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Engineering Si-compatible materials based on transparent nitrides and conductive oxides (TNCOs) for broadband active plasmonic and metamaterials applications

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Dissertation

ENGINEERING Si-COMPATIBLE MATERIALS BASED ON TRANSPARENT NITRIDES AND CONDUCTIVE OXIDES (TNCOS) FOR BROADBAND ACTIVE PLASMONICS AND METAMATERIALS APPLICATIONS

by

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Dedicated to

My Family and Friends
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ABSTRACT

Alternative plasmonic materials of Transparent Nitrides and Conductive Oxides (TNCOs) including Indium Tin Oxide (ITO), Al-doped ZnO (AZO) and Titanium Nitride (TiN), have been proposed as novel material platforms for Si-compatible plasmonics and metamaterials, showing enhanced light-matter interaction over a broad spectral range.

It has been recently shown that these materials feature reduced optical losses compared with conventional noble metals such as Au and Ag in the visible and near-infrared spectral range. However, it is still an open challenge to tailor the structural and optical properties of these materials, and to further reduce their optical losses, in order to effectively utilize them in photonic devices. In this thesis work, I demonstrate wide tunability of the optical and structural properties of ITO, AZO and TiN thin films, by using post-deposition annealing treatments, enabling significant reduction of their optical losses. By measuring the optical bandgaps of the investigated materials, I show that the tunability of the optical properties originates from the modulation of the free carrier concentration induced by the annealing treatment. Moreover, I perform XRD
characterization of the fabricated films, indicating that the annealing also effectively tunes the grain size, which is consistent with the change of the optical properties. Eventually, I investigate the role of the annealing gases for ITO and AZO, demonstrating that free-carrier modulation in ITO and AZO is due to the change in the density of oxygen vacancies after post-deposition annealing.

In particular, TNCOs possess epsilon-near-zero (ENZ) condition in near-infrared range with optical loss $\epsilon' < 1$, thus providing enhanced internal fields in the medium at the ENZ condition. In collaboration with Prof. Nader Engheta and the previous post-doc in our group Dr. Antonio Capretti, we demonstrate enhanced second-harmonic generation (SHG) and third-harmonic generation (THG) from ITO thin films driven by ENZ condition. It results that the SHG generation efficiency is comparable with that of a crystalline quartz plate of thickness 0.5 mm, and that the THG generation efficiency is $\sim$600 times larger than crystalline silicon.

As an application for the fabricated TiN material, I investigate PL intensity and lifetime in Hyperbolic Metamaterials (HMMs) coupled with emitting Si Quantum Dots (QDs). In collaboration with Hiroshi Sugimoto in Prof. Minoru Fujii’s group and the previous post-doc in our group Dr. Sandeep Inampudi, we demonstrate up to 1.6-times enhanced decay rate of QDs emission. Photonic devices based on TNCO plasmonic materials offer an effective approach for the engineering of novel Si-based photonic devices with enhanced light-matter coupling over a broad spectral range.

As an application for the fabricated ITO, in collaboration with Hongwei Zhao in Prof. Jonathan Klamkin’s group, electro-absorption modulators are numerically
investigated to show high extinction ration of greater than 6dB, while insertion loss is less than 1.3dB for wavelength range from 1.25 µm to 1.42 µm.

Additionally, we demonstrate tunable optical properties of ITO thin films in mid-infrared spectrum by thermal annealing of ITO in oxygen environment. In collaboration with Sajan Shrestha and Adam Overvig in Prof. NanFang Yu’s group, we fabricate 2D periodic arrays of ITO and show wide tuning of plasmonic resonances of ITO nanostructure from 4 µm to 10 µm. Combining with the tunability of ITO thin films in near-infrared, the ITO material platform provides a promising method for the control and engineering of Si-based tunable plasmonic and metamaterial devices in the infrared spectrum.

Finally, in collaboration with my colleague Ren Wang, we experimentally demonstrate silicon nanodisk arrays with tunable anapole mode excitation in the visible spectrum. The proposed high index nanostructures can be used to enhance absorption rate for applications in semiconductor photodetector.
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List of Abbreviations

3D Three Dimensional
a-Si:H Hydrogenated Amorphous Silicon
AOM Acousto-Optic Modulator
Au Gold
AZO Aluminum Doped Zinc Oxide
Cr Chrome
EBL Electron Beam Lithography
EMT Effective Medium Theory
ENZ Epsilon-Near-Zero
FDTD Finite Difference Time Domain
FTIR Fourier Transform Infrared Spectroscopy
HMM Hyperbolic Metamaterials
IR Infrared
ITO Indium Tin Oxide
LDOS Local Density of States
LPF Long-Pass Filter
MIBK Methylisobutyle Ketone
MOS Metal-Oxide-Semiconductor
MSE Mean-Squared Error
NIR Near-Infrared
NSOM Near-Field Scanning Optical Microscopy
**OPO** Optical Parametric Oscillator  
**PL** Photoluminescence  
**PMMA** Poly Methyl Methacrylate  
**QDs** Quantum Dots  
**RF** Radio Frequency  
**RIE** Reactive Ion Etch  
**SC** Standard Clean  
**SE** Spectroscopic Ellipsometry  
**SEM** Scanning Electron Microscopy  
**SHG** Second Harmonic Generation  
**Si** Silicon  
**SPF** Short-Pass Filter  
**TCO** Transparent Conductive Oxides  
**THG** Third Harmonic Generation  
**Ti** Titanium  
**TiN** Titanium Nitride  
**TNCO** Transparent Nitrides and Conductive Oxides  
**TOA** Tip-On-Aperture  
**XRD** X-Ray Diffraction  
\( \lambda_{\text{ENZ}} \) Epsilon-near-zero (ENZ) wavelength  
\( \lambda_{\text{PS}} \) Screened plasma wavelength
Chapter 1

1 Introduction

1.1 Motivation

The quest for the high-density integration of optical and electrical devices for compact photonics transducers and ultrasensitive chemical sensors has significantly driven the recent advancements of plasmonics and metamaterials technologies. Plasmonics merges the high bandwidth offered by photonics and nano-scale integration provided by nanoelectronics by coupling electromagnetic waves to free electron oscillations at metal-dielectric interface, creating subwavelength oscillating mode, known as plasmon [1]. Plasmonics exploits the unique optical properties of metallic nanostructures to manipulate and confine at nanometer scales, which drives the development of novel class of devices with unprecedented functionalities including hyperlens [2,3], invisibility [4–6], plasmonic waveguides [7,8], etc.

The ability to concentrate light has been traditionally in the domain of dielectric lens. Due to the fundamental laws of diffraction, dielectric lens cannot focus patterns that are smaller than half of the wavelength of light (~\(\lambda/2\)), where \(\lambda\) is the wavelength of light in the dielectric medium. Plasmonic nanostructures do not have these limitations because they can convert optical radiation into localized field distributions and enable coupling to subwavelength modes. Besides, plasmonic nanostructures can dramatically change light-matter interaction. Due to the possibility to confine light in subwavelength mode-volume
cavities, plasmonic devices can benefit to have high optical quality-factors (Q) with ultrasmall volume $v_m$.

Subwavelength imaging is among the first practical applications of plasmonics. For example, near-field scanning optical microscopy (NSOM) uses subwavelength apertures in metal-coated optical probes and shows spatial resolution, which is determined by the size of the aperture instead of the wavelength of light. Figure 1.1(a) demonstrates the application of NSOM for nanolithography system. The integration of plasmonic nanostructures with scanning components enables precise control over intense nanoscale optical fields while minimizing the diffraction-limited background light. Even though subwavelength aperture can have extremely high spatial resolution, the minimum aperture dimension is limited by optical throughput, which means the power transmitted through subwavelength aperture is inversely proportional to the square of the aperture area. Therefore, in apertureless NSOM (aNSOM), light with polarization along the tip’s long axis illuminates the metal tip. The lightning-rod effect generates highly localized near-field at tip’s apex which is superimposed with broad diffraction-limited light spot. Using nonlinear effect, non-localized background can be suppressed and the resolution of aNSOM is largely determined by tip radius. Deep-subwavelength ($\sim \lambda/3000$) spatial resolution imaging has been demonstrated at infrared spectrum, as shown in Figure 1.1(c). Recently, aNSOM has been used in high-resolution imaging for carbon nanotubes and DNA (Figure 1.1(b)). By depositing a metal protrusion adjacent to NSOM aperture, aperture fields can be further localized, because this structure combines the background suppression offered by conventional apertures with the tip-limited spatial resolution of
new apertureless technique. This approach is called tip-on-aperture (TOA), which has been recently used in new near-field microscopy and light delivery to small volumes. Figure 1.1(d) shows a SEM image of TOA probe.

**Figure 1.1:** (a) Schematics of plasmonic nanolithography system. An array of plasmonic nanostructures are placed at the end of the writing head and focus UV light to subwavelength spots. (b) A near-field Raman image of carbon nanotubes using aNSOM technique. (c) An NSOM image of multiple transistors cross-section. The aNSOM technique can distinguish the structures with different doping densities with subwavelength resolution. (d) A SEM image of TOA probe [9].

As plasmonic nanostructures can manipulate light beyond the classical diffraction limits, a number of silicon photonic components such as plasmon-enhanced photodetectors, plasmonic modulators have been realized using nanofabrication
techniques. For photodetectors, its speed is generally limited by two factors: carrier-transit time (the time of photogenerated carriers to transit to the detector’s intrinsic region), resistor-capacitor (RC) time constant (the time to charge the device’s effective capacitance). Among the two factors, carrier-transit time is proportional to the length of device, and RC time constant scales with device capacitance, which is proportional to device area. Therefore, reducing the detector size in both lateral and vertical dimension will benefit to increase the detector’s speed, and reduce its power consumption. Figure 1.2(a) shows the schematics of one plasmon-enhanced photodetector. This structure can concentrate light in both lateral and vertical directions, thus shrinking its detector size and boosting its speed.

Likewise, Figure 1.2(b) demonstrates the use of resonant plasmonic structures based on surface plasmon polariton (SPP) antennas to effectively concentrate light to deep-wavelength photodetector region. The concentric grating coupler can couple SPP into silicon photodetector underneath and increase its photoresponse by a factor of more than 20.

Alternatively, Figure 1.2(c) illustrates another approach of plasmon-enhanced photodetectors. Deep-subwavelength volume of Ge is embedded in the arms of sleeve-dipole antenna to resonate at 1.31 μm. By measuring polarization dependent photoresponse, resonant antennas effects have been observed with polarization contrast around 20. This device has very small footprint and can be integrated in a large scale in practical photodetector structures.
Figure 1.2: (a) Normalized energy density of plasmonic slit with width 50 nm in 100 nm thick Al film on silicon substrate. This structure can confine light both laterally and vertically. (b) Concentric grating coupler couples SPP into Si photodetector. The resulted photoresponse is improved by a factor of more than 20. (c) Plasmon-enhance Ge photodetector using sleeve-dipole antenna to resonate at 1.31 μm. (d) Schematics of nanoscale plasmonic modulators. The electrical signals are encoded into optical data stream by external applied voltage across active nonlinear medium sandwiched between metallic components in MDM waveguide [9].

Together with photodetectors, high-speed and power-efficient optical modulators are essential for highly integrated silicon photonics. Plasmonic nanostructures allow designs of more compact and efficient modulators. Figure 1.2(d) gives a conceptual design of nanoscale plasmonic modulators. By using a metal-dielectric-metal (MDM) geometry, the electric signals can be encoded into optical data stream by changing the optical properties of nonlinear active medium, which is sandwiched between metal components of MDM plasmonic waveguide.
Because the plasmon behavior in all of these devices originates from the collective oscillations of free electrons in the material, metals have been the primary components due to their abundant free electrons. However, metals exhibit high extinction losses in the visible and near-infrared spectral ranges, limited tunability, and lack of compatibility with the widespread silicon technology, severely limiting practical device implementations. For metals, the primary loss mechanism is attributed to conduction electrons and bound electron interband transitions. Among them, the conduction electron loss comes from the interactions of electron-electron, electron-photons and scatterings of lattice defects. For interband transitions, it occurs when d-electrons jump to higher energy levels with the absorption of incident photons. In metals, the loss is introduced when the bound electron absorbs incident photon and shifts to higher energy level. Figure 1.3 shows the impact of interband transitions on the losses of copper. Left axis is the imaginary part of the permittivity. The peak of at 2.1 eV corresponds to the interband transition. It is due to the electronic transitions from L3 band to Fermi surface [1,10,11].
Figure 1.3: The imaginary part of permittivity of copper. Contribution to optical loss in copper is attributed to free electron loss and interband transition loss [1,10,11].

In recent years, transparent conductive oxides (TCOs), such as Indium Tin Oxide (ITO) and Al-doped ZnO (AZO), and transition-metal nitrides, such as Titanium Nitride (TiN), have emerged as alternative plasmonic materials featuring reduced optical losses compared with conventional noble metals such as Au and Ag in the visible and near-infrared spectral range [1,12–14]. Figure 1.4 shows the comparison of optical properties of alternative plasmonic materials and conventional metals.
Figure 1.4: Comparison of optical properties of alternative plasmonic materials with conventional metals. (a) Real and (b) imaginary part of permittivity of transparent conductive oxides (TCO) and transition nitrides. The losses in TCOs are a few times smaller than those of conventional metals, while the losses of nitrides are comparable to metals in the optical range [15].

These materials also feature outstanding thermal and chemical stability [16,17], and their optical properties depend on several parameters: carrier concentration and carrier mobility. For plasmonic applications, their carrier concentration has to be high enough so that the real part of dielectric permittivity is negative. Besides, it has to be tunable to allow carrier concentration to either increase or decrease. Higher carrier mobility results in lower material losses. Additional optical losses can be introduced by interband transitions and are highly detrimental. Figure 1.5 shows the map of material parameters for typical plasmonic materials. Ideal materials for plasmonic applications should have small interband loss, high carrier mobility, which lie at the horizontal plane of the left end of the plot.
Figure 1.5: The map of material parameters (i.e. interband loss, carrier concentration and carrier mobility) of plasmonic materials. Ideal plasmonic material should have small interband loss and high carrier mobility [18].

In general, these materials are non-stoichiometric in nature and therefore their optical properties significantly depend on their deposition conditions [16,17]. For instance, ITO, AZO and TiN have demonstrated tunable optical dispersion by controlled deposition temperature [15,19]. Due to the unique advantages of their materials including CMOS compatibility, tunability of optical and structural properties, reduced optical losses, transparent nitrides and conductive oxides (TNCOs) have found widespread applications in plasmonics, metamaterials and nonlinear optics, such as negative refraction [20], single photon source [21], perfect absorption of light [22], spontaneous emission control [23,24], and nonlinear generation enhancement [25,26].
Metamaterials are artificial engineered materials with subwavelength building blocks. These materials have been proposed as a novel approach to manipulate electromagnetic fields, with applications to energy squeezing [27], imaging [28], scattering [29,30], and nonlinear optics [31–35]. Among them, a highly anisotropic metamaterial which consists of subwavelength metallic-dielectric multilayer structures can effectively act as metallic material in one or two directions and dielectric in the third direction. In such metamaterials, light experiences extreme anisotropy, which results in hyperbolic dispersion, and can cause dramatic change of light propagation in the materials. This classes of metamaterials is called hyperbolic metamaterial (HMM), and has found applications in negative refraction [36], hyperlens [2,37], single-photon sources [21], etc. Figure 1.6 shows the use of HMM in these applications.

**Figure 1.6:** Applications of hyperbolic metamaterial (HMM). (a) Experimental results of negative refraction using HMM, (d) schematics of negative refraction, (b) partial focusing using HMM: simulated (left) and experimentally measured (right) spatial maps of electric field, (e) schematics of partial focusing experiment, (c) hyperlens experiment using HMM [38].
Recently, enhancement of harmonic generation in nonlinear epsilon-near-zero (ENZ) media has been theoretically predicted [31,33–35,32] and phase mismatch-free propagation has been demonstrated experimentally [39]. However, current designs for near-infrared and optical frequencies [40–42] rely on the use of metallic materials with large extinction losses or on three-dimensional nano-manufacturing, limiting the compatibility with silicon technology and integrated planar devices.

In this thesis, we demonstrate the material engineering of transparent nitrides and conductive oxides (TNCOs) to achieve tunability of optical and structural properties with reduced optical losses. Besides, we investigate the applications of enhanced second and third harmonic generation in ITO films at telecommunication wavelengths. Furthermore, we demonstrate TiN-based hyperbolic metamaterials for broadband enhancement of local density of states. Finally, we explore other applications using TNCOs for high-speed electro-optical modulators and plasmonic resonance in mid-infrared spectrum.

1.2 Outline

This thesis begins with a review of fundamental concepts in electromagnetics followed by an introduction of the physical processes of thin film growth and sputtering, as well as optimization of deposition parameters for ITO, AZO and TiN thin films.

Chapter 4 describes the optical and structural characterization of ITO, AZO and TiN thin films by using post-deposition annealing treatments in controlled gaseous atmospheres. It will be shown that this method provides wide tunability of the optical and
structural properties of ITO, AZO and TiN thin films and a significant reduction of their optical losses. By measuring the optical bandgaps of the investigated materials, we show that the tunability of their optical properties originates from the modulation of the free carrier concentration upon annealing treatment. Then, we perform XRD characterization of the fabricated films that indicates that annealing can also effectively tunes the grain size as a function of annealing temperature, which is consistent with the modification of the optical properties. At last, we investigate the role of annealing gases for ITO and AZO, demonstrating that the free-carrier modulation in ITO and AZO is due to the change in the density of oxygen vacancies induced by the post-deposition annealing.

Chapter 5 shows the enhanced second- and third-harmonic generations tailored by the ENZ response of Si-compatible ITO films at telecommunication wavelengths, without the need of specialized nanofabrication. It provides a simple and cost-effective approach to control the ENZ behavior resulting in highly-efficient, nonlinear generation on Si.

As an application of alternative plasmonic material, TiN-based hyperbolic metamaterial (HMM) will be presented in Chapter 6. The intensity and the wavelength-dependent dynamics of the broadband QDs light emission across the HMMs hyperbolic dispersion regime is investigated to demonstrate Si compatible active structures that feature broadband enhancement of the photonic local density of states (LDOS). Chapter 7 covers the application of ITO for broadband electro-optical modulator. The numerical study of extinction ratio (ER) and insertion loss (IL) of the proposed electro-optical modulator based on ITO will be investigated.
Chapter 8 will discuss the post-deposition annealing of ITO thin films in oxygen atmosphere which leads to the tuning of their ENZ point throughout the near-infrared and short-wavelength mid-infrared (i.e., from 1 \( \mu \text{m} \) to 4 \( \mu \text{m} \)) bands with reduced optical losses. Tunable plasmonic resonances in mid-infrared from 4 \( \mu \text{m} \) to 10 \( \mu \text{m} \) will be shown with potential applications including metasurfaces, sensing and nonlinear generation. Chapter 9 will provide preliminary results of silicon nanostructures for broadband absorption enhancement using non-radiative anapole modes. Final conclusion and future perspectives will be discussed in the last chapter.
Chapter 2

2 Theoretical Background

In this chapter, I summarize the fundamental concepts of electromagnetics theory, which serves as the necessary basis for this thesis. In particular, I will review the basic concepts of electrodynamics such as optical fields and Maxwell’s equations, then I will discuss the optical properties of materials and review models for different medium.

2.1 Maxwell’s Equations

Light manifests itself in the forms of wave and particles. To describe the optical radiation, it is most sufficient to adopt the wave picture of light, which allows us to use the classical field theory based on Maxwell’s equations. In macroscopic electrodynamics, the behavior of time-varying electromagnetic field is governed by space- and time-dependent macroscopic Maxwell’s equations, in the absence of space charges and currents, they are given by [43]

\[ \nabla \cdot \mathbf{D} = \rho \]  \hspace{1cm} (2.1)

\[ \nabla \cdot \mathbf{B} = 0 \]  \hspace{1cm} (2.2)

\[ \nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \]  \hspace{1cm} (2.3)

\[ \nabla \times \mathbf{H} = \mathbf{J} + \frac{\partial \mathbf{D}}{\partial t} \]  \hspace{1cm} (2.4)

Where \( \mathbf{E} \) denotes the electric field, \( \mathbf{D} \) the electric displacement, \( \mathbf{H} \) the magnetic field, \( \mathbf{B} \) the magnetic induction, \( \mathbf{J} \) the current density and \( \rho \) the charge density. In
addition, the response of a medium to an electromagnetic field generates the polarization \( \mathbf{P} \) and magnetization \( \mathbf{M} \). They are connected to the field quantities through the following relations:

\[
\mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P} \quad (2.5)
\]

\[
\mathbf{B} = \mu_0 \mathbf{H} + \mu_0 \mathbf{M} \quad (2.6)
\]

Where \( \varepsilon_0 \) is the electric permittivity of free space (~8.854 \( \times \) 10\(^{-12} \) F/m) and \( \mu_0 \) is the magnetic permeability of free space (~1.257 \( \times \) 10\(^{6} \) H/m). By substituting the fields \( \mathbf{D} \) and \( \mathbf{B} \) into Maxwell’s curl equations (Equations 2.3 and 2.4) by the expressions in Equations 2.5 and 2.6, and combining the two resulting equations, we obtain the inhomogeneous wave equations

\[
\nabla \times \nabla \times \mathbf{E} + \frac{1}{c^2} \frac{\partial \mathbf{E}^2}{\partial t^2} = -\mu_0 \frac{\partial}{\partial t} \left( \mathbf{J} + \frac{\partial \mathbf{P}}{\partial t} + \nabla \times \mathbf{M} \right) \quad (2.7)
\]

\[
\nabla \times \nabla \times \mathbf{H} + \frac{1}{c^2} \frac{\partial \mathbf{H}^2}{\partial t^2} = \nabla \times \mathbf{j} + \nabla \times \frac{\partial \mathbf{P}}{\partial t} + \mu_0 \frac{\partial \mathbf{M}}{\partial t} \quad (2.8)
\]

Where \( c \) is the speed of light in vacuum \( (c = \frac{1}{\sqrt{\varepsilon_0 \mu_0}}) \). In addition, we have the following constitutive relations for non-dispersive linear and isotropic medium:

\[
\mathbf{D} = \varepsilon_0 \varepsilon \mathbf{E} \quad (2.9)
\]

\[
\mathbf{B} = \mu_0 \mu_0 \mathbf{H} \quad (2.10)
\]

\[
\mathbf{P} = \varepsilon_0 \chi_\varepsilon \mathbf{E} \quad (2.11)
\]

\[
\mathbf{M} = \chi_m \mathbf{E} \quad (2.12)
\]

\[
\mathbf{J} = \sigma \mathbf{E} \quad (2.13)
\]
Where Equation 2.9 relates displacement field $\mathbf{D}$ and electric field $\mathbf{E}$ through dielectric constant $\varepsilon$. Equation 2.10 relates magnetic induction $\mathbf{B}$ and magnetic field $\mathbf{H}$ through magnetic permeability $\mu$. Equation 2.11 relates polarization $\mathbf{P}$ and electric field $\mathbf{E}$ through dielectric susceptibility $\chi_e = \varepsilon - 1$. Equation 2.12 relates magnetization $\mathbf{M}$ and electric field $\mathbf{E}$ through magnetic susceptibility $\chi_m = \mu - 1$. The last equation 2.13 relates current density $\mathbf{J}$ with electric field $\mathbf{E}$ by electric conductivity $\sigma$. For nonlinear media, the right sides of these equations can be supplemented using higher order terms. While for anisotropic media, tensorial forms of $\varepsilon$ and $\mu$ will be used in these equations.

