrier depletion effect in ITO layer cannot fully explain the minimum voltage phenomenon in Figure 8-2(a) and 8-2(b) because 0.015 V is much less than 1 V.

8.3 AZO Film Characterization

In order to obtain the complex refractive index change for AZO under bias voltages and reduce the ITO effect, an ellipsometry measurement was performed on a film of 100 nm AZO/5 nm Al$_2$O$_3$/n-type Si substrate (with a carrier concentration of $2 \times 10^{15}$ cm$^{-3}$). The reason of using silicon instead of metal is the fabrication ease of cleaving out sections of the film/substrate to achieve a device with no electrical shorting.

Characterization of AZO films was done by spectroscopic ellipsometry (V-VASE from J. A. Woollam). The model fitting software includes both Drude and Lorentz oscillator models for silicon with amplitude parameters in these two models that can be modified during the fitting thus isolating the AZO and Al$_2$O$_3$ fittings from silicon. During the ellipsometry measurements, the silicon was grounded and bias voltage $v$ was applied to AZO. When $v=0$V and -3V, the complex permittivity as a function of wavelength between 300 and 1700 nm was fitted through models for AZO, Al$_2$O$_3$ and n-type Si. The fitting results gave us a thickness of 99.994 nm for AZO and 4.987 nm for Al$_2$O$_3$ with a mean square error of 1.532 at 0V and a thickness of 102.97 nm for AZO and 4.949 nm for Al$_2$O$_3$ with a mean square error of 1.906 at -3V, very close to ALD fabrication parameters for AZO and Al$_2$O$_3$. 
8.4 Accumulated Carrier Concentration Under Bias

In order to obtain the spatial distribution of complex permittivity and complex refractive index in AZO, the Poisson’s equation was solved and compared with the ellipsometry data. For the case of accumulation, the potential in AZO as a function of depth \( x \) can be calculated by solving Poisson’s equation:

\[
\frac{d^2 \phi(x)}{dx^2} = -\frac{\rho(x)}{\varepsilon_t} \approx \frac{q}{\varepsilon_t} N_d \left\{ e^{q\phi(x)/(kT)} - 1 \right\}
\]

where \( \phi(x) \) is the potential in the AZO as a function of depth, \( N_d \) is the bulk carrier concentration of AZO, and \( \varepsilon_t \) is the static dielectric constant of the spacer layer.

![Figure 8-3 Calculated carrier concentration using Poisson equation as a function of depth into AZO from the AZO/Al₂O₃ interface when the AZO is negatively biased.](image)

The induced charge distribution inside the AZO can be calculated using the potential calculated by equation 8.4 using: \( N_v(x) = N_d e^{q\phi(x)/(kT)} \) [168]. In the calculation, the thickness of the Al₂O₃ layer was 5 nm and the static permittivity for AZO was \( \varepsilon = 8\varepsilon_o \) [169]. Poisson equation based calculations were first verified by reproducing the charge distribution of Figure 1(b) in reference [160]. Then the surface potential at the AZO/Al₂O₃ interface was used as a variable to
match the carrier concentration in AZO with the measured value by the ellipsometry. Using the surface potential of $\phi_s=0.0896$ V, and a value of 1 nm for the Debye length, the results from the Poisson equation calculation can repeat the experimental data of carrier concentrations in AZO and results are shown in Figure 8-3. When $x > 4$ nm, the carrier concentration approaches to the $3.92 \times 10^{26}$ m$^{-3}$, which is the value when $v=0$ V is applied to the AZO.

For $v=-3.5$ V, we changed the surface potential to $0.0896 \times 3.5/3=0.1045$ V in the Poisson equation based simulation. Using Equation (8.1) and data in Figure 8-3, the plasma frequency of the AZO under -3.5 V was calculated, which increased from 1.19 eV at the depth $x=10$ nm to 4.10 eV at $x=0.25$ nm and further to 9.07 eV at $x=0$ nm. Based on equation (8.3) and at the wavelength of 532 nm, the complex refractive index $n=n'+in''$ for AZO under -3.5 V was also calculated. It changed from 1.761+i 0.108 at $x=10$ nm to 0.629+i 0.371 at $x=0.25$ nm and further to 0.122+i 3.437 at $x=0$ nm, for example. The absorption coefficient $\alpha$ is related to the imaginary part of the refractive index by $\alpha=4\pi n''/\lambda$. Based on the spatial distribution of complex refractive index in AZO, the transmission through the 87.5 nm AZO was calculated to be 90.77% at 0 V and 80.07% at -3.5 V. By considering the absorption due to the imaginary part of the complex refractive index and the grating cycle of 400/915, the diffraction efficiency at 0 V and -3.5 V was modified to 2.08%/95.96%=2.167% and 1.6%/91.28%=1.75%, respectively for laser polarization parallel to the grating.

