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High Quality Aluminum Doped Zinc Oxide Plasmonic and Hyperbolic Metamaterials via Atomic Layer Deposition

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High Quality Aluminum Doped Zinc Oxide Plasmonic and Hyperbolic Metamaterials via Atomic Layer Deposition

A dissertation submitted in partial satisfaction
of the requirements for the degree

Doctor of Philosophy

in

Chemical Engineering

by

Conor T. Riley

Committee in charge:

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2016
The Dissertation of Conor T. Riley is approved and it is acceptable in quality and form for publication on microfilm and electronically:

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Co-chair

Chair

University of California, San Diego

2016
DEDICATION

In dedication to my friends and family
**TABLE OF CONTENTS**

Signature page ........................................................................................................ iii

Dedication ........................................................................................................ iv

Table of Contents ................................................................................................ v

List of Figures .................................................................................................... vii

List of Tables .................................................................................................... ix

Acknowledgements ............................................................................................ x

Vita .................................................................................................................... xi

Abstract ............................................................................................................ xiii

Introduction ....................................................................................................... 1

Chapter 1  Plasmonics ...................................................................................... 4
  1.1 Background ............................................................................................ 4
  1.2 Surface Plasmonics .............................................................................. 7
  1.3 Plasmonic Materials ........................................................................... 10

Chapter 2  Atomic Layer Deposition .............................................................. 15
  2.1 Background ............................................................................................ 15
  2.2 ZnO Growth Mechanism .................................................................. 16
  2.3 ZnO Doping ........................................................................................... 17
  2.4 Permittivity Values of AZO Deposited by ALD ................................ 18

Chapter 3  Optical Properties of AZO Grown by ALD .............................. 20
  3.1 Properties of AZO Deposited by ALD ................................................ 20
  3.2 Post Processing Procedures ................................................................ 27
  3.3 ZnO Buffer Layers ............................................................................... 32
  3.4 Methods ................................................................................................ 33
Chapter 4 Localized Surface Plasmon Resonant Cavities ........................................... 36
  4.1 Nanosphere Lithography ..................................................................................... 37
  4.2 Coated Silicon Nanopillars .................................................................................. 38
  4.3 Improved Silicon Coated Nanopillars ................................................................. 46
  4.4 ZnO Buffer Layers .............................................................................................. 50
  4.5 AZO Nanotubes .................................................................................................. 51
  4.6 Methods ............................................................................................................. 54

Chapter 5 Hyperbolic Metamaterials ............................................................................ 57
  5.1 Theory and Background ...................................................................................... 57
  5.2 Negative Refraction ............................................................................................. 63
  5.3 ALD Grown AZO/ZnO Multilayer Structure ...................................................... 67
  5.4 Embedded AZO Nanowire HMM ........................................................................ 71
  5.5 Methods ............................................................................................................. 73

Chapter 6 Hyperbolic Metamaterial Nanoparticles ...................................................... 75
  6.1 Introduction ........................................................................................................ 75
  6.2 Background ....................................................................................................... 76
  6.3 Broadband Absorption from Hyperbolic Nanotubes .......................................... 78
  6.4 Transfer of Hyperbolic Nanotube Arrays .......................................................... 87
  6.5 Other Systems ................................................................................................... 90
  6.6 Conclusion ......................................................................................................... 91
  6.7 Methods ............................................................................................................ 92

Chapter 7 Conclusion .................................................................................................. 95
  7.1 Dissertation Summary ....................................................................................... 95
  7.2 Outlook ............................................................................................................. 96

References ................................................................................................................ 98
LIST OF FIGURES

Figure 1 (A) SPP wave created from incident excitation radiation. (B) Localized surface mode due to LSPR on a nanosphere with a diameter much smaller than a wavelength of the incident radiation ........................................................................................................ 9

Figure 2 XRD pattern of a planar silicon wafer coated with an AZO film deposited with a 1:20 Al$_2$O$_3$:ZnO cycle ratio at 200 °C ........................................................................................................ 22

Figure 3 XRD patterns of 50 nm AZO coatings on planar silicon deposited at varying Al$_2$O$_3$:ZnO cycle ratios. The data shows all peaks shifting to larger diffraction angles and an a-axial [increase in (100) peak] preference as Al$_2$O$_3$ cycle occurrence is increased ........................................................................................................ 22

Figure 4 XRD patterns of Al$_2$O$_3$:ZnO films with a 1:15 cycle ratio on planar silicon deposited at varying temperatures. The data shows all peaks shifting to larger diffraction angles and c-axial preference [increase in (002) peak] as the deposition temperature is increased ........................................................................................................ 23

Figure 5 (100) Wurtzite diffraction angle as a function of (left) Al cycle frequency and (right) deposition temperature ........................................................................................................ 23

Figure 6 Hall measurements showing carrier concentration and hall mobility of a 50 nm AZO coating on a planar glass substrate for (a) different aluminum cycle frequencies (1:15-1:30 Al$_2$O$_3$:ZnO cycle ratios) and (b) different ALD deposition temperatures at a constant Al cycle frequency of 6.25% (1:15 Al$_2$O$_3$:ZnO cycle) ........................................................................................................ 25

Figure 7 Real and imaginary dielectric constants determined by ellipsometry for a 1:15 Al$_2$O$_3$:ZnO cycle ratio AZO-coated planar substrate deposited at 250˚C ........................................................................................................ 27

Figure 8 (a) Real and (b) imaginary dielectric constants of AZO and thermally processed AZO at 825 °C for 15 s. Both samples are coated with HfO$_2$ ........................................................................................................ 29

Figure 9 (a) PL spectrum of an unprotected AZO film before (red) and after (black) thermally processing at 825 °C for 15 s. (b) PL spectrum of an AZO film protected with HfO$_2$ before (blue) and after (black) thermally processing at 825 °C for 15 s ........................................................................................................ 31

Figure 10 (a) Real and (b) imaginary dielectric constants for thermally processed AZO films with varying ZnO buffer layer thicknesses ........................................................................................................ 32

Figure 11 Schematic showing the process for fabricating AZO coated SiNP arrays ........................................................................................................ 38
Figure 12 SEM image of (a) the top and (b) cross-section of a representative AZO-coated SiNP array (D = 303 nm). (c) HRTEM image of an ALD-deposited AZO layer. The AZO is being imaged from an area that peeled away from the nanopillar during cleavage of the silicon substrate. (d) cross-sectional image ...

Figure 13 IR extinction spectra of AZO-coated SiNPs deposited at (a) constant temperature (200 °C) and varying Al/Zn compositions and (b) constant Al/Zn composition (1:20 Al₂O₃:ZnO cycle ratio) at different deposition temperatures. (c) Log-log plot of carrier concentration vs. resonant wavelength for various............40

Figure 14 (a) FDTD simulations showing a comparison of the experimental (black) and simulated (green) extinction spectra for a SiNP (D = 200 nm) coated with a 50 nm thick, 1:15 Al₂O₃:ZnO cycle ratio AZO film. (b) Cross-section of an AZO-coated SiNP nanopillar while excited with linearly polarized light at peak....42

Figure 15 IR extinction spectra for AZO-coated SiNP arrays (grown at 250°C with a 1:15 Al₂O₃:ZnO cycle ratio) at different incident angles for (a) TE polarized light and (b) TM polarized light........................................................................................................43

Figure 16 (a) IR extinction spectra of a 1:15 Al₂O₃:ZnO cycle ratio AZO-coated SiNP array with different diameters. The increase in extinction at ~ 2200 nm for the 681 nm diameter pillars is attributed to the photonic modes of the silicon core. (b-d) SEM images of AZO-coated SiNPs with diameters of (b) 303 nm, (c) 490.44

Figure 17 IR extinction spectra of a 1:15 Al₂O₃:ZnO cycle ratio AZO-coated SiNP array deposited at 225 °C with varying AZO shell thicknesses. Due to a smaller AZO shell filling fraction, the optical density of the spectra are normalized for better comparison............................................................................................................................45

Figure 18 (a) IR extinction spectra of a 1:20 Al₂O₃:ZnO cycle ratio AZO-coated SiNP array deposited at 200°C with different gap sizes. Data points from 2690 nm to 2800 nm are excluded due to hydroxyl impurities in our set-up. SEM images of AZO-coated SiNPs with (b) 12 nm (c) 38 nm and (d) 92 nm gap......46

Figure 19 (a) Cross-sectional and (b) top-down SEM image of an SiNP array coated by an AZO/HfO2 (56/12 nm) film........................................................................................................................................47

Figure 20 IR extinction spectra of thermally processed AZO/HfO₂ (56 nm/12 nm) after deposition on a SiNP array and treated with a (a) 15 s thermal pulse with varying temperatures, (b) held at a constant temperature of 825 °C but varying pulse times, and (c) varying Al:Zn compositions (825 °C, 15s). (d) Comparison,49

Figure 21 (a) IR extinction spectra of a 56 nm/12 nm AZO/HfO₂ (green), 56 nm/12 nm ZnO/HfO₂ (blue), and HfO₂ (12nm) coated SiNP array. All samples in this graph were thermally treated with a 15 s pulse at 825 °C. (b) FDTD simulation extinction spectra comparing the LSPR peak of an AZO coated........49
Figure 22 IR extinction spectra of thermally processed AZO/HfO$_2$ (20 nm/12 nm) layer deposited on a SiNP array with varying ZnO buffer layer thicknesses....51

Figure 23 Fabrication scheme of AZO nanotubes.....................................................52

Figure 24 SEM images of top down (a, b, c) and cross sectional (d, e, f) view of AZO nanotubes for sample A, B and C, respectively..........................53

Figure 25 Normalized optical density spectrum of (a) simulated and (b) experimental AZO nanotubes as shown in figure 24.................................54

Figure 26 Isofrequency surfaces of (a) dielectric (b) type I HMM and (c) type II HMM mediums..............................................................61

Figure 27 Schematics of (a) multilayer and (b) nanowire array geometries capable of hyperbolic dispersion..................................................62

Figure 28 Schematic of the razor blade experiment showing negative refraction.................................................................66

Figure 29 (a) SEM image of multilayer ZnO/AZO HMM comprised of 8 ZnO/AZO (56nm/56nm) (b) TM polarization transmission ratio of partially blocked beam/full beam showing a clear peak indicative of negative refraction and (c) TE polarization transmission ratio of partially blocked beam/full beam showing the...68

Figure 30 Real and imaginary effective permittivity elements for an (a) AZO/ZnO multilayer with fill fraction f=0.5..................................................68

Figure 31 SMM field plots ($|E|^2$) for TE and TM-polarized light of different wavelengths, incident from air, at 25° from normal, onto 50 period structure of alternating 56nm ZnO and AZO layers. Losses are omitted for clarity........70

Figure 32 SMM field plots ($|E|^2$) for TE and TM-polarized light of wavelength 1470nm, incident from air at different angles from normal, onto 50 period structure of alternating 56nm ZnO and AZO layers. Losses are omitted for clarity..........................................................71

Figure 33 SEM images taken at different steps during the fabrication of AZO nanowires embedded in ZnO including (a) ZnO-coated silicon nanowires , (b) etched silicon leaving behind nanoholes, and (c) AZO-filled nanoholes. (d) Real and (e) imaginary optical constants as predicted by EMT (dashed)........72

Figure 34 (a) Schematic of coupled HNTs. SEM images of the HNT arrays as viewed in the plane (b) parallel and (c) perpendicular to the nanotube axis............79

Figure 35 (a) Absorption spectra of HNT arrays deposited at a temperature of 185 °C and 200 °C along with a spectrum of a pure AZO nanotube array
deposited at 200 °C. (b) Schematic of the incident radiation at angle $q$ showing TM polarization. Wide-angle absorption spectra for (c) TM and (d) TE.................80

Figure 36 (a) IR reflection spectrum of an HNT array. (b) Absorption spectrum of HNT arrays measured by an integrating sphere (A=1-T-R) and specularly (A=1-R)...........................................................................................................81

Figure 37 Simulated absorption of (a) the exact structure and EMA to describe the HNT shell, (b) EMA HNT arrays with air cores and solid hyperbolic metamaterial nanowires, and (c) exact structure HNT arrays with smooth and roughened tops (RMS = 200 nm). Unless otherwise stated simulated.........................82

Figure 38 Simulated absorption of (a) exact structure HNTs with increasing $n$ from 1-8 (blue to yellow) and 13 (black) with constant $g$, (b) exact structure HNT arrays with varying $a$ and constant $D_t$, and (c) EMA solid hyperbolic nanowire arrays of varying diameter. Unless otherwise stated parameters $L, D_t, D_c, g, a$..84

Figure 39 Simulated absorption using the exact structure of (a) HNTs with a varying $ff_m$ in the shell, (b) common HMMs compared with the HNTs, and (c) HNTs with varying length. Unless otherwise stated parameters $L, D_t, D_c, g, a, n, t_m$ and $t_d$ are kept constant at 1.5 µm, 740 nm, 220 nm, 30 nm, 770 nm, 10........84

Figure 40 SEM image of sample B as viewed in the plane (a) perpendicular and (b) parallel to the nanotube axis and sample C as viewed from the plane (c) perpendicular and (d) parallel to the nanotube axis.........................................................87

Figure 41 (a) Comparison of experimental and simulated absorption spectra for sample A. (b) Transmission and (c) absorption spectra for samples A-C with parameters as described in Table 1 after flexing several times as shown in (e). Photograph of sample A showing (d) visible transparency and (e) mechanical...89

Figure 42 Exact structure simulated absorption spectra of a closely packed TiN/(Al,Sc)N based (a) HNT arrays and (b) hyperbolic nanosphere arrays. The HNT array parameters $L, D_t, D_c, g, a, n, t_m$ and $t_d$ used in the simulation were 750 nm, 500 nm, 60 nm, 30 nm, 530 nm, 11, 10nm, and 10nm, respectively.................91
TABLE OF CONTENTS

Chapter 1: Introduction......................................................1

Chapter 2: Methodology......................................................7

Chapter 3: Results.............................................................15

Chapter 4: Discussion.........................................................23

Chapter 5: Conclusion..........................................................28

A.1: Supplementary Information..........................................39

Appendix A: Data Tables....................................................45

Appendix B: Figures............................................................60

References.................................................................65

List of Tables........................................................................89

List of Figures......................................................................94

Symbols and Abbreviations..................................................100

Index....................................................................................105
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ABSTRACT OF THE DISSERTATION

High Quality Aluminum Doped Zinc Oxide Plasmonic and Hyperbolic Metamaterials via Atomic Layer Deposition

by

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Doctor of Philosophy in Chemical Engineering

University of California, San Diego, 2016

Professor Donald Sirbuly, Chair
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The ability to transform energy from electromagnetic radiation into oscillations of free electrons at the surface of certain materials forms the basis of surface plasmonics. The majority of research in this area has utilized noble metals such as gold and silver owing to their appropriate optical response and
low loss at visible frequencies. However, these materials are not suited for many applications operating out of the visible spectrum and at high temperatures. Therefore many researchers are investigating new plasmonic materials. At the forefront of this search is aluminum-doped zinc oxide. By adjusting the free electron concentration, this high melting point material can be tuned to operate throughout the infrared spectrum up to the important telecommunication wavelength (ca. 1550 nm) with lower loss than any other material studied. However, to date, high quality aluminum-doped zinc oxide capable of operating at telecommunications wavelengths has only been demonstrated with the non-scalable and non-conformal method of pulsed laser deposition. Herein, a simple process is devised that enables the use of atomic layer deposition, an ultraconformal, highly scalable technique, to synthesize tunable aluminum doped zinc oxide thin films with plasmonic properties that rival the best films achieved by pulsed laser deposition. This method is proven to be a powerful tool for plasmonic applications by exploiting the ultraconformal properties of atomic layer deposition to make materials that cannot be made by any other process. This is accomplished by creating tunable localized surface plasmonic resonant cavities made of vertically aligned aluminum doped zinc oxide coated silicon nanopillars and solid aluminum doped zinc oxide nanotubes. In addition, hyperbolic metamaterials comprised of aluminum doped zinc oxide and zinc oxide are created in the multilayer and the embedded nanowire geometry. Finally, this method is used to create the first demonstration of a new class of transferable
hyperbolic metamaterials particles in the form of vertically aligned hyperbolic nanotubes. When closely packed, these particles show broadband absorbance with a single monolayer. More importantly, they can be transferred to virtually any substrate paving the way for flexible and visibly transparent materials.
Introduction