In the constitutive equations, the complex dielectric constant is given by $\varepsilon = \varepsilon_1 + i\varepsilon_2$, where $\varepsilon_1$ and $\varepsilon_2$ are the real and imaginary parts of dielectric constant, respectively. An equivalent form of representation is given by complex refractive index $\tilde{n} = n + ik$, where $n$ and $k$ are the ratio of the speed of light in the vacuum to the speed of light in the medium, and the extinction coefficient of light in the medium, respectively. To relate these two expressions, we have the following relations:

$$\varepsilon_1 = n^2 - k^2$$  \hspace{1cm} (2.13)

$$\varepsilon_1 = 2nk$$  \hspace{1cm} (2.14)

$$n = \frac{\varepsilon_1 + \sqrt{\varepsilon_1^2 + \varepsilon_2^2}}{2}$$  \hspace{1cm} (2.15)

$$k = \frac{\varepsilon_2}{2n}$$  \hspace{1cm} (2.16)
2.2 Optical Properties of Materials

A simple model for the dielectric properties of a material can be obtained by considering the motion of bound electron in the presence of an applied electric field. Electric dipole moment will be created when electric field separates the electron from positively charged nucleus. A simple model for the dynamics of the displacement $x$ of the bound electron is as follows ($\ddot{x} = \frac{dx}{dt}$):

$$m \ddot{x} = eE - kx - m\gamma \dot{x}$$  \hspace{1cm} (2.17)

Where the term $kx$ is a spring-like restoring force due to binding of electrons to nucleus, $m\gamma \dot{x}$ is the friction-type force proportional to the velocity of electron. Spring constant $k$ is related to resonance frequency of spring by $\omega_0 = \sqrt{\frac{k}{m}}$. Equation 2.17 can be rewritten as

$$\ddot{x} + \gamma \dot{x} + \omega_0^2 x = \frac{e}{m} E$$ \hspace{1cm} (2.18)

If we assume the electric field $E(t)$ is sinusoidal with frequency $\omega$ ($E(t) = E e^{j\omega t}$), then the solution of equation 2.18 will be $x(t) = xe^{j\omega t}$, then equation 2.18 is rewritten as

$$-\omega^2 x + j\omega \gamma x + \omega_0^2 x = \frac{e}{m} E$$ \hspace{1cm} (2.19)

Then the solution will be

$$x = \frac{e E}{\omega_0^2 - \omega^2 + j\omega \gamma}$$ \hspace{1cm} (2.20)

The polarization per unit volume $P$ and electric displacement field $D$ will be

$$P = np = nx = \frac{ne^2 E}{\omega_0^2 - \omega^2 + j\omega \gamma} = \varepsilon_0 x(\omega)E$$ \hspace{1cm} (2.21)
\[
\mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P} = \varepsilon_0 (1 + \chi_e(\omega)) \mathbf{E} = \varepsilon(\omega) \mathbf{E} \quad (2.22)
\]

Where the effective permittivity \( \varepsilon(\omega) \) is:

\[
\varepsilon(\omega) = \varepsilon_0 + \frac{\frac{n_e^2}{m}}{\omega_0^2 - \omega^2 + j \omega \gamma} = \varepsilon_0 + \frac{\varepsilon_0 \omega_p^2}{\omega_0^2 - \omega^2 + j \omega \gamma} \quad (2.23)
\]

Where \( \omega_p \) is the plasma angular frequency. For different materials, the above model equation 2.23 can be described as the following cases:

a. Dielectrics, \( \omega_0 \neq 0, \gamma \neq 0 \).

b. Conductors, \( \omega_0 = 0, \gamma \neq 0 \).

c. Collisionless plasmas, \( \omega_0 = 0, \gamma = 0 \).

For Drude-Lorentz model, we need to add an interband term, which is given by

\[
\frac{\varepsilon(\omega)}{\varepsilon_0} = 1 + \frac{\omega_p^2}{j \omega (\gamma + j \omega)} + \sum_{l=1}^{k} \frac{\alpha_{\omega_p,k}^2}{\omega_0^2 - \omega^2 + j \omega \gamma_k} \quad (2.24)
\]

2.3 Epsilon-Near-Zero (ENZ) Condition and Screened Plasma Wavelength

ITO and AZO have been used widely as transparent contacts in microelectronic industry [44,45], while TiN has been utilized as a coating material to improve surface properties [46], and as a conductive barrier in microelectronics [47]. The near-infrared (NIR) permittivity \( \varepsilon(\omega) \) of ITO, AZO and TiN can be adequately described by Drude-Sommerfeld model [17]:

\[
\varepsilon(\omega) = \varepsilon_1(\omega) + i \varepsilon_2(\omega) = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2 + j \omega \gamma} \quad (2.25)
\]

Here \( \varepsilon_\infty \) is the background permittivity (high frequency limit of \( \varepsilon \)), \( \omega_p \) is the plasma angular frequency and \( \gamma \) describes the charge carrier collision rate, which results
in the optical losses inside the material. The plasma angular frequency can be expressed as:

$$\omega_p^2 = \frac{n e^2}{\varepsilon_0 m^*}$$  \hspace{1cm} (2.26)

Where $e$ is elementary charge, $n$ is the carrier concentration (which can be experimentally inferred from ellipsometry), $m^*$ is the effective mass of electron (which in ITO, AZO and TiN is approximately 0.35 $m_0$ [48], 0.38 $m_0$ [49], 1.10 $m_0$ [50], respectively. $m_0$ is the free electron mass), and $\varepsilon_0$ is the permittivity of free space.

In general, a large free carrier concentration of the order of $10^{20} - 10^{22}$ cm$^{-3}$ is needed to achieve negative permittivity, \textit{i.e.} a metallic behavior in the optical spectrum. In TCOs, such high doping levels are very challenging due to the fundamental solid-solubility limit [1,17]. Therefore, TCOs typically display metal behavior in the NIR range. On the contrary, it has been shown that TiN supports a carrier concentration of approximately $\sim10^{22}$ cm$^{-3}$ and it shows metal-like properties even in the visible spectrum. However, this functionality comes at the cost of a significantly increased value of optical losses, since equation 2.25 implies that $\varepsilon_2 \propto \omega_p^2 \propto n$, \textit{i.e.} $\varepsilon_2$ grows linearly with the free carrier concentration.

The frequency at which the real part of the permittivity $\varepsilon_1$ goes to zero is known as screened plasma frequency $\omega_{ps}$, and it can be expressed as $\omega_{ps}^2 = \frac{\omega_p^2}{\varepsilon_\infty - \gamma^2}$. For TiN, the imaginary permittivity $\varepsilon_2$ at the screened plasma wavelength $\lambda_{ps}$ is larger than 1. On the contrary, it has been demonstrated that ITO and AZO can show an epsilon-near-zero (ENZ) condition, denoted by $\lambda_{ENZ}$, at the screened plasma frequency [1,17,51]. For
these materials, not only the real part of permittivity $\varepsilon_1$ is zero, but also the imaginary part of the permittivity $\varepsilon_2$ is significantly smaller than one. In particular, the condition $\varepsilon_2 < 1$ guarantees enhanced internal fields in nanolayers composed of materials that supports the ENZ condition. Achieving the ENZ condition in a widely tunable spectral range is important for applications to optical cloaking [30,52,53], molecular emission control [54,55] and nonlinear optics [25,56].
Chapter 3

3 Deposition of ITO, AZO and TiN Thin Films

In my thesis work, a large number of samples of ITO, AZO and TiN were deposited using either RF or reactive DC magnetron sputtering, followed by post-deposition annealing in pure N₂ (99.999%), Ar (99.999%) or O₂ (99.999%) atmospheres. Therefore, it is critical to understand the thin film growth and sputtering processes. This chapter provides the optimization of deposition parameters including chamber pressure, cathode power of the targets and their effects on the optical properties (ENZ wavelength) of thin films. I will start with the substrate cleaning, the first step before thin film deposition, then briefly introduce the physical processes of thin film growth and sputtering. At last, I will explain the key deposition parameters of sputtering of these thin films. It is important to note that this chapter only focuses on the optimization of sputtering parameters for as-deposited samples. In order to further tailor the optical and structural properties of these thin films, post-deposition annealing is essential to modulate the free carrier concentration and thus influence the material properties, more details of annealing to control the material properties will be discussed in Chapter 4.

3.1 Substrate Cleaning

Using automated dicing saw (Disco DAD 3220) with 2" hubbed resin bond diamond blade (CA-006-325-XXX-H), 4" substrates of Si, fused silica and quartz are diced into 1×1 cm² pieces. Prior to sputtering, each substrate piece needs to be thoroughly cleaned to remove surface impurities during shipping, handling and dicing.
Standard RCA process has been adopted to clean these substrates. At first, the substrates are sonicated in de-ionized (DI) water for 5 minutes to remove particles that exist on the surfaces. Then the substrates are placed into a solution of 1:1:5 volume mixture of ammonium hydroxide (NH₄OH, 29% by wt.), hydrogen peroxide (H₂O₂, 30% by weight) and de-ionized (DI) water at 75°C for 10 minutes, this step is to remove organic contaminants and it is called SC-1 step. Following that, only for bare Si substrates, an optional second setup is to shortly immerse substrates in 1:50 solution of aqueous HF (hydrofluoric acid) at room temperature for 15s to remove thin native oxide layer. Subsequently, the substrates are immersed into a solution of 1:1:6 volume mixture of hydrochloric acid (HCl, 37% by wt.), hydrogen peroxide (H₂O₂, 30% by weight) and de-ionized (DI) water at 75°C for 10 minutes, to get rid of the ionic contaminants which were introduced previously, this step is called SC-2. Finally, the substrates are rinsed by DI water and dried by nitrogen (N₂).

3.2 Thin Film Deposition Process

Thin film deposition process typically involves three main steps: 1) Production of appropriate atomic, molecular or ionic species; 2) Transport of these produced species to substrate through a medium; 3) Condensation of these species on substrate to form solid deposition, either directly or indirectly through chemical and/or electrochemical reaction. Formation of thin film usually takes place through nucleation and growth process. The general sequence of growth process can be summarized as follows [57]:
1. The species lose velocity components that are normal to the substrate upon the impact of substrate, provided that the incident energy isn’t too high so that the species can be physically adsorbed on the substrate surface.

2. Initially, the adsorbed species aren’t in thermal equilibrium with substrate so that they can move over the surface of the substrate. The species interact with themselves and therefore form bigger clusters.

3. Nucleation stage: These clusters are thermodynamically unstable. Depending on the deposition parameters, they may tend to desorb in time. These clusters will grow in size if the deposition parameters are appropriate to allow cluster collides with other adsorbed species before getting adsorbed. After reaching certain critical size, the cluster becomes thermodynamically stable to overcome the nucleation barrier.

4. Islands stage: The critical nuclei in nucleation stage will grow in number and size until a saturation nucleation density is reached. The density of nucleation and the size of average nucleus depend on several parameters including the energy and rate of the impinging species, the activation energies of absorption, desorption, thermal diffusion, and the temperature, etc. By direct impingement of the incident species, a nucleus can grow perpendicular to the substrate, and it can also grow parallel to it by surface diffusion of the adsorbed species.

5. Coalescence stage: The small islands formed previously start to coalesce with each other to reduce substrate area. They tend to agglomerate to form bigger islands
and this process can be enhanced by increasing the substrate temperature to increase the surface mobility of the adsorbed species.

6. Formation of continuous film: Larger islands grow together to leave the channels and holes of uncovered substrate. The structure of the films changes from discontinuous island to porous network. Continuous film is formed by filling of the channels and holes.

Thornton Zone model was developed to describe the growth and structural variation of sputtered thin film as a function of the substrate temperature, kinetic energy of ions and the deposition rate [58], as shown by Figure 3.1. It illustrates the effect of the individual physical processes on structure and the dependence on substrate temperature (T), Argon gas pressure (P).

Figure 3.1: Schematic representation of the Thornton growth zone model of sputtered deposited materials. (T/Tm) is the ratio of deposition temperature (T) to the melting temperature (Tm) of the sputtered material [58].
In Zone I of the Thornton model, as a result of shadowing effects which overcome insufficient adatom surface diffusion, the structures can occur in amorphous and crystalline deposits. High points on growing surface receive more flux of coating than the valleys, thus creating shadowing effects and inducing open boundaries. The thin films in Zone I consist of tapered crystals with domed tops, which are separated by voided boundaries.

In Zone II, surface diffusion dominates the shadowing effect. By a sequence of morphology changes, thin films grow from discrete nuclei that have favorable growth properties. It consists of columnar grains separated by distinct and dense boundaries.

In Zone III, thin film growth is dominated by bulk lattice and grain-boundary diffusional process, which allows the high temperature recovery and recrystallization. It consists of equiaxed recrystallized grains.

In Zone T, it is considered to be the transition region between Zone I and II. The adatom diffusion largely overcomes the roughness of substrate and initial nucleation, so that the material property is governed by energetic ion bombardment from sputtering target under low gas pressures. As a result, grain structure appears to be fibrous without voided boundaries, which results in high-density films in Zone T. In this thesis, most of the fabricated samples are located in Zone T or Zone I (deposition at room temperature and low gas pressure).
3.3 Sputtering

Sputtering is a process where particles from solid target material are ejected due to ion bombardment by energetic particles, such as gas ions (Ar\(^+\) in our cases). A sputtering event is initiated by first collision between incident ions and target surface atoms, followed by sequential collisions between target surface atoms. Figure 3.2 shows the process of sputtering collisions in the target surface.

Sputtering deposition usually consists of three steps: 1) Emission of particles from target surface by momentum transfer from gas ions impacting on the target surface. 2) Transport of sputtered particles to substrate through ambient gas molecules (Ar atoms). 3) Transformed particles deposited onto substrate surface. In general, several kinds of sputtering systems are available for thin film deposition, such as direct current (DC), radio frequency (RF) diode and magnetron sputtering.

Figure 3.2: Schematic representation of the sputtering process.
3.3.1 DC Diode Sputtering

The DC diode sputtering system consists of a pair of planar electrodes, one is cathode and another one is anode. The target is usually on top of cathode and the substrates are placed on the anode. When the sputtering chamber is kept at certain pressure with certain applied DC voltage, the glow discharge is initialized to generate plasma. Then, Ar ions in the glow discharge are accelerated to bombard the target surface to produce sputtered particles from the target, which eventually results in the sputtering deposition of thin film on the substrates. In DC diode sputtering, the target has to be electrically conductive to avoid surface charging which will disturb the ion bombardment of target surface.

3.3.2 RF Diode Sputtering

By simply substituting insulating target for metal target in DC diode sputtering system, the sputtering glow discharge can’t be sustained because the surface charge will be built up on target surface. Therefore, to sustain glow discharge for insulating targets, DC power supply is replaced with RF power supply. In RF diode sputtering, the electrons oscillate to acquire sufficient energy to be ionized and sustain plasma. RF electric field for the glow discharge increases the collision probability between secondary electrons and gas molecules, so RF diode sputtering uses electrons more efficiently to produce plasma. In particular, RF diode sputtering system requires impedance-matching network between power supply and discharge chamber. In practical systems, radio frequencies
(13.56MHz) is used for plasma processing in RF diode sputtering system. RF diode sputtering is usually used to deposit dielectric materials.

3.3.3 Magnetron Sputtering

Magnetron sputtering became widely used after the seminal work by Thornton [59]. By introducing magnetic field using magnets inside the cathode target, the glow discharge in magnetron sputtering system is concentrated in the high-magnetic-field region and a circular cathode glow is formed. This high flux of electrons can generate extremely high-density plasma, which enhances the chemical reaction at the substrate during film growth. In the deposition of ITO films, Ar gas is supplied to sustain the plasma to sputter the ITO target (99.99% purity). While for AZO deposition, co-sputtering of Al (99.99% purity) and ZnO (99.99% purity) targets are utilized to form stoichiometric thin films with tunable optical properties. Figure 3.3 shows the configuration of ITO and AZO thin films sputtering. The angle between the normal of the substrate surface and target is 60°, and the substrate is placed on top of a rotating stage to obtain uniform thin film.
Figure 3.3: Schematic representation of ITO (ITO target only) and AZO (Al and ZnO targets) magnetron sputtering.

3.3.4 Reactive Sputtering

Reactive sputtering is a process that allows the deposition of material compounds by introducing reactive gas (N\textsubscript{2} in our cases) to the plasma, which is typically an inert gas (Ar in our cases). During the process, reactive gas is activated by plasma and chemically reacts with the target surface, which subsequently is sputtered away. By careful control of the relative amounts of inert and reactive gas, the composition of sputtered thin film can be altered in a controllable way. We use reactive sputtering at room temperature of Ti target (99.99% purity) in pure N\textsubscript{2} atmosphere to deposit TiN thin films, as shown in Figure 3.4.
Figure 3.4: Schematic representation of N\textsubscript{2} reactive RF magnetron sputtering for TiN thin film deposition.

3.3.5 The Sputtering System Used in This Thesis

The Denton sputtering system used in this thesis has three magnetron sputter cathodes (3 inch, water cooled) in a confocal arrangement, which is coupled to RF generator operating at 13.56 MHz. The system has RF power supplies with automatch network and rack mounted control panel (500 W). The sputtering chamber is pumped with a mechanical roughing and a turbomolecular pumps, to be able to operate with base pressure \( \sim 10^{-7} \) mbars, it also supports liquid N\textsubscript{2} trap with enhanced water vapor pumping speed. Three gases (N\textsubscript{2}, H\textsubscript{2} and O\textsubscript{2}) are available for reactive sputtering with purities of 99.999%, their flow rates are controlled by independent mass-spectrometers. The
chamber has variable speed (0–25 RPM) rotating substrate stage to provide excellent film uniformity during deposition.

3.4 Thermal Annealing

After sputtering deposition, ITO and AZO thin films are treated with post-deposition annealing in rapid thermal annealing (RTA) furnace under pure N₂ (99.999%), Ar (99.999%) or O₂ (99.999%) atmospheres, with temperature from room temperature to 750°C for 60 min. For TiN thin films, they are annealed in Mellen thermal furnace in vacuum with pressure 2.3×10⁻³ Torr at temperatures between room temperature and 900°C for 60 min, with ramp-time fixed at 1 min. The annealing will produce a large tunability of the measured optical dispersion properties of the ITO, AZO and TiN layers in the visible and NIR spectrum, and result in a significant reduction of their optical loss as well.

The effect of annealing temperature and atmospheres on the optical and structural properties of ITO, AZO and TiN will be discussed with more details in Chapter 4.

3.5 Sputtering Parameters

In this part, I will investigate the effect of gas pressure, sputtering cathode power to obtain ITO, AZO and TiN as deposited thin films with optimum optical properties ($\lambda_{ENZ}$ in this case). All the samples are fabricated at room temperature. Since post-deposition annealing can further tailor the optical properties to modulate $\lambda_{ENZ}$ and reduce
optical loss, one challenge in this research is to push $\lambda_{\text{ENZ}}$ into lower limit for as deposited samples. Therefore the goal of the optimization of sputtering parameters in this study is to minimize the $\lambda_{\text{ENZ}}$ with considerable optical loss reduction. All the depositions parameters are summarized in Tables 3.1 to 3.4.