We then considered the effect of the change of optical path difference on the change of diffraction efficiency. Assuming the grating is a square-wave phase grating (experimentally grating duty cycle is 400/915=0.44 versus 0.5 in square-wave case), then the phase $\phi(x) = \phi_0+\Delta\phi \sqrt{r-sin(2\pi x/\Lambda)}$. The diffraction efficiency DE is given by the equation, $DE=(2\sin(D\phi)/\pi)^2$ for
+1 and -1 diffraction orders [170]. Based on the change of refractive index in AZO, the DE change for AZO grating under voltages from 0V to -3.5V was calculated to 0.29%, compared with the modified experimental change of DE of 0.417% (2.167% -1.75%).

8.5 Capacitance-Voltage Characterization

Capacitance-voltage (C-V) measurements in the dark on the sample 100 nm AZO/5 nm Al₂O₃/n-type Si confirm the threshold voltage that can be seen in Figure 8-2(a) and 8-2(b). The C-V measurement on the freshly fabricated sample is shown in Figure 8-4(a). The silicon was grounded and the bias voltage was applied to AZO. At high frequencies of 5 kHz and 10 kHz, the capacitance increases with higher bias voltage. At 1 kHz, capacitance was observed to rise quickly starting from the voltage of -1V and reach a constant at -3.5 V, the same voltage range where a continuous change in diffraction efficiency occurs in Figure 8-2(a) and 8-2(b). The threshold voltage of -1V might be due to the trapped positive charges at the interface.

![Figure 8-4 Capacitance measurement only days after being fabricated (a) and after four-month (b) films of 100 nm AZO/5 nm Al₂O₃/n-type silicon at different frequencies. The silicon is grounded.](image-url)
After the sample of 100 nm AZO/5 nm Al₂O₃/n-type Si was exposed to ambient environment at room temperature for four months, C-V curve was re-measured as shown in Figure 4(b). The slope of yellow dash line in Figure 8-4(b) became smaller, indicating the increase of interface states in the sample after four months [17]. The threshold voltage for the capacitance was also shifted from -1V in Figure 8-4(a) to -1.8V in Figure 8-4(b). We are currently fabricating new devices and will study the relationship among the interface states, threshold voltage for changes in DE, device tuning speed, and reliability.

In summary, we have observed the continuous dropping of diffraction efficiency in AZO grating when the AZO is negatively biased from -1V to -3.5 V. The dropping of the diffraction efficiency has been explained by the carrier concentration dependent complex refractive index changes, obtained through ellipsometry measurement and Poisson equation based calculations. These results will lead toward the integration of AZO in optoelectronics for post-fabrication electrical tuning for active optical or plasmonic devices.
CHAPTER 9

CONCLUSION

As the age of the modern electronics based on silicon integrated circuits is nearing its end this work sheds light on photonics as potential candidate for its replacement.

To show the fabrication feasibility of photonics, a simple single reflective optical element capable of high-throughput, large scale fabrication of micro- and nano-sized structure templates using holographic lithography is introduced and developed. It is specifically shown to be capable of fabricating 3D photonic templates with 4, 5, and 6 fold symmetry and have the versatility and robustness to handle many more configurations. It is also proven to be capable of fabricating subwavelength features including nano-antenna templates with its ability to tune the phase of individual beams to control the interference of compound lattices.

To show the possible coupling of current photonics technology with the macroscale optical communications technology already available this research demonstrates the fabrication and characterization of patterned near-IR plasmonic materials to help integrate the two technologies. We first demonstrated the presence of surface plasmon resonances in a square lattice hole array of the transparent conducting oxide Aluminum Zinc Oxide (AZO). We then utilized this AZO and lithographic patterning technique to demonstrate device level tunability of diffraction efficiency via electrical biasing of patterned diffraction gratings.