Although it was poorly understood at the time, the earliest advancements in the field of optics were achieved by exploring different materials to manipulate the reflection, transmission and absorption of light. This led to the creation of many of the common objects we still use today such as mirrors, stained glass and lenses. Within the last 3,000 years the fields of optics and photonics have expanded considerably giving us the ability to communicate over long distances at near-light speeds, harvest renewable energy from the sun and create detection devices sensitive enough to identify a single molecule. Many of the significant modern discoveries have been found by examining the interesting phenomena that occurs when light interacts with a solid material engineered to have structures much smaller than the wavelength of light. When operating in the visible and infrared, this is known as the field of nanophotonics. One subdivision of nanophotonics is called plasmonics. This specific case utilizes materials with large electron densities that, when impinged upon by light of proper momentum, will create a highly confined and intense electric field leading to many exciting applications such as ultra-low concentration sensing, subdiffraction waveguiding [1] and imaging [2] and advanced biomedical research for the treatment of devastating diseases such as cancer [3]. Until recently, the field of plasmonics has remained relatively myopic in terms of materials due to the favorable optical properties of gold and silver at visible wavelengths. However, due to the needs
for high temperature, corrosion resistant and infrared plasmonic applications, recent research efforts have expanded in order to explore alternative candidates [4]. One of the most promising candidates for high temperature, corrosion resistance and infrared plasmonic applications is aluminum-doped zinc oxide (AZO). However, not many fabrication methods are capable of producing AZO with optical properties suitable for applications in the important telecommunication region. The methods that have been demonstrated thus far either have high dissipation losses, only work for relatively thick films and/or are challenging to scale up into commercially available devices. Atomic layer deposition is a method of great interest to the scientific community due to its ability to grow uniform, pinhole free thin films on very large substrates (> 1 m² has been demonstrated), control the film thickness on the angstrom scale and easily incorporate foreign atomic dopant species into the material matrix. In addition, being a gas phase deposition method, atomic layer deposition has the unmatched ability to conform to very small feature sizes; an extremely powerful tool in the field of nanophotonics. However, prior to this work, high quality AZO grown by atomic layer deposition has not produced films capable of operating at telecommunication wavelengths.

Therefore, this dissertation outlines a simple process for creating high quality AZO grown by atomic layer deposition and describes methods for using the films to make high quality nanoplasmonic and hyperbolic metamaterials that cannot be made by any other process. Chapter 1 gives a brief overview of the
basic history and theory of plasmonics and reviews the materials currently being used. Chapter 2 gives a brief background in atomic layer deposition and reviews the previous work on AZO grown by this method. Chapter 3 discusses the basic properties of AZO created by atomic layer deposition and demonstrates a simple process for improving these properties to access high quality, ultraconformal films plasmonically active at telecommunication wavelengths. Next, chapter 4 applies these principles to created localized surface plasmon resonant cavities. Chapter 5 introduces hyperbolic metamaterials and demonstrates AZO/ZnO based materials created by atomic layer deposition. Next, chapter 6 introduces a new type of hyperbolic metamaterial that cannot be made by any other process. Finally, chapter 7 summarizes the work and discusses the outlook.
Chapter 1

Plasmonics

This chapter gives a brief overview into the background and theory of plasmonics. This starts with the Drude model for bulk plasmons and continues to surface plasmonics. This serves as the fundamental theory that lays the foundation for the remaining chapters. In addition the currently available plasmonic materials are summarized followed by a brief review on the currently available AZO deposition methods and corresponding optical properties.

1.1 Background

Plasmonic materials are materials that contain a large amount of charged particles such that the charged species can be treated as a plasma within the material. Although highly doped p-type semiconductors have been shown to possess plasmonic behavior [5, 6], for simplicity, this dissertation will focus on metals and n-type semiconductors where unbound electrons are the charged particles. In this case, the unbound electrons in the plasma respond heavily to electric fields allowing it to become polarized. In general, the dielectric displacement, \( \mathbf{D} \), of a material in the presence of an external electric field, \( \mathbf{E} \), can be written as:
\[ D = \varepsilon_0 E + P \quad (1) \]

Where \( \varepsilon_0 \) is the vacuum permittivity and \( P \) is the macroscopic polarization response in terms of the electrical dipole moment per unit volume. For a plasma of unbound electrons, this is expressed as:

\[ P = -ne \quad (2) \]

Where \( n \) is the unbound electron concentration, \( e \) is the charge of the electron and \( x \) is the displacement. Using equations 1 and 2, the interaction of light and plasmonic materials can then be understood by the Drude model [7-9]. Here the equation of motion for an electron of mass \( m \) within the plasma with an applied external electric field, \( E \) is given by:

\[ m \frac{d^2x}{dt^2} + my \frac{dx}{dt} = -eE \quad (3) \]

Where \( \gamma \) is the damping coefficient that takes into account the collisions of the electrons. Since \( E \) is provided by the incident radiation, it is assumed to be harmonic, time dependent and given as, \( E(t) = E_0 e^{-i\omega t} \). Consequently, the response of the electron must be of similar form; \( x(t) = x_0 e^{-i\omega t} \). Where \( E_0 \) and \( x_0 \) represent the amplitudes of the electric field and electron oscillation, respectively.
Therefore, solving equation 3 with the described solutions gives a new form for the time dependent displacement as:

\[ x(t) = \frac{e}{m(\omega^2 + iy\omega)} E(t) \]  \hspace{1cm} (4)

Next, using equations 1, 2 and 4, the dielectric displacement can be expressed as:

\[ D = \varepsilon_0 E \left( 1 + \frac{n_e^2}{m\varepsilon_0 (\omega^2 + iy\omega)} \right) \]  \hspace{1cm} (5)

Next, the plasma frequency, \( \omega_p \), is defined as:

\[ \omega_p = \frac{n_e^2}{\sqrt{m\varepsilon_0}} \]  \hspace{1cm} (6)

Using the constitutive relations, \( D \) is generally expressed in terms of the dielectric permittivity of the material, \( \varepsilon \), as \( D = \varepsilon E \varepsilon_0 \). Therefore, the dielectric constant can be written as:

\[ \varepsilon(\omega) = 1 + \frac{\omega_p^2}{(\omega^2 + iy\omega)} \]  \hspace{1cm} (7)
However, the actual material is comprised of a neutral plasma consisting of unbound electrons surrounding their atomic cores. The polarization of these cores are significant, particularly at higher frequencies [9], and must be taken into account. This is accomplished by adding an extra polarization term ($P_b = \varepsilon_0 E (\varepsilon_b - 1)$) to equation 1 where $\varepsilon_b$, is the background permittivity. This leads to the permittivity of an actual plasmonic material:

$$\varepsilon(\omega) = \varepsilon_b + \frac{\omega_p^2}{(\omega^2 + i\gamma \omega)}$$  \hspace{1cm} (8)

Finally, the dielectric constant can be decomposed into it’s real an imaginary parts:

$$\varepsilon(\omega) = \varepsilon' + i\varepsilon'' = \varepsilon_b - \frac{\omega_p^2}{(\omega^2 + i\gamma \omega)} + i \frac{\omega_p\gamma}{(\omega^2 + i\gamma \omega)\omega}$$  \hspace{1cm} (9)

Where $\varepsilon'$ and $\varepsilon''$ signify the real and imaginary parts of the dielectric constant.

1.2 Surface Plasmonics

The theory described in section 1.1 outlines a method to obtain the bulk dielectric permittivity within a Drude metal. However, a very interesting consequence of these properties occurs along the dielectric/metal interface. This is known as surface plasmonics. Essentially, when transverse-magnetic (TM)
polarized electromagnetic excitation with large enough momentum impinges upon a metal/dielectric interface, a surface plasmon-polariton (SPP) will form and propagate along the interface with an evanescent decay into the dielectric due to the grouping of electrons in the material as shown in figure 1a. The dispersion relation for such waves are given as:

\[ \beta = k_0 \sqrt{\frac{\varepsilon_1 \varepsilon_2}{\varepsilon_1 + \varepsilon_2}} \] (10)

Where \( \beta \) is the propagation constant of the SPP, \( k_0 \) is the vacuum wave vector, \( \varepsilon_1 \) and \( \varepsilon_2 \) are the dielectric functions of the metal and dielectric, respectively. Since the dispersion of the incident radiation is given by \( \beta = k_0 \sqrt{\varepsilon_2} \), the momentum of incident radiation will always be of lower magnitude. Therefore additional fabrication efforts are needed to create propagating SPPs. This was first demonstrated in 1968 using the Otto configuration [10] and Kretschmann method [11] which use a prisms to attain the additional momentum needed for excitation. In addition to prisms, gratings [12] and surface roughness [9] can also be used to overcome the momentum barrier. Regardless of the fabrication opsticles, the resultant SPPs create an intense electric field that is highly confined to the surface. Therefore many devices have been used with these configurations for applications including sensing [13], subdiffraction waveguiding [1] and imaging [2].
When plasmonic materials are engineered to have features much smaller than the excitation wavelength, a dipole moment will form inside the structure in response to an electromagnetic wave. This causes the particle to become polarized, forming a localized plasmonic standing wave that occurs at the surface as shown in figure 1b. Due to a restoring force, a resonant condition arises making the plasmonic material a resonant cavity. This is known as localized surface plasmon resonance (LSPR). Much like propagating waves, a large electrical field is created and highly confined to the surface. However, these modes are excited by direct illumination, which eliminate some of the fabrication challenges that must be considered for propagating surface plasmons. In addition to the material properties of the plasmonic material and surrounding dielectric, the resonance can also be tuned by varying the particles physical dimensions.

Figure 1 (A) SPP wave created from incident excitation radiation. (B) Localized surface mode due to LSPR on a nanosphere with a diameter much smaller than a wavelength of the incident radiation.
1.3 Plasmonic Materials

The choice of plasmonic materials play a large role in the performance and operating spectral region of the devices based on both SPP and LSPR. Since the materials response is best characterized by the dielectric constant, a more explicit examination of equation 9 is necessary.

In equation 9, the real part of the permittivity is related to the polarization response of the material and the imaginary part describes the optical loss. The crossover wavelength, $\lambda_c$, is defined as the wavelength in which the real part is equal to zero. At wavelengths longer than $\lambda_c$ the polarization response of the plasma oscillations are fast enough to interact with the oscillation of incident electromagnetic radiation and the material behaves like a metal. At wavelengths shorter than $\lambda_c$ the material becomes transparent and behaves as an insulator. Technically, materials can be plasmonically active at all wavelengths longer than $\lambda_c$, however, since the permittivity is inversely related to the impedance by $Z = \sqrt{\frac{\mu_m}{\varepsilon}}$ (where $\mu_m$ is the magnetic permeability which is unity for the non-magnetic materials discussed in this dissertation), impedance matching becomes a challenge at wavelengths much longer than $\lambda_c$. Consequently, the resultant large reflection is not desirable for many applications. Since $\lambda_c$ is related to $\omega_p^2 \propto n$, as seen in equations 6 and 9, choosing materials with an appropriate $n$ is paramount to a working plasmonic device. Conventional metals such as gold and silver which have $n \approx 1 \times 10^{22} - 1 \times 10^{23}$ cm$^{-3}$ are therefore useful for visible and
NIR applications. However, semiconductors are used for longer wavelengths due to their tunable carrier concentrations lower than \( n \approx 1 \times 10^{21} \text{ cm}^{-3} \).

Also seen in equation 9, \( \varepsilon'' \) is proportional to \( \gamma \) which can be related by the carrier mobility, \( \mu \), by:

\[
\gamma = \frac{e}{\mu m_e} \quad (10)
\]

However it should be noted that other factors are responsible for optical loss such as intra- and inter-band transitions, surface roughness, substrate adhesion and metal-substrate contact surface area [14].

For SPP devices the main parameters that affect the device performance are it’s propagation length and confinement width. A large \( \varepsilon'' \) will create a more dampened propagating wave while a small \( \varepsilon' \) will cause a larger penetration into the lossy metal. Therefore figure of merits (FOM) have been cited as \( (\varepsilon')^2/\varepsilon'' \) [4]. The LSPR properties can be explained by Mie theory that shows that the resonant wavelength (wavelengths at which the extinction cross-section reaches a maximum) can also be tuned by increasing the carrier concentration. Analogous to guided modes in dielectric resonators, the quality factor \( \left( \frac{\lambda_r}{\Delta \lambda} \right)^2 \) (where \( \lambda_r \) is the resonant wavelength and \( \Delta \lambda \) is the full width half max of the resonance) of a plasmonic resonator can be tuned by varying the optical loss [15, 16]. Although highly significantly on the geometry of the resonant nanostructures,
FOMs for LSPR typically are in the form: $(\varepsilon')^N/\varepsilon''$ [4] (where N is an integer based on the particle geometry).

Therefore the material used can have a profound effect on the performance of a plasmonic device. In addition, other factors must be examined when choosing a material such as air sensitivity and corrosion protection which have been shown to degrade plasmonic materials. For those reasons noble metals such as gold and silver have been the material of choice at visible wavelengths. However, gold and silver are expensive, rare, have low melting temperatures and are not considered to be compatible with CMOS processing [17]. Therefore other materials have been considered for visible wavelength applications. These mainly include Cu [18], Al [19], TiN [20] and various alloys [21-23]. For operating wavelengths longer than 1200 nm semiconductors are typically used. This has included doped Si [24], InAs [25], ZnO [17], SnO$_2$ [17, 26], GaAs [27], and Ge [28]. In addition 2D materials such as graphene have also been proven to generate plasmonic behavior [29].

One spectral region that is of particular interest is the telecommunication window (1260-1675 nm). This is due to a transmission window in SiO$_2$ fiber optics which are used for high speed communication. Plasmonic materials working in this region are therefore sought after for enhancement of gain media, optical transmitters/photodetectors and subdiffraction waveguiding. Specifically, erbium, a commonly used material in gain media and lasing, has an emission peak at 1550 nm. However, an appropriate plasmonic material must have a
sufficiently large $n$ value ($> 1 \times 10^{21} \text{cm}^{-3}$) to operate in this spectral region. Unfortunately, obtaining such high values of $n$ can be challenging for many semiconductors. This is because at large dopant concentrations the dopant material will eventually reach a solid solubility limit at which point the dopant species will begin to precipitate into clusters resulting in a diminished value of $n$. Therefore $\varepsilon_b$, $m$ and $\mu$ must also be taken into account. Unfortunately, Si, GaAs and Ge have large values of $\varepsilon_b$ and/or cannot overcome the solubility limits needed to achieve sufficient values of $n$ for plasmonics activity in this region. Therefore only few materials with $\lambda_c$ near telecommunication windows have been experimentally demonstrated as viable materials including transparent conducting oxides (TCO) such as In doped SnO$_2$ (ITO), Ga doped and Al doped ZnO, (GZO, AZO, respectively). Although these materials have been demonstrated to work within the telecommunications region, AZO has been shown to operate with significantly lower optical loss [17].