3.5.1 Sputtering Parameters of ITO Thin Films

One of the most important parameters during deposition of ITO is the sputtering cathode power. Table 3.1 summarizes the deposition parameters of ITO thin films under different sputtering power, while keeping the chamber pressure (2.4 mT) and thickness (91 nm $\pm$ 5 nm) as constants. It is shown that when the sputtering power initially increases from 80 W to 120 W, $\lambda_{\text{ENZ}}$ decreases from 2001 nm to 1907 nm. When the sputtering power further increases to 250 W, $\lambda_{\text{ENZ}}$ saturates around 1875 nm, as shown from the inset of Figure 3.5. This result demonstrates that 150W is enough to minimize the $\lambda_{\text{ENZ}}$ of sputtered ITO thin films. It should be noted that all the samples have been fabricated at different times to ensure the reproducibility of the sputtering recipe.

Table 3.1: Sputtering parameters of ITO thin films deposited under different sputtering cathode power

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>ITO cathode power (W)</th>
<th>Chamber gas pressure (mT)</th>
<th>Thickness (nm)</th>
<th>$\lambda_{\text{ENZ}}$ (nm)</th>
<th>Deposition rate (nm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>182</td>
<td>80</td>
<td>2.4</td>
<td>88</td>
<td>2001</td>
<td>8</td>
</tr>
<tr>
<td>180</td>
<td>120</td>
<td>2.4</td>
<td>88</td>
<td>1907</td>
<td>13.2</td>
</tr>
<tr>
<td>183</td>
<td>150</td>
<td>2.4</td>
<td>86</td>
<td>1875</td>
<td>17.2</td>
</tr>
<tr>
<td>185</td>
<td>200</td>
<td>2.4</td>
<td>95</td>
<td>1875</td>
<td>21.5</td>
</tr>
<tr>
<td>184</td>
<td>250</td>
<td>2.4</td>
<td>86</td>
<td>1874</td>
<td>23.75</td>
</tr>
</tbody>
</table>
The $\lambda_{\text{ENZ}}$ of as deposited ITO samples is in the range of 1800–2000 nm. To tune the $\lambda_{\text{ENZ}}$, post-deposition annealing is applied to modulate the free electron density in these thin films, it also results in significant optical loss reduction. Typically, low sputtering power of ITO yields slower deposition rate, so we preferred to use higher power (200 W) in this study to achieve moderate deposition rate, with the ability to optimize $\lambda_{\text{ENZ}}$ for as deposited ITO samples.

To investigate the effect of gas pressure on the influence of optical dispersion properties ($\lambda_{\text{ENZ}}$), we keep the ITO sputtering cathode power (120 W) and thickness (91 nm $\pm$ 5 nm) the same, while the gas pressures are varied from 2 mT to 4.1 mT, as listed in Table 3.2.

**Figure 3.5:** Real (a) and imaginary (b) part of permittivity of ITO samples on Si substrate fabricated with different sputtering power: 80 W (black), 120 W (red), 150 W (green), 200 W (blue), 250 W (cyan). All the samples have similar thickness around 91 nm $\pm$ 5 nm.
Table 3.2: Sputtering parameters of ITO thin films deposited under different gas pressure

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>ITO cathode power (W)</th>
<th>Chamber gas pressure (mT)</th>
<th>Thickness (nm)</th>
<th>$\lambda_{ENZ}$ (nm)</th>
<th>Deposition rate (nm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>176</td>
<td>120</td>
<td>4.1</td>
<td>96</td>
<td>2205</td>
<td>14.4</td>
</tr>
<tr>
<td>177</td>
<td>120</td>
<td>3.1</td>
<td>94</td>
<td>1931</td>
<td>14.1</td>
</tr>
<tr>
<td>178</td>
<td>120</td>
<td>2.4</td>
<td>88</td>
<td>1924</td>
<td>13.2</td>
</tr>
<tr>
<td>179</td>
<td>120</td>
<td>2.0</td>
<td>87</td>
<td>1946</td>
<td>13.05</td>
</tr>
</tbody>
</table>

As the chamber pressure changes, the $\lambda_{ENZ}$ varies from 1946 nm to 2205 nm. It can be seen from Figure 3.6 that the thin film deposited at gas pressure of 2.4 mT has the smallest $\lambda_{ENZ}$.

Figure 3.6: Real (a) and imaginary (b) part of permittivity of ITO samples on Si substrate fabricated under different chamber pressure: 4.1 mT (black), 3.1 mT (red), 2.4 mT (green), 2.0 mT (blue). All the samples have similar thickness around 91 nm±5 nm.
Dielectric permittivity of ITO thin films with different thickness is shown in Figure 3.7. The $\lambda_{\text{ENZ}}$ of ITO films decreases with increased thickness of ITO. The thickness dependence of optical properties is well known for TCOs due to trapping states at the interface of TCOs and substrates, which will be discussed in Chapter 4.

**Table 3.3**: Sputtering parameters of ITO thin films with different thickness

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>ITO cathode power (W)</th>
<th>Chamber gas pressure (mT)</th>
<th>Thickness (nm)</th>
<th>$\lambda_{\text{ENZ}}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>185</td>
<td>200</td>
<td>2.4</td>
<td>16</td>
<td>1958</td>
</tr>
<tr>
<td>187</td>
<td>200</td>
<td>2.4</td>
<td>35</td>
<td>1915</td>
</tr>
<tr>
<td>191</td>
<td>200</td>
<td>2.4</td>
<td>94</td>
<td>1875</td>
</tr>
<tr>
<td>405</td>
<td>200</td>
<td>2.4</td>
<td>298</td>
<td>1823</td>
</tr>
</tbody>
</table>

The deposition parameters of ITO thin films with different thickness are listed in Table 3.3, the sputtering cathode power and gas pressure are kept the same for all the samples.

**Figure 3.7**: Real (a) and imaginary (b) part of permittivity of ITO samples on Si substrate with different thickness: 16 nm (black), 35 nm (red), 94 nm (green), 298 nm (blue). All the samples are fabricated using same sputtering power under same deposition pressure.
3.5.2 Sputtering Parameters of AZO Thin Films

The deposition parameters of AZO thin films are summarized in Table 3.4 and 3.5. Similar to ITO, we keep constant gas pressure (2.4 mT) for all the depositions of AZO to ensure fabricated AZO thin films are structurally located in Zone T of the Thornton diagram. Co-sputtering of Al and ZnO targets is used to fabricate AZO thin films, therefore it is important to independently optimize the Al and ZnO sputtering targets power. Different powers of Al and ZnO targets produce stoichiometric AZO thin films, which affect the optical properties ($\lambda_{ENZ}$ in this case).

**Table 3.4**: Sputtering parameters of AZO thin films deposited under different Al power

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Al cathode power (W)</th>
<th>Chamber gas pressure (mT)</th>
<th>Thickness (nm)</th>
<th>$\lambda_{ENZ}$ (nm)</th>
<th>Deposition rate (nm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>124</td>
<td>25</td>
<td>2.4</td>
<td>35</td>
<td>NA (longer than 2400 nm)</td>
<td>9</td>
</tr>
<tr>
<td>126</td>
<td>29</td>
<td>2.4</td>
<td>37</td>
<td>2125</td>
<td>9.4</td>
</tr>
<tr>
<td>117</td>
<td>30</td>
<td>2.4</td>
<td>38</td>
<td>2028</td>
<td>9.7</td>
</tr>
<tr>
<td>123</td>
<td>31</td>
<td>2.4</td>
<td>41</td>
<td>2205</td>
<td>10.5</td>
</tr>
</tbody>
</table>

Table 3.4 lists all the deposition parameters of AZO thin films with different Al sputtering power, it can be seen that 30 W Al sputtering power is optimal to minimize the $\lambda_{ENZ}$ (2028nm). It should be noted that due to the wavelength coverage limit of the ellipsometer used in BU shared facility (Up to 2400 nm), the $\lambda_{ENZ}$ of sample 124 (25 W Al sputtering power) can't be precisely provided, but it can be estimated that this sample has $\lambda_{ENZ}$ longer than 2400 nm, as shown in Figure 3.8.
Figure 3.8: Real (a) and imaginary (b) part of permittivity of ITO samples on Si substrate with different thickness: 16 nm (black), 35 nm (red), 94 nm (green), 298 nm (blue). All the samples are fabricated using same sputtering power under same deposition pressure.

Similarly, we keep Al sputtering power constant at 30 W to optimize the ZnO sputtering power, while gas pressure is chosen to be 2.4 mT. All the fabricated AZO thin films have thickness 36 nm±5 nm.

Table 3.5: Sputtering parameters of AZO thin films deposited under different ZnO power

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>ZnO cathode power (W)</th>
<th>Chamber gas pressure (mT)</th>
<th>Thickness (nm)</th>
<th>λ_{ENZ} (nm)</th>
<th>Deposition rate (nm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>159</td>
<td>115</td>
<td>2.4</td>
<td>32</td>
<td>2345</td>
<td>8.2</td>
</tr>
<tr>
<td>118</td>
<td>119</td>
<td>2.4</td>
<td>41</td>
<td>NA (longer than 2400 nm)</td>
<td>10.5</td>
</tr>
<tr>
<td>158</td>
<td>120</td>
<td>2.4</td>
<td>34</td>
<td>2360</td>
<td>8.7</td>
</tr>
<tr>
<td>117</td>
<td>123</td>
<td>2.4</td>
<td>38</td>
<td>2028</td>
<td>9.7</td>
</tr>
</tbody>
</table>
As shown from Figure 3.9, the $\lambda_{ENZ}$ of AZO thin film with ZnO sputtering power (123 W) is the smallest to be 2028nm, but all others have $\lambda_{ENZ}$ longer than 2300 nm.

![Figure 3.9: Real (a) and imaginary (b) part of permittivity of AZO samples on Si substrate fabricated with different ZnO sputtering power: 115 W (black), 119 W (red), 120 W (green), 123 W (blue). All the samples have similar thickness around 36 nm±5 nm.](image)

Table 3.6 summarizes the deposition parameters of AZO thin films with different thickness. The depositions parameters of Al power (30 W), ZnO power (123 W) and gas pressure (2.4 mT) are kept as constants.

**Table 3.6: Sputtering parameters of AZO thin films with different thickness**

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Al cathode power (W)</th>
<th>ZnO cathode power (W)</th>
<th>Chamber gas pressure (mT)</th>
<th>Thickness (nm)</th>
<th>$\lambda_{ENZ}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>117</td>
<td>30</td>
<td>123</td>
<td>2.4</td>
<td>38</td>
<td>2030</td>
</tr>
<tr>
<td>116</td>
<td>30</td>
<td>123</td>
<td>2.4</td>
<td>73</td>
<td>1868</td>
</tr>
<tr>
<td>115</td>
<td>30</td>
<td>123</td>
<td>2.4</td>
<td>141</td>
<td>1805</td>
</tr>
<tr>
<td>110</td>
<td>30</td>
<td>123</td>
<td>2.4</td>
<td>288</td>
<td>1743</td>
</tr>
</tbody>
</table>
Figure 3.10 shows the dielectric permittivity of AZO thin films with different thickness. Again, the $\lambda_{\text{ENZ}}$ decreases as the thickness of AZO increases. Analogously to ITO, AZO features thickness dependent optical properties too. However, it needs to be noticed that the $\lambda_{\text{ENZ}}$ is in the near-IR range for as deposited AZO thin films.

![Figure 3.10: Real (a) and imaginary (b) part of permittivity of AZO samples on Si substrate with different thickness: 38 nm (black), 73 nm (red), 141 nm (green), 288 nm (blue). All the samples are fabricated using same sputtering power under same deposition pressure.](image)

3.5.3 Sputtering Parameters of TiN Thin Films

We use DC sputtering of Ti target in N$_2$ reactive gas to deposit TiN thin films, the total power is always controlled at 200W (DC voltage×DC current). Higher power (>200 W) isn’t selected because we noticed the flickering of sputtering target. On the contrary, we didn’t use lower value (<200W) because 200 W of Ti benefits to provide energetic
atoms incident on substrates to form smoother TiN thin films with moderate deposition rate. Again, chamber gas pressure at 2.4 mT is used for all TiN thin film deposition to make sure the fabricated thin films are structurally attributed to Zone T in the Thornton diagram.

**Table 3.7:** Sputtering parameters of TiN thin films with different thickness

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Ti cathode power (W)</th>
<th>N₂ gas flow (sccm)</th>
<th>Chamber gas pressure (mT)</th>
<th>Thickness (nm)</th>
<th>λ&lt;sub&gt;ENZ&lt;/sub&gt; (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>364</td>
<td>200</td>
<td>10</td>
<td>2.4</td>
<td>16</td>
<td>1091</td>
</tr>
<tr>
<td>363</td>
<td>200</td>
<td>10</td>
<td>2.4</td>
<td>20</td>
<td>849</td>
</tr>
<tr>
<td>361</td>
<td>200</td>
<td>10</td>
<td>2.4</td>
<td>40</td>
<td>738</td>
</tr>
<tr>
<td>337</td>
<td>200</td>
<td>10</td>
<td>2.4</td>
<td>57</td>
<td>725</td>
</tr>
</tbody>
</table>

The dielectric permittivity of TiN thin films with different thickness has been shown in Figure 3.11. TiN has smaller thickness dependence when its thickness is larger than 40 nm. Its λ<sub>ENZ</sub> moves from near-IR into visible spectrum when thickness is increased from 16 nm to 57 nm. Table 3.7 lists all the deposition parameters of TiN thin films with different thickness.
Figure 3.11: Real (a) and imaginary (b) part of permittivity of AZO samples on Si substrate with different thickness: 38 nm (black), 73 nm (red), 141 nm (green), 288 nm (blue). All the samples are fabricated using same sputtering power under same deposition pressure.

3.6 Conclusion

In conclusion, ITO, AZO and TiN thin films have been fabricated using RF and DC sputtering. The sputtering parameters (chamber gas pressure, sputtering cathode power) have been optimized to minimize \( \lambda_{ENZ} \). The thin films are deposited at low chamber pressure (2.4 mT) and at room temperature, therefore these thin films are structurally located in Zone T of Thornton model.

For ITO thin films, it has been found out that the \( \lambda_{ENZ} \) saturates for ITO cathode power larger than 200 W. Besides, the chamber gas pressure has also been optimized to further reduce the \( \lambda_{ENZ} \). Similar to ITO, Al (30 W) and ZnO (123 W) cathode powers are optimized to provide the smallest \( \lambda_{ENZ} \). The fabricated samples of ITO, AZO and TiN in
this chapter are fabricated at low gas pressure and room temperature. Post-deposition annealing of these thin films to tailor the optical dispersion and structural properties will be discussed in the Chapter 4.

The thickness dependent optical properties have also been discussed in this chapter. ITO, AZO and TiN thin films feature thickness dependent $\lambda_{\text{ENZ}}$. In general, as the thickness is increased, $\lambda_{\text{ENZ}}$ is decreased and saturates in particular wavelength range, which is near-IR for ITO and AZO films, visible for TiN films.
Chapter 4

4 The Optical and Structural Properties of ITO, AZO and TiN Thin Films

This chapter provides the optical and structural characterization of ITO, AZO and TiN thin films using spectroscopic ellipsometry (SE), X-ray diffraction (XRD). Firstly, the optical dispersion of as deposited and annealed thin films are characterized by spectroscopic ellipsometry to obtain its thickness, optical permittivity, $\lambda_{ENZ}$ and optical loss $\varepsilon_2$. Subsequently, we measure optical bandgaps to show thermal annealing can dramatically modulate free carrier concentration in these materials. Finally, X-ray diffraction is performed to characterize crystallite grain sizes and demonstrates that thermal annealing can also effectively control the structural properties of these materials.

Segments of this Chapter have been adapted from the 2015 Optical Material Express publication *Wide tuning of the optical and structural properties of alternative plasmonic materials* which can be found here [60]. I would like thank Prof. Soumendra Basu for insightful discussions of using X-ray diffraction for structural characterization of materials.

4.1 Spectroscopic Ellipsometry

Ellipsometry is a very sensitive technique that uses polarized light to characterize complex refractive index (or dielectric functions) of thin films, it also can be used to characterize composition, roughness, thickness and other material properties.
Ellipsometry measures the change in polarization state of reflected light from the surface of a sample. It measures the complex reflectance ratio $\rho$, which is parameterized by the amplitude ratio $\psi$ and the phase difference $\Delta$. The polarization state of light can be decomposed into s and p components, where s, p components oscillate perpendicular and parallel to the plane of incidence, respectively. The amplitudes of s and p components are denoted as $r_p$ and $r_s$, respectively. The complex ratio is given by

$$\rho = \frac{r_p}{r_s} = \tan(\psi)e^{i\Delta}$$

(4.1)

Where $\tan(\psi)$ is the amplitude ratio and $\Delta$ is the phase difference upon reflection.

A typical ellipsometry setup is shown in Figure 4.1. Light source emits electromagnetic radiation and it gets linearly polarized by a polarizer, light is incident onto the sample after passing through an optional compensator (retarder or quarter wave plate) which changes linearly polarized light to be elliptically polarized, but it is only used when the material contains anisotropy. After light reflects from the sample, it passes another optional compensator and a second polarizer (called analyzer here), then falls in to a detector that measures the polarization state of light to extract the complex ratio of $\rho$. 
In this thesis, all the samples have been measured using the Variable Angle Spectroscopic Ellipsometry (VASE, J.A. Woollam Co., Inc.). It has all the components as depicted in Figure 4.1. The combination of variable angle of incidence and spectroscopic measurement allows us to acquire a larger amount of data. More importantly, the spectral acquisition range and angles of incidence can be optimized to determine certain sample parameters such as layer thickness. For example, to determine ITO thin film thickness, spectral acquisition measurements in the visible spectrum at different angles are performed to fit the thickness using Cauchy model, which is given by [61]

$$n(\lambda) = A_n + \frac{B_n}{\lambda^2} + \frac{C_n}{\lambda^3}$$  \hspace{1cm} (4.2)

This procedure works very well because ITO features good transparency in the visible spectrum, so spectral measurement in the visible is essential to help determine the
thickness of ITO, often the fitted thickness is compared against the measured thickness from surface profilometer and finds very good match. Figure 4.2 shows the measured $\psi$ and $\Delta$ at angles of $55^\circ$, $65^\circ$, $75^\circ$ between 500–800 nm, as well as the fitted data of Cauchy model to determine the ITO thickness.

**Figure 4.2:** The measured and fitted $\psi$ (left) and $\Delta$ (right) at angles of $55^\circ$, $65^\circ$, $75^\circ$ between 500–800 nm of one representative ITO sample to determine its thickness.

In particular, VASE spectroscopic ellipsometry has been used in the wavelength range of 400–2400 nm to characterize the dielectric permittivity, thickness of fabricated ITO, AZO and TiN thin films. Drude-Sommerfeld model has been used to fit the optical dispersion in this wavelength range for these materials, as discussed in Chapter 2. Because ellipsometry is a model dependent technique where mathematical model such as Drude-Lorentz model is required to obtain useful physical information about the sample. Therefore, it is critical to define a quantity that represents the quality of match between the data calculated from the model and the experimental data. The maximum likelihood estimator must be positive and should go to 0 (or at least an absolute minimum) when the calculated data matches the experimental data exactly. VASE ellipsometer uses the mean-squared error (MSE) to describe maximum likelihood estimator:
\[
\text{MSE} = \sqrt{\frac{1}{2N-M} \sum_{i=1}^{N} \left( \frac{\psi_{\text{mod}}^i - \psi_{\text{exp}}^i}{\sigma_{\psi,i}} \right)^2 + \left( \frac{\Delta_{\text{mod}}^i - \Delta_{\text{exp}}^i}{\sigma_{\Delta,i}} \right)^2} = \sqrt{\frac{1}{2N-M} \chi^2}
\]  

(4.3)

Where \( N \) is the number of \((\psi, \Delta)\) pairs, \( M \) is the number of variable parameters in the model, and \( \sigma \) are the standard deviations on the experimental data points. It represents a sum of the squares of the differences between the measured and calculated data, with each difference weighted by the standard deviation of that measured data point. For the MSE of fabricated samples, usually MSE<15 can be considered as a good fitting. Figure 4.3 provides the measured \( \psi \) and \( \Delta \) of a representative sample of ITO at angles of 55°, 65°, 75° between 500–2000 nm, as well as the fitted data of Drude-Lorentz model for this sample annealed at 350°C in N\(_2\) for 1h, with a MSE of 5.04.

**Figure 4.3:** The measured and fitted (Drude-Lorentz model) \( \psi \) (left) and \( \Delta \) (right) at angles of 55°, 65°, 75° between 500–2000 nm of a representative ITO sample annealed at 350°C in N\(_2\) for 1h to determine its optical dispersion. The MSE in this case is 5.04, which indicates very good match between fitted and measured data.

### 4.2 X-Ray Diffraction

X-rays are waves of electromagnetic radiation with wavelength range from \(10^{-2}\) nm to 10 nm, and crystals are regular arrays of atoms. Upon the incidence of X-rays on
crystals, atoms scatter X-ray waves through atoms’ electrons. When X-ray strikes on electrons, it produces secondary spherical waves that emanate from the electrons. This process is known as elastic scattering and electrons are called scatterers. Atoms with regular array of scatterers produce regular array of spherical waves, and due to the constructive interference of these waves in specific conditions, it will result in intense peaks (Bragg peaks) of reflected X-rays at certain wavelength and incident angles. This leads to Bragg’s law which is given by

$$2d \sin \theta = n\lambda$$  \hspace{1cm} (4.4)

Where d is the spacing between diffraction planes, $\theta$ is the incidence angle, n is any integer and $\lambda$ is the wavelength of the beam. This phenomenon was first observed and explained by William L. Bragg and his father William H. Bragg in 1912 [62]. Figure 4.4 shows the diagram of Bragg diffraction, where two beams with identical wavelength and phase are incident on a crystalline solid and constructive interference occurs when the length difference $2d \sin \theta$ is equal to an integer multiple of wavelength of X-ray radiation, as described from Equation 4.4.
Figure 4.4: The diagram of Bragg diffraction. Two beams with identical wavelength and phase are incident on a crystalline solid and constructive interference occurs when the length difference $2d \sin \theta$ is equal to an integer multiple of wavelength of X-ray radiation.