This research extends the robust CMOS compatible fabrication techniques of holographic lithography into tunable conductive materials, and contributes to the core technology of future integrated photonics.
APPENDIX

MATLAB CODE FOR INTERFERENCE OF MULTIPLE BEAMS
MATLAB code that simulates the interference pattern created by ROE output beams

General_ROE_Intensity_Pattern.m

```matlab
Variable Definitions

clear;
NOSB=6; \% Number of Symmetric Beams

BeanPhase=[0, 0, 0, 0, 0, 0]; \% Phase of Beams in multiples of pi: BeanPhase[beam1, beam2, ..., beamN]
BlockSideBeams=[0, 0, 0, 0, 0, 0]; \% to block nth side beam = (1) or allow nth side beam = (0)
angleI=[76, 76, 76, 76, 76, 76]; \% Phase of Beams in multiples of pi: BeanPhase[beam1, beam2, ..., beamN]
Blockcenter=0; \% to block center beam = (1) or allow center beam = (0)
level=0.002; \% determines fill fraction
Picture=0; \% to save picture = (1) or not save picture = (0)
Inverse=0; \% to do inverse structure = (1) or not use inverse structure (0)

AmpSide=[1, 1, 1, 1, 1, 1]; \% relative Intensity of side Beams
AmpCenter=2; \% relative amplitude of center beam

Nt=[4.25, 4.25, 4.25, 4.25, 4.25, 4.25]; \% Index of refraction for reflective surface
%{
Common used index of refraction for various wavelengths
silicon: (4.25)514nm \ (4.34)488nm \ (4.15)532nm \ (4.577)460nm
GaAs: (4.710)457.9 nm \ (4.15)532nm
%}

Choose the Center Beam Polarization you desire:
\% CBP=1 Linear Polarization with Linear Angle measured from x axis
\% CBP=2 Elliptical Polarization with Linear Angle Measured from x axis (Right Handed helicity)
% CBP=2;
```
LinearAngle = 45;

lamb = 514.5e-9; %wavelength of laser
ni = 1; % index of refraction for air

angleT = ones(1, NOSB);
for L = 1: NOSB
    angleT(L) = asind((ni) / (Nt(L)) * sind(angleI(L))); % angle of transmittance
end

firstorder = ones(1, NOSB);
for L = 1: NOSB
    firstorder(L) = 180 - 2 * angleI(L); % polar angle denoting side beam k-vector from ROE
end

angles = 360 / NOSB; % azimuthal angle spacing between side beams, = 360/number of beams

shift = 0; % shift is starting point of azimuthal angle denoting side beam k vectors, helps set lattice structure??

X, Y, Z limits

xs = 0.3; ys = xs; zs = 0; % Starting position of x, y, z
xt = 4.5; yt = xt; % Terminating position of x, y, z
zt = 5; %

yi = 0.05; xi = yi; % Step Interval of x, y, z
zi = 0.25;

x = (xs: xi: xt) * 1e-6;
y = (ys: yi: yt) * 1e-6;
z = (zs: zi: zt) * 1e-6;

Wave Vector Setup

k = 2 * pi / lamb;

% Creating and Defining k-vector geometry for ki (central beam)
ki x = 0; ki y = 0; ki z = k;

% Defining k-vector geometry for kn
% Note in Matlab: phi = elevation angle; theta = azimuthal angle
knx = ones(1, NOSB);
kny=ones(1,NOSB);
knez=ones(1,NOSB);

for L = 1:NOSB
theta = (shift+(L-1)*angles)*pi/180;
phi = (90-firstorder(L))*pi/180;
[knx(L),kny(L),knz(L)] = sph2cart(theta,phi,-k);
end

Initial Phase Delay Set Up

%defining Phase for each beam from inputed Beamphase in 'Variable Def'
Phase=ones(1,NOSB); for L = 1:NOSB
Phase(L)= BeamPhase(L)*pi;
end

Polarization Setup

initial=LinearAngle; % initial angle of polarization from x-axis ; 45 if circular

% Central Beam polarization (CBP) used. Defined in 'Variable Definitions'
if CBP==1 % Linear polarization
Eivx=AmpCenter*cosd(initial);
Eivy=AmpCenter*sind(initial);
Eivz= 0;
end
if CBP==2 % Elliptical polarization
Eivx=AmpCenter*cosd(initial);
Eivy=AmpCenter*sind(initial)*1i;
Eivz= 0;
end