For these reasons the optical properties of AZO have been studied for different deposition methods. The work accomplished prior to the research reported in this dissertation is summarized in table 1. Because AZO is a non-stoichiometric material, the value of $\lambda_c$, varies widely with different deposition methods, thicknesses, and post processing procedures. AZO plasmonics was first proposed by West et. al [30]. Here, the authors theoretically predicted $\lambda_c > 1400$ nm with $\varepsilon'' < 0.5$ at $\lambda_c$, by extracting data from previously reported values [31]. Soon after, the first demonstration of AZO as a plasmonic material
was achieved with pulsed laser deposition (PLD) for films thicknesses > 150 nm [17, 32]. This method was shown to create high carrier concentration AZO with λ_c~1400 nm and corresponding ε'' ~0.4. The carrier concentration was also shown to be tunable with aluminum concentration and post deposition thermal processes. Plasmonic behavior at telecommunication wavelengths was also demonstrated by sputtering [33]. By carefully adjusting the oxygen partial pressure, the authors showed carrier concentrations of 1.25x10^{21} cm^{-3} with films thickness of 120 nm, leading to λ_c~1410 nm. However, higher losses (ε'' = 0.65 at λ_c) were shown with this method. It is worth noting that AZO nanoparticles with plasmonic behavior near telecommunication wavelengths have also been synthesized from solution methods [34]. However, integrating these nanoparticles into many of the devices mentioned earlier is a major challenge, therefore, the focus will remain on thin film deposition methods of AZO for this dissertation.

Portions of Chapter 1 have been submitted for publication as: J. S. T. Smalley, C. T Riley, D. J. Sirbuly, Z. Liu, Y. Fainman, “Active and Tunable Near-Infrared Hyperbolic Metamaterials.”
Chapter 2

Atomic Layer Deposition

Being a laser based deposition method, scalability with PLD presents a major challenge for fabricating commercially available devices. Additionally, both PLD and sputtering do not have the ability to conform to nanoscale features, which can be important for many nanostructures required for nanoplasmic materials. Another deposition method that has the potential to circumvent these issues is atomic layer deposition (ALD). Unlike the physical deposition methods described above, ALD is a gas phase deposition method which utilizes unique surface reactions to create smooth, pinhole free, tunable, and ultra-conformal films with thickness control on the angstrom scale [35]. These unmatched abilities have recently afforded ALD as a popular choice for many electrical applications in the semiconductor industry, however, prior to this work, little research using ALD for plasmonic material deposition has been conducted.

2.1 Background

ALD is a gas phase process that relies on sequential, self-limiting surface reactions provided by chemical pulses. In most cases the surface reactions start with a first reactant, A, forming a monolayer at the substrate surface. Next, a second reactant, B, is introduced into the chamber where it reacts with A. The
chemicals are engineered such that only A can react with B and vice versa. Therefore, the film is grown by oscillating sequential chemical pulses of A and B until the desired film thickness is achieved. Unlike the conventional chemical vapor deposition method (CVD), all chemical reactions are completed solely at all unreacted surface sites and not with their own species. This allows the chemical pulses to freely diffuse throughout the sample and sufficiently react with available surface sites within high aspect ratio structures. This results in excellent step coverage which leads to pinhole free, continuous films [35]. In addition, the substrate scale is only limited by the reactor size which has led to ALD growth on substrates > 1m² [36].

The first material to be grown by ALD was ZnS in 1974 [35]. However, it was in 1980 that the first materials produced by ALD was published [37]. Due to the sequential, self-limiting requirement of ALD the majority of materials grown have been diatomic such as SiO₂, ZnO [38], TiO₂ [39], Al₂O₃ [35]. However, self-limiting methods using hydrogen radicals have been created for transition metal deposition [40, 41].

2.2 ZnO Growth Mechanism

The most common precursors for ZnO growth are diethyl zinc (DEZ) as the zinc source and deionized water as the oxygen source. In this case a gas phase H₂O pulse is first introduced into the system such that it hydroxylates the surface of the substrate. Next, the DEZ is pulsed into the chamber where it reacts
with the hydroxyl groups on the substrate surface. The overall chemical reaction for one cycle is given as:

\[
\text{Zn}(CH_2CH_3)_2 + H_2O \rightarrow \text{ZnO} + 2C_2H_6 \quad \Delta H = -70 \text{kcal}
\]  

(11)

Since this reaction is exothermic the deposition takes place at relatively low temperatures with typical depositions taking place from 100 – 200 °C. However, room temperature deposition has been achieved [42]. Other than the obvious implications for substrate compatibility, the deposition temperature has also been observed to tune the electronic properties, crystallinity and growth rate of the ZnO [35, 43]. In addition to DEZ and H₂O other chemicals have been used. For the zinc source this includes zinc acetate [44] and dimethyl zinc [45]. However these reactions are less favorable and therefore require higher deposition temperature. For the oxygen source O₂ [45], O₃ [46] and N₂O [47] have also been used with higher deposition temperatures as well.

2.3 ZnO Doping

Chemical doping is easily achieved with ALD by replacing one of the chemical pulses with another source material. This has been achieved for ZnO with many dopant materials such as aluminum [48], nitrogen [49], phosphorus [50], titanium [51], gallium [52] and germanium [53]. For aluminum doping in AZO, a trimethyl aluminum (TMA) pulse, replaces a DEZ pulse. Although the
exact mechanism of aliovalent doping by aluminum still remains a research topic, it is thought that an aluminum atom is substituted in place of a zinc atom in order to add one unbound electron to the AZO system.

2.4 Permittivity Values of AZO Deposited by ALD

The optical properties of AZO grown by ALD determined by ellipsometry prior to the work done in this dissertation are shown in table 1. Unfortunately, AZO films grown by ALD have relatively high $\varepsilon''$ values and long wavelength $\lambda_c$. The first reports of the plasmonic properties of AZO deposited by ALD showed that the carrier concentrations of the films could be easily tuned by adjusting the aluminum concentration [51]. However the demonstrated $\lambda_c\sim2000$ nm for 250 nm thick films with $1.0 < \varepsilon'' < 2.0$ were inferior to PLD and sputtering results. Later, the sensitive thickness dependence on the carrier concentration was shown by dramatically tuning $\lambda_c$ from $\lambda_c\sim2200$ nm for $\sim95$ nm thick films to $\lambda_c\sim1600$ nm for $\sim577$ nm thick films with corresponding of $\varepsilon''\sim3.5$ and $\varepsilon''\sim0.9$, respectively [54]. However the high loss, inappropriate working spectral range and/or large thicknesses of these films do not provide much use for many applications in many plasmonic devices. Therefore the focus of this dissertation is to create high quality AZO films by ALD that can operate within the telecommunications window.
Portions of Chapter 2 have been submitted for publication as: J. S. T. Smalley, C. T Riley, D. J. Sirbuly, Z. Liu, Y. Fainman, “Active and Tunable Near-Infrared Hyperbolic Metamaterials.”

Table 1: Summary of plasmonic properties of AZO

<table>
<thead>
<tr>
<th>Ref</th>
<th>Deposition Method</th>
<th>$\lambda_c$ (nm)</th>
<th>$\varepsilon''$@ $\lambda_c$</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[17]</td>
<td>PLD</td>
<td>1400</td>
<td>0.35</td>
<td>&gt; 150</td>
</tr>
<tr>
<td>[33]</td>
<td>Sputter</td>
<td>1410</td>
<td>0.65</td>
<td>120</td>
</tr>
<tr>
<td>[54]</td>
<td>ALD</td>
<td>1600</td>
<td>0.9</td>
<td>577</td>
</tr>
<tr>
<td>[51]</td>
<td>ALD</td>
<td>2000</td>
<td>1.2</td>
<td>250</td>
</tr>
</tbody>
</table>
Chapter 3

Optical Properties of AZO Grown by ALD

In this chapter the plasmonic properties of AZO grown by ALD are discussed. The optical properties are examined by correlating them to both the electrical and structural properties. The optical, electronic and structural data are all shown to be in good agreement solidifying the theories outlined in chapter 1. Further, a simple process to obtain low loss AZO active at the telecommunications region is demonstrated and explained.

3.1 Properties of AZO Deposited by ALD

As described earlier, ALD requires sequential surface reactions in order to grow thin films. This is done by flowing gaseous source materials across a substrate at a certain temperature and pressure. To grow ZnO, separate and oscillating zinc (diethyl zinc) and oxygen sources (DI water) are pulsed into the reaction chamber until the desired thickness is reached. Therefore, one ZnO cycle is equivalent to one zinc and oxygen source pulse. To dope the zinc oxide with aluminum, an aluminum source pulse (trimethyl aluminum) is periodically added in place of the zinc source pulse. How often the aluminum replaces the zinc source controls the dopant concentration. In this section the AZO coatings were created by depositing one Al₂O₃ cycle for every 15-30 ZnO cycles onto
planar substrates at 200-250°C. Confirmation of the AZO films comes from X-ray diffraction (Fig. 2) which shows peaks (for a 1:20 Al₂O₃:ZnO cycle ratio AZO coating) that correspond to wurtzite ZnO. Importantly, there is no evidence of crystalline impurities such as Al₂O₃ or ZnAl₂O₄. Additional XRD runs were carried out on planar AZO films synthesized at 200°C with 1:15-1:30 Al₂O₃:ZnO deposition cycle ratios to monitor any variations in the diffraction peaks as the Al incorporation was altered (Fig. 3-5). As the Al cycle frequency increases, all of the wurtzite diffraction peaks shift to higher angles. Since the ionic radius of Al³⁺ is considerably smaller (0.53 Å) than Zn²⁺ (0.74 Å), a decrease in the d-spacing between atomic planes is expected to occur when Zn sites are substituted by Al atoms. When the Al cycle frequency is kept constant at 1:15, and the temperature is increased from 200°C to 275°C, similar shifts to higher angles are also seen. This can be explained by higher incorporation of Al at elevated temperatures or by an increase in oxygen vacancies which has been observed in ZnO films deposited by ALD [55].
**Figure 2** XRD pattern of a planar silicon wafer coated with an AZO film deposited with a 1:20 Al$_2$O$_3$:ZnO cycle ratio at 200 °C.

**Figure 3** XRD patterns of 50 nm AZO coatings on planar silicon deposited at varying Al$_2$O$_3$:ZnO cycle ratios. The data shows all peaks shifting to larger diffraction angles and an a-axial [increase in (100) peak] preference as Al$_2$O$_3$ cycle occurrence is increased.
Figure 4 XRD patterns of Al$_2$O$_3$:ZnO films with a 1:15 cycle ratio on planar silicon deposited at varying temperatures. The data shows all peaks shifting to larger diffraction angles and c-axial preference [increase in (002) peak] as the deposition temperature is increased.

Figure 5 (100) Wurtzite diffraction angle as a function of (left) Al cycle frequency and (right) deposition temperature.
To further investigate the effect of Al doping on the carrier concentration, Hall measurements were performed on 50 nm ALD films prepared under different conditions. It was found that by increasing the Al cycle occurrence from 1:30 to 1:15 Al$_2$O$_3$:ZnO the carrier concentration increased linearly from $1.5 \times 10^{20}$ to $3.6 \times 10^{20}$ cm$^{-3}$ (Fig. 6a). At cycle ratios above 1:15, and a growth temperature of 200 °C, there were no further increases observed in the carrier concentration indicating that an upper limit on Al doping had been achieved. Above this concentration AlO$x$ suboxide clusters may form, creating an insulating character within the film which leads to a decreased carrier concentration [56]. When keeping the deposition temperature constant and increasing the aluminium cycle frequency, the Hall mobility drops and the carrier concentration increases. The decrease in mobility is expected due to an increase in electron-impurity scattering. By increasing the temperature from 200 °C to 250 °C, and holding the Al cycle ratio constant at 1:15, the carrier concentration can be further increased from $3.6 \times 10^{20}$ to $9.3 \times 10^{20}$ cm$^{-3}$ (Fig. 6b). All of the Hall measurements support the XRD data which show similar trends (i.e., higher conductivity, smaller d-spacing) when the carrier concentration is increased. This is strong evidence that the substitution of Al into the ZnO lattice is not only causing changes in the crystal lattice parameters but also significantly altering the electronic properties of the material.
Figure 6 Hall measurements showing carrier concentration and hall mobility of a 50 nm AZO coating on a planar glass substrate for (a) different aluminum cycle frequencies (1:15-1:30 Al₂O₃:ZnO cycle ratios) and (b) different ALD deposition temperatures at a constant Al cycle frequency of 6.25% (1:15 Al₂O₃:ZnO cycle ratio).

Next, the permittivity values for the AZO layer is extracted using ellipsometry. The sample characterized was deposited at 250°C with a 1:15 Al₂O₃:ZnO cycle ratio. Optical constants were then determined from the measured ψ and Δ values by modeling the AZO film on silicon using a series of Kramers-Kronig consistent oscillators using the Drude-Lorentz equation:

\[
\varepsilon(\omega) = \varepsilon_b - \frac{\omega_p^2}{\omega(\omega + i\gamma_p)} + \frac{f_1\omega_1^2}{\omega_1^2 - \omega^2 - i\omega\gamma_1} (12)
\]

Where \(\gamma_p\) is the Drude dampening coefficient, \(\gamma_1\) is the Lorentz dampening coefficient and \(f_1\) is the oscillator strength. The parameters of equation 11 are summarized in table 2.
Table 2 Drude lorentz parameters of a 1:15 Al$_2$O$_3$:ZnO cycle ratio AZO film deposited by ALD at 250 °C.

<table>
<thead>
<tr>
<th>$\omega_p$</th>
<th>$\gamma_p$</th>
<th>$f_t$</th>
<th>$\varepsilon_b$</th>
<th>$\omega_i$</th>
<th>$\gamma_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.231</td>
<td>0.281</td>
<td>0.699</td>
<td>2.855</td>
<td>4.392</td>
<td>0.064</td>
</tr>
</tbody>
</table>

The experiments showed a $\lambda_c$ of 2160 nm with a corresponding imaginary dielectric constant ($\varepsilon''$) of 2 (Fig. 7). Although this loss is considerably lower than noble metals at this wavelength, crossover wavelengths smaller than 1550 nm with lower losses have been reported using PLD [17]. Since these values are similar to other ALD studies [51] it is thought that the higher loss is due to the lower crystal quality inherent to the ALD deposition process. Furthermore, the optical loss has been shown to be inversely proportional to the electron mobility which often reflects the crystalline quality of a material. Highly doped AZO films deposited by ALD possess mobilities < 10 cm$^2$/V·s whereas AZO films created via PLD have been shown to have mobilities as high as 47.6 cm$^2$/V·s [57]. In addition, unlike other thin film deposition methods, it has been shown that the aluminum dopants deposited by ALD maintain their layered configuration which may not be ideal for achieving high carrier concentrations [58]. Although the PLD method has shown better plasmonic properties, the ability of ALD to coat/fill small feature sizes, paramount to the growing field of nano-optics, is still unmatched by any other thin film deposition process. Therefore post process procedures are needed in order to keep all the synthetic advantages of ALD, while achieving lower losses and negative permittivity at 1550 nm.
Figure 7 Real and imaginary dielectric constants determined by ellipsometry for a 1:15 Al$_2$O$_3$:ZnO cycle ratio AZO-coated planar substrate deposited at 250˚C.