The X-ray Diffraction (XRD) system used in this thesis is Bruker D8 Discover. It is a state-of-the-art, high quality system equips with the optimum components (X-ray 4-Bounce monochromator, high-precision two-circle goniometer) to provide high resolution X-ray diffraction, grazing incidence diffraction measurements. When the diffraction peaks are measured, Scherrer equation is used to infer the size of the crystallite grain, which is given by [63]

$$\tau = \frac{K \lambda}{\beta \cos \theta}$$

(4.5)

Where $\tau$ is the mean crystallite grain size, $K$ is a dimensionless shape factor with typical value 0.9, it may vary with the actual shape of the crystallite, $\lambda$ is the X-ray wavelength, $\beta$ is the linewidth broadening at the full width half maximum (FWHM), $\theta$ is
the Bragg angle. It states that the peak width is inversely proportional to the crystal thickness measured perpendicular to the reflecting planes, which means a smaller crystal results in a more broadened peak. We use Scherrer equation to calculate the crystallite grain sizes of fabricated ITO, AZO and TiN thin films after post-deposition annealing, thus demonstrating the structural properties of these materials can be reliably tuned by thermal annealing treatments.

4.3 Optical and Structural Properties of ITO, AZO and TiN

In the following, we systematically investigate a set of ITO, AZO and TiN thin films deposited by magnetron sputtering. By measuring their dielectric permittivity using Spectroscopic Ellipsometry (SE) and their crystallite size using X-ray Diffraction (XRD), we show that post-deposition annealing allows to effectively modulate the free carrier concentration in these materials, and to achieve full tunability of their optical and structural properties. In this thesis, for simplicity, in all the tables that summarize our annealing parameters, we use the symbol $\lambda_{PS}$ to represent both the ENZ condition and screened plasma wavelength, as discussed in Chapter 2.

4.3.1 Optical Properties of ITO and AZO

We deposited ITO and AZO thin films using RF magnetron sputtering at room temperature in a Denton Discovery 18 confocal-target system, and we tailored their optical dispersion properties by post-deposition annealing. ITO and AZO thin films were
grown on Si substrates in Ar atmosphere, the chosen sputtering targets for ITO, AZO thin films were ITO (99.99% purity), Al (99.99% purity)/ZnO (99.99% purity), respectively. The sputtering power for ITO thin films was held constant at 200 W, as for AZO thin films, the Al/ZnO targets power were 30 W/123 W, respectively. The details of sputtering power optimization can be found in Chapter 3. The base pressure was $1.0\times10^{-7}$ Torr and the Ar gas flow was kept at 12 sccm. For all the fabricated samples, two different thicknesses have been grown at 37 nm ± 5 nm (thin) and 300 nm ± 5 nm (thick), irrespective of the deposition conditions.

Post-deposition annealing treatments have been performed using a rapid thermal annealing (RTA) furnace, which resulted in a large tunability of the measured optical dispersion for ITO and AZO in the near-IR spectrum. The film thickness remains almost constant after annealing (thickness error: ± 5 nm), as independently verified by surface profilometry. For ITO thin films, annealing processes were performed in Ar gas atmosphere at temperatures between 350 and 750°C for 30 min, while for AZO thin films, they were performed in N$_2$ gas atmosphere at temperatures between 100 and 400 °C for 60 min. The annealing conditions of ITO and AZO samples are listed in Table 4.1 and Table 4.2, respectively. (We did not list annealing parameters of AZO annealed at 400°C, 300°C, 100°C and as deposited, because their $\lambda_{ENZ}$ exceeds the wavelength range 400–2000 nm of our ellipsometer, as shown in Figure 4.5(a).)
Table 4.1: ITO thin films annealing parameter on Si substrate

<table>
<thead>
<tr>
<th>Thickness(nm)</th>
<th>(\lambda_{PS}) (nm)</th>
<th>(\varepsilon_2 \at \lambda_{PS})</th>
<th>Annealing Temp. (°C)</th>
<th>Annealing Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>37</td>
<td>1264</td>
<td>0.541</td>
<td>750</td>
<td>30</td>
</tr>
<tr>
<td>300</td>
<td>1283</td>
<td>0.347</td>
<td></td>
<td></td>
</tr>
<tr>
<td>37</td>
<td>1390</td>
<td>0.483</td>
<td>550</td>
<td>30</td>
</tr>
<tr>
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<td>0.352</td>
<td></td>
<td></td>
</tr>
<tr>
<td>37</td>
<td>1671</td>
<td>0.53</td>
<td>350</td>
<td>30</td>
</tr>
<tr>
<td>300</td>
<td>1609</td>
<td>0.49</td>
<td></td>
<td></td>
</tr>
<tr>
<td>37</td>
<td>1920</td>
<td>0.951</td>
<td></td>
<td>As Deposited</td>
</tr>
<tr>
<td>300</td>
<td>1826</td>
<td>0.845</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4.2: AZO thin films annealing parameter on Si substrate

<table>
<thead>
<tr>
<th>Thickness(nm)</th>
<th>(\lambda_{PS}) (nm)</th>
<th>(\varepsilon_2 \at \lambda_{PS})</th>
<th>Annealing Temp. (°C)</th>
<th>Annealing Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>37</td>
<td>1825</td>
<td>1.47</td>
<td>275</td>
<td>60</td>
</tr>
<tr>
<td>300</td>
<td>1403</td>
<td>0.78</td>
<td></td>
<td></td>
</tr>
<tr>
<td>37</td>
<td>1818</td>
<td>1.8</td>
<td>250</td>
<td>60</td>
</tr>
<tr>
<td>300</td>
<td>1375</td>
<td>0.69</td>
<td></td>
<td></td>
</tr>
<tr>
<td>37</td>
<td>1914</td>
<td>2.15</td>
<td>225</td>
<td>60</td>
</tr>
<tr>
<td>300</td>
<td>1382</td>
<td>0.66</td>
<td></td>
<td></td>
</tr>
<tr>
<td>37</td>
<td>1917</td>
<td>2.19</td>
<td>200</td>
<td>60</td>
</tr>
<tr>
<td>300</td>
<td>1405</td>
<td>0.77</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The experimentally measured optical permittivity data for ITO and AZO samples are shown in Figure 4.5 and in Figure 4.6, which display the effect of annealing on the real \((\varepsilon_1)\) and imaginary \((\varepsilon_2)\) parts of the complex permittivity. Two values of sample thickness have been investigated, 37 nm (continuous lines) and 300 nm (dashed lines) in order to demonstrate consistency. Our data demonstrate that the \(\lambda_{ENZ}\) of all the ITO and AZO samples can be largely tuned in the range of NIR (1200–2000 nm for ITO, 1400–2000 nm for AZO), depending on the post deposition annealing conditions.
Figure 4.5: Real (a) and imaginary (b) part of permittivity of ITO samples on Si substrate annealed at different temperatures: As Deposited (black), 350 °C (red), 550 °C (green), 750 °C (blue). The annealing is performed in Ar atmosphere for 30 min for all samples. Continuous lines are for samples with thickness 37 nm, dashed lines are for samples with thickness 300 nm [60].

Figure 4.6: Real (a) and imaginary (b) part of permittivity of AZO samples on Si substrate annealed at different temperatures: As Deposited (black), 100 °C (red), 200 °C (green), 225 °C (blue), 250 °C (cyan), 275 °C (magenta), 300 °C (dark yellow), 400 °C (orange). The annealing is performed in N₂ atmosphere for 60 min for all samples. Continuous lines are for samples with thickness 37 nm, dashed lines are for samples with thickness 300 nm [60].
It is well known that the optical properties of TCOs have thickness dependence, due to reasons including the trapping states at the interface of TCOs and substrates [64, 65], and different microstructures of thin films [66]. The developed fabrication process has largely solved this problem, as evidenced in Figure 4.7 that shows the $\lambda_{\text{ENZ}}$ and $\varepsilon_2$ as a function of annealing temperature for both thick and thin samples. The data indicates that as the annealing temperature is increased, both the $\lambda_{\text{ENZ}}$ and $\varepsilon_2$ are decreased. Most importantly, ITO thin films show very small thickness dependence of their optical properties upon post-deposition annealing, as can be seen clearly from Figure 4.5. We also note that the imaginary parts of the permittivity $\varepsilon_2$ assumes at $\lambda_{\text{ENZ}}$ values in the range 0.541–0.951 for thin ITO, 0.347–0.845 for thick ITO (see Table 4.1), which are significantly smaller than what previously reported in plasmonic metals in the targeted telecommunication window [67].

On the other hand, we found that AZO materials have a larger thickness dependence of their optical properties compared with ITO, as evidenced in Figure 4.8. Differently from ITO, there is an optimal annealing temperature (250 °C) where we can achieve the smallest $\lambda_{\text{ENZ}}$. Similarly to ITO, the imaginary parts of the permittivity $\varepsilon_2$ at $\lambda_{\text{ENZ}}$ are 1.47–2.19 for thin samples, and 0.66–0.78 for thick AZO (see Table 4.2), which are improved compared to typical plasmonic metals in the same wavelength range [67]. However, it should be noticed that thin-film AZO does not support the ENZ condition ($\varepsilon_2 < 1$), while thick AZO samples display the ENZ condition $\lambda_{\text{ENZ}}$ ($\varepsilon_2 < 1$). We ascribe this difference to the improved crystallinity degree of the thick AZO samples.
Figure 4.7: $\lambda_{\text{ENZ}}$ (black curves on left axis) and $\varepsilon_2$ (blue curves on right axis) as a function of the annealing temperature. Solid triangular lines are for ITO samples with thickness 37 nm, and solid circle lines are for ITO samples with thickness 300 nm [60].

Figure 4.8: $\lambda_{\text{ENZ}}$ (black curves on left axis) and $\varepsilon_2$ (blue curves on right axis) as a function of the annealing temperature. Solid triangular lines are for AZO samples with thickness 37 nm, solid circle lines are for AZO samples with thickness 300 nm [60].
4.3.2 Optical Properties of TiN

TiN thin films on fused silica and Si substrates were deposited using DC reactive sputtering with Ti target (99.99% purity) in N₂ atmosphere at room temperature. The base pressure was 2.5×10⁻⁷ Torr and the N₂ gas flow was kept at 10sccm. Similar to ITO and AZO, two different thicknesses have been prepared at 40 nm ± 5 nm (thin) and 300 nm ± 5 nm (thick), irrespective of the deposition conditions. Post-deposition annealing processes have been performed using a Mellen thermal furnace, which again resulted in a large tunability of the screened plasma wavelengths λₚₛ in the 500–720 nm spectral range. Annealing processes were performed in vacuum with pressure 2.3×10⁻³ Torr at temperatures between room temperature and 900 °C for 60 min. Again, the film thickness stays almost constant after annealing (thickness error: ± 5 nm). The annealing conditions are the same for samples on both Si and fused silica substrates, and its corresponding annealing parameters are included in Table 4.3 and 4.6, respectively.
Table 4.3: TiN thin films annealing parameter on Si substrate

<table>
<thead>
<tr>
<th>Thickness(nm)</th>
<th>$\lambda_{PS}$ (nm)</th>
<th>$\varepsilon_2$ @ $\lambda_{PS}$</th>
<th>Annealing Temp. ($^\circ$C)</th>
<th>Annealing Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>510</td>
<td>2.27</td>
<td>900</td>
<td>60</td>
</tr>
<tr>
<td>300</td>
<td>560</td>
<td>4.52</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>551</td>
<td>2.14</td>
<td>800</td>
<td>60</td>
</tr>
<tr>
<td>300</td>
<td>541</td>
<td>3.52</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>558</td>
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<td>700</td>
<td>60</td>
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<tr>
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<td>553</td>
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<tr>
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<td>500</td>
<td>60</td>
</tr>
<tr>
<td>300</td>
<td>633</td>
<td>4.60</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>626</td>
<td>2.76</td>
<td>400</td>
<td>60</td>
</tr>
<tr>
<td>300</td>
<td>659</td>
<td>5.04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>643</td>
<td>3.04</td>
<td>300</td>
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</tr>
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</tr>
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<td>3.75</td>
<td>200</td>
<td>60</td>
</tr>
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<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>706</td>
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<td>As Deposited</td>
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<tr>
<td>300</td>
<td>717</td>
<td>8.27</td>
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</tbody>
</table>

The measured permittivity is shown in Figure 4.9 and Figure 4.10 for TiN samples with thickness 40 nm and 300 nm on Si substrate, respectively. It is important to notice that for all the TiN samples the imaginary permittivity $\varepsilon_2$ has values larger than 1, and therefore the ENZ condition was not met. In fact, TiN thin films do not show any ENZ condition due to their higher optical losses ($\varepsilon_2 < 1$) compared to ITO/AZO thin films.
Figure 4.9: Real (a) and imaginary (b) part of permittivity of TiN samples with thickness 40 nm on Si substrate annealed at different temperatures: As Deposited (black), 200 °C (red), 300 °C (green), 400 °C (blue), 500 °C (cyan), 600 °C (magenta), 700 °C (dark yellow), 800 °C (navy), 900 °C (purple). The annealing is performed in vacuum for 60 min for all samples [60].

Figure 4.10: Real (a) and imaginary (b) part of permittivity of TiN samples with thickness 300 nm on Si substrate annealed at different temperatures: As Deposited (black), 200 °C (red), 300 °C (green), 400 °C (blue), 500 °C (cyan), 600 °C (magenta), 700 °C (dark yellow), 800 °C (navy), 900 °C (purple). The annealing is performed in vacuum for 60 min for all samples [60].
Figure 4.11 clearly visualizes the effect of the post-deposition annealing on the thin film optical properties. For TiN samples with thickness 40 nm and 300 nm, as annealing temperature increases the corresponding $\lambda_{PS}$ decreases, as well as the imaginary permittivity $\varepsilon_2$. We note that the differences of $\lambda_{PS}$ are small between the 40 nm and 300 nm TiN samples, showing that TiN has small thickness-dependence for the screened plasma wavelength after the annealing treatment. In particular, for TiN films (both thin and thick samples) the optical losses can be reduced by almost a factor of 2 compared to the as-deposited samples. However, it should be noticed that the losses of the 300 nm-thick TiN sample is about twice that of the 40 nm-thin TiN sample, which indicates that TiN exhibits larger thickness-dependence for optical losses upon annealing. However, the data in Fig. 7 demonstrate that post-deposition annealing is an effective way to reduce the optical losses for both thicknesses and tune the optical properties of plasmonic TiN materials.

**Figure 4.11:** $\lambda_{PS}$ (black curves on left axis) and $\varepsilon_2$ (blue curves on right axis) as a function of the annealing temperature. Solid triangular lines are for TiN samples with thickness 40 nm, solid circle lines are for TiN samples with thickness 300 nm [60].
The modulation of optical losses is vividly demonstrated by the optical photographs in Figure 4.12, which correspond to 40nm-thick TiN samples on Si annealed at different temperatures. Samples annealed above 700 °C exhibit Au-like metallic luster, which demonstrates the fundamental role of the annealing process in tuning the material properties of TiN, which can result in plasmonic behavior in the visible spectral range. A similar trend has also been observed for TiN samples with 300 nm thickness.

**Figure 4.12:** Optical image of TiN samples with thickness 40 nm on Si substrate annealed at different temperatures from room temperature to 900 °C. For samples annealed above 700 °C, Au-like metallic luster starts to present [60].

By using post-deposition annealing, our findings demonstrate large tunability of the optical properties of these materials in terms of the ENZ conditions (for ITO/AZO), screened plasma wavelength (for TiN), and optical losses. In the following sections, we will address the origin of these effects and clarify the role of annealing treatments on the optical bandgaps and structural properties of the different plasmonic materials.
4.4 Optical Bandgap and Structural Properties

4.4.1 Optical Bandgap

In order to understand the connection between the annealing and the optical properties of our materials we experimentally measured the optical bandgaps of the fabricated ITO, AZO and TiN thin films on fused silica substrates using the Tauc’s method [68,69]. Due to the wide bandgap nature of the materials, we see that the optical gaps can be accurately estimated by considering a linear fit of the Tauc plots in the region $E_g > 3\text{eV}$ extrapolated to zero absorption (See Figure 4.13(a), 4.14(a), 4.15(a)). Table 4.4, 4.5 and 4.6 summarize the annealing parameters for ITO, AZO and TiN thin films, respectively.

**Table 4.4: ITO thin films annealing parameter on fused silica substrate**

<table>
<thead>
<tr>
<th>Thickness(nm)</th>
<th>$\lambda_{PS}$ (nm)</th>
<th>$\varepsilon_2 @ \lambda_{PS}$</th>
<th>Annealing Temp. ($^\circ$C)</th>
<th>Annealing Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>37</td>
<td>1160</td>
<td>0.53</td>
<td>200</td>
<td>13</td>
</tr>
<tr>
<td>37</td>
<td>1250</td>
<td>0.46</td>
<td>350</td>
<td>13</td>
</tr>
<tr>
<td>37</td>
<td>1360</td>
<td>0.71</td>
<td>200</td>
<td>3</td>
</tr>
<tr>
<td>37</td>
<td>1810</td>
<td>1.26</td>
<td>160</td>
<td>13</td>
</tr>
<tr>
<td>37</td>
<td>2000</td>
<td>1.37</td>
<td>As Deposited</td>
<td></td>
</tr>
</tbody>
</table>

**Table 4.5: AZO thin films annealing parameter on fused silica substrate**

<table>
<thead>
<tr>
<th>Thickness(nm)</th>
<th>$\lambda_{PS}$ (nm)</th>
<th>$\varepsilon_2 @ \lambda_{PS}$</th>
<th>Annealing Temp. ($^\circ$C)</th>
<th>Annealing Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>1441</td>
<td>0.86</td>
<td>290</td>
<td>60</td>
</tr>
<tr>
<td>300</td>
<td>1548</td>
<td>0.98</td>
<td>200</td>
<td>60</td>
</tr>
<tr>
<td>300</td>
<td>1698</td>
<td>1.295</td>
<td>140</td>
<td>60</td>
</tr>
<tr>
<td>300</td>
<td>1749</td>
<td>1.63</td>
<td>As Deposited</td>
<td></td>
</tr>
</tbody>
</table>
Table 4.6: TiN thin films annealing parameter on fused silica substrate

<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>$\lambda_{PS}$ (nm)</th>
<th>$\varepsilon_2$ @ $\lambda_{PS}$</th>
<th>Annealing Temp. (°C)</th>
<th>Annealing Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>509</td>
<td>3.08</td>
<td>900</td>
<td>60</td>
</tr>
<tr>
<td>40</td>
<td>546</td>
<td>3.53</td>
<td>800</td>
<td>60</td>
</tr>
<tr>
<td>40</td>
<td>576</td>
<td>3.68</td>
<td>700</td>
<td>60</td>
</tr>
<tr>
<td>40</td>
<td>602</td>
<td>4.25</td>
<td>600</td>
<td>60</td>
</tr>
<tr>
<td>40</td>
<td>612</td>
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<tr>
<td>40</td>
<td>624</td>
<td>5.68</td>
<td>400</td>
<td>60</td>
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<td>638</td>
<td>6.4</td>
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<tr>
<td>40</td>
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<td>6.9</td>
<td>200</td>
<td>60</td>
</tr>
<tr>
<td>40</td>
<td>647</td>
<td>8.15</td>
<td>As Deposited</td>
<td></td>
</tr>
</tbody>
</table>

The optical transmittance $T$ of thin films fabricated on fused silica substrates has been measured at normal incidence. The absorption coefficient $\alpha$ has been calculated using the formula:

$$T = (1 - R)e^{-\alpha t}$$  \hspace{1cm} (4.6)

Where $R$ is the overall reflectance coefficient, and $t$ is the film thickness. The optical bandgap $E_g$ for direct transitions can be expressed as function of frequency by the formula:

$$\alpha h \omega = (h \omega - E_g)^{1/2}$$  \hspace{1cm} (4.7)

Figure 4.13(a) and 14(a) show the bandgaps of ITO and AZO can be largely tuned by post-deposition annealing (3.63–3.94 eV for ITO, 3.68–3.93 eV for AZO). In the inset of Figure 4.13 (a) and 14(a), we report the bandgaps of ITO and AZO as a function of the optical free-carrier concentration $N^{2/3}$, which describes the bandgap shift due to the increased free carrier density in the material, known as Burstein-Moss shift [70,71]:
\[ E_g = E_{g0} + \frac{\hbar^2}{2m^*}(3\pi^2 N)^{2/3} \] (4.7)

In Figure 4.13(b) and 14(b), we additionally plot the optical bandgaps versus the plasma frequency (expressed in energy units) for the measured ITO and AZO thin films. Finally, we correlate the values of the measured \( \lambda_{ENZ} \) for all the samples with the measured optical bandgaps, thus directly demonstrating the critical role played by the annealing conditions in determining the ENZ transition wavelengths of ITO and AZO thin films. The increase of optical bandgaps is in accordance with the increase of their plasma frequency, which reduces the \( \lambda_{ENZ} \) accordingly.