%Defining Amplitude of Center beam
%Eiamp= sqrt(Eivx^2+Eivy^2+Eivz^2);

%fresnell eqn include polarization phase shift of 0 or pi upon reflection
rs=zeros(1,NOSB);
rp=zeros(1,NOSB);
for L=1:NOSB
rs(L)=(ni*cosd(angleI(L))-Nt(L)*cosd(angleT(L)))/(ni*cosd(angleI(L))+Nt(L)*cosd(angleT(L)));
rp(L)=(-ni*cosd(angleT(L))+Nt(L)*cosd(angleI(L)))/(ni*cosd(angleT(L))+Nt(L)*cosd(angleI(L)));
end

% Defining Eno (side Beam) Magnitudes
% Implementing Experimental measured magnitudes and blocked beams
Amplit = ones(1, NOSB);
for L = 1: NOSB
    if BlockSideBeams(L) == 0
        Amplit(L) = sqrt(AmpSide(L));
    else
        Amplit(L) = 0;
    end
end

% Side Beam S polarized
Enos = ones(1, NOSB);
for L = 1: NOSB
    Enos(L) = Amplit(L) * (rs(L) * Eivx * sind(angles*(L-1)) + rs(L) * Eivy * cosd(angles*(L-1)));
end

% Side Beam P polarized
Enop = ones(1, NOSB);
for L = 1: NOSB
    Enop(L) = Amplit(L) * (rp(L) * Eivx * cosd(angles*(L-1)) + rp(L) * Eivy * sind(angles*(L-1)));
end

% Defining Env (for s and p separately)
% where Env = Envs + Envp
% p-polarization of side beams
Envpx = ones(1, NOSB);
Envpy = ones(1, NOSB);
Envpz = ones(1, NOSB);
for L = 1: NOSB
    thetaEp = (shift + 180 + (L-1) * angles) * pi / 180;
    phiEp = (firstorder(L)) * pi / 180;
    [Envpx(L), Envpy(L), Envpz(L)] = sph2cart(thetaEp, phiEp, Enop(L));
end

% s-polarization of side beams
Envsx = ones(1, NOSB);
Envsy = ones(1, NOSB);
Envsz = ones(1, NOSB);
for L = 1: NOSB
    thetaEs = (shift + 90 + (L-1) * angles) * pi / 180;
    phiEs = 0;
    [Envsx(L), Envsy(L), Envsz(L)] = sph2cart(thetaEs, phiEs, Enos(L));
end

% Defining Env: Total Side Beam Polarizations
Interference SetUp

% where Env = Envs + Envp

Envx = ones(1, NOSB);
Envy = ones(1, NOSB);
Envz = ones(1, NOSB);
for L = 1: NOSB
    Envx(L) = Envpx(L) + Envsx(L);
    Envy(L) = Envpy(L) + Envsy(L);
    Envz(L) = Envpz(L) + Envsz(L);
end

% deleting some variables to free memory
varlist =
    {'thetaEs', 'phiEs', 'thetaEp', 'phiEp', 't het aEs', 'phi Es', 't het aEp', 'phi Ep', 'Envpx', 'Envpy', 'Envpz', 'Envsx', 'Envsy', 'Envsz', 'Enos', 'Enop', 'rs', 'rp'};
clear(varlist{:});

% Defining En = Enamp * e^{phase}

Enx = ones(length(x), length(y), length(z), NOSB);
Eny = ones(length(x), length(y), length(z), NOSB);
Enz = ones(length(x), length(y), length(z), NOSB);
Eix = ones(length(x), length(y), length(z));
Eiy = ones(length(x), length(y), length(z));
Eiz = ones(length(x), length(y), length(z));

for j = 1:length(x)
    for v = 1:length(y)
        for f = 1:length(z)
            for L = 1: NOSB
                Enx(j, v, f, L) = Envx(L) * exp(1i * (knx(L) * x(j) + kny(L) * y(v) + knz(L) * z(f) + Phase(L)));
                Eny(j, v, f, L) = Envy(L) * exp(1i * (knx(L) * x(j) + kny(L) * y(v) + knz(L) * z(f) + Phase(L)));
                Enz(j, v, f, L) = Envz(L) * exp(1i * (knx(L) * x(j) + kny(L) * y(v) + knz(L) * z(f) + Phase(L)));
            end
        end
    end
end