3.2 Post Processing Procedures

In the last section the synthesis and plasmonic tunability of AZO films created by ALD was demonstrated. However, attaining thin films (< 60 nm) with crossover wavelengths below 2100 nm and low loss ($\varepsilon'' < 1$) could not be achieved. The smallest value of $\lambda_c$ obtained for a 56 nm film was at 2160 nm with a corresponding $\varepsilon''$ of ~ 2. To improve these properties the effects of thermal pulses by rapid thermal processing (RTP) was investigated. It was found that any thermal processing over 500˚C on the as-made AZO led to a decrease in the carrier concentration. However, if a 10 nm or thicker film of HfO$_2$ was deposited over the AZO by ALD, $\lambda_c$ could be tuned to higher energies and lower losses after RTP up to 900˚C. Figure 8 compares the optical constants obtained from ellipsometry for two 56 nm HfO$_2$ coated AZO films, one with (AZO-TP) and the
other without (AZO) a post-synthetic thermal treatment at 825 °C for 15 s. After the RTP treatment $\lambda_c$ shifts by over 600 nm from 2150 nm to 1545 nm. In addition, the losses for the thermally treated films are significantly reduced. According to the Drude theory a blueshift in $\lambda_c$ should be accompanied by an increase in the carrier concentration (Equation 9). Therefore Hall measurements were carried out on thermally processed and as-made AZO/HfO$_2$ films (600 nm/12 nm). In order to ensure that the bulk AZO material was probed, the HfO$_2$ layer was removed by RIE. Subsequently, the top 100 nm of the AZO was removed by wet etching to ensure no contaminants from the RIE process were present. The results of the Hall measurements are summarized in Table 3 which show that the carrier concentration increases from $1.0 \times 10^{21}$ cm$^{-3}$ to $1.5 \times 10^{21}$ cm$^{-3}$ after thermal processing.

**Table 3** Hall measurement results for AZO and ZnO, along with Drude model fitting parameters for AZO, before and after rapid thermal processing. All samples were thermally processed with a 12 nm HfO$_2$ protection layer. The protection layer was removed before carrying out the Hall measurement.

<table>
<thead>
<tr>
<th></th>
<th>$n \times 10^{21}$ (cm$^{-3}$)</th>
<th>$\mu$ (cm$^2$/V·s)</th>
<th>$p \times 10^{-4}$ (Ω·cm)</th>
<th>$\varepsilon_b$</th>
<th>$\omega_p$ (eV)</th>
<th>$\gamma$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AZO Before RTP</td>
<td>1.0</td>
<td>10.1</td>
<td>6.1</td>
<td>4.0</td>
<td>1.28</td>
<td>0.28</td>
</tr>
<tr>
<td>AZO After RTP</td>
<td>1.5</td>
<td>9.8</td>
<td>3.8</td>
<td>4.5</td>
<td>1.7</td>
<td>0.096</td>
</tr>
<tr>
<td>ZnO Before RTP</td>
<td>0.029</td>
<td>16.5</td>
<td>127.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ZnO After RTP</td>
<td>0.0087</td>
<td>16.8</td>
<td>429.7</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Consequently, ultralow resistivity films are created after thermal processing with a resistivity of 3.8x10^{-4} \, \Omega\cdot\text{cm}, which is the lowest reported value for ALD synthesized AZO to date. The Drude model fitting parameters of non-thermally processed and thermally processed AZO (825 °C, 15s) are also listed in Table 3 which shows an increase in $\omega_p$ and a decrease in $\gamma$ after thermal processing, qualitatively consistent with the optical constants described in Figure 8 and the carrier concentration values obtained from Hall measurements.

**Figure 8** (a) Real and (b) imaginary dielectric constants of AZO and thermally processed AZO at 825 °C for 15 s. Both samples are coated with HfO$_2$.

Further investigation into the enhanced carrier concentrations was carried out through PL studies. Information about the defect concentration of ZnO-based materials can be inferred by examining the visible portion of the PL emission spectrum. The most commonly referred defects in ZnO are oxygen vacancies ($V_o$), zinc interstitials ($Zn_i$), oxygen interstitials ($O_i$), oxygen antisites ($O_{Zn}$) and
zinc vacancies ($V_{Zn}$) [59, 60]. $V_o$ and $Zn_i$ are known to be electron donating whereas $O_i$, $V_{Zn}$ and $O_{Zn}$ are found to be electron accepting. Here, to ensure the PL signal was coming only from the AZO, RIE was carried out to remove the HfO$_2$ protection layer.

As seen in figure 9, films thermally processed at 825 °C for 15 s without the HfO$_2$ layer show a strongly enhanced PL signal at 600 nm. This PL emission is attributed to the $O_i$ defects which has been observed previously for thermally treated ZnO at 700 °C [61]. The formation of these particular defects has been reported to be caused by the creation of metallic zinc and it’s subsequent evaporation leaving behind accepting $O_i$ defects which reduce the carrier concentration [62]. On the other hand, the AZO films thermally processed with the HfO$_2$ layer show a slight decrease in the visible defect emission. This supports the argument that the HfO$_2$ serves as a protection layer preventing zinc evaporation. However, this does not explain why the carrier concentration increases after thermal processing. In addition to the Hall measurements for AZO, Table 3 also reports the results for pure ZnO. In contrast to AZO films, the ZnO carrier concentration decreases after thermally treating the HfO$_2$ protected samples. This suggests that carrier enhancement in the AZO is due to the activation of the aluminum dopants. It has been demonstrated that the amount of aluminum atoms contributing free electrons is far lower for ALD than other synthetic methods [58, 63]. Using an effective field model, it has been proposed that this discrepancy is due to the unique layer-by-layer configuration of
aluminum dopants [64] as opposed to randomly oriented dopants in other methods such as chemical vapor deposition, PLD, or sputtering. This model shows that the close proximity of adjacent aluminum atoms causes electronic repulsion that suppresses the donation of free electrons and decreases the carrier concentration. Therefore it is hypothesized that the boost in carrier concentration after the thermal processing is caused by the diffusion of aluminum atoms into the ZnO layers configuring the dopants into randomly oriented positions more suitable for supporting higher carrier concentrations. Experimentally derived diffusion constants from literature [65] support this theory by showing that the aluminum atoms are capable of traveling more than one half of a ZnO/Al₂O₃ period (~2nm) under the thermal conditions used in our experiments.

Figure 9 (a) PL spectrum of an unprotected AZO film before (red) and after (black) thermally processing at 825 °C for 15 s. (b) PL spectrum of an AZO film protected with HfO₂ before (blue) and after (black) thermally processing at 825 °C for 15 s.
3.3 ZnO Buffer Layers

The effects on the conductivity of aluminum-doped [66] and gallium-doped [67] ZnO films due to ZnO buffer layers (intermediate layer between substrate and AZO) has previously been studied. It has been shown that the grain size of ZnO buffer layers become larger with increasing thickness which translates to AZO film growth with larger grain sizes. Larger grain sizes decrease the amount of grain boundaries that create electronic traps and barriers which results in a more conductive film. This generates highly conductive AZO films that arise from an increase in both the carrier concentration and electron mobility. Therefore, according to Drude theory, a blueshift of $\lambda_c$ and lower loss is expected by the use of ZnO buffer layers. Figure 10a-b demonstrates this effect for HfO$_2$ protected and thermally processed (825 °C, 15 s) 56nm AZO films. Here $\lambda_c$ shifts from 1545 nm to 1450 nm when a 112 nm ZnO buffer layer is used. In addition, the optical loss is significantly decreased from 0.53 to 0.46 at 1550 nm.

![Graph](image)

**Figure 10** (a) Real and (b) imaginary dielectric constants for thermally processed AZO films with varying ZnO buffer layer thicknesses.
3.4 Methods

AZO films were deposited on the silicon nanopillar templates via ALD using a Beneq TFS200 atomic layer deposition system where the zinc, aluminum and oxygen sources were diethylzinc (DEZ), trimethylaluminum (TMA) and water, respectively. The films were grown by applying either a zinc or aluminum cycle before a water cycle at temperatures spanning from 200°C to 250°C. The aluminum concentration was controlled by changing the frequency of the TMA precursor cycle. For example, a film of ~ 2 wt% Al/Zn (nominal) was synthesized by using 1 TMA cycle for every 20 DEZ cycles (20:1 Zn:Al).

Hall measurements were performed on a home-built set-up using the van der Pauw method at room temperature with a magnetic field of 3000–5000 G. Silver ohmic contacts were used for all samples. The films in section 3.2 were 56 nm thick and deposited on sapphire or glass. Both 600 nm AZO and ZnO samples were deposited on sapphire and coated with 12 nm of HfO₂. HfO₂ layers were removed using reactive ion etching (RIE) via an Oxford P80 with CHF₃ and Ar gases. The top ~ 100 nm of ZnO based material was removed using dilute hydrochloric acid. The remaining thickness (~ 500 nm) was confirmed by ellipsometry. All photoluminescent (PL) measurements were taken from films deposited on RCA cleaned p-type (5 Ω·cm) prime silicon. To characterize the defect emission, the HfO₂ layers were first removed by RIE. Next, dilute HCl was used to etch away any contaminants from the RIE process. The samples were
then excited with a continuous-wave helium cadmium laser (Kimmon electric) and the PL spectra were captured using a thermoelectrically cooled (-75 °C) Princeton Instrument spectrometer. The laser beam was focused onto the sample (~ 50 µm spot size) at an angle of 45° and power density of ~ 1 W/cm².

All AZO film thicknesses were quantified on planar silicon substrates via ellipsometry using a filmetrics F20. For the permittivity values obtained in section 2.1, ellipsometry measurements were carried out using a commercial Woolam VASE ellipsometer that scanned from 300 nm to 2000 nm on a 90 nm thick AZO films (1:15 Al₂O₃:ZnO cycle ratio) deposited at 250°C. The remaining optical constants from 2000 nm – 3000 nm were extrapolated from the ellipsometry data using the Lorentz-Drude model. For the remaining sections measurements were extended to longer wavelengths (1600 nm – 3000 nm) using a second J.A. Woollam IR ellipsometer coupled to a Bruker v/66s Fourier transform infrared spectrometer. In order to obtain the optical constants for the multilayer samples (Si/AZO/HfO₂ and Si/ZnO/AZO/HfO₂), ellipsometry was first preformed on the bare, cleaned silicon. Next, the optical constants of ZnO and HfO₂ were obtained from Si/HfO₂ and Si/ZnO samples. The complex permittivity of AZO was then obtained by modeling the multilayer system where AZO was the only unknown. All models were carried out on the J.A. Woollam VASE software where Kramers Kronig consistent oscillators were fit to the experimentally obtained ψ and Δ values. XRD patterns were taken with a Rigaku Rotaflex using the Cu K-alpha wavelength.
All thermally treated AZO films were grown with a 20:1 Zn:Al ratio unless otherwise specified. After growth, rapid thermal processing was done using an AG Associates Heat Pulse 610 with a 1.5 L/min nitrogen flow rate. The maximum ramp up and ramp down speeds were used which took less than 15 s to reach the maximum temperature and less than 20 s to cool down to 300 °C.

Portions of Chapter 3 is a reprint of materials as it appears in the following publications: Conor T. Riley, Tien A. Kieu, Joseph S.T. Smalley, Si Hui Athena Pan, Sung Joo Kim, Kirk W. Post, Alireza Kargar, Dimitri N. Basov, Xiaoqing Pan, Yeshaiahu Fainman, Deli Wang and Donald J. Sirbuly, Plasmonic tuning of aluminum doped zinc oxide nanostructures by atomic layer deposition” Phys. Status Solidi RRL, 2014, 11, 948-952. The dissertation author was the primary investigator and the first author of these papers. Conor T. Riley, Joseph S. T. Smalley, Kirk W. Post, Dimitri N. Basov, Yeshaiahu Fainman, Deli Wang, Zhaowei Liu and Donald Sirbuly, “High-Quality, Ultraconformal, Aluminum-Doped Zinc Oxide Nanoplasmonic and Hyperbolic Metamaterials” Small, 2016, 12, 892-901. The dissertation author was the primary investigator and the first author of these papers.
Chapter 4
Localized Surface Plasmon Resonant Cavities

One of the main advantages of ALD is its ability to conform to high aspect ratio nanostructures. For LSPR, this ability can be a very powerful tool since the material itself no longer needs to be structured but the material can be conformed to a previously structured substrate. This feature is important since creating anisotropic etching conditions can be very challenging for certain materials whereas creating such profiles in other materials such as silicon has been studied for many decades. However, despite these advantages, relatively very few studies have reported LSPR by ALD grown films. In this chapter the AZO films grown by ALD demonstrated in chapter 3 are used to conformally coat nanostructures to create LSPR cavities. All the materials in this chapter and subsequent chapters use forms nanosphere lithography (NSL) to create the nanostructured templates. The LSPR cavities are created by the inherent films characterized in section 2.1 and later protected and thermally treated for improved cavities. In addition ZnO buffer layers are used to further improve the LSPR cavities and shift the resonant wavelength to the important telecommunication region.
4.1 Nanosphere Lithography

The ability to create nanostructures have revolutionized the majority of technology based fields. Therefore, many processes have been demonstrated which include focused ion beam lithography [68], electron beam lithography [69], nanoimprint lithography [70], immersion lithography [71], and nanoparticle self-assembly processes [72]. Focused ion beam lithography and electron beam lithography have the distinct advantage of being able to create high resolution (<10 nm) structures with many different geometries. However, scaling up to larger substrates sizes is expensive and time consuming with these methods. On the other hand, nanoimprint lithography uses a master mould created from either electron beam or focused ion beam lithography to create a stamp. This stamp can be used to scale up to larger substrate. In addition immersion lithography uses an immersion oil and high energy light in order to decrease the resolution limitied by the diffraction limit. Both of these methods create nanostructures on the order of < 50 nm and are currently either in use or being investigated for use in computer processors. However, these methods require the use of complicated and expensive setups limiting the throughput of samples created for small scale fundamental research projects. However, NSL uses combines self-assembly techniques with lithography to create a nanopatterning technique that uses relatively cheap materials and equipment allowing for large area samples to be made quickly and inexpensively.
NSL was first demonstrated by Hsu et. al. in 2008 [73]. As shown in figure 11, Stöber particles are grown from standard processes [74, 75] and self-assembled onto a substrate. Next the Stöber particles are decreased in diameter by RIE using gases that are selective to etch the Stöber particles only. The unmasked silicon is then etched with RIE, this time using a gas composition that is selective only to silicon. The remaining Stöber particle masks are removed with hydrofluoric acid leaving behind a silicon nanopillar (SiNP) template. Finally, the SiNP template is used to create LSPR cavities by coating the pillars with the plasmonically active AZO demonstrated in the chapter 1.

![Diagram](image)

**Figure 11** Schematic showing the process for fabricating AZO coated SiNP arrays.

4.2 Coated Silicon Nanopillars

As in chapter 3, the AZO coatings were created by depositing one Al\textsubscript{2}O\textsubscript{3} cycle for every 15-30 ZnO cycles at 200-250°C onto either planar substrates or the SiNPs created by NSL. In this section, unless specified otherwise, SiNPs with ~200 nm diameters, 540 nm lengths and a 480 nm pitch were used. These
dimensions were chosen to be small enough to eliminate any photonic modes in the SiNP [76] yet large enough to create well defined SiNPs. A representative array of SiNPs is shown in Fig. 12a-b. The cross-sectional image in Fig. 12c of a larger SiNP (to allow easier cleavage for imaging) shows that the AZO coatings are highly conformal, whereas the high-resolution transmission electron micrograph (Fig. 12d) reveals the AZO crystal structure with a lattice spacing of 0.26 nm corresponding to the (001) plane of the wurtzite crystal structure.

**Figure 12** SEM image of (a) the top and (b) cross-section of a representative AZO-coated SiNP array (D = 303 nm). (c) HRTEM image of an ALD-deposited AZO layer. The AZO is being imaged from an area that peeled away from the nanopillar during cleavage of the silicon substrate. (d) cross-sectional image of a larger diameter (D = 662 nm) AZO-coated SiNP showing a highly conformal film deposited by the ALD process.
Extinction spectra of 50 nm AZO-coated SiNPs are shown in Fig. 13a-b. The spectra have well defined LSPR bands that can be tuned by changing the Al/Zn cycling ratios and/or growth temperature. Bare SiNP arrays and undoped ZnO-coated SiNP arrays were also carried out as controls which showed no optical responses at these frequencies (Fig. 13c).