**Figure 4.13:** (a) Tauc plot for a set of ITO samples, where the linear fit (dashed lines) extrapolates the optical bandgap \( E_g = 3.94 \text{ eV (red, } \lambda_{ENZ} = 1160 \text{ nm), } E_g = 3.90 \text{ eV (blue, } \lambda_{ENZ} = 1250 \text{ nm), } E_g = 3.81 \text{ eV (green, } \lambda_{ENZ} = 1360 \text{ nm), } E_g = 3.68 \text{ eV (cyan, } \lambda_{ENZ} = 1810 \text{ nm), } E_g = 3.63 \text{ eV (magenta, } \lambda_{ENZ} = 2000 \text{ nm). Inset: Burstein-Moss shift of the bandgap } E_g \text{ as a function of the carrier concentration } N^{2/3}. \) (b) \( \lambda_{ENZ} \) (circles on left axis) and plasma frequency (triangles on right axis in energy units) as a function of the bandgap \( E_g \) [60].
Figure 4.14: (a) Tauc plot for a set of AZO samples, where the linear fit (dashed lines) extrapolates the optical bandgap $E_g = 3.93$ eV (red, $\lambda_{ENZ} = 1441$ nm), $E_g = 3.82$ eV (blue, $\lambda_{ENZ} = 1548$ nm), $E_g = 3.7$ eV (green, $\lambda_{ENZ} = 1698$ nm), $E_g = 3.68$ eV (cyan, $\lambda_{ENZ} = 1749$ nm). Inset: Burstein-Moss shift of the bandgap $E_g$ as a function of the carrier concentration $N^{2/3}$. (b) $\lambda_{ENZ}$ (circles on left axis) and plasma frequency (triangles on right axis in energy units) as a function of the bandgap $E_g$ [60].

Figure 4.15(a) shows that the optical bandgap of TiN can also be tuned in a wide range (3.53–3.83 eV) by post-deposition annealing in vacuum. As the annealing temperature is increased from room temperature to 900 °C, not only the screened plasma wavelength $\lambda_{PS}$ decreases, but also the optical bandgap $E_g$ increases.
Figure 4.15: (a) Tauc plot for a set of TiN samples, where the linear fit (dashed lines) extrapolates the optical bandgap $E_g$=3.83 eV (black, $\lambda_{PS}$ = 509 nm), $E_g$=3.78 eV (red, $\lambda_{PS}$ =546 nm), $E_g$ =3.82 eV (green, $\lambda_{PS}$ =576 nm), $E_g$ =3.72 eV (blue, $\lambda_{PS}$ =602 nm), $E_g$ =3.65 eV (cyan, $\lambda_{PS}$ =612 nm), $E_g$ =3.64 eV (magenta, $\lambda_{PS}$ =624 nm), $E_g$ =3.62 eV (dark yellow, $\lambda_{PS}$ =638 nm), $E_g$ =3.56 eV (navy, $\lambda_{PS}$ =637 nm), $E_g$ =3.53 eV (purple, $\lambda_{PS}$ =647 nm). (b) $\lambda_{PS}$ (circles on left axis) and optical bandgap (triangles on right axis in energy units) as a function of the annealing temperature [60].

4.4.2 Structural Properties

The structural properties of ITO, AZO and TiN have been investigated using X-ray diffraction with Cu-K$_\alpha$ (Bruker D8 Discover) in 2$\theta$ mode. Figure 4.16(a), 17(a) and 18(a) show the X-ray spectra of ITO, AZO and TiN samples with thickness 300 nm on Si substrate under different annealing conditions, respectively. For ITO, several peaks appear including (211) at $2\theta$=21.45º, (222) at $2\theta$=30.63º, (400) at $2\theta$=35.46º, (332) at $2\theta$=41.88º, (431) at $2\theta$=45.63º, (440) at $2\theta$=51º, (622) at $2\theta$=60.6º. These spectra clearly reveal the polycrystalline nature of the sputtered ITO samples. From Scherrer
equation [72], we extract the estimated grain sizes from the full-width half-maximum (FWHM) at (211) peak. Figure 4.16(b) correlates the grain sizes for all the samples with $\lambda_{\text{ENZ}}$ as a function of annealing temperature. Grain size of ITO is increased from 21 to 29.6 nm as the annealing temperature increases from room temperature to 750 °C. The trend and grain size of ITO are in agreement with other findings as well [69,73,74].

**Figure 4.16:** (a) X-ray diffraction pattern for a set of ITO samples with thickness 300 nm on Si substrate, with $\lambda_{\text{ENZ}}$=1826 nm (black, As Deposited), 1609 nm (red, 350 °C 30 min in Ar), 1476 nm (green, 550 °C 30 min in Ar), 1283 nm (blue, 750 °C 30 min in Ar). (b) ITO (211) crystallite size and $\lambda_{\text{ENZ}}$ as a function of annealing temperature [60].

As for AZO, the main peak is at (002) at $2\theta=34.48^\circ-34.70^\circ$ depending on the annealing temperature, the small shift can be attributed to slightly different Al doping concentration for samples annealed at different temperature [75,76]. Figure 4.17(b) shows (002) grain size is increased from 17.7 to 26.2 nm from room temperature to 250 °C, and then decreased to 22 nm from 250 to 300 °C, which is consistent with the change of $\lambda_{\text{ENZ}}$. 
Figure 4.17: (a) X-ray diffraction pattern for a set of AZO samples with thickness 300 nm on Si substrate, with $\lambda_{\text{ENZ}} = 1620$ nm (black, As Deposited), 1525 nm (red, 100 °C 60 min in N$_2$), 1405 nm (green, 200 °C 60 min in N$_2$), 1382 nm (blue, 225 °C 60 min in N$_2$), 1375 nm (cyan, 250 °C 60 min in N$_2$), 1403 nm (magenta, 275 °C 60 min in N$_2$), 1423 nm (dark yellow, 300 °C 60 min in N$_2$), N.A. (orange, 400 °C 60 min in N$_2$). (b) AZO (002) crystallite size and $\lambda_{\text{ENZ}}$ as a function of annealing temperature [60].

For TiN, the main peak is at (200) at $2\theta = 42.32°$–$42.72°$, where the small shift is due to the decreased lattice constant after annealing [77–80]. Similarly, Figure 4.18(b) depicts (200) grain size and $\lambda_{\text{PS}}$ as a function of annealing temperature. The increase of annealing temperature can not only decrease the screened plasma wavelength $\lambda_{\text{PS}}$, but also significantly increase the crystallite size, which is also consistent with the trend of optical loss $\varepsilon_2$ in Figure 4.11.
Figure 4.18: (a) X-ray diffraction pattern for a set of TiN samples with thickness 300 nm on Si substrate, with $\lambda_{ps} =$717 nm (black, As Deposited), 691 nm (red, 200 °C 60 min in vacuum), 672 nm (green, 300 °C 60 min in vacuum), 659 nm (blue, 400 °C 60 min in vacuum), 633 nm (cyan, 500 °C 60 min in vacuum), 591 nm (magenta, 600 °C 60 min in vacuum), 553 nm (dark yellow, 700 °C 60 min in vacuum), 541 nm (navy, 800 °C 60 min in vacuum), 560 nm (purple, 900 °C 60 min in vacuum). (b) TiN (200) crystallite size and $\lambda_{ps}$ as a function of annealing temperature [60].

Our findings demonstrate that post-deposition annealing treatments can effectively modulate the free carrier density in the material, thus enabling control over the plasma frequency, the optical bandgap, the ENZ condition (for ITO and AZO), and the screened plasma wavelength (for TiN), as well as the materials grain sizes.

4.5 Effect of Annealing Gas

Several mechanisms have been proposed to account for carrier concentration and mobility in ITO including oxygen vacancies, structural deformations and tin
dopants [71,73,81–83]. However, it has recently been demonstrated that the morphology of sputtered ITO thin films, which can be directly modified with the annealing temperature, plays a key role [71,73]. This is because free electrons in as-deposited ITO are trapped at the grain boundaries. With increasing annealing temperature the grain size increases, the density of grain boundaries decreases, and fewer carriers remain trapped resulting in a higher free carrier density. Moreover, grain boundaries behave as traps for free carriers and barriers for carrier transport, which explains the observed increase of carrier mobility with annealing temperature [71,73,81–83]. We notice to this regard that the measured optical band-gaps and free carrier concentrations for our samples are in good agreement with reported values for sputtered films [71,73].

For AZO, several other mechanisms have been proposed to explain the contribution of carrier concentration, such as Al$^{3+}$ substitution sites, Al interstitial atoms and oxygen vacancies [84,85]. In order to further understand the mechanism that allows for tailoring the free-carrier concentration in our samples, we performed post-deposition annealing of thin ITO and AZO films on Si substrate in different gas atmospheres, at fixed temperature (750 °C for ITO, 250 °C for ITO) and time (60 min). The reason we choose 750 °C (for ITO)/250 °C (for AZO) is because it is the temperature we used to achieve the smallest $\lambda_{\text{ENZ}}$ (see Table 4.1 and Table 4.2). For ITO, the permittivity of the annealed samples measured by ellipsometry is shown in Figure 4.19. The two samples annealed in Ar and N$_2$ show a similar permittivity, with a clear ENZ condition around 1160 nm. On the contrary, the sample annealed in O$_2$ displays a purely dielectric behavior (i.e. positive $\varepsilon_1$). Similar trend has also been observed for the AZO thin films, as shown
in Figure 4.20. This is a strong indication that the conduction mechanism in the fabricated ITO and AZO thin films is certainly due to O\textsubscript{2} vacancies, and that the free-carriers are strongly reduced by O\textsubscript{2} annealing, consistently with the published literature [1,86].

**Figure 4.19**: Real (a) and imaginary (b) part of permittivity of ITO thin (37 nm) film on Si substrate at a fixed temperature 750 °C for 60 min under different annealing gas ambient O\textsubscript{2} (red), Ar (black), N\textsubscript{2} (green) [60].

**Figure 4.20**: Real (a) and imaginary (b) part of permittivity of AZO thin (37 nm) film on Si substrate at a fixed temperature 250 °C for 60 min under different annealing gas ambient O\textsubscript{2} (red), Ar (black), N\textsubscript{2} (green) [60].
On the other hand, for TiN, we kept annealing time 60 min fixed and tried different annealing atmosphere including vacuum, Ar, N\textsubscript{2} and O\textsubscript{2}. Our results showed that only vacuum annealing treatments resulted in good quality TiN films with good film uniformity, while other annealing gases gave rise to surface non-uniformities.

4.6 Conclusion

In this Chapter, we have reviewed Spectroscopic Ellipsometry (SE) and X-ray Diffraction (XRD) to characterize the optical and structural properties of ITO, AZO and TiN thin films. We have demonstrated that by using post-deposition annealing treatments, the optical and the structural properties of ITO, AZO and TiN thin films can be effectively tuned in a wide range with a significant reduction of their optical losses, due to the modulation of free-carrier concentration. In particular, ITO and AZO can serve as good candidates of plasmonic materials in NIR range, while TiN can be used in visible spectrum. Besides, we show that upon annealing, the measured optical properties ITO feature small thickness-dependence, while the ones of AZO possess larger thickness-dependence. Furthermore, we discovered that TiN exhibits small thickness-dependence for $\lambda_{\text{ENZ}}$, but larger thickness-dependence for optical loss $\varepsilon_2$. By measuring the optical bandgaps of the investigated materials, we show that the tunability of their optical properties originates from the modulation of the free carrier concentration upon annealing treatment. Then, we perform XRD characterization of the fabricated films, which indicates that annealing can also effectively tune the grain size as a function of annealing temperature, which is consistent with the modification of the optical properties. At last,
by investigating the optical dispersion in different annealing gases, we show that oxygen vacancies are responsible for the free-carrier modulation in both ITO and AZO thin films. Our findings demonstrate the critical importance of annealing treatments to provide wide tunability of both optical and structural properties of ITO, AZO and TiN, thus providing a simple and promising method for the control and engineering of Si-based tunable plasmonic and metamaterial devices.
Chapter 5

5 The Nonlinear Generation of ITO and TiN

In this chapter, the nonlinear Second Harmonic Generation (SHG) and Third Harmonic Generation (THG) properties of ITO and TiN will be investigated. The second- and third- order susceptibilities are quantified by the previous post-doc in our group, Dr. Antonio Capretti. Here we demonstrate enhanced second- and third-harmonic generation tailored by the ENZ response of Si-compatible ITO films at telecommunication wavelengths, without the need of specialized nanofabrication.

Segments of this section have been adapted from the 2015 Optical Letters publication titled Enhanced third-harmonic generation in Si-compatible Epsilon-Near-Zero ITO nanolayers [25] and 2015 ACS Photonics publication Comparative Study of Second-Harmonic Generation from Epsilon-Near-Zero Indium Tin Oxide and Titanium Nitride Nanolayers Excited in the Near-Infrared Spectral Range [26].

5.1 Sample Deposition and Annealing Processes

We use RF magnetron sputtering to deposit ITO thin films on Si substrate from an ITO target in Ar atmosphere, as discussed in Chapter 4. Similarly, we deposit TiN thin films using DC reactive sputtering, from a Ti target in N₂ atmosphere, with a gas flow at 10 sccm. The thickness of the fabricated samples is fixed at 37 nm ± 5 nm for ITO, and 40 nm ± 5 nm for TiN. In order to tailor the optical properties of the fabricated samples, we perform post-deposition thermal annealing processes, with increasing annealing time and temperature, as detailed in Table 5.1 for ITO, and in Table 5.2 for TiN. We measure
the electric permittivity \( \varepsilon(\omega) \) of all the fabricated samples by using variable angle spectroscopic ellipsometry. The post-deposition annealing processes results in a large tunability of the optical dispersions for both materials.

**Table 5.1: Fabrication parameters for ITO nanolayers**

| \( \lambda_{\text{ENZ}} \) (nm) | \(|\varepsilon| = \varepsilon^* @ \lambda_{\text{ENZ}}\) | Anneal. Temp. (°C) | Anneal. Time (min) | Ramp-up Time (s) |
|---|---|---|---|---|
| 1150 | 0.53 | 750 | 60 | 15 |
| 1270 | 0.52 | 750 | 30 | 15 |
| 1390 | 0.48 | 550 | 30 | 15 |
| 1550 | 0.61 | 350 | 60 | 15 |
| 1670 | 0.54 | 350 | 30 | 15 |

**Table 5.2: Fabrication parameters for TiN nanolayers**

| \( \lambda_{\text{ps}} \) (nm) | \(|\varepsilon| = \varepsilon^* @ \lambda_{\text{ps}}\) | Anneal. Temp. (°C) | Anneal. Time (min) | Ramp-up Time (min) |
|---|---|---|---|---|
| 510 | 3.10 | 900 | 60 | 1 |
| 545 | 3.55 | 800 | 60 | 1 |
| 565 | 3.65 | 700 | 60 | 1 |
| 615 | 5.07 | 500 | 60 | 1 |
| 640 | 6.51 | 300 | 60 | 1 |
| 645 | 8.12 | As deposited |

The ellipsometric data for all the ITO and TiN nanolayers are fitted with a very good accuracy using the standard Drude-Sommerfeld model for the free charge carriers, as discussed in Chapter 2:

\[
\varepsilon(\omega) = \varepsilon'(\omega) + i\varepsilon''(\omega) = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\gamma\omega} \tag{5.1}
\]

Where \( \omega_p \) is the plasma angular frequency and \( \gamma \) is the collision rate of the carriers. Here, \( \varepsilon_\infty \) represents the background permittivity, which accounts for the effects
of the electron transitions occurring at higher frequencies. In the Drude-Sommerfeld model, the zero of the real permittivity \( \varepsilon' = 0 \) is generally referred as screened plasma wavelength \( \lambda_{ps} \), which is given by the relation \( \frac{2\pi c}{\lambda_{ps}} = \frac{\omega_p^2}{\varepsilon_\infty} - r^2 \). In the following, we also define an ENZ condition as the minimum of the absolute permittivity \( |\varepsilon(\omega)| = |\varepsilon'(\omega) + i\varepsilon''(\omega)| \), with the necessary requirement that \( |\varepsilon(\omega)| < 1 \). Differently from the screened plasma wavelength, this condition guarantees the enhancement of the normal component of the internal electric field, which drives the unique properties of the ENZ media. For the simple model in Equation (5.1), the ENZ condition corresponds with the screened plasma wavelength \( \lambda_{ps} \) only if the imaginary permittivity is less than unity (\( |\varepsilon(\omega)| = \varepsilon'' < 1 \)).
**Figure 5.1:** Real part $\varepsilon'$ (a) and imaginary part $\varepsilon''$ (b) of the electric permittivity for the ITO nanolayers with $\lambda_{\text{ENZ}} = 1150$ nm (red), 1270 nm (blue), 1390 nm (green), 1550 nm (cyan), 1670 nm (magenta). Real part $\varepsilon'$ (c) and imaginary part $\varepsilon''$ (d) of the electric permittivity for the TiN nanolayers with $\lambda_{\text{ps}} = 510$ nm (red), 545 nm (blue), 565 nm (green), 615 nm (cyan), 640 nm (magenta) and 645 nm (orange) [26].

The experimental complex permittivity $\varepsilon(\omega)$ is shown in Figure 5.1, with the real part $\varepsilon'$ on the left column and the imaginary part $\varepsilon''$ on the right column. The permittivity of the ITO nanolayers is shown in Figure 5.1 (a) and (b). These samples feature a $\lambda_{\text{ENZ}}$ in the range between 1150 nm and 1670 nm, demonstrating that the ENZ condition can be largely tailored with the post deposition annealing process. At the ENZ wavelength, the absolute permittivity $|\varepsilon(\omega)| = \varepsilon''$ is in the range 0.48 – 0.61, which is much smaller than noble metals in the targeted infrared spectra. The permittivity of the TiN nanolayers is shown in Figure 5.1 (c) and (d). The fabricated TiN samples show a screened plasma wavelength that is tailored in the visible spectrum, between 510 nm and 645 nm. The
absolute permittivity $|\varepsilon(\omega)| = \varepsilon^*$ at the ENZ wavelength is larger than unity for all samples.

5.2 Second Harmonic Generation of ITO and TiN

The potential of both ITO and TiN materials as platforms for second-order optical nonlinearities have been investigated. Specifically, I fabricate ITO nanolayers featuring a tailorable ENZ condition $\lambda_{\text{ENZ}}$ in the near-infrared, and together with Dr. Antonio Capretti, we experimentally demonstrate enhanced second-harmonic generation (SHG) driven by their ENZ response. Moreover, we investigate the SHG properties of TiN nanolayers with a metallic behavior in the same spectral range. The results of our comparative study show that the SHG from the ITO nanolayers is 50 times more efficient than TiN, with an intensity comparable to that of a crystalline quartz plate of thickness 0.5mm, used as a reference. Moreover, Dr. Antonio Capretti quantifies the second-order susceptibility of the fabricated samples by using the rigorous Green-function formalism for surface optics.

5.2.1 Calculated Internal Electric Field

Dr. Antonio Capretti performed accurate electromagnetic calculations in order to quantify the electric field inside the fabricated nanolayers at the excitation wavelength, which drives the optical nonlinearities investigated in this thesis [87]. Specifically, we considered a free-space ($m=0$) / nanolayer ($m=1$) / substrate ($m=2$) geometry illuminated...
by an incident plane wave with wavevector $\mathbf{k}_0$ lying in the $xOz$ plane. We adopt the same spatial coordinates as in Ref. [50], with the $i$ axis perpendicular to the layer surface (the interface between the free-space and the nanolayers is at $z=-d_1=0$, while the interface between the nanolayer and the substrate is at $z=-d_2=D$). Similarly to what we did in [25], here we express the electric field in the generic medium $m$ as:

$$\mathbf{E}_m(x, y, z) = A_{m}^{TE} \left[ 1 + \bar{R}_{m,m+1}^{TE} e^{2i k_{m,x} (d_{m+2})} \right] e^{i(k_{m,x}x - k_{m,z}z)} \hat{y}$$

Equation (5.2) is for the case of s-polarized incident plane wave, and Equation (5.3) for the case of p-polarization. The generic medium $m$ is characterized by its wavenumber $k_m$ and impedance $\zeta_m$. The spatial components of the wavevector $\mathbf{k}_m$ in medium $m$ (indicated by the $x,y,z$ subscripts) are determined by the Snell’s law. The complete expressions for the coefficients $A_m$ and $\bar{R}_{m,m+1}$ are well known for both s- and p-polarizations [87]. In this work, the fields are normalized with respect to the amplitude of the incident electric field $|\mathbf{E}_{inc}|$ (i.e. we assume $A_0^{TE} = 1$ and $\bar{R}_0^{TE} = \zeta_0^{-1}$). We used the experimental values of the permittivity obtained from our ellipsometric data to calculate the amplitude of the electric field $\mathbf{E}_1$ inside the fabricated nanolayers, when the incident wave is p-polarized (for simplicity we will drop the subscript 1). The results are displayed in Figure 5.2(a–b) for ITO and in Figure 5.2(c–d) for TiN. The field amplitude and phase are, with good approximation, constant along the nanolayer thickness, due to their subwavelength extent. Here, the normal ($E_n$) and the tangent ($E_t$) components of the field calculated at the interface with free space ($z=0$).
Figure 5.2: Amplitude of the internal electric field components $E_z$ (a) and $E_x$ (b) as function of the incident wavelength, for the ITO nanolayers with $\lambda_{ENZ} = 1150$ nm (red), 1270 nm (blue), 1390 nm (green), 1550 nm (cyan), 1670 nm (magenta); $E_z$ (c) and $E_x$ (d) for the TiN nanolayers with $\lambda_{ps} = 510$ nm (red), 545 nm (blue), 565 nm (green), 615 nm (cyan), 640 nm (magenta) and 645 nm (orange) [26].