% Determines size of ELL so that it will not change size over loops
TComb = NOSB; % initial value counting all I## pairs equal where ## but not center beam
for L = 1: NOSB
for N=L:NOSB;
    if N>L
        TComb=TComb+1;
    end
end
if Blockcenter ==0
    TComb=TComb+NOSB+1;
end
ELL=ones(length(x),length(y),length(z),TComb);

for L=1:NOSB
    ELL(:,:,L) =
        (Enx(:,:,L).*conj(Enx(:,:,L))+Eny(:,:,L).*conj(Eny(:,:,L))+Enz(:,:,L).*conj(Enz(:,:,L)))*0.5 ;
end
Lth=NOSB;  % keeps track of the current number of 2 Beam interactions
for L=1:NOSB
    for N=L:NOSB;
        if N>L
            Lth=Lth+1;
            ELL(:,:,Lth) =
                (Enx(:,:,L).*conj(Enx(:,:,N))+Eny(:,:,L).*conj(Eny(:,:,N))+Enz(:,:,L).*conj(Enz(:,:,N)));
        end
    end
end
% utilizing blockcenter to incorporate or Not incorporate Ei into sum
if Blockcenter ==0
    for L=1:NOSB
        ELL(:,:,Lth+L) =
            (Enx(:,:,L).*conj(Eix)+Eny(:,:,L).*conj(Eiy)+Enz(:,:,L).*conj(Eiz));
    end
    ELL(:,:,Lth+NOSB+1) = (Eix.*conj(Eix)+Eiy.*conj(Eiy)+Eiz.*conj(Eiz))*0.5 ;
end
for L=1:TComb
    if L==1
        It=ELL(:,:,L);
    else
        It=It+ELL(:,:,L);
    end
end
% deleting some variables to free memory
varlist =
    {'knx','kny','knz','Envx','Envy','Envz','Exx','Eny','Enz','Exy','Ey','Ez','Exz','Eyv','Evy','Exv','Ehz','ELL'};
clear(varlist{:})
%
It = It./max(max(max(It)));
It = real(It);

if Inverse==1
    Iti = 1-It; % inverse structure
    It = Iti;
end

Plotting Intensity Field

Figure(1)
clf
data = smooth3(It,'box',1);
p1 = patch(isosurface(x,y,z,data,level), ... 
    'FaceColor','b','EdgeColor','none');
p2 = patch(isocaps(x,y,z,data,level), ... 
    'FaceColor','interp','EdgeColor','none');
isonormals(x,y,z,data,p1);alpha 1;
view(90,90) % view angle
axis on; box off; camlight; lighting phong;
material shiny; %colorbar

Figure(3)

% for x = 1:10
% disp(x)
% end
% clf
data = smooth3(It,'box',1);
p1 = patch(isosurface(x,y,z,data,level), ... 
    'FaceColor','b','EdgeColor','none');
p2 = patch(isocaps(x,y,z,data,level), ... 
    'FaceColor','interp','EdgeColor','none');
isonormals(x,y,z,data,p1);alpha 1;
view(3) % view angle
axis equal;
axis on; box off; camlight; lighting phong;
material shiny; %colorbar

Save Figures
if Blockcenter==1
    s1='Beams';
else
    s1='+1Beams';
end

if Inverse==0
    s2='';
else
    s2='_Inverse_';
end

if Picture==1
    filename1txt=['n+1_Phase','-2D','_xi=',num2str(xi),'_xt=',num2str(xt),'_zi=',num2str(zi),'_zt=',num2str(zt),'_TS=',num2str(timeStamp(6)),'.jpg'];
    filename2txt=['n+1_Phase','-3D','_xi=',num2str(xi),'_xt=',num2str(xt),'_zi=',num2str(zi),'_zt=',num2str(zt),'_TS=',num2str(timeStamp(6)),'.jpg'];
    saveas(Figure(2),filename2txt)
    saveas(Figure(1),filename1txt)
end

End

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BIBLIOGRAPHY


[89] D. George, J. Lutkenhaus, D. Lowell, M. Moazzezi, M. Adewole, U. Philipose, Huiliang Zhang, and and Y. Lin, “3D photonic crystals through interference of multibeam with 4+1,5+1, and 6+1 configurations,” Optics Express, vol. 14, No.19 (2014), and