**Figure 13** IR extinction spectra of AZO-coated SiNPs deposited at (a) constant temperature (200 °C) and varying Al/Zn compositions and (b) constant Al/Zn composition (1:20 Al$_2$O$_3$:ZnO cycle ratio) at different deposition temperatures. (c) Log-log plot of carrier concentration vs. resonant wavelength for various AZO-coated SiNP arrays showing a linear relationship (dashed line) in accordance with the Drude model. Here, the resonant wavelength is defined as the wavelength at peak optical density. (d) IR extinction spectra of AZO (250°C, 1:15 Al:Zn) deposited on SiNPs and planar silicon, ZnO coated SiNPs, and uncoated SiNPs.
Furthermore, a coated SiNP (1:15 Al2O3:ZnO) was deposited at 200°C and annealed for 1 hour at 250 °C in the reactor chamber resulting in no significant change to the optical or electrical properties. This indicates that the doping occurs as a result of the ALD crystal growth, and temperature dependent sticking coefficients of the source chemicals, as opposed to temperature activation of the dopants [35]. Further, the blue shift in the LSPR frequency from 3200 nm to 2100 nm as the carrier concentration is increased is predicted by the Drude model (eqn. 9). The log-log plot in figure 13d shows that the LSPRs are tunable from the mid-wavelength IR to the NIR and have a linear relationship that matches well with the Drude model. More importantly the XRD, Hall measurements and spectroscopic data all show that as the aluminum concentration and substrate temperature increase more unbound electrons are added into the wurtzite lattice, blue shifting the plasmonic frequency.

Next, the obtained permittivity shown in figure 7 were used in finite-different time-domain (FDTD) simulations on an individual nanostructure with similar dimensions as the experiment. The calculated extinction spectrum of the simulated AZO-coated SiNP is shown in Fig. 14a which has a maximum peak at a similar wavelength as the experimental array. The broader experimental peak is mainly attributed to sample inhomogeneities (e.g., lattice disordering, surface roughness), as compared to the perfect simulated array, but inter-pillar coupling could also be contributing to a broader linewidth. A more detailed analysis is required for determining the exact origin of the discrepancies and will be a topic
of future work. In these studies it was observed that the predominant LSPR mode at normal incidence is due to the lateral dipole oriented perpendicular to the excitation wavevector with an electric field enhancement factor greater than 3 at the resonant wavelength (Fig. 15b).

**Figure 14** (a) FDTD simulations showing a comparison of the experimental (black) and simulated (green) extinction spectra for a SiNP (D = 200 nm) coated with a 50 nm thick, 1:15 Al₂O₃:ZnO cycle ratio AZO film. (b) Cross-section of an AZO-coated SiNP nanopillar while excited with linearly polarized light at peak resonance (2085 nm).

In addition, a significantly stronger light-matter interaction is observed with increasing incident angle under TM polarization (Fig. 15) which is a characteristic of the plasmonic modes observed in the simulations [9].
The AZO coating is the only part of the nanostructure that can support a LSPR mode and show a band that is tunable by impurity doping. Therefore, it is expected that additional tuning can be achieved by adjusting the dimensions of the nanostructure array. There was found to be no significant dependence of the LSPR resonant wavelength on the diameter of the SiNPs (Fig. 16a-f).

Figure 15 IR extinction spectra for AZO-coated SiNP arrays (grown at 250°C with a 1:15 Al₂O₃:ZnO cycle ratio) at different incident angles for (a) TE polarized light and (b) TM polarized light.
Figure 16 (a) IR extinction spectra of a 1:15 Al$_2$O$_3$:ZnO cycle ratio AZO-coated SiNP array with different diameters. The increase in extinction at ~ 2200 nm for the 681 nm diameter pillars is attributed to the photonic modes of the silicon core. (b-d) SEM images of AZO-coated SiNPs with diameters of (b) 303 nm, (c) 490 nm, and (d) 681 nm. (e) Histogram showing the diameter distributions of AZO coated SiNPs with average diameters ~300nm. (f) FDTD simulations of AZO coated SiNPs with varying diameters spanning the size distribution displayed in the previous histogram showing little optical variation of the resonant wavelength.
However, significant red-shifting was observed when the AZO film was increased from 40 nm to 75 nm (Fig. 17).

![IR extinction spectra of a 1:15 Al₂O₃:ZnO cycle ratio AZO-coated SiNP array deposited at 225 °C with varying AZO shell thicknesses. Due to a smaller AZO shell filling fraction, the optical density of the spectra are normalized for better comparison.](image)

**Figure 17** IR extinction spectra of a 1:15 Al₂O₃:ZnO cycle ratio AZO-coated SiNP array deposited at 225 °C with varying AZO shell thicknesses. Due to a smaller AZO shell filling fraction, the optical density of the spectra are normalized for better comparison.

This indicates that the excited dipole is mainly confined within the AZO shell and not within the silicon core for the dimensions probed. Furthermore, when the inter-pillar distance was decreased, the LSPR broadens and redshifts which is indicative of a plasmonic coupling effect (Fig. 18).
Figure 18 (a) IR extinction spectra of a 1:20 Al$_2$O$_3$:ZnO cycle ratio AZO-coated SiNP array deposited at 200°C with different gap sizes. Data points from 2690 nm to 2800 nm are excluded due to hydroxyl impurities in our set-up. SEM images of AZO coated SiNPs with (b) 12 nm (c) 38 nm and (d) 92 nm gap sizes.

4.3 Improved Silicon Coated Nanopillars

In section 3.2, we deposited the unprotected AZO onto SiNPs created by NSL to investigate the LSPR modes. Here, we use the same approach to verify our results and show how adjusting the thermal conditions can tune and increase the quality factor of the LSPR for protected AZO films. We demonstrate this using a SiNP array template with an average length, diameter and pitch of 702 nm, 201
nm and 445 nm, respectively. The standard deviation of the SiNP diameter was found to be 34 nm. Although this size distribution is significant it has been found to have no impact on the LSPR modes. After fabricating the nanopillars they were coated with a 56 nm thick layer of AZO and 12 nm of HfO$_2$ (Fig. 19)

![SEM image of SiNP array coated by AZO/HfO$_2$](image)

**Figure 19** (a) Cross-sectional and (b) top-down SEM image of an SiNP array coated by an AZO/HfO$_2$ (56/12 nm) film.

Figure 20a shows the LSPR of both as-made (25 °C) and thermally processed AZO coated/protected SiNPs. Consistent with the ellipsometric data discussed earlier, a clear blueshift is observed after thermal processing indicating an increase in carrier concentration. In addition, due to smaller losses in the post processed AZO, the quality factor is increased. Moreover, the tuning of the LSPR is demonstrated in Figure 20a-c. First, by varying the thermal processing temperature (15 s) it is clear that there is a significant blueshift and increase in the quality factor in the temperature range of 700-900 °C (Figure 5a). Below 700
little change is observed and above 950 °C the LSPR is no longer observed within the wavelength range probed. We find that the largest blueshift occurs between 825 °C and 900 °C. Moreover, when the temperature is held constant at 825 °C and the time is varied the ideal conditions are found to be 15 s - 30 s (Fig. 20b). Less than 15 s the aluminum atoms are not fully activated and the carrier concentration is still increasing. Above 30 s the quality factor of the peak begins to decrease. Therefore we find that the optimal thermal conditions for lowest loss and highest energy crossover frequency is achieved when the protected AZO films are processed at 825 °C for 15 s. It is therefore theorized that at these thermal conditions aluminum is allowed to migrate into a configuration that supports higher carrier concentration while suppressing donating defects. Moreover, ε” is reduced by improved AZO-substrate adhesion and/or improvements in the crystal structure. However, the exact mechanism for the improvements is still under investigation. In addition, similar to the non-processed AZO, the LSPR properties can also be tuned by adjusting the aluminum dopant concentration. Here the maximum blueshift and quality factor is achieved at a 20:1 Zn:Al chemical pulse ratio (Fig. 20c). At higher aluminum concentrations the carrier concentration is found to decrease most likely due to aluminum suboxide formation and clustering [56].
Figure 20 IR extinction spectra of thermally processed AZO/HfO$_2$ (56 nm/12 nm) after deposition on a SiNP array and treated with (a) a 15 s thermal pulse with varying temperatures, (b) held at a constant temperature of 825 °C but varying pulse times, and (c) varying Al:Zn compositions (825 °C, 15s). (d) Comparison of experimental IR extinction spectra and a FDTD simulation of an AZO/HfO$_2$ (56 nm/12 nm) layer coated on a SiNP (in experiment the sample was thermally processed at 825 °C for 15 s).

Figure 21 (a) IR extinction spectra of a 56 nm/12 nm AZO/HfO$_2$ (green), 56 nm/12 nm ZnO/HfO$_2$ (blue), and HfO$_2$ (12nm) coated SiNP array. All samples in this graph were thermally treated with a 15 s pulse at 825 °C. (b) FDTD simulation extinction spectra comparing the LSPR peak of an AZO coated SiNP with a 12nm HfO$_2$ layer (blue) and without HfO$_2$ (black).
In order to further investigate the LSPRs in the AZO/HfO$_2$ coated SiNP samples, finite difference time domain (FDTD) simulations were carried out using the optical constants obtained from ellipsometry and on dimensions identical to those measured in the experiments. As shown in Figure 20d there is excellent agreement between the simulation and experimental data for both the spectral positioning and quality factor. Importantly, controls were carried out on thermally treated samples that included SiNPs coated with only HfO$_2$ and SiNPs coated with ZnO/HfO$_2$ which did not show any optical activity in the NIR region (Fig. 21a). Since experimentally removing the HfO$_2$ from the sidewalls is extremely difficult and enhanced plasmonic properties with protection layers below 10nm is not observed, the impact of the HfO$_2$ on the LSPR is studied through the FDTD simulations. The data shows that a 12 nm HfO$_2$ layer shifts the resonant wavelength by 25 nm due to a larger dielectric constant of the media surrounding the AZO (Fig. 21b). However, the linewidth stays relatively the same indicating the HfO$_2$ does not increase the quality factor due to any cladding effects.

4.4 ZnO Buffer Layers

Following the approaches of section 2.3, the use of ZnO buffer layers to improve the permittivities are reflected in LSPR modes on the SiNPs for protected 20 nm AZO films thermally processed at 825 °C for 15 s. Here the resonant wavelength is shifted from 1670 nm to telecommunication wavelengths (ca. 1550 nm) by adding a 50 nm ZnO buffer layer (Fig. 22).
Figure 22 IR extinction spectra of thermally processed AZO/HfO$_2$ (20 nm/12 nm) layer deposited on a SiNP array with varying ZnO buffer layer thicknesses.

4.5 AZO Nanotubes

By again exploiting the ultra conformal properties of ALD, NSL can be employed to make free standing vertically aligned AZO nanotubes. Following the fabrication scheme outlined below (Fig. 23) a silicon hole array template is made by first using depositing the Stöber particles with an LB trough and shrinking them with RIE. Next, a thin nickel film is deposited over the Stöber particles. The Stöber particles are then removed mechanically by sonication and a cleanroom q-tip leaving behind a hole pattern in a triangular lattice. The holes are deepened with RIE and the nickel mask is removed by wet etching. The hole arrays are then filled with the HMM multilayers by exploiting the ultra-conformal properties of ALD. Next, reactive ion etching (RIE) is used to remove the top layers and
expose the underlying silicon. The silicon surrounding the HNTs is then removed by RIE leaving a vertically aligned triangular array of closely packed HNTs.

The fabrication process leads to a smaller diameter at the top of the silicon nanoholes compared to the diameter at the middle. Therefore, as the AZO is deposited into the hole arrays, layer by layer via ALD, the top is sealed before the middle, which leaves a small hollow core. In order to study the LSPR tuning three samples were fabricated. The total diameter, $D_t$, of the nanotubes were adjusted by changing the Stöber particle etching time. The three samples have varying $D_t$ and slightly varying lengths, $L$. As shown in figure 24 the resultant AZO nanotubes have $D_t$ of 395 nm, 490 nm, 545 nm for sample A, B and C, respectively. The $L$ for the nanotubes for sample A, B and C were 570 nm, 597
nm and 603 nm. The core size for all the samples were similar at ~ 40 nm. The lattice period, $a$, is given by the original Stöber particle diameter which was the same for all samples and is 595 nm. Therefore the interpillar gap, $g$, is a function of $D_t$ and $a$ and expressed as $g = a - D_t$.

![Figure 24](image)

**Figure 24** SEM images of top down (a, b, c) and cross sectional (d, e, f) view of AZO nanotubes for sample A, B and C, respectively.

Figure 25 shows the normalized extinction for samples A, B and C. In accord with theory, the resonant wavelength of the peak blue shifts as the diameter decreases. In addition the peaks are seen to broaden as $g$ decreases. This is most likely due to coupling between the structures as observed before for the AZO coated silicon pillars in section 4.2.
Figure 25 Normalized optical density spectrum of (a) simulated and (b) experimental AZO nanotubes as shown in figure 24

4.6 Methods

SiNP templates were fabricated using NSL by a method adapted from literature [73]. Silica nanoparticles (~ 440 nm diameter) were grown by the well-known Stöber process [74, 75]. Next, the particles were functionalized with aminopropyl-methyldiethoxysilane (APMDES) and deposited onto p-type (5 Ω·cm) prime silicon using a Langmuir Blodgett trough (KSV NIMA). The silica particles were then shrunk using RIE with CHF$_3$ and Ar gases using an oxford P80. Next, using an Oxford P100 with SF$_6$ and C$_4$F$_8$ gases, the exposed silicon was etched creating nanopillars. Any remaining SiO$_2$ was removed using hydrofluoric acid. Before ALD all samples were cleaned using the RCA cleaning procedure. All extinction measurements were carried out from 1200 nm to 2500 nm on the nanopillar array using a Perkin Elmers Lambda 1050. Finite-difference time-domain (FDTD) simulations were carried out using the Lumerical software package. A single AZO/HfO$_2$ core shell nanopillar was modeled with periodic
boundary conditions using identical dimensions to those observed in the experiments. Plane wave excitation was launched at normal incidence. All nanostructure imaging was carried out using an FEI XL30 ultrahigh resolution SEM. The atomic-scale structural analyses were carried out using a high-resolution transmission electron microscopy (HRTEM, JEOL JEM3100F) operating at 300 kV.

AZO nanotube arrays were fabricated using silicon nanohole templates created by nanosphere lithography. Stöber particles (595 nm diameter) were grown, functionalized, assembled and shrunk as described before. Next, a 45 nm thick nickel film was then deposited on the sample using a Temescal BJD 1800 electron beam evaporator. The Stöber particles where then mechanically removed with a cleanroom q-tip and sonication. Next, using an Oxford P100 with SF$_6$ and C$_4$F$_8$ gases, the exposed silicon was etched creating the nanohole template. After removing the nickel mask using TFB nickel etchant the AZO was deposited into the nanoholes with a Beneq TFS200 atomic layer deposition system operating at a reactor temperature of 200°C. Diethylzinc, trimethylaluminum, and deionized water were used as the zinc, aluminum and oxygen sources, respectively. The Zn:Al pulse ratio for the AZO films was kept constant at 20:1 for all experiments. The film thicknesses were first determined for each material on planar silicon substrates by ellipsometry using a Rudolph Auto EL ellipsometer at each temperature. A total AZO thickness of ~350 nm was deposited on the nanohole template such that the nanoholes were completely
sealed. Next, a 20 nm protection layer of HfO$_2$ was deposited via ALD by using tetrakis(dimethylamido)hafnium(IV) and water as the hafnium and oxygen sources, respectively. After depositing the AZO and protection layer, rapid thermal processing was carried out to activate the aluminum dopants$^{21}$ using an AG Associates Heat Pulse 610 with a 1.5 L min$^{-1}$ nitrogen flow rate. The top layers of HfO$_2$ and AZO where then removed using RIE with CHF$_3$ and Ar gases using an oxford P80 until the top silicon was exposed. The exposed silicon was removed using an Oxford P100 with SF$_6$ and C$_4$F$_8$ gases leaving behind the AZO nanotube array. Before measurements, dilute HCl was applied to the back of the samples to remove any contaminates that may have been generated during the ALD process.