We already showed in Ref. [25] that the normal component $E_z$ inside the ITO nanolayers has a maximum in correspondence with the ENZ wavelength, at incident angles in the range $45^\circ$ – $55^\circ$ with respect to the surface normal. This angle corresponds to the quasi-Brewster mode [43], whose dispersion is described by the upper polariton branch of the investigated layered material. All the calculations in Figure 5.2 are performed at an incident angle of $45^\circ$. The normal component $E_z$ inside the ITO nanolayers is shown in Figure 5.2(a) and it is maximized at the ENZ wavelength for each investigated sample. For the ITO nanolayers the amplitude of $E_z$ is larger than the
incident electric field by a factor between 1.5 and 1.8. In Figure 5.2(b) we show the amplitude of the tangent component $E_x$, which, contrary to the normal component, is considerably reduced with respect of the incident field by a factor $\sim$0.5. The $E_z$ and $E_x$ components of the electric field inside the TiN samples are shown in Figure 5.2(c) and Figure 5.2(d), respectively. For all the fabricated samples, both components are reduced with respect of the incident field. The $E_x$ component dominates over the $E_z$ component by a factor $\sim$2, due to the metallic behavior of the TiN samples in the investigated spectral range. For each TiN sample, the electric field in the TiN samples slightly increases in proximity of the screened plasma wavelength $\lambda_{ps}$. However, both field components remains lower than the incident field, due to the high material losses (see Table 5.2).

5.2.2 Second-Harmonic Generation Spectroscopy

The calculations of the internal electric field in the previous section pointed out the different behavior of the ITO and of the TiN nanolayers in the investigated near-infrared regime. In the following we experimentally characterize the nonlinear optical responses of the fabricated samples using SHG spectroscopy. Figure 5.3(a) shows a schematic of the experimental setup, which utilizes an Optical Parametric Oscillator (OPO, Inspire Auto 100, Spectra-Physics) pumped by a Ti:Sapphire laser (Mai Tai, Spectra-Physics), delivering ultrafast pulses of 150 fs duration at a 81 MHz repetition rate. We use as the excitation beam the OPO idler output, scanning the 1000–1700 nm spectral range. A 1000 nm long-pass filter (LPF) removes any spurious signal from the excitation beam, which has an average power of 10 mW. A 20x microscope objective
(OBJ) focus the beam onto the sample under investigation, resulting in a peak intensity in the focused beam spot of approximately \( I_{peak}^{(\omega)} = 42 \text{ MW/cm}^2 \). The incident angle is 45° for all the acquisitions, and the SHG signal is collected in reflection configuration through a 30 mm lens (L1). The collected light is then coupled into a monochromator (Cornerstone 260, Newport) through a 180 mm lens (L2). A 1000 nm short-pass filter (SPF) is placed in front of the monochromator slits to reject the excitation wavelength. The SHG spectra have been detected with a lock-in amplifier (M-70100, Oriel Merlin) coupled to a low-light photomultiplier tube (PMT, 77348 Oriel Instrumentation). Figure 5.3(b) shows a schematic of the polarization configuration for both the excitation (red) and the collected SHG signal (blue). The excitation beam is linearly polarized, and the polarization is defined by the angle \( \beta \), such that \( \beta = 0^\circ \) determines an incident \( p \)-polarization and \( \beta = 90^\circ \) an incident \( s \)-polarization.
With the experimental setup described above, the ITO nanolayers are excited in the spectral range of their $\lambda_{ENZ}$. On the contrary, the TiN samples are excited in a spectral range where their response is metallic, and the SHG signal is generated in proximity of their screened plasma wavelength $\lambda_{ps}$. For these reasons, the fabricated ITO and TiN materials represent a complementary choice to investigate the SHG processes while scanning the incident wavelength in the near-infrared. In Figure 5.4(a) we show representative SHG spectra collected under p-polarized incidence ($\beta=0^\circ$) for the ITO sample with $\lambda_{ENZ} = 1390$ nm. Analogously to our THG case reported in Ref. [50], the intensity exhibits a maximum at the incident wavelength around $\lambda_{ENZ}$. In Figure 5.4(b) we...
show representative SHG spectra collected under p-polarized incidence for the TiN sample with \( \lambda_{ps} = 545 \text{ nm} \). In this case, the SHG signal is very low and it is close to the noise background of our experimental configuration. The SHG intensity grows monotonically when the incident wavelength is reduced from 1200 nm to 1000 nm. As a normal practice, we substitute the investigated samples with their substrate, in order to show that the SHG signals are indeed generated inside the fabricated ITO and TiN nanolayers. No SHG signal is detected under the same excitation conditions in the substrate.

**Figure 5.4:** (a) SHG signals of the ITO nanolayer with \( \lambda_{ENZ} = 1390 \text{ nm} \) at incident wavelength \( \lambda = 1200 \text{ nm} \) (black), 1250 nm (magenta), 1300 nm (green), 1350 nm (red), 1400 nm (blue), 1450 nm (pink). (b) SHG signals of the TiN nanolayer with \( \lambda_{ps} = 545 \text{ nm} \) at incident wavelength \( \lambda = 1025 \text{ nm} \) (black), 1050 nm (red), 1075 nm (green), 1100 nm (blue), 1125 nm (cyan), 1150 nm (magenta), 1175 nm (yellow), 1200 nm (dark yellow) [26].
The SHG intensities are summarized in Figure 5.5 for all the investigated samples. Figure 5.5(a) displays the case of the ITO nanolayers, showing a characteristic trend that peaks at the corresponding $\lambda_{\text{ENZ}}$ for each sample, analogous to the THG case for such ITO nanolayers [25]. This data confirms that the control of the ENZ condition in homogeneous ITO nanolayers allows reliable tuning of their second-order nonlinear optical properties in a wide spectral range, which is interesting for telecommunication applications. The behavior of the SHG intensity with respect to the incident wavelength has been investigated for all the TiN nanolayers. The samples annealed at temperatures lower than 700 °C shows no detectable SHG signal. For all the remaining samples, the SHG intensity increases as the incident wavelength decreases, as summarized in Figure 5.5(b). Remarkably, the maximum achieved SHG efficiency for the TiN nanolayers is a factor of 50 lower than the best ITO nanolayer. The trends of the SHG intensity are consistent with the electric field calculations previously discussed, for both ITO and TiN materials.
Figure 5.5: (a) SHG intensity as function of the incident wavelength for the ITO nanolayers with $\lambda_{ENZ} = 1150$ nm (red), 1270 nm (blue), 1390 nm (green), 1550 nm (cyan), 1670 nm (magenta). (b) SHG intensities as function of the incident wavelength for the TiN nanolayer with $\lambda_{ps} = 510$ nm (blue), 545 nm (green), 565 nm (red) [26].

5.2.3 Second-Order Susceptibility

By measuring the dependence of the SHG intensity on the polarization of the incident beam, Dr. Antonio Capretti calculated the components of the second-order susceptibility. Specifically, we performed SHG measurements for both s- and p-detection configurations as function of the angle of polarization $\beta$ of the incident beam. In this experiment, the incident beam polarization is rotated by using a $\lambda/4$ waveplate followed by a Glan-Laser polarizer. The incident polarization is defined by the angle $\beta$, 
such that $\beta=0^\circ$ determines a p-polarization and $\beta=90^\circ$ a s-polarization. The collected SHG signal is analyzed in its $p$- and s-components by a polarizer. In Figure 5.6(a) and 6(b) the collected SHG $p$-and s-components are shown versus $\beta$ for the representative ITO sample excited at its ENZ wavelength $\lambda_{\text{ENZ}} = 1150$ nm. We notice that the intensity of the SHG s-component is zero for both $p$ ($\beta=0^\circ$) and s ($\beta=90^\circ$) incident polarizations. This follows from the fact that the fabricated films possess in-plane isotropy ($C_{\alpha\nu}$ symmetry group). Consequently, there are three allowed and independent components for the second-order susceptibility: namely $\chi^{(2\omega)}_{zzz}$, $\chi^{(2\omega)}_{zzx} = \chi^{(2\omega)}_{zxy}$ and $\chi^{(2\omega)}_{xxz} = \chi^{(2\omega)}_{xxy} = \chi^{(2\omega)}_{yyz}$. Moreover, the SHG p-component is zero for the s ($\beta=90^\circ$) incident polarization, and the $\chi^{(2\omega)}_{zxx} = \chi^{(2\omega)}_{zzy}$ component is negligible. Here, the maximum intensity of the SHG p-component (at $\beta=0^\circ$) is approximately 20 times more intense than the s-component (at $\beta=45^\circ$). In conclusion, the two relevant components of the second-order susceptibility are $\chi^{(2\omega)}_{zzz}$ and $\chi^{(2\omega)}_{zxx}$ for both materials. This result confirms that the SHG signal is mainly driven by the normal component $E_z$ of the electric field. It has not been possible to conduct a similar analysis for the TiN samples with the same experimental apparatus, due their low SHG intensity.
Figure 5.6: Intensity of the SHG p- (a) and s- (b) components as function of the polarization angle of the incident beam $\beta$ for the ITO nanolayer with $\lambda_{ENZ} = 1150$ nm at incident wavelength $\lambda = \lambda_{ENZ}$ [26].

In order to further confirm the effect of the ENZ-enhancement of the electric field over the SHG process, we calculate the SHG intensity as function of the excitation wavelength for all the fabricated samples. We fix the incident polarization at $\beta=0^\circ$ (p-polarization) and the incident angle at $45^\circ$, as in the experimental section discussed previously. We consider the same multilayer planar geometry as before, where an incident plane wave illuminates the structure from free-space, inducing a second-order nonlinear bulk polarization $\mathbf{p}^{(2\omega)}$ inside the nanolayer:

$$\mathbf{p}^{(2\omega)} = \epsilon_0 \chi^{(2\omega)} \cdot \mathbf{E} \cdot \mathbf{E}$$  \hspace{1cm} (5.4)

Where $\chi^{(2\omega)}$ is the bulk second-order susceptibility and $\mathbf{E}$ is the electric field inside the nanolayer (we dropped the subscript 1) calculated at the excitation wavelength
from Equations (5.2) and (5.3). The SHG field reflected back to free space can be expressed by using the rigorous Green-function formalism for surface optics [88,89]:

\[
E_r^{(2\omega)} = \frac{i k_0^{(2\omega)} D}{2} \frac{t_0^{(2\omega)} e^{2ik_{1,z}^{(2\omega)} D} \int_{-D}^{0} (e^{-k_{1,z}^{(2\omega)} z'} q_1^{(2\omega)} + r_{12}^{(2\omega)} e^{2ik_{1,z}^{(2\omega)} D} q_1^{(2\omega)} e^{2ik_{1,z}^{(2\omega)} z'} p_0^{(2\omega)}) \frac{e^{(2\omega)}}{e_0} d z'}
\]

\( (5.5) \)

Where the subscripts \( m=0, 1, 2 \) are the same as in the previous sections, and all the quantities with the \( (2\omega) \) superscript are related to the second-harmonic fields: \( k_0^{(2\omega)} \) is the free-space wavenumber, \( k_{1,z}^{(2\omega)} \) is the \( z \)-component of the wavevector inside the nanolayer, \( t_{ij}^{(2\omega)} \) and \( r_{ij}^{(2\omega)} \) are the Fresnel transmission and reflection coefficients for the electric field at the interface between two media \( i \) and \( j \) (the appropriate coefficient have to be selected for p- and s- polarizations), \( q_{1,\pm}^{(2\omega)} \) describes the polarization state of the generated light (as defined in Ref. [52]). The integration variable \( z' \) goes from \(-D\) (corresponding to the interface between the nanolayer and the substrate) to \( 0 \) (corresponding to the interface between the free-space and the nanolayer) in the coordinate system adopted throughout this manuscript. Given the subwavelength thickness of the investigated nanolayers, we assume that \( k_{1,z}^{(2\omega)} \ll 1 \) and that the \( \mathbf{E} \) field is constant along the \( z \) direction. Consequently, the second-order bulk polarization \( p^{(2\omega)} \) is constant across the nanolayers thickness, and Equation (5.5) can be approximated as:

\[
E_r^{(2\omega)} = \frac{i k_0^{(2\omega)} D}{2} \frac{t_0^{(2\omega)} e^{2ik_{1,z}^{(2\omega)} D} (q_1^{(2\omega)} + r_{12}^{(2\omega)} e^{2ik_{1,z}^{(2\omega)} D} q_1^{(2\omega)} p_0^{(2\omega)}) \frac{e^{(2\omega)}}{e_0} |_{z=0}}
\]

\( (5.6) \)

Where \( p^{(2\omega)} \) is calculated inside the nanolayer, at the interface with free-space. The calculated SHG intensity is shown in Figure 5.7 for the ITO nanolayers, as function
of the incident wavelength. This calculation is performed for each of the allowed second-order susceptibility components separately from the others. In Figure 5.7(a), we used the set of parameters \((\chi_{zzz}^{(2\omega)} \neq 0, \chi_{xzx}^{(2\omega)} = 0, \chi_{xzx}^{(2\omega)} = 0)\). Analogously, we used the set of parameters \((\chi_{zzz}^{(2\omega)} = 0, \chi_{xzx}^{(2\omega)} \neq 0, \chi_{xzx}^{(2\omega)} = 0)\) for Figure 5.7(b) and \((\chi_{zzz}^{(2\omega)} = 0, \chi_{xzx}^{(2\omega)} = 0, \chi_{xzx}^{(2\omega)} \neq 0)\) for Figure 5.7(c). Each of the allowed components of \(\chi^{(2\omega)}\) exhibit maximum SHG generation when the samples are pumped at the \(\lambda_{\text{ENZ}}\), in agreement with the experimental results showed in Figure 5.5. However, the width of the SHG peak is shorter for the \(\chi_{zzz}^{(2\omega)}\) component in Figure 5.7(a), and it increases for \(\chi_{xzx}^{(2\omega)}\) in Figure 5.7(b). The bandwidth further increases for the \(\chi_{zxx}^{(2\omega)}\), which also features a much shorter SHG intensity. These results are easily explained by considering the amplitude of the \(E_z\) and \(E_x\) components shown in Figure 5.2. We notice that for the \(\chi_{zzz}^{(2\omega)}\) component shown in Figure 5.7(a), our calculations predict a SHG intensity enhanced by approximately 4 orders of magnitude, compared to wavelengths detuned from the ENZ condition. It is also important to note that the SHG from the fabricated ITO nanolayers benefits from both from the enhanced electric field of the excitation and from the improved extraction of the SHG light. As a matter of fact, the fabricated ITO samples are transparent in the visible spectrum.
Figure 5.7: Calculated SHG intensity as function of the incident wavelength for the ITO nanolayers with $\lambda_{ENZ} = 1150$ nm (red), 1270 nm (blue), 1390 nm (green), 1550 nm (cyan), 1670 nm (magenta). The second-order susceptibility components are $\chi^{(2)}_{zzz} \neq 0, \chi^{(2)}_{xxx} = 0, \chi^{(2)}_{zxx} = 0$ (a), $\chi^{(2)}_{zzz} = 0, \chi^{(2)}_{xxx} \neq 0, \chi^{(2)}_{zxx} = 0$ (b), $\chi^{(2)}_{zzz} = 0, \chi^{(2)}_{xxx} = 0, \chi^{(2)}_{zxx} \neq 0$ (c) [26].

We performed a similar analysis for the TiN nanolayers. Figure 5.8 shows the calculated SHG intensity as function of the incident wavelength. In Figure 5.8(a), we used the set of parameters $\chi^{(2)}_{zzz} \neq 0, \chi^{(2)}_{xxx} = 0, \chi^{(2)}_{zxx} = 0$. Analogously, we used the set of parameters $\chi^{(2)}_{zzz} = 0, \chi^{(2)}_{xxx} \neq 0, \chi^{(2)}_{zxx} = 0$ for Figure 5.8(b) and $\chi^{(2)}_{zzz} = 0, \chi^{(2)}_{xxx} = 0$ for Figure 5.8(c).
$\chi^{(2\omega)}_{zxx} \neq 0$) for Figure 5.8(c). The TiN nanolayers display a metallic behavior in the investigated spectral range. For this reason, the SHG intensity monotonically decreases as the incident wavelength increases for all the investigated components of the second-order susceptibility. It is interesting to note that, assuming equal amplitude for $\chi^{(2\omega)}_{zzz}$, $\chi^{(2\omega)}_{xzx}$ and $\chi^{(2\omega)}_{zxx}$, the SHG intensity due to the $\chi^{(2\omega)}_{zzz}$ component is 3 orders of magnitude lower than the others. This is due to the metallic behavior of the TiN nanolayers in the near infrared, which negatively affects the extraction of SHG light. Moreover, the second-order polarization induced by $\chi^{(2\omega)}_{zzz}$ depends on the normal component $E_z$ of the electric field at the incident wavelength, which is strongly reduced inside the TiN nanolayers, as already shown in Figure 5.2(c).
In order to quantify the second-order susceptibility of the investigated nanolayers, we performed relative measurements with a reference material, as detailed in Chapter 4 of Ref. [90]. Specifically, we considered the reflected SHG intensity from a Y-cut quartz plate of thickness 0.5mm. We measured the SHG s-component \( I^{(2\omega)}_{\text{quartz}} \) generated by an s-polarized incident beam, when the quartz standard axis 1 is parallel to the s-direction. We assumed the value \( \chi_{111} = 0.6 \ pmV^{-1} \) for the second-order susceptibility of quartz, where
the subscripts refer to the standard crystallographic axes [91]. We obtained that the SHG intensity \( I_{\text{ITO}}^{(2\omega)} \) of the best ITO nanolayer (with \( \lambda_{\text{ENZ}} = 1150 \text{ nm} \)) is comparable with the quartz plate (our experimental measurements indicated that \( I_{\text{ITO}}^{(2\omega)}/I_{\text{ITO}}^{(2\omega)} \approx 1/3.5 \), when both are pumped at \( \lambda = 1100 \text{ nm} \). This is a remarkable performance for the ITO nanolayers, considering that the quartz plate thickness is as large as 0.5 mm. As a comparison, in Ref. [92] the SHG from arrays of silver nanoparticles and islands excited at \( \lambda = 1060 \text{ nm} \) resulted to be \( \approx 2\times 10^{-3} \) lower than a quartz sample (with unspecified orientation) [92]. By comparing the calculated and the experimental values of the SHG intensity, we estimated that the second-order susceptibility components are \( \chi_{zzz}^{(2\omega)} = 0.18 \text{ pm} V^{-1} \) and \( \chi_{xzz}^{(2\omega)} = 0.05 \text{ pm} V^{-1} \) (in good agreement with previous studies [93]) and that the SHG efficiency is \( \eta_{\text{SHG}} = \frac{I^{(2\omega)}}{I^{(\omega)}} = 3 \times 10^{-13} \text{ at } I_{\text{peak}}^{(\omega)} = 42 \text{ MW/cm}^2 \). Since the SHG is a second-order nonlinear process, \( \eta_{\text{SHG}} \) increases linearly with the incident intensity and the slope has a constant value \( \eta_{\text{SHG}}/I_{\text{peak}}^{(\omega)} = 7 \times 10^{-21} \text{ cm}^2/W \). As a comparison, the arrays of nanowires investigated in Ref. [94] have a maximum \( \eta_{\text{SHG}}/I_{\text{peak}}^{(\omega)} = 3.5 \times 10^{-21} \text{ cm}^2/W \) with the excitation at \( \lambda = 800 \text{ nm} \), whereas the nanoantenna recently reported in Ref. [95] has a maximum \( \eta_{\text{SHG}}/I_{\text{peak}}^{(\omega)} = 2.1 \times 10^{-21} \text{ cm}^2/W \) in the same 940–1480 nm spectral range targeted here (although enhanced values are reported for longer wavelengths). The comparison with the results obtained by other groups is affected by the different experimental conditions, especially the spectral and temporal properties of the excitation beam. However, it is clear from our results that ITO nanolayers provide an excellent nonlinear optical performance even without utilizing
surface nanostructuring. This is a direct consequence of the enhanced internal electric field at the ENZ wavelength. For the TiN samples, the SHG efficiency is \( \eta_{SHG} = \frac{f^{(2\omega)}}{f^{(\omega)}} = 6.5 \times 10^{-15} \) at \( f_{\text{peak}}^{(\omega)} = 42\text{MW/cm}^2 \), with a slope \( \eta_{SHG}/f_{\text{peak}}^{(\omega)} = 1.4 \times 10^{-22}\text{cm}^2/\text{W} \).

Crystalline TiN is a centrosymmetric medium, and therefore the bulk second-order susceptibility is zero in the dipolar approximation. The SHG from centrosymmetric conductors is generally attributed to surface effects and to nonlocal bulk effects. The samples investigated here are polycrystalline, and the grain boundaries also play important effects in optical nonlinearities. We attribute the low second-order optical nonlinearity of the fabricated TiN nanolayers to the grain centrosymmetry and to the significant optical losses associated with the large imaginary part of the permittivity.

### 5.3 Third Harmonic Generation of ITO

Similar to SHG, I assisted Dr. Antonio Capretti to demonstrate Third-Harmonic Generation (THG) from ITO nanolayers with an efficiency ~600 times larger than crystalline silicon. The enhanced optical nonlinearity is driven by the nanolayers ENZ condition at telecommunication wavelengths. However, no Third Harmonic Generation from TiN has been observed.
5.3.1 Third-Harmonic Generation Spectroscopy

We select the samples of ITO with $\lambda_{\text{ENZ}} = 1270$ nm, 1390 nm and 1550 nm to investigate (See Table 5.1) Third Harmonic Generation properties. In order to experimentally demonstrate the relevance of the ENZ condition for the control and the enhancement of the nonlinear frequency generation, we characterized the nonlinear optical responses of the ITO thin films using ultrafast third-harmonic generation spectroscopy, similar to second-harmonic generation spectroscopy shown in Figure 5.3. The collected light at the incident wavelength is rejected by a 1000 nm short-pass filter placed in front of the monochromator slits. The incident angle was kept at 45° for all the acquisitions. In order to demonstrate that the THG signals are generated in the fabricated ITO films, we substituted the investigated samples with a bulk Si substrate. In this case no signal is detected under the same excitation power.