Chapter 5

Hyperbolic Metamaterials

In this chapter the plasmonically active films are demonstrated for further use by being incorporated into a class of materials called hyperbolic metamaterials. This is demonstrated in two different geometries: (i) The multilayer, where negative refraction is observed, and (ii) embedded nanowires, where hyperbolic dispersion is experimentally verified with ellipsometry.

5.1 Theory and Background

Metamaterials are artificially designed materials engineered to have properties that do not exist in nature. Specifically, optical metamaterials have enabled the advancement of many applications such as optical magnetism [77], cloaking [78] and super resolution [79] through the engineered combination of plasmonic and dielectric materials with features much smaller than the wavelength of light. Initial research utilized advanced 3D geometries to tailor both the magnetic permeability and electric permittivity to have negative values (double negative media) resulting in a negative index of refraction. However, fabricating 3D metamaterials that fulfill this size criterion in the NIR-Vis wavelength range presents a challenge. Therefore many researchers have focused on the use of hyperbolic metamaterials (HMM) in order to ease synthetic
requirements. Unlike double negative media, HMMs utilize extreme optical anisotropy that arises from the combination of non-magnetic materials with permittivity of opposing sign. This is described using a permittivity tensor as shown below.

\[
\varepsilon^{\text{eff}} = \begin{bmatrix}
\varepsilon_{xx} & 0 & 0 \\
0 & \varepsilon_{yy} & 0 \\
0 & 0 & \varepsilon_{zz}
\end{bmatrix}
\] (13)

This research focuses its attention on uniaxial material where two of the axes are identical and notated as \( \varepsilon_{yy} = \varepsilon_{zz} = \varepsilon_\parallel \) and one axes is unique \( \varepsilon_{xx} = \varepsilon_\perp \) and described as the optical axis. The dispersion of such a material can be described by first assuming that the electric and magnetic fields are of the form:

\[
E = E_0 e^{i(\omega t - kr)} 
\] (14)

\[
H = H_0 e^{i(\omega t - kr)} 
\] (15)

Where \( H \) is the magnetic field, \( k \) is the wavevector, \( r \) is the position vector and \( H_0 \) and \( E_0 \) are the electric and magnetic field amplitudes. Using Maxwell’s curl equations for the electric field and magnetic field and the constitutive relations for non-magnetic uniaxial materials:
\[ D = \varepsilon_0 \varepsilon^{\text{eff}} E \] (16)
\[ B = \mu_0 H \] (17)

The following expression is obtained:

\[ \mathbf{k} \times (\mathbf{k} \times \mathbf{E}) + \omega^2 \mu_0 \varepsilon_0 \varepsilon^{\text{eff}} \mathbf{E} \] (18)

This leads to the dispersion relation for ordinary waves (TE polarization) and extraordinary waves (TM polarization):

**TE Polarization:**
\[ k_x^2 + k_y^2 + k_z^2 = \varepsilon_\parallel \frac{\omega^2}{c^2} \] (19)

**TM Polarization:**
\[ \frac{k_x^2}{\varepsilon_\parallel} + \frac{k_y^2 + k_z^2}{\varepsilon_\perp} = \frac{\omega^2}{c^2} \] (20)

Here, the TM polarization has its electric field components in the xy plane and therefore depend on both \( \varepsilon_\perp \) and \( \varepsilon_\parallel \). On the other hand, TE polarization has an electric field component in the y-axis only. Therefore, the dispersion relation for TE polarization only depends upon \( \varepsilon_\parallel \). In the absence of resonance, when a uniaxial material is made up of common dielectrics all the permittivity values are positive and an isofrequency wavevector plot (Fig. 26) is elliptical for both polarizations. However when \( \varepsilon_\parallel \) and \( \varepsilon_\perp \) have opposing signs the isofrequency
wavevector plot becomes hyperboloidal for TM polarizations as shown in figure 26b-c. Therefore these metamaterials are called hyperbolic. This is achieved in two ways allowing for classifications of type I and type II HMMs as follows:

Type I - $\varepsilon_\perp < 0; \varepsilon_\parallel > 0$ (21)

Type II - $\varepsilon_\perp > 0; \varepsilon_\parallel < 0$ (22)

Type I wavevector plots have a two fold hyperbola resulting in a low k-vector cutoff whereas type II wavevector plots result in a one fold hyperbola connected at lower wavevectors. In both cases, in contrast to common materials, there exists no upper bound on the allowed wavevectors. Therefore, these materials possess very large photonic density of states (PDOS).

This is very important for diffraction limited based applications. The diffraction limit states that under normal conditions the smallest feature size resolved, $d$, is given by:

$$d = \frac{\lambda}{2nsin\theta}$$  (23)

Where $\theta$ is the angle of incidence, $n$ is the index of refraction and $\lambda$ is the wavelength of light. When light is incident upon features smaller than $d$, large and imaginary k vector evanescent waves are produced at the surface. Therefore,
conventional optics cannot restore this information. The ability of HMMs to interact with these fields is what allows many interesting applications such as photoluminescent enhancement [80], invisibility [81], subdiffraction imaging [79] and negative refraction [82, 83].

![Figure 26](image)

**Figure 26** Isofrequency surfaces of (a) dielectric (b) type I HMM and (c) type II HMM mediums.

Although both types of HMMs support the propagation of large wave vector modes, each type has unique characteristics that can be advantageous to specific applications. For example, negative refraction and hyperlensing are only observed in type I HMMs while large reflectivity is observed in type II HMMs [83-85]. The latter feature makes type II useful for asymmetric transmission [86] as well as gain-compensated wave-guiding [87]. Such materials are typically created
by two prominent geometries, as shown in figure 27: a planar layered structure in which alternating layers of plasmonic and dielectric materials are stacked or a wire structure in which plasmonic nanowires are embedded in a dielectric media. In both cases the characteristic dimensions (layers thickness or wire diameter) must be much smaller than the wavelength of incident light. The layered geometry has the advantage of simpler fabrication. On the other hand, the nanowire geometry has the advantage of displaying type I properties away from resonance providing lower loss which may greatly benefit hyperlensing applications [88]. Furthermore, the nanowire geometry has been demonstrated to be a superior biosensor compared to conventional surface plasmon-polariton based devices [89].

![Figure 27](image)

**Figure 27** Schematics of (a) multilayer and (b) nanowire array geometries capable of hyperbolic dispersion.
Under the assumption that the features are deeply subwavelength, the optical properties of an HMM can be described using an effective medium theory (EMT). Here, the properties of HMMs depend only on the metal filling fraction as well as the permittivity of the dielectric and metallic materials. For the layered structure the transverse and longitudinal permittivity elements are:

\[
\varepsilon_{\parallel} = f \varepsilon_m + (1 - f) \varepsilon_d; \quad \varepsilon_{\perp} = \left( f \frac{1}{\varepsilon_m} + \frac{1-f}{\varepsilon_d} \right)^{-1}
\]

where \( f \) is the filling fraction of the metallic component and \( \varepsilon_m \) and \( \varepsilon_d \) are the permittivity of the metallic and dielectric materials, respectively. For the nanowire structure the permittivity elements arising from the Maxwell-Garnet approximation are:

\[
\varepsilon_{\parallel} = \frac{(1+f)\varepsilon_m + (1-f)\varepsilon_d}{(1-f)\varepsilon_m + (1+f)\varepsilon_d}; \quad \varepsilon_{\perp} = f \varepsilon_m + (1-f) \varepsilon_d
\]

5.2 Negative Refraction

One of the more interesting properties of HMMs is that under certain circumstances negative refraction is possible. Physically this is due to conservation of tangential momentum which states that \( k_z \) must be equal at the HMM/dielectric interface. Using this boundary condition and Fresnel's equations
for anisotropic uniaxial materials it is possible to derive two different refractive indices, the group index, $n_g$, and the phase index, $n_p$ [90, 91].

$$n_g = \frac{\varepsilon_\perp}{\varepsilon_\parallel} \sqrt{\varepsilon_\parallel - \frac{\varepsilon_\perp}{\varepsilon_\parallel} \left(1 - \frac{\varepsilon_\perp}{\varepsilon_\parallel}\right) \sin^2 \theta} \quad (26)$$

$$n_p = \sqrt{\varepsilon_\parallel + \left(1 - \frac{\varepsilon_\perp}{\varepsilon_\parallel}\right) \sin^2 \theta} \quad (27)$$

Where, $n_g$, describes the direction of the energy of the wave as related to the Poynting vector within the HMM, and $n_p$ describes the index within the material as related to the wave vector. Experimentally, $n_g$ describes the intensity and the direction of the wave, whereas $n_p$ describes the phase change due to refraction of the wave. Therefore, for type I material, $n_g$ is negative leading observed negative refraction, however, $n_p$ remains positive. The negative direction of the Poynting vector and the wave vector can be seen by examining the tangential component of the Poynting vector, $S_z$ as follows [92]:

$$S_z = \frac{k_0 H_0^2}{\varepsilon_\perp 2\omega \varepsilon_0} \quad (28)$$
Here, since $\varepsilon_\perp$ is negative the sign of $S_z$ must be opposite of $k_z$. Therefore, once the propagating wave crosses the HMM/dielectric interface, the direction of $S_z$ must flip relative to $k_z$ causing the observed negative refraction.

Consequently, experimental demonstrations of negative refraction in HMMs have been reported. This was first accomplished by Hoffman et. al [82] with a multilayer comprised of 80 nm oscillating layers of In$_{0.53}$Ga$_{0.47}$As and Al$_{0.48}$In$_{0.52}$. The total thickness of the sample was 8.1 µm and operating in the infrared at ~ 9 - 12 µm. In accord with theoretical predictions, the negative refraction was validated by the razor blade experiment. In this experiment the sample is placed between a light source and detector and the transmission is studied at different angles in the presence and absence of a razor blade which blocks half of the light transmitted through the sample (Fig. 28). Therefore, with this configuration, if negative refraction occurs the light is shifted away from the razor blade so that more light is incident upon the detector causing a peak in the transmission ratio of the partially blocked beam/full beam for TM polarized light only. Many experimental demonstrations reverse the position of the razor blade to show a dip in the transmission. In all cases TE polarizations serve as a control to show the lack of the peak. Later, the nanowire geometry was also verified to have negative refraction [88]. This sample was comprised of 60 nm silver nanowires embedded in an Al$_2$O$_3$ matrix. In this case negative refraction was experimentally demonstrated by observing the shift of a laser beam at visible wavelengths.
In addition to the HMMs previously discussed, many other systems have been demonstrated including multilayers comprised of Au/Al₂O₃ [93], Au/TiO₂ [94], Ag/PMMA [95], Ag/SiO₂ [96], Ag/Si [80] and Ag/Ge [97]. For operation at telecommunication wavelengths the low loss and polarization response of AZO has many benefits. Due to a near perfect match of lattice parameters, the most obvious choice for a HMM dielectric component used in conjunction with AZO is ZnO. This was first demonstrated with PLD [83]. Here, a multilayer structure comprised of 8 periods of alternating 60 nm AZO/ZnO layers was fabricated. In agreement with EMA, type I hyperbolic dispersion occurred in the wavelength range of 1.84 µm < \lambda₀ < 2.4 µm and type II at longer wavelengths. This material was validated by ellipsometry and the observation of negative refraction at \lambda₀~1.8 µm using the razor blade method for TM polarization. In addition to PLD grown AZO based HMMs, GZO based HMMs have also been created by molecular beam epitaxy [98]. By using a figure of merit defined by Hoffman et. al [82], different HMM materials have been

Figure 28 Schematic of the razor blade experiment showing negative refraction.
compared where hyperbolic dispersion exists [4]. It was concluded that the AZO/ZnO material system is superior to other HMMs in the $1400 < \lambda_0 < 2000$ nm range. However, prior to this work, conformal ALD grown AZO/ZnO multilayer or nanowires had not been demonstrated.

5.3 ALD Grown AZO/ZnO Multilayer Structure

To demonstrate hyperbolic dispersion with the ALD grown films, a simple layered structure comprised of 8 periods of ZnO and AZO alternating stacks grown on silicon was investigated. The thickness of each layer is 56 nm giving a total thickness of 896 nm. After growing the HMM it is protected with a 50 nm layer of HfO$_2$ and annealed at 825°C for 20 s. The electron micrograph in Figure 29a captures the contrast between the alternating AZO and ZnO layers. Using the permittivity values obtained for AZO grown on a 112 nm ZnO buffer layer, EMT (Equation 23) predicts type I hyperbolic dispersion from 1460 nm to 2000 nm and type II dispersion for wavelengths longer than 2080 nm (Fig. 30).
Figure 29 (a) SEM image of multilayer ZnO/AZO HMM comprised of 8 ZnO/AZO (56nm/56nm) (b) TM polarization transmission ratio of partially blocked beam/full beam showing a clear peak indicative of negative refraction and (c) TE polarization transmission ratio of partially blocked beam/full beam showing the lack of a peak (d) Angle of refraction predicted by EMT and TMM.

Figure 30 Real and imaginary effective permittivity elements for an (a) AZO/ZnO multilayer with fill fraction f=0.5
In order to show the functionality of the high quality HMM films, negative refraction is demonstrated using the razor blade experiment as described in the previous section. As expected a clear peak is observed for TM polarized light (Fig. 29b) while transverse-electric (TE) polarized light show no peaks (Fig. 29c). The transmission data also shows good agreement with FDTD simulations that were carried out on the identical layered structure using the permittivites of AZO grown on 112 nm ZnO buffer layers. As predicted by EMT, none of the properties depend on the thickness of each individual layer as samples with layer thicknesses as thin as 15 nm where synthesized with little impact on the negative refraction performance. In addition, analytical calculations based on both the transfer matrix (TMM) and scattering matrix (SMM) methods confirm the experimental and FDTD results. The angle of refraction determined using the derivative of the transmitted phase with respect to the angle of incidence [64] is shown in Figure 29d. The complex amplitude transmittance is calculated via the TMM [99] using the experimentally obtained optical constants. Additionally, the refraction angle predicted by EMT is shown. The predicted angle of maximum negative refraction, and therefore the largest transmission ratio is slightly red-shifted from the experimental results. The small discrepancy is likely due to the approximation of the method where accuracy depends upon the total thickness of the multilayer [100].
The SMM, while generally more difficult to implement than the TMM, is known to be more accurate [101]. Figure 31 compares the squared magnitude of both TE and TM polarized electric fields, incident at an angle of 25 °, for several different wavelengths. The fields are determined using a modified version of an open-access SMM implementation [102]. The incident beam undergoes greatest negative refraction at a wavelength of 1470 nm, in very good agreement with experimentally observed transmission ratio. For clarity, only the real parts of the experimentally determined optical constants are used and the structure consists of 50-periods of alternating 56 nm thick ZnO and AZO layers. It is clear from an analysis of TE and TM fields at various angles of incidence with a fixed wavelength of 1470 nm that only the TM mode undergoes negative refraction (Fig. 32).