In Figure 5.9(a) we show representative THG spectra collected under p-polarized incidence for the sample with $\lambda_{\text{ENZ}} = 1390$ nm. The intensity exhibits a maximum if the incident wavelength is equal to $\lambda_{\text{ENZ}}$, and it scales cubically with the incident power, as shown in the inset of Figure 5.9(b). These findings directly demonstrate that the enhanced electric field component $E_z$ achieved at the tailored $\lambda_{\text{ENZ}}$ can be utilized to boost the THG emitted intensities.
Figure 5.9: (a) THG signals of the ITO film with $\lambda_{\text{ENZ}} = 1390$ nm at incident wavelength $\lambda = 1250$ nm (magenta), 1300 nm (green), 1350 nm (red), 1400 nm (blue), 1450 nm (pink), 1500 nm (cyan), 1550 nm (olive). (b) THG intensity as function of the incident average power [25].

The behavior of the THG intensity with respect to the incident wavelength has been investigated for all the fabricated samples and is summarized in Figure 5.10. The THG intensities show a characteristic trend that peaks for each sample approximately at the corresponding $\lambda_{\text{ENZ}}$. Finally, we notice that the THG curves are not symmetric. This is mainly due to the lack of symmetry of the material optical linear response around $\lambda_{\text{ENZ}}$, i.e. $\varepsilon_1$ is negative for $\lambda>\lambda_{\text{ENZ}}$ (plasmonic) and is positive for $\lambda<\lambda_{\text{ENZ}}$ (dielectric). These data demonstrate that the control of the ENZ condition in homogeneous ITO thin films allows reliable tuning and enhancement of their nonlinear optical properties in the telecommunication window.
Figure 5.10: THG intensities as function of the incident wavelength for the ITO nanolayers with $\lambda_{ENZ} = 1270$ nm (blue), 1390 nm (green), 1550 nm (cyan). The estimated relative error for the measured SHG and THG intensities is less than 20% for all the investigated samples [25].

In order to quantify the optical nonlinearity of the fabricated nanolayers, we considered as a reference the reflected THG intensity from a polished (100) Si wafer. As already stated previously, no signal is detected from the Si wafer under an average power of 10 mW. In order to detect the THG from Si with a reasonable signal-to-noise ratio, we increased the incident power up to 30 mW (the THG intensity grows with the third power of the incident power), and we used an incident wavelength of 1060 nm, where experimental estimations of the third-order susceptibility are available for crystalline Si [96,97]. Specifically, we measured the p-component of the THG intensity generated by a p-polarized incident beam with the Si wafer [100] axis in the plane of incidence. It resulted that the THG efficiency of the best ITO nanolayer (with $\lambda_{ENZ} = 1550$ nm) is ~
586 higher than the Si wafer, which is an outstanding performance considering that the wafer thickness is \( \sim 300 \mu m \).

5.3.2 Third-Order Susceptibility

Dr. Antonio Capretti quantified the third-order susceptibilities of the investigated ITO films by using the Green-function formalism of Ref. [88]. The reflected THG field from the investigated ITO thin films can be expressed as:

\[
E_{r,ITO}^{(3\omega)} = \frac{i k_0^{(3\omega)} z_0}{2 k_{1z}^{(3\omega)}} \frac{\ell_{10}^{(3\omega)}}{1-r_1^{(3\omega)} r_2^{(3\omega)}} e^{i k_{1z}^{(3\omega)} D} (q_{11+}^{(3\omega)} + r_{12}^{(3\omega)} e^{2i k_{1z}^{(3\omega)} D} q_{11-}^{(3\omega)}) \frac{p^{(3\omega)}}{\varepsilon_0} \quad (5.7)
\]

Where \( D \) is the film thickness, \( z_0 \) is the free-space impedance, and all the quantities with \( (3\omega) \) superscript are related to third-harmonic fields: \( k_0^{(3\omega)} \) is the free-space wavenumber, \( k_{1z}^{(3\omega)} \) is the \( z \)-component of the wavevector in the ITO region, \( \ell_{ij}^{(3\omega)} \) and \( r_{ij}^{(3\omega)} \) are the Fresnel transmission and reflection coefficients for the electric field at the interface between two media \( i \) and \( j \) for p-polarization, \( q_{11+}^{(3\omega)} \) describes the polarization of the generated light as defined in Ref. 6. \( p^{(3\omega)} \) is the third-order nonlinear polarization given by:

\[
p^{(3\omega)} = \varepsilon_0 \chi^{(3\omega)} : E E E \quad (5.8)
\]

Where \( E=(E_x, E_y, E_z) \) is the electric field at the incident wavelength and \( \chi^{(3\omega)} \) is the effective bulk third-order susceptibility. Following Ref. [96], we consider:

\[
p^{(3\omega)} = \varepsilon_0 \left( \chi_{1111}^{(3\omega)} - 3 \chi_{1122}^{(3\omega)} \right) E^3 + \varepsilon_0 3 \chi_{1122}^{(3\omega)} E (E \cdot E) \quad (5.9)
\]
Where \( i=1,2,3 \) refers to the three cubic axes. We calculated the THG intensity as function of the incident wavelength for the three ITO nanolayers, as shown in Figure 5.11. We performed the calculations by addressing each of the two terms in Equation (5.9) separately. In Figure 5.11(a), we only considered the first term, or equivalently we assumed \( \chi^{(3\omega)}_{1111} \gg 3\chi^{(3\omega)}_{1112} \). In Figure 5.11(b) we only considered the second term, or equivalently we assumed material isotropy \( \chi^{(3\omega)}_{1111} - 3\chi^{(3\omega)}_{1112} = 0 \). Interestingly, for both cases all the samples display maximum THG when the incident wavelength is equal to their respective \( \lambda_{\text{ENZ}} \), in good agreement with the experimental results showed in Figure 5.10. These results are easily explained by considering the dependence of the normal \((E_z)\) component on the incident wavelength, which has been previously discussed and is shown in Figure 5.2. For the first term of Equation (5.9) shown in Figure 5.11(a), the THG intensity at \( \lambda_{\text{ENZ}} \) is more than 2 orders of magnitude higher than wavelengths far from the ENZ condition. It is also interesting to notice that the second term of Equation (5.9) shown in Figure 5.11(b) features a dip in the THG intensity, resulting from a minimum of \( \mathbf{E} \cdot \mathbf{E} = E_x^2 + E_z^2 \), which can be obtained for incident p-polarization at a wavelength different than \( \lambda_{\text{ENZ}} \).
Figure 5.11: Calculated THG intensities as function of the incident wavelength for the ITO thin films with $\lambda_{ENZ} = 1270$ nm (blue), 1390 nm (green), 1550 nm (cyan). Panel (a) assumes $\chi^{(2)_{\omega}} > 3\chi^{(3)_{\omega}}$, panel (b) assumes material isotropy [25].

The THG efficiencies of the fabricated ENZ materials result from the combination of: a) enhanced internal electromagnetic field at the ENZ wavelength; b) significantly improved light extraction achieved at the harmonic frequencies due to the ITO transparency.

Dr. Antonio Capretti quantified the third-order susceptibility of the ITO film on Si substrate with $\lambda_{ENZ} = 1550$ nm by comparing the calculated and the experimental values of the THG efficiency. As we have already discussed, at the ENZ wavelength $E_z >> E_x$, and Equation (5.9) can be approximated as:

$$P^{(3\omega)} \approx \chi^{(3\omega)}_{1111} E_z \hat{z}$$  \hspace{1cm} (5.10)

Our calculations indicate a third-order susceptibility of
\[ \chi^{(3\omega)}_{1111} = 3.5 \times 10^{-18} \text{ m}^2\text{V}^{-2}, \]
resulting in a THG efficiency that is \(~600\) times larger than in crystalline Si. Consequently, ITO films with engineered ENZ behavior represent an ideal platform for applications to integrated nonlinear optics and sensing, relying on full compatibility with Si technology and enhanced nonlinear optical response in the telecommunication spectrum.

5.4 Conclusion

In conclusion, we experimentally showed that both ITO and TiN nanolayers can be fabricated to have tailorable optical dispersion in the near-infrared. Dr. Antonio Capretti also theoretically predicted that the SHG process in ITO is enhanced by approximately 4 orders of magnitude if the excitation wavelength matches the ENZ condition of the material. Remarkably, the ITO nanolayers generate an SHG signal of comparable intensity with that of a crystalline quartz plate of thickness 0.5 mm, while TiN shows a much lower SHG intensity. Besides, when operating at ENZ wavelength, ITO nanolayers have a THG efficiency that is \(~600\) times larger than in crystalline Si. Hence, ITO is an efficient and compelling Si compatible material platform for surface optical nonlinearities, which is compatible with Si fabrication technology and it is applicable for scalable and planar-integrated metamaterial structures. We have shown a simple and cost-effective approach to control the ENZ behavior, resulting in highly efficient harmonic generation. This study will open practical and powerful avenues for largely scalable and highly integrated frequency conversion and optical modulation using silicon-based materials.
Chapter 6

6 Tin-Based Hyperbolic Metamaterial for Broadband Enhancement of Local Density of States

In this chapter, in collaboration with Hiroshi Sugimoto in Prof. Minoru Fujii’s group, by using steady-state and time-resolved photoluminescence spectroscopy as a function of emission wavelength, we investigate the light emission of silicon quantum dots by colloidal synthesis that were uniformly spin-coated into a 20 nm-thick film and deposited atop a hyperbolic metamaterial of alternating TiN and SiO$_2$ sub-wavelength layers. In partnership with rigorous electromagnetic modeling of dipolar emission developed by the previous post-doc in our group Dr. Sandeep Inampudi, we demonstrate enhanced Local Density of States and coupling to high-k modes in a broad spectral range.

Sections of this chapter have been adapted from the 2015 Applied Physics Letters publication titled *Broadband enhancement of local density of states using silicon-compatible hyperbolic metamaterials* [24].

6.1 Hyperbolic Metamaterial

Metamaterials are artificially engineered media composed of arrays of identical and resonant building blocks of sub-wavelength size. By carefully controlling their shape and composition, it is possible to create artificial materials that feature unique optical phenomena and give rise to unprecedented functionalities, such as cloaking [98], negative refraction [99,100], molecular sensing [101], super-resolution imaging [16,49], and
In recent years, a specific class of metamaterials, known as hyperbolic metamaterials (HMMs), has attracted considerable attention. HMMs are meta-crystals with extreme anisotropy in their optical response due to the opposite sign of the dielectric tensor components along two orthogonal directions [37]. The name is from the isofrequency curve of the medium, which is hyperbolic as opposed to circular in isotropic media. As a result, HMMs support hyperbolic iso-frequency dispersion curves that can potentially modify light-matter interaction over a broad spectral range [52–55]. Applications of these fascinating concepts to the enhancement of single photon sources [21], nonlinear processes [57], and sub-wavelength focusing [106,107] have been recently demonstrated.

For the dielectric tensor components of HMM, it has dielectric properties ($\varepsilon > 0$) in one direction, and metallic properties ($\varepsilon < 0$) in orthogonal directions. It can be described by the dielectric response of a uniaxial crystal ($\varepsilon_{xx} = \varepsilon_{yy} = \varepsilon_\perp, \varepsilon_{zz} = \varepsilon_\parallel, \varepsilon_\perp \neq \varepsilon_\parallel$) with extreme anisotropy ($\varepsilon_\perp \varepsilon_\parallel < 0$), which is given by [104] [38]:

$$\varepsilon = \begin{bmatrix} \varepsilon_\perp & 0 & 0 \\ 0 & \varepsilon_\perp & 0 \\ 0 & 0 & \varepsilon_\parallel \end{bmatrix}$$  \hspace{1cm} (6.1)

Such property doesn’t exist in nature at optical frequencies and the term “hyperbolic” originates from the isofrequency surface of extraordinary waves in such medium, which is given by

$$\frac{k_x^2 + k_y^2}{\varepsilon_\parallel} + \frac{k_z^2}{\varepsilon_\perp} = \left(\frac{\omega}{c}\right)^2$$  \hspace{1cm} (6.2)
Note that for isotropic medium \((\varepsilon_{xx} = \varepsilon_{yy} = \varepsilon_{zz} = \varepsilon_{\parallel})\), the isofrequency surface is a sphere. While for HMM, it opens up into a hyperboloid because the sign of dielectric constants are opposite along orthogonal directions. Depending on in which direction the dielectric component is metallic, there are two kinds of HMM: type I \((\varepsilon_{xx} = \varepsilon_{yy} = \varepsilon_{\perp} > 0, \varepsilon_{zz} = \varepsilon_{\parallel} < 0)\), type II \((\varepsilon_{xx} = \varepsilon_{yy} = \varepsilon_{\perp} < 0, \varepsilon_{zz} = \varepsilon_{\parallel} > 0)\). Figure 6.1 shows the isofrequency contours of the isotropic medium and HMM.

**Figure 6.1:** Isofrequency surfaces for (a) isotropic medium, (b) type I HMM with extreme anisotropy \((\varepsilon_{xx} = \varepsilon_{yy} = \varepsilon_{\perp} > 0, \varepsilon_{zz} = \varepsilon_{\parallel} < 0)\), (c) type II HMM with extreme anisotropy \((\varepsilon_{xx} = \varepsilon_{yy} = \varepsilon_{\perp} < 0, \varepsilon_{zz} = \varepsilon_{\parallel} > 0)\). HMM in (b) and (c) can support waves with unbounded wavevectors because the isofrequency surface opens up as hyperboloid. HMM behaves as metals to reflect waves with wavevector smaller than \(k_{\text{min}}\) [108].

From the isofrequency surface curve, it can be seen that HMM can support waves with wavevectors far exceeding free space wavevector \((k_0 = \omega / c)\). There states are referred as “high-\(k\)” states of HMM, which are evanescent in vacuum and decay exponentially, but can propagate within HMM. In particular, the local density of states
(LDOS) of HMM has contributions from large wavevector states up to the wavevector $k_{\text{max}} \gg k_0$ and is given by

$$\rho(\omega) \sim k_{\text{max}}^3$$

(6.3)

For HMM, the isofrequency surface opens up as hyperboloid which has infinite volume and leads to a broadband singularity in density of states. Therefore, HMM can be used to enhance LDOS for broadband engineering of spontaneous emission of light emitters due to the coupling with electromagnetic states unique to HMM. This approach of controlling the rate of spontaneous emission is fundamentally different from many methods like photonic crystals [109], resonant cavities [110], and slow light waveguides [111].

In metals, the real part of the dielectric permittivity is negative below plasma frequency. In hyperbolic regime, the components of dielectric tensor are negative in one or two directions, which can be achieved by restricting free-electron motion to these directions. Therefore, the most common approach to realize HMM is to use layered metal-dielectric structures. Figure 6.2 shows an example of layered metal-dielectric structure.
Figure 6.2: Realization of Hyperbolic Metamaterial (HMM) by using periodically layered metal-dielectrics structures. $d_m$ and $d_d$ are the thickness of metallic and dielectric components, respectively.

From effective medium theory (EMT) [112], the effective dielectric tensor components in the parallel and perpendicular directions to anisotropy axis are given by

$$
\varepsilon_\perp = \frac{\varepsilon_mD_m + \varepsilon_d d_d}{d_m + d_d}, \quad \varepsilon_\parallel = \frac{d_m + d_d}{d_m/\varepsilon_m + d_d/\varepsilon_d}
$$

(6.4)

Where $\varepsilon_m$ and $\varepsilon_d$ are the dielectric permittivity of metallic and dielectric components, $d_m$ and $d_d$ are the thickness of metallic and dielectric components. The effective medium approximation of Equation 6.4 is valid in long-wavelength limit, which means the variation of electromagnetic field over one period is small.
6.2 Design of TiN-Based Hyperbolic Metamaterial

To attain hyperbolic regime, one needs to turn the parameter $\varepsilon_L \varepsilon_{||} < 0$. Hence, currently most HMM devices utilize metallic components as their sub-wavelength building blocks. However, they are characterized by significant absorption losses in the visible and near-infrared spectral ranges, limited tunability, and lack of compatibility with the widespread silicon technology. Alternative plasmonic materials such as transparent conductive oxides (TCOs) and transition metal nitrides have recently emerged as a viable solution to conventional metal-based plasmonic structures, for both linear \cite{14,17,113} and nonlinear device applications \cite{25,26}. Among them, titanium nitride (TiN) has been used as a good plasmonic material in visible spectrum due to its compatibility with Si processing, excellent thermal and chemical stability, and largely tunable optical properties \cite{15,16}.

The HMM structure consists of a multilayer stack of 10 alternating layers (5 periods) of TiN and SiO$_2$ deposited on a glass substrate. The uppermost layer is SiO$_2$, which works as a spacer to avoid non-radiative quenching by the TiN layer. Both TiN and SiO$_2$ layers were grown at room temperature in a Denton Discovery 18 confocal-target system. TiN thin films were deposited using DC reactive sputtering with Ti (99.99% purity) target in N$_2$ atmosphere, while SiO$_2$ thin films were deposited using RF sputtering with SiO$_2$ (99.99% purity) target in Ar atmosphere. The thickness of each layer has been kept fixed at 15 nm, irrespective of the deposition conditions. The base pressure was 1.0×10$^{-7}$ Torr and both the N$_2$/Ar gas flow were kept at 10sccm, while the Ti and SiO$_2$ targets power were fixed at 200 W. Post-deposition thermal annealing processes...
have been performed using a Mellen thermal furnace, which resulted in a large tunability of the measured optical dispersion properties of the TiN layers in the visible spectrum, and in a significant reduction of their optical loss coefficient as well. Annealing processes were performed at 900 °C for 1h, in a vacuum of pressure $2.3 \times 10^{-3}$ Torr.

The optical properties of the constituent TiN thin films were experimentally determined by variable angle spectroscopic ellipsometry that allowed us to determine the relative dielectric permittivity of the material by a standard fitting procedure using the Lorentz oscillator model [17]. Figure 6.3(a) displays the extracted values of the permittivity of the TiN layers, which exhibit an electron plasma behavior ($\varepsilon' < 0$) for wavelengths larger than 550nm. The dielectric permittivity of the HMM multilayered structure was calculated using Equation 6.4 by effective medium theory (EMT), resulting in the in-plane ($\varepsilon_{//}$) and out-of-plane ($\varepsilon_{\perp}$) components shown in Figure 6.3(b). We notice that the real part of the in-plane relative permittivity ($\varepsilon'_{//}$) turns negative for wavelengths larger than 658 nm, giving rise to the hyperbolic dispersion regime that we are interested to investigate in relation to LDOS modifications in active Si-compatible structures [23,55,114].
Figure 6.3: (a) Real (black) and imaginary (violet) parts of dielectric permittivity for the constituent TiN layer in HMM structure. (b) Real (blue) and imaginary (olive) parts of dielectric permittivity for HMM structure. In HMM structure, the dielectric permittivity has in-plane ($\varepsilon_{\parallel}$) and out-of-plane ($\varepsilon_{\perp}$) components [24].

In order to experimentally demonstrate LDOS enhancement effects, a thin film of light emitting Si QDs was spin coated (2000 rpm) from a colloidal solution (0.4 mg/mL) atop the HMM structure. In collaboration with Prof. Minoru Fujii’s group, the QD-layer is prepared by spin-coating QDs dispersions in methanol (0.4 mg/mL) at a spin speed of 2000 rpm. After the evaporation of methanol, a film of Si-QDs with 20 nm thickness characterized by SEM was obtained, as shown in Figure 6.4(a).

The QDs allow us to investigate the dynamics of light emission coupled to the HMM hyperbolic regime. The detailed preparation procedure of colloidal Si QDs has been described elsewhere [117,118]. In this work, in order to overlap the emission spectrum and the hyperbolic regime we select the QDs with a diameter of 3.2 nm that result in a room temperature Photoluminescence (PL) quantum yield in solution of
approximately 7% [118]. For comparison purpose, a control sample consisting of identically prepared QDs spun atop one period of TiN/SiO$_2$ and a reference sample consisting of QDs atop a glass substrate were also prepared. Figure 6.4(b) represents the cross-sectional SEM of 10 alternating layer of TiN/SiO$_2$ HMM structure.

![Figure 6.4: Cross-section SEM image of (a) single layer Si-QDs (b) 10 alternating layer of TiN/SiO$_2$ HMM structure. (scale bar: 100 nm)](image)

6.3 Steady-State and Time-Resolved Photoluminescence (PL) Spectroscopy

PL measurements were performed using an Ar ion laser (Spectra Physics, 177–602) pumping at 488 nm focused with a 35 mm focus lens. For time-resolved PL, the laser beam was modulated by an acousto-optic modulator (AOM) at a frequency of 1 kHz. PL emitted from the sample was collected and collimated using a 2-inch diameter plano-convex lens (L1), and focused by second lens (L2) onto the input slit of a monochromator (Oriel Cornerstone 260) equipped with a photomultiplier tube (Oriel Instrumentation 77348). A 500 nm long-pass filter (LPF) was placed in the front of the slit to reject the
pump laser light. Figure 6.5 depicts the schematics of PL measurement setup.