![Figure 31](image)

**Figure 31** SMM field plots ($|E|^2$) for TE and TM-polarized light of different wavelengths, incident from air, at 25° from normal, onto 50 period structure of alternating 56nm ZnO and AZO layers. Losses are omitted for clarity.
5.4 Embedded AZO Nanowire HMM

Lastly, the conformal properties of ALD were further exploited to fabricate the nanowire geometry required for HMM. To accomplish this, NSL was first employed to create a silicon nanopillar array. The gaps were then filled with ZnO (Fig. 33a) which was etched using RIE to expose the silicon on the top of the nanopillars. RIE was used again with a different gas composition to remove the silicon nanopillars leaving nanoholes (Fig. 33b). The nanoholes were then filled with AZO and the top layer of AZO was removed to improve the transmission (Fig. 33c). The average length, pitch and diameter of the AZO nanowires are 907 nm, 407 nm and 250 nm, respectively. As seen in Figure 33d, this leads to an AZO filling fraction of 0.3. EMT (Equation 24) predicts type II hyperbolic
dispersion from 1.84 µm to 2.32 µm and type I hyperbolic dispersion at wavelengths longer than 2.58 µm. Extracted values from ellipsometry (Fig. 33d and 33e) show similar behavior as predicted from EMT. However, discrepancies are expected due to rough nanowire walls and the polycrystalline structure of the AZO generated via ALD. The extinction measurements (Fig. 33f) show a clear peak centered at 2335 nm which is in an identical location to where the maximum loss is predicted by EMT for this geometry.

Figure 33 SEM images taken at different steps during the fabrication of AZO nanowires embedded in ZnO including (a) ZnO-coated silicon nanowires, (b) etched silicon leaving behind nanoholes, and (c) AZO-filled nanoholes. (d) Real and (e) imaginary optical constants as predicted by EMT (dashed) and extracted from ellipsometry (solid). (f) IR extinction spectra of AZO nanowires embedded in ZnO showing optical losses identical to that predicted by EMT.
5.5 Methods

Layered hyperbolic metamaterials were synthesized on DSP and SSP p-type (5 Ω·cm) prime silicon. 8 periods (16 total layers) of alternating ZnO and AZO films were grown at 250 °C and capped with a 50 nm HfO₂ protection layer. All AZO components were grown with a 20:1 Zn:Al ratio. The whole sample was then thermally processed at 825 °C for 20 s. Negative refraction tests were carried out using a Perkin Elmer Lambda 1050. The sample was placed at the halfway point between the monochromator exit and PbS detector and the angle of the sample was varied from 0 – 20°. The beam was partially blocked by placing a razor blade at the halfway point between the sample and the detector such that the TE polarization at 0° was half of the full beam transmission.

Embedded AZO nanowires were created by first synthesizing a nanowire template using NSL as described above. Next, 200 nm of ZnO was deposited at 250°C to fill in the gaps. The top layer of ZnO was removed by RIE with CHF₃ and Ar gases using an oxford P80 to expose the silicon nanowire tips. Next, using an Oxford P100 with SF₆ and C₄F₈ gases, the exposed silicon was etched leaving nanoholes. The holes were filled with AZO at a 20:1 Zn:Al ratio at 250 °C and capped with a 50 nm HfO₂ protection layer. The sample was then thermally processed at 825 °C for 20 s and the top layer of HfO₂ and AZO was removed using RIE. Extracted optical constants were obtained using ellipsometry as described above. All models were carried out on the J.A. Woollam VASE
software using a uniaxial model where Kramers Kronig consistent oscillators were fit to the experimentally obtained $\psi$ and $\Delta$ values.

Portions of Chapter 5 is a reprint of materials as it appears in the following publication: Conor T. Riley, Joseph S. T. Smalley, Kirk W. Post, Dimitri N. Basov, Yeshiahu Fainman, Deli Wang, Zhaowei Liu and Donald Sirbuly, “High-Quality, Ultraconformal, Aluminum-Doped Zinc Oxide Nanoplasmonic and Hyperbolic Metamaterials” Small, 2016, 12, 892-901. The dissertation author was the primary investigator and the first author of this paper.
Chapter 6

Hyperbolic Metamaterial Nanoparticles

In this chapter a new material is introduced in the form of hyperbolic metamaterial particles. This is demonstrated with hyperbolic nanotubes made up of the AZO/ZnO films characterized in chapter 5. When closely packed they exhibit broadband near perfect absorption due to a coupling of hyperbolic and plasmonic modes. It is also shown that this new class of materials can be applied to other material systems and geometries for a broader range of applications.

6.1 Introduction

Selective and broadband perfect absorbers generally use advanced plasmonic geometries on top of metallic reflectors and/or dielectric spacers. However, this limits their ability to be scaled up to larger surface area devices and transferred to more desirable substrates. Here we introduce a new class of materials in the form of transferable hyperbolic metamaterial particles (THMMP). We show that these materials form broadband yet selective, omni-directional absorption when they are closely packed and do not require metallic back reflectors; allowing them to be transferable and mechanically flexible given their discontinuous nature. This is demonstrated using vertically aligned, closely packed, hyperbolic metamaterial nanotube (HNT) arrays comprised of alternating
layers of aluminum-doped zinc oxide and zinc oxide shells deposited by atomic layer deposition. We first realize the concept by fabricating the HNTs on silicon substrates and then transfer the arrays to a thin elastomer to create a flexible, visibly transparent material that maintains near perfect absorption at telecommunication wavelengths (ca. 1550 nm). In addition, different materials systems and geometries are discussed leading to a broader range of applications.

6.2 Background

Perfect broadband absorbers have the ability to efficiently capture radiation within a large spectral range at all angles. The captured energy can then be redirected and manipulated leading to many exciting applications such as thermophotovoltaics (TPV) [103, 104], thermal emitters [105, 106], camouflage [107], and thermal detectors [108]. Currently, carbon nanotubes (CNTs) provide perfect ultra-broadband absorption [109]. However, the CNT films are relatively thick and do not allow any control over the operating wavelengths of the absorber which is critical for creating visibly transparent IR absorbers and materials for many other applications including thermophotovoltaics that require selective yet broadband absorption [110].

Hyperbolic metamaterials (HMM) can provide an alternative to creating selective and broadband absorption. Recently, selective broadband absorbers have been created via HMM pyramids [111-113]; however, these materials are
made with low melting point metals which would not be able to withstand high temperature applications such as thermal emitters, have shown limited absorption at telecommunication wavelengths (~85%), have not yet shown large angle absorption, and have only been demonstrated on metallic back reflectors making simultaneous broadband absorbance and visible transparency challenging. Perfect absorbing metamaterials have also been used to demonstrate broadband absorption by the convolution of multiple loss mechanisms [110]. However, these materials require dielectric spacers and metallic back reflectors, and use advanced nanostructured geometries, making it difficult to scale up the fabrication for larger area applications and/or transfer the materials to more desirable substrates. More favorable architectures include nanoparticle monolayers and vertically aligned nanowires which can be assembled and transferred via inexpensive techniques to different substrates while maintaining mechanical flexibility due to the gaps between the independent structures [114, 115]. In addition, the substrate/nanoparticle interfacial surface area is reduced, mitigating problems that arise due to lattice mismatch. This is particularly important for high temperature applications such as heat generating absorbers and thermal emitters which put extreme stresses on interfaces within the device.

Here we report the first broadband, selective absorber created by closely packed transferable hyperbolic metamaterial particles (THMMP) in the form of vertically aligned, closely packed hyperbolic nanotube (HNT) arrays comprised of
aluminum-doped zinc oxide (AZO) and ZnO. We use this material to demonstrate tunable, omni-directional, selective, near perfect absorption at telecommunication wavelengths (ca. 1550). We also show that this material can be made visibly transparent and mechanically flexible by transferring the HNT arrays to a thin polymer substrate. Numerical simulations are used to verify the experimental behavior and to provide insight on other material systems/geometries that find applications in different regions of the electromagnetic spectrum (e.g., visible).

6.3 Broadband Absorption from Hyperbolic Nanotubes

A HNT is defined in terms of its length, \( L \), total diameter, \( D_t \), and air core diameter, \( D_c \) (Fig. 34a). The shell is comprised of \( n \) HMM periods with alternating AZO and ZnO concentric layers of thicknesses \( t_m \) and \( t_d \), respectively. Therefore one period has a thickness, \( p \), equal to \( t_m + t_d \) and the total shell thickness is given as the product of \( n \) and \( p \). When oriented in an array the lattice period, \( a \), and HNT gap, \( g \), are also defined where \( a = g + D_t \). In section 4.3 a simple process for making high quality, planar AZO/ZnO HMM multilayers via atomic layer deposition (ALD) that displayed negative refraction due to hyperbolic dispersion was displayed. Similar films were used to fabricate the HNT array. The scheme outlined in figure 23 is used to create the HNTs except that oscillating 10 nm ZnO and AZO HMM films are deposited into the silicon nanoholes in place of the pure AZO. The air cores in this case are larger due to the higher aspect ratio of the hole at \( D_c \) is \( \sim 220 \) nm however, the core is of little consequence to the
absorption as will be described later. Fig. 34b-c shows the resulting vertically aligned HNTs with $D_c$, $a$, and $L$ equal to 235 nm, 770 nm and 1730 nm, respectively. $D_t$ varies from 770 nm at the top to 650 nm at the bottom.

**Figure 34** (a) Schematic of coupled HNTs. SEM images of the HNT arrays as viewed in the plane (b) parallel and (c) perpendicular to the nanotube axis.

As stated in this dissertation and other reports [116-118], the carrier concentration of the AZO is dependent on the ALD deposition temperature, $T_d$, allowing for the absorption of the HNT array to be tuned. Utilizing an integrating sphere, figure 35a captures the true absorption spectrum ($\text{absorption}(\%) = 100\% - \text{transmission}(\%) - \text{reflection}(\%)$) of HNT arrays deposited at a $T_d$ of 200 °C and 185 °C. Broadband absorption > 87% from 1200 nm to over 2200 nm is demonstrated with a maximum absorption of 98.1% at 1550 nm for a $T_d$ of 200 °C. For a $T_d$ of 185 °C, broadband absorption > 87% is observed from 1500 nm to over 2200 nm with a maximum absorption of 96.3% at 1700 nm. As a control, pure AZO nanotubes are also plotted which exhibit only a modest absorption maximum of 82.5% at 1400 nm with a narrow spectral width. The HNTs show excellent selectivity by displaying increased reflection at longer wavelengths (Fig. 36a). This is due to an increased impedance mismatch as the real permittivity
becomes decreasingly lower at longer wavelengths as described in chapter 3. The angular dependence was also studied by sputtering a 100 nm gold film on the back of the silicon. This allowed only the specular reflectance to be considered when calculating the absorption \[ \text{absorption}(%) = 100\% - \text{reflectance}(\%) \]. This method is valid within 1% from 1500 nm to 2400 nm and within 6% from 1400 nm to 1500 nm, however, at wavelengths shorter than 1400 nm we found that this method is not accurate due to photon scattering (Fig. 36b).

\[ \text{Figure 35} \] (a) Absorption spectra of HNT arrays deposited at a temperature of 185 °C and 200 °C along with a spectrum of a pure AZO nanotube array deposited at 200 °C. (b) Schematic of the incident radiation at angle \( \theta \) showing TM polarization. Wide-angle absorption spectra for (c) TM and (d) TE
polarizations of an HNT array deposited at 200 °C. The color corresponds to the percent absorption.

**Figure 36** (a) IR reflection spectrum of an HNT array. (b) Absorption spectrum of HNT arrays measured by an integrating sphere (A=1-T-R) and specularly (A=1-R).

As shown in Fig. 35c-d, HNTs possess omnidirectional absorption for both TM and TE polarizations. For TM polarization, the absorption is maintained above 85% at all angles and wavelengths measured. For TE polarization the absorption is diminished at higher angles and longer wavelengths, however, an absorption > 70% is maintained across the measured wavelengths and angles smaller than 50°.

Using the complex permittivity values previously described in chapter 3, the simulated absorption of a closely packed HNT array is shown in Fig. 37a using the parameters $L=1.5 \, \mu m$, $D_t = 740 \, \text{nm}$, $D_c = 220 \, \text{nm}$, $g = 30 \, \text{nm}$, $a = 770$ nm, $n = 13$, and $t_m = t_d = 10$ nm.
Figure 37 Simulated absorption of (a) the exact structure and EMA to describe the HNT shell, (b) EMA HNT arrays with air cores and solid hyperbolic metamaterial nanowires, and (c) exact structure HNT arrays with smooth and roughened tops (RMS = 200 nm). Unless otherwise stated simulated parameters \( L, D_h, D_c, g, a, n, t_m \) and \( t_d \) were kept constant at 1.5 \( \mu \text{m} \), 740 nm, 220 nm, 30 nm, 770 nm, 10, 10 nm, and 10 nm, respectively. (d) Experimental absorption spectra of an as-processed HNT array and an array that was further roughened with RIE (deposition temperature was 200 \(^\circ\text{C}\)). The inset shows a SEM image of a roughened HNT array.

The data shows absorption values greater than 90% from 1400 – 2000 nm. In addition to simulations that explicitly compute for a structure described by each individual ZnO and AZO layer (exact structure), simulations were carried out where the permittivity of the shell material is replaced with the permittivity tensor derived from EMA for curved multilayer structures. This is accomplished following
literature [119] which shows that the conversion from the curvilinear nature of the HNT to Cartesian coordinates can be accomplished by the following tensor:

\[
\mathbf{\varepsilon}^{eff} = \begin{bmatrix}
\varepsilon_{\perp} \cos^2(\phi) + \varepsilon_{||} \sin^2(\phi) & (\varepsilon_{\perp} - \varepsilon_{||}) \sin(\phi) \cos(\phi) & 0 \\
(\varepsilon_{\perp} - \varepsilon_{||}) \sin(\phi) \cos(\phi) & \varepsilon_{\perp} \sin^2(\phi) + \varepsilon_{||} \cos^2(\phi) & 0 \\
0 & 0 & \varepsilon_{||}
\end{bmatrix}
\] (29)

As shown, the exact structure agrees well with EMA. This allowed us to simulate the structure with less computational expense and study the effects of adjusting \(D_t\) and \(D_c\) without changing \(n\) and \(p\).

Importantly, the simulations also showed that the existence of the core has little effect on the absorption (Fig. 36b). By varying some of the parameters described in figure 34a, simulations show that the absorption observed is the result of multiple peaks converging into one broadband peak. All parameters are kept at the values stated above unless otherwise stated. As shown in figure 38a, as \(n\) decreases from 8 to 1 with constant \(g\), the broadband absorption separates into two peaks at 1.45 \(\mu\)m and \(\sim\)2-3 \(\mu\)m. Moreover, when \(n\) and \(D_t\) are held constant, but \(a\) is increased from 770 nm to 3500 nm, we observe a deconvolution of the peaks (Fig. 38b). In order to study whether the lattice constant affects the coupling strength between HNTs, or the coupling of incident light (via diffraction), we first use the EMA to eliminate the effect of \(n\) and replace the air core with the effective medium. Using solid HMM nanowires, no significant effect on the absorption band is observed when \(D_t\) is varied from 740 nm to 260
nm with constant $g$ (Fig. 38c). Therefore, while the lattice constant affects the coupling strength between HNTs, it does not affect the coupling of incident light.

**Figure 38** Simulated absorption of (a) exact structure HNTs with increasing $n$ from 1-8 (blue to yellow) and 13 (black) with constant $g$, (b) exact structure HNT arrays with varying $a$ and constant $D_h$, and (c) EMA solid hyperbolic nanowire arrays of varying diameter. Unless otherwise stated parameters $L, D_h, D_o, g, a, n, t_m$ and $t_d$ were kept constant at 1.5 µm, 740 nm, 220 nm, 30 nm, 770 nm, 10, 10 nm, and 10 nm, respectively.

**Figure 39** Simulated absorption using the exact structure of (a) HNTs with a varying $f_m$ in the shell, (b) common HMMs compared with the HNTs, and (c) HNTs with varying length. Unless otherwise stated parameters $L, D_h, D_o, g, a, n, t_m$ and $t_d$ are kept constant at 1.5 µm, 740 nm, 220 nm, 30 nm, 770 nm, 10, 10 nm, and 10 nm, respectively.
Broadband absorbance is achieved with a sufficient amount of periods and when the HNTs are packed close enough to allow strong resonance coupling. Physically, $g$ is responsible for the intercoupling of the HNTs and $n$ is responsible for the number of higher order plasmon-polaritons modes supported by the HMM\textsuperscript{27}. The bandwidth of high wavevector modes supported by the HMM depends upon $p$ but not $n$. However, as $n$ increases the discrete modes supported by the HMM are expected to coalesce. If there were no losses each mode would have a sharp profile, but due to the high losses the discreteness vanishes and a single absorption band appears. The shorter wavelength peak located at 1.45 $\mu$m corresponds to $\lambda_c$ of AZO and shows little tunability. Therefore, we conclude that the short wavelength peak arises due to excitation of bulk and/or surface plasmon-polaritons in the AZO. Conversely, the longer wavelength peak intensifies as $n$ gets larger (Fig. 38a), increasing the accuracy of EMA (i.e., the material possesses hyperbolic dispersion). In addition, only the long wavelength peak changes with the metal filling fraction, $ff_m$ (Fig. 38a). This supports our theory that the long wavelength peak arises due to coupling between lossy modes that exist because of hyperbolic dispersion of the HNT. Although high absorption has been obtained for planar HMMs [120, 121], our simulations show that the absorption occurs within a narrower band when similar length scales (1.5 $\mu$m) are used for both the planar and embedded nanowire HMM geometries (Fig. 38b). Furthermore, planar HMMs do not have the many benefits of nanoparticle films as mentioned above. Simulations also show that the
length of the HNTs does not contribute much to the absorption when greater than 1.5 μm. However, at lengths smaller than 1.0 μm the absorption decreases due to increased transmission (Fig. 38c).

The experimental values are in good agreement with the simulated values from 1400 nm to 2000 nm. However, out of this spectral range the simulated absorption is significantly lower. At shorter wavelengths this is due to the silicon substrate (discussed in more detail later); whereas at longer wavelengths the higher absorption can be attributed to scattering by the roughened surface. The effects due to roughening can be observed in the absorption profile from both the numerical simulations and experiments (Fig. 37c-d). It is clear from the simulations that the shorter wavelengths are unaffected by the increased surface roughness, but at longer wavelengths (> 2000 nm) there is a much higher absorption for a roughened surface. To validate this experimentally, the as-processed arrays were further roughened by over etching during the RIE process (Fig. 37d). Although the HNTs are shorter by 260 nm after etching, the absorption is much higher at longer wavelengths as compared to the smoother and longer HNTs. However, at shorter wavelengths the absorption of the roughened HNTs is diminished due to the shorter length of the HNTs. This is because the absorption is sensitive to the length at shorter wavelengths as it is closer to the crossover frequency where the polarization response and loss are lower. The absorption of photons by scattering into modes of the HMMs has been previously studied and,
following Fermi’s golden rule, is attributed to the high photonic density of states in these materials [120, 122].

6.4 Transfer of Hyperbolic Nanotube Arrays

To investigate if the HNT arrays could operate as a stand-alone material after being removed from the growth substrate, we transferred the arrays to a thin, flexible and visibly transparent substrate by spin coating 60 µm of polydimethylsiloxane (PDMS) onto the top of the arrays and removing the silicon via RIE. This was carried out for three different arrays with various parameters as described in Table 4 and observed from the direct imaging (Fig. 40).

![SEM image of sample B as viewed in the plane (a) perpendicular and (b) parallel to the nanotube axis and sample C as viewed from the plane (c) perpendicular and (d) parallel to the nanotube axis.](image)

**Figure 40** SEM image of sample B as viewed in the plane (a) perpendicular and (b) parallel to the nanotube axis and sample C as viewed from the plane (c) perpendicular and (d) parallel to the nanotube axis.
Sample A and B both have the same geometry (i.e., constant $L$, $D_h$ and $D_c$) but a different $T_d$, similar to what was used in Fig. 35. Sample C has a $T_d$ of 185 °C but a larger $g$ and a smaller $L$ compared to samples A and B. The absorption spectra of sample A and a simulated exact structure (with a similar structure to sample A, but with a rounded top to replicate experimental conditions) have excellent agreement (Fig. 41a). This suggests that the shorter wavelength discrepancy seen earlier is due to the silicon substrate either from reflection back into the HNTs or absorption of the textured surface created during the HNT fabrication. The transmission and absorption spectra of the three samples (Fig. 41b-c) illustrates that a large transmission window is observed from 500 to 1300 nm, with the broadest IR absorption band belonging to sample A at the expense of a narrower and weaker transmission window. The transmission can be slightly increased by lowering $T_d$ and keeping the geometry constant, but the largest gain in transmission is observed when $L$ is decreased and $g$ is increased (sample C). All the constituent materials (AZO, ZnO and PDMS) in the free-standing HNT have large optical transparencies throughout the visible, and reflection accounts for < 12% of the decreased transparency, therefore we believe the additional absorption stems from silicon contaminates leftover from the transfer process and/or sub-band levels (defects states) in the ZnO/AZO layers. With further refinement in the synthesis, etching, and transferring steps we anticipate a significant improvement in the visible transparency. After transferring the HNT array to the PDMS film, they can be
reproducibly flexed while still maintaining their excellent broadband absorption in the NIR, and transmission in visible, as well as their physical interface with the polymer (Fig. 41d-f).

Table 4: Parameters of PDMS supported HNTs

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<th>D_t (nm)</th>
<th>D_c (nm)</th>
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<th>t_n (nm)</th>
<th>t_d (nm)</th>
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Figure 41 (a) Comparison of experimental and simulated absorption spectra for sample A. (b) Transmission and (c) absorption spectra for samples A-C with parameters as described in Table 1 after flexing several times as shown in (e). Photograph of sample A showing (d) visible transparency and (e) mechanical flexibility. (f) SEM image of an HNT array (Sample B) after transferring to a flexible PDMS substrate and flexing several times as shown in (e).
6.5 Other Systems

Beyond the AZO/ZnO HNT system, selective and broadband absorption can be applied to many other material systems and geometries. For example, the TiN/(Al,Sc)N material system has been shown to produce very high quality epitaxial HMMs with refractory qualities [123]. THMMP arrays with these materials could be advantageous for applications such as TPV and visible emitters that require many cycles at elevated temperatures (> 1000 °C). Current research in this area focuses on non-selective absorbers [103] and plasmonic metamaterials [110], however, these planar materials either loose efficiency due to parasitic radiation at higher temperature or can crack and delaminate due to thermal expansion mismatch between the absorber layer and substrate. A major advantage of a THMMP array is that it has a reduced substrate contact area that minimizes the impact of thermal expansion mismatches and would allow for a wider selection of substrates to be used while promoting the use of facile transfer techniques. Simulations reveal that TiN/(Al,Sc)N based HNT arrays \((L=750 \text{ nm},\ D_f=500 \text{ nm},\ D_c=30 \text{ nm},\ n=11,\ t_m=t_d=10 \text{ nm},\ a=530 \text{ nm})\) have absorption > 93% throughout the entire visible spectrum while suppressing absorption at longer wavelengths (Fig. 42a). In comparison to the HNT geometry, closely packed hyperbolic nanospheres could be particularly useful since they are expected to have less angular dependence and can be deposited onto substrates via low cost/scalable processes such as nanoparticle self-assembly and spray-on techniques. Simulations also reveal that these types of arrays made from a
TiN/(Al,Sc)N material system have a large absorption (> 89% throughout the entire visible spectrum) while suppressing absorption in the NIR with only a 540 nm thick single monolayer (Fig. 42b).

**Figure 42** Exact structure simulated absorption spectra of a closely packed TiN/(Al,Sc)N based (a) HNT arrays and (b) hyperbolic nanosphere arrays. The HNT array parameters $L$, $D_h$, $D_c$, $g$, $a$, $n$, $t_m$, and $t_d$ used in the simulation were 750 nm, 500 nm, 60 nm, 30 nm, 530 nm, 11, 10 nm, and 10 nm, respectively. The $D_h$, $D_c$, $g$, $a$, $n$, $t_m$, $t_d$ used for the hyperbolic nanosphere simulation were 540 nm, 60 nm, 30 nm, 570 nm, 12, 10 nm and 10 nm, respectively.

6.6 Conclusion

In conclusion, we have successfully demonstrated a new class of metamaterials, THMMP, that have tunable, selective and broadband near perfect omni-directional absorption. The broadband absorption is a result of the coalescence of absorption due to bulk or surface plasmon-polaritons in the AZO and lossy modes that exist due to the hyperbolic dispersion of the arrays. With
the ability to remove these particles from their growth substrates, we were able to
demonstrate that the arrays could be transferred to visibly transparent and
mechanically flexible substrates while maintaining their broadband absorption in
the NIR. We believe the synthetic strategies presented here are universal and
can be applied to other nanoparticle systems. Not only would this enable a host
of different materials that operate at distinct parts of the electromagnetic
spectrum, but it is anticipated that novel light-matter interactions would be
uncovered that have yet to be explored.

6.7 Methods

HNT arrays were fabricated as described in section 3.5 using silicon
nanohole templates with 770 nm Stöber particles. The ZnO/AZO HMM was
deposited into the nanoholes with a Beneq TFS200 atomic layer deposition
system operating at a reactor temperature of 185 °C or 200°C. Diethylzinc,
trimethylaluminum, and deionized water were used as the zinc, aluminum and
oxygen sources, respectively. The Zn:Al pulse ratio for the AZO films was kept
constant at 20:1 for all experiments. The film thicknesses were first determined
for each material on planar silicon substrates by ellipsometry using a Rudolph
Auto EL ellipsometer at each temperature. A total HMM thickness of ~350 nm
(each individual ZnO and AZO layer was 10 nm) was deposited on the nanohole
template such that the nanholes were completely sealed. Next, a 20 nm
protection layer of HfO₂ was deposited via ALD by using
tetrakis(dimethylamido)hafnium(IV) and water as the hafnium and oxygen sources, respectively. After depositing the HMM and protection layer, rapid thermal processing was carried out to activate the aluminum dopants\textsuperscript{21} using an AG Associates Heat Pulse 610 with a 1.5 L min\textsuperscript{-1} nitrogen flow rate. The top layers of HfO\textsubscript{2} and ZnO/AZO were then removed using RIE with CHF\textsubscript{3} and Ar gases using an oxford P80 until the top silicon was exposed. The exposed silicon was removed using an Oxford P100 with SF\textsubscript{6} and C\textsubscript{4}F\textsubscript{8} gases leaving behind the HNT array. The roughened HNTs were created by additional etching of the HNTs (deposited at a temperature of 200 °C) using RIE with CHF\textsubscript{3} and Ar gases. Before measurements, dilute HCl was applied to the back of the samples to remove any contaminates that may have been generated during the ALD process.

Simulations of the exact structure were carried out using finite-difference time-domain (FDTD) methods (Lumerical) and EMA simulations were implemented with COMSOL using the finite element method (FEM). All simulations used plane wave excitation with periodic boundary conditions at normal incidence. The optical constants used for AZO and ZnO were experimentally determined via ellipsometry as reported in chapter 3. TiN and Al(Sc)N optical constants were obtained from literature\textsuperscript{[123]}. All structures were simulated in a vacuum without any substrate.

The HNT were transferred to a flexible polymer films by depositing a ~ 60 µm film of PDMS and etching away the silicon substrate. First, the PDMS film was coated on the top of the HNT array by spin coating at 1000 RPM for 45 s
and curing at 125 °C for 8 minutes. The back silicon was then cleaned with O₂ plasma (Oxford P100) and removed using a Xactix XeF₂ Etcher.

All experimental absorption measurement between 1200 nm and 2400 nm where taken using a Perkin Elmers Lambda 1050 UV/Vis/NIR spectrometer. For non-angle dependent data a 150 mm Spectralon coated integrating sphere with a PMT (visible wavelengths) and InGaAs (NIR wavelengths) detector was used. For angle dependent measurements a universal reflectance accessory was used with an InGaAs detector. IR reflectance was determined using a Bruker LUMOS FTIR. All SEM imaging was carried out on a FEI XL30 ultrahigh resolution SEM.

Chapter 6, in full, has been submitted for publication as: C. T. Riley, J.S.T Smalley, J. R. J. Brodie, Y. Fainman, D. J. Sirbuly, Z. Liu “Near Perfect Broadband Absorption from Flexible and Transferable Hyperbolic Metamaterial Nanoparticles.” The dissertation author was the primary investigator and the first author of these papers.
Chapter 7

Conclusion

This chapter concludes the dissertation by summarizing the work and giving a brief outlook on the future research direction of ALD grown AZO based plasmonic and hyperbolic metamaterials.

7.1 Dissertation Summary

The purpose of this dissertation was to demonstrate a method for synthesizing, high quality, low loss ALD AZO suitable for applications operating at or near telecommunication wavelengths. This was accomplished by applying thin HfO$_2$ films followed by a thermal treatment via rapid thermal processing. This allowed for the aluminum dopants to be activated while suppressing any electron accepting defects that would normally occur without the protection layer.

Once high quality films were made, the conformal properties of ALD were demonstrated by creating tunable LSPR cavities by coating the films on SiNP templates created by NSL. These materials were demonstrated to be highly tunable from 3200 nm to 1550 nm by adjusting the interpillar gap distance, AZO thickness, aluminum concentration, deposition temperature, thermal treatment temperature, thermal treatment time and ZnO buffer layer thickness. In addition, LSPR cavities were also demonstrated by fabricating solid AZO nanotubes by
varying the NSL process. These materials were also shown to be tunable by adjusting the total diameter. In all cases the theory outlined in chapter 1 predicted the optical behavior which was also verified by numerical simulations.

The high quality films were then used to make HMMs. This was first accomplished in the multilayer geometry. Here, negative refraction was demonstrated and verified by FDTD, TMM and SMM calculations. In addition, an AZO/ZnO embedded nanowire HMM was also created for the first time via ALD and experimentally verified by ellipsometry.

The ultraconformal properties of ALD was again exploited to create a new class of metamaterial particles named THMMPs. This was experimentally demonstrated using HNTs comprised of AZO/ZnO multilayers. Here it was shown that these materials possess broadband, selective, omni-directional absorption when closely packed with a single monolayer and can be transferred to different substrates. These materials were also shown to have universal properties that can be applied to other material systems and geometries.

7.2 Outlook

The AZO films created could be further used in many applications. For example the lowest resistance achieved was $3.8 \times 10^{-4} \, \Omega \cdot \text{cm}$ which is the lowest reported value for AZO created by ALD. This can be used in many fields that require transparent conductive nanostructured films such solar energy harvesting. In addition the LSPR cavities created may have the ability to show
high Purcell factors and radiative enhancement. One area this might be useful for is visual light communication [124] (VLC). Currently VLC is being proposed as an alternative to WiFi due to its large, unrestricted bandwidth. Although visual light is only being considered currently, NIR could also be used with many advantages, however emitters in this region have low internal quantum efficiency [125]. Both LSPR and HMM cavities created in chapter 4, 5 and 6 are expected to have large Purcell effects which can enhance both the radiative intensity and modulation speed of the emitters [80].

As seen in chapter 6, ultraconformal HMMs can be used to create many unique forms of metamaterials. In particular, THMMPs have been shown to be able to create near perfect, omnidirectional broadband, yet selective absorption with one single, flexible and transferable monolayer. However, the full range of uses for this material may be much more diverse. For instance these particles are much like from solid metal particles in that they display an intensely confined electric field at resonance and can be self assembled into many unique configurations however they are also impedance matched with air within a large spectral range. This can have many implications for applications such as camouflage [107], cancer therapeutics [3] and thermophotovoltaics [103].
References