![Schematics of PL measurement setup](image)

**Figure 6.5**: Schematics of PL measurement setup

Figure 6.6(a) shows the measured PL spectra of the reference (black lines), control (red lines) and HMM samples (blue lines). The QDs feature a broad PL spectrum peaked around 740 nm, which allows us to study the PL properties of the samples across the hyperbolic dispersion transition (i.e., where the dispersion switches from elliptical to hyperbolic around 658 nm). The QDs film thickness is fixed to 20 nm on all samples and the reflections of substrates at the incident angle of PL measurements are comparable and within the range of 16% to 22% for all samples. Notice that an almost negligible PL enhancement (within the uncertainty of the error-bars) was observed at the hyperbolic threshold. We also notice that the PL spectra of the QDs coupled to the HMM and the
control sample are blue-shifted 20 nm with respect to the PL spectra on silica glass. This shift is related to the increased TiN material losses at longer wavelengths.

![Figure 6.6](image)

**Figure 6.6:** (a) PL spectra of QD films on silica glass, control and HMM substrates. PL spectra measured at 5 distinct points on each substrate are shown. Inset: Decay curves of silica glass (black) and HMM (blue) samples measured at 720 nm with fitting curves (red). (b) Average PL lifetimes of silica glass, control and HMM samples as a function of detection wavelength. (c) Decay rate enhancement of HMM sample with respect to that of the silica glass and control samples. The colored area shows hyperbolic dispersion range of HMM sample. The error bars in panels (b) and (c) are obtained by measuring 5 distinct points on the substrate and include the error during the fitting process (less than 3%) [24].

### 6.4 Electromagnetic Simulation of Emission Rate of Dipole in HMM

To accurately interpret our experimental findings, Dr. Sandeep Inampudi performed a rigorous theoretical analysis of the decay rate enhancement by calculating the LDOS of different samples over the experimental wavelength range. Considering the
QDs emission as due to randomly oriented classical dipoles, the LDOS normalized to the free space density of states (i.e., LDOS enhancement) can be found by computing the ratio of energy dissipation in a non-homogeneous structure and in free space [119]. In the case of dipoles atop of the HMM structure we can express the dissipation ratio as [119]:

\[
\frac{P}{P_0}(\omega, h) = 1 + \frac{1}{2} \int_0^1 \frac{s}{s_z} Re\left\{ e^{2i s z k_0 h} \left[ r_s + (2s^2 - 1) r_p \right] \right\} ds + \frac{1}{2} \int_1^\infty \frac{s}{|s_z|} e^{-2|s_z| k_0 h} Im\left[ r_s + (2s^2 - 1) r_p \right] ds
\]  

(6.5)

Where \( Re\{\} \) and \( Im\{\} \) denote the real and imaginary parts of the respective terms. In the above equation, the integrals are carried over the entire angular emission spectrum, where \( s(= k_x/k_0) \) represents transverse wavevector components including low-\( k \) propagating modes (\( s \leq 1 \)) and high-\( k \) evanescent (\( s > 1 \)) modes in the spectrum, and \( s_z(= \sqrt{1 - s^2}) \) represents the longitudinal components of the wavevector. The quantities \( r_s \) and \( r_p \) are the complex reflection coefficients for Transverse Electric (TE) and Transverse Magnetic (TM) polarized waves which are calculated as in Ref. [120]. The parameter \( h \) is the dipole position above layers. Since in our experiments we have Si QDs randomly dispersed in a 20nm-thick active layer, we considered in the calculations the positional average of the power ratio with respect to \( h \). We also notice that equation 6.5 already contains the statistical average with respect to the dipole orientations in all possible directions (parallel and perpendicular to the layers) [43], which appropriately represent the case of randomly distributed QDs. The first two terms on the right hand side of Equation 6.5 represent the contributions from the propagation parts of the PL angular spectrum, given by \((P/P_0)_{\text{low-}k}\) and measured through far-field PL experiments, while the third term represents the evanescent and high-\( k \) \((P/P_0)_{\text{high-}k}\) contributions of sub-
wavelength modes that the decay in the near-field region of the emitters. Using the calculated energy dissipation ratio as given by Equation 6.5, the spontaneous decay rate enhancements of dipolar emitters with a quantum yield $\eta$ can be expressed as [23]:

$$\frac{\Gamma}{\Gamma_0} = (1 - \eta) + \eta \frac{P}{P_0}$$  \hspace{1cm} (6.6)

Where $\Gamma$ represents the spontaneous decay rate on the sample and $\Gamma_0$ is the spontaneous decay in vacuum.

To analyze the effect of the hyperbolic dispersion on the QDs PL, we compare the experimental and theoretical results in Figure 6.7. Figure 6.7(a) shows the comparison between measured (symbols) and calculated (solid line) decay rate enhancements with respect to the control sample ($\Gamma_{\text{HMM}}/\Gamma_{\text{control}}$), where a similar trend is observed in both cases during the transition from the elliptical to the hyperbolic regime. This demonstrates broadband coupling of energy into evanescent high-$k$ modes supported by the HMM structure. As shown by our calculations (Figure 6.7(b)), no appreciable increase in the PL intensity is expected during the transition from elliptical to hyperbolic regimes, in agreement with the experimental data shown in Figure 6.6(a) and Figure 6.7(b). In contrast to previous reports of enhanced PL decay rates using Si compatible HMMs at specific emission wavelengths [23], we demonstrated here a broadband effect that evidences the continuous transition of the layered metamaterial from the elliptical to the hyperbolic regime.
Figure 6.7: (a) Total decay rate enhancement measured (symbols) from time resolved experiments and calculated (solid line) using Equation (6.5) and (6.6) of HMM sample with respect to control sample ($\Gamma_{\text{HMM}}/\Gamma_{\text{control}}$). (b) Calculated LDOS normalized by control sample ($P_{\text{HMM}}/P_{\text{control}}$) for both low-k and high-k modes (solid lines). Measured PL intensity ratio of HMM sample to control sample is also shown (red-symbols). The dashed lines in both panels (a) and (b) are calculated results with reduced absorption losses in TiN [24].

In order to better understand the role of the material absorption losses we theoretically calculated the LDOS (or energy dissipation ratio) using Equation 6.5 also for the case of an HMM structure with losses in the TiN layers reduced by a factor of two. This new situation leads to only a slight modification of the transition region between the elliptical and hyperbolic regimes. No appreciable enhancement is noticed in the ratio of total decay rates (dashed lines in Figure 6.7(a)) in the hyperbolic regime due to the low quantum yield of the Si-QDs. However, the calculated LDOS spectrum features further enhancement of the coupling to the high-k modes in comparison to the radiative power (dashed lines in Figure 6.7(b)) in the system with reduced losses.
6.5 Future Plan

As discussed in this chapter, the LDOS of HMM can be greatly enhanced by incorporating plasmonic material with dielectric material. We know from Chapter 4 that ITO is good plasmonic material with low loss in near-IR. Therefore, I propose an active hyperbolic metamaterial (HMM) based on ITO and embedded Er doped Zinc Oxide (Er:ZnO) materials, which emits at optical communication wavelength 1.55 µm.

By selecting appropriate ITO, the effective permittivity of active HMM which comprises ITO and Er:ZnO can have hyperbolic dispersion at 1.55 µm, as shown in Figure 6.8. Thus, we expect to see enhanced LDOS at 1.55 µm with increased light emission. Additionally, as shown in Chapter 5, because ITO generates SHG and THG very efficiently at ENZ wavelength, it is very interesting to explore the nonlinear generation properties in the hyperbolic regime of this active HMM device. This work could lead to a new approach to realize active HMM for silicon photonic light emission application.
The proposed active hyperbolic metamaterial (HMM) which comprises ITO and Er doped Zinc Oxide (Er:ZnO) light emitting materials. (b) The simulated Real part of dielectric permittivity for active HMM structure. In HMM structure, the dielectric permittivity has in-plane $\varepsilon_{//}$ (blue) and out-of-plane $\varepsilon_{\perp}$ (red) components.

6.6 Conclusion

In conclusion, we have demonstrated that TiN-based HMMs coupled to Si QDs are a viable platform for LDOS engineering with Si-compatible active materials. We performed wavelength dependent PL intensity and lifetime measurements of broadband emitting Si QD in HMMs structures and demonstrated up to 1.6-times enhanced decay rate of QDs emission when coupled to the high-k modes of HMM compared with identical QDs deposited on a silica glass sample. The results are also validated with electromagnetic calculations of the emission rate of embedded dipoles. The demonstrated active metamaterials with hyperbolic dispersion represent a promising first step towards the engineering of novel Si-compatible devices with enhanced light–matter coupling for
applications to on-chip optical communication, processing and sensing. These findings provide an alternative approach for the engineering of novel Si-compatible broadband sources that leverage the control of radiative transitions in hyperbolic metamaterials and the flexibility of the widespread Si platform.
Chapter 7

7 Broadband Electro-Absorption Modulators Design Based on Epsilon-Near-Zero (ENZ) Indium Tin Oxide

In this chapter, a high-confinement silicon (Si) electro-absorption modulator based on slot waveguide with epsilon-near-zero (ENZ) indium tin oxide (ITO) materials is proposed by our collaborator HongWei Zhao in Prof. Jonathan Klamkin’s group. The ITO modulator utilizes the “epsilon-near-zero” (ENZ) state, which enables a higher extinction ratio. Sections of this Chapter have been adapted from the 2015 IEEE Journal of Quantum Electronics publication titled Broadband Electro-Absorption Modulators Design Based on Epsilon-Near-Zero Indium Tin Oxide [14].

Firstly, I characterize ITO thin films with different carrier concentrations and HongWei designs ITO modulator structure using the experimentally extracted parameters. Then, HongWei investigates both butt coupling and evanescent coupling of the proposed device with conventional Si strip waveguides. In both coupling schemes, the compact electro-absorption modulators designs, with device length \( \leq 1.5\mu\text{m} \), demonstrate a high extinction ratio over a wide optical bandwidth while maintaining relatively low insertion loss.

7.1 Plasmonic Modulator

Silicon photonics has been used in single-chip, CMOS-compatible photonic integrated circuits platform for optical communication applications [121–123]. Low-loss
waveguides, germanium-on-Si photodetectors and Si optical modulator have been realized based on silicon photonics platform. Conventionally, Mach-Zehnder modulators have been widely used but suffer from problems including low efficiency, high insertion loss, and large footprint [124]. Even though the footprint can be significantly reduced by utilizing a micro-ring resonator, these devices exhibit narrow optical bandwidth and are thermally unstable [125]. Electro-absorption modulators based on tensile strained Ge quantum wells or bulk Ge/Si materials are promising, but it requires sophisticated epitaxial growth [126,127]. Metal-Insulator-Metal (MIM) based plasmonic modulator has also been proposed to manipulate light on subwavelength scale, but such devices suffer from limited propagation length due to large losses associated with metal layers.

In recent years, in order to overcome limited propagation length and higher loss of plasmonic modulator, CMOS-compatible transparent conducting oxides (TCOs) [e.g. indium tin oxide (ITO), aluminum zinc oxide (AZO), and gallium zinc oxide (GZO)] based modulator have emerged [128–132]. It utilizes metal-oxide-semiconductor (MOS) stack on top of silicon waveguide to form hybrid-plasmonic modulator. By using TCOs as functional switching part in the MOS stack, the dielectric permittivity of TCOs can be tuned by controlling its carrier density through applied electric field at the TCO/oxide interface (i.e. electron-accumulation layer). Its modulation speed is solely limited by RC delay. Lu et al. has reported a numerical study of aluminum-doped zinc oxide (AZO) slot waveguide. The simulation shows 3.7 dB modulation depth, and 0.82 dB insertion loss with device length of 0.25 µm [128]. Vasudev et al. proposed electro-absorption modulator with "epsilon-near-zero" ITO that shows a 3 dB extinction ratio with a 27-µm
long device at the wavelength of $1.55 \mu m$ [133]. In their work, the ITO layer along with a thin HfO$_2$ are deposited on top of a silicon strip waveguide, which provides a small optical confinement inside the active ITO material thus limits the device performance.

Figure 7.1 shows the layout of MOS based electro-optical modulator [134]. By applying an electric bias between metal and silicon layers, an accumulation layer is formed between ITO/SiO$_2$ interface. Hence, the carrier density of ITO can be modulated by changing the electric bias, thus inducing effective change of its index from dielectric to quasi-metallic. Several electro-optical modulators based on ITO MOS structures have been reported [135,136].

**Figure 7.1:** Design of compact hybrid-plasmonic electro-optical modulator. This structure comprises a MOS stack of ITO-SiO$_2$-metal. (a) Accumulation layer is formed at ITO/SiO$_2$ interface with applied electric field. (b) Schematics of RC-delay limited electro-optical modulator. (c) SEM image of fabricated MOS based electro-optical modulator [132].

### 7.2 Material Synthesis and Characterization

The permittivity of the ITO films is described by the Drude-Sommerfeld model, as discussed in Chapter 2.
\[ \varepsilon = \varepsilon_r + j\varepsilon_i = \varepsilon_\infty - \frac{\omega_p^2}{\omega(\omega+j\gamma)} \]  

(7.1)

Where the plasma frequency, \( \omega_p \), is given by \( \omega_p^2 = \frac{N e^2}{\epsilon_0 m^*} \), \( \varepsilon_\infty \) is the high frequency permittivity, \( \gamma \) is the electron scattering rate, \( N \) is the free-carrier concentration in the material, and \( m^* \) is the effective mass of the electron. According to Equation 7.1, the permittivity of ITO can be tuned by actively changing the carrier concentration. With such an ITO layer embedded in a dielectric waveguide, the light absorption will be modulated accordingly. ITO samples were prepared by radio-frequency magnetron sputtering (Denton Discovery 18) on Si substrates from an ITO (99.99%) disc target of four inches in diameter. The ITO target power was 200 W, and post-deposition annealing treatments were applied to tune the optical dispersion of the films. The permittivity was directly measured using spectroscopic ellipsometry (Woollam VASE). The measured wavelength dependent permittivity of ITO with different carrier concentrations (extracted from the measured plasma frequency), are shown in Figure 7.2. Form \( N_1 \) to \( N_4 \), the ENZ wavelengths, where \( \varepsilon_r = 0 \), are 1920 nm, 1550 nm, 1390 nm and 1260 nm, respectively. With an appropriate bias voltage to increase the carrier concentration from \( N_1 \) to \( N_3 \), the magnitude of the permittivity is changed by a factor of \( |\varepsilon_3 / \varepsilon_1| = 0.8 \) for a wavelength of 1.55 \( \mu m \). at the wavelength of 1.31 \( \mu m \), for an increase in carrier concentration from \( N_1 \) to \( N_4 \), the magnitude is changed by the ratio \( |\varepsilon_4 / \varepsilon_1| = 0.29 \).
Figure 7.2: The dielectric permittivity of ITO with different carrier concentrations ($N_1 = 1.78 \times 10^{21} \text{cm}^{-3}$, $N_2 = 2.69 \times 10^{21} \text{cm}^{-3}$, $N_3 = 3.37 \times 10^{21} \text{cm}^{-3}$ and $N_4 = 3.69 \times 10^{21} \text{cm}^{-3}$), measured by spectroscopic ellipsometry [14].

7.3 Mode Analysis and Modulator Design

Figure 7.3(a) shows a cross-section schematic of the proposed slot-waveguide modulator based on ITO. The structure consists of a Si strip waveguide (of thickness $t_1 = 220 \text{ nm}$) on a buried oxide layer, an active ITO layer ($t_{ITO} = 10 \text{ nm}$), two thin silicon dioxide ($\text{SiO}_2$) buffer layers ($t_b = 10 \text{ nm}$) and a poly-Si capping layer ($t_2 = 160 \text{ nm}$). The width of the modulator is 500 nm. The optical intensity of the TM modes is well confined in the slot, which effectively enhances the overlap of the optical modes and the ITO active medium. A voltage applied across the doped Si and the ITO layer tunes the permittivity of the ITO layer by carrier accumulation at the ITO/buffer layer interface, thereby modulating the optical loss of the modulator structure. We assume the thickness of the carrier concentration layer at the ITO/$\text{SiO}_2$ interface is 5 nm, therefore the
permittivity of the ITO layer beyond the accumulation layer will not be tuned by the voltage.

Figure 7.3: (a) Schematic of the modulator structure, the profiles of fundamental TM mode at $\lambda=1310$ nm at different carrier concentrations. (b) The absorption loss of modulator for different carrier concentrations based on 2D FDTD mode solver analysis [14].

The optical loss of the fundamental TM mode ($\alpha_m$) of the slot-waveguide modulator is primarily due to free-carrier absorption in the active ITO layer. This loss can
be approximated by the product of the optical mode confinement factor (Γ) and the material absorption of the bulk ITO (α_b):

\[ \alpha_m = \Gamma \cdot \alpha_b \]  \hspace{1cm} (7.2)

Where \( \alpha_b = 2k_0 \cdot \text{Im}[\varepsilon^{1/2}] \). The confinement factor, \( \Gamma \), depends on \( |\varepsilon| \) and the waveguide structure (the active layer thickness, the buffer material and thickness) [133]. As the permittivity is tuned to induce absorption modulation, both \( \Gamma \) and \( \alpha_b \) are altered. A smaller \( |\varepsilon| \) can lead to an enhancement of the electric field (\( E \)) magnitude confined in the ITO layer due to the continuity of the normal component of the electric displacement field (\( D = \varepsilon E \)). Therefore, it is important to engineer the ENZ condition so that a minimum \( |\varepsilon| \) is achieved for a state with high optical loss. As shown in Figure 7.3(a), the electrical intensity of the fundamental TM mode is confined in the \( \text{SiO}_2/\text{ITO}/\text{SiO}_2 \) slot when \( N_1 = 1.78 \times 10^{21} \text{cm}^{-3} \), resulting in a small absorption loss (0.6 dB/\( \mu \text{m}^{-1} \)) at the wavelength of 1.31 \( \mu \text{m} \). When the carrier concentration is tuned to be \( N_4 = 3.69 \times 10^{21} \text{cm}^{-3} \), the \( \varepsilon_r \) of the ITO is near zero. The electrical intensity is mostly confined only in the ENZ ITO material, thus a high absorption loss (9.8 dB/\( \mu \text{m}^{-1} \)) is obtained at this state.

Utilizing the measured permittivity results of the ITO films, a 2D mode solver was employed to simulate the optical loss of the fundamental TM mode (TM\(_0\)) of the modulator. Figure 7.3(b) shows the optical loss of the TM\(_0\) mode of the slot-waveguide structure with ITO carrier concentration \( N_1 = 1.78 \times 10^{21} \text{cm}^{-3} \), \( N_2 = 2.69 \times 10^{21} \text{cm}^{-3} \), \( N_3 = 3.37 \times 10^{21} \text{cm}^{-3} \) and \( N_4 = 3.69 \times 10^{21} \text{cm}^{-3} \). Over the entire optical
fiber communications band, the mode absorption loss \((\alpha_m)\) is fairly low for a carrier concentration of \(N_1\), and is relatively high for carrier concentrations of \(N_2\), \(N_3\), and \(N_4\). Therefore, we define the state with carrier concentration \(N_1\) as the ON state. As shown in Figure 7.3(b), the maximum optical loss for \(N_2\), \(N_3\), and \(N_4\) are achieved at 1.58 \(\mu\)m, 1.42 \(\mu\)m, and 1.29 \(\mu\)m, respectively. Therefore we can optimize the OFF state of the modulator for different wavelengths of operation. The performance of the electro-absorption modulator is then determined from the ratio of the optical loss in the ON state and OFF state where:

\[
\alpha_{ON} = \alpha_m(N_1)
\]

\[
\Delta \alpha = \alpha_m(N_i) - \alpha_m(N_1) \quad (i = 2, 3, 4)
\]

(7.3) \hspace{1cm} (7.4)

For the slot-waveguide structure, \(\Gamma\) depends on the buffer layer thickness and its refractive index. Therefore, we have evaluated the performance of the modulator with two different process compatible buffer materials, SiO\(_2\) and silicon nitride (Si\(_3\)N\(_4\)), and two different buffer thicknesses, 10 nm and 7 nm. The corresponding \(\alpha_{ON}\) and \(\Delta \alpha\) are plotted in Figure 7.4. Generally, with the same thickness, the structure with the Si\(_3\)N\(_4\) buffer shows higher \(\alpha_{ON}\) as well as higher \(\Delta \alpha\). For a given buffer material, the 10-nm thickness shows lower \(\alpha_{ON}\) and lower \(\Delta \alpha\). The modulator with 10-nm thick SiO\(_2\) buffers demonstrates the minimum \(\alpha_{ON}\), which is only 0.55 dB\(\mu\)m\(^{-1}\) at wavelength of 1.31 \(\mu\)m, and 1.68 dB\(\mu\)m\(^{-1}\) at the wavelength of 1.55 \(\mu\)m. The maximum \(\Delta \alpha\) is achieved with 7-nm thick Si\(_3\)N\(_4\) buffers: 15.9 dB\(\mu\)m\(^{-1}\) at 1.31 \(\mu\)m (for carrier concentration increase from \(N_1\) to \(N_4\)) and 8.9 dB\(\mu\)m\(^{-1}\) at 1.55 \(\mu\)m (for carrier concentration increased from \(N_1\) to \(N_2\)).
For a specific application and wavelength of interest, several parameters such as the carrier concentration for the OFF state, and the material and thickness of the dielectric buffers should be selected accordingly. For instance, if the target operating wavelength is 1.31 $\mu$m, a modulator with 7-nm thick Si$_3$N$_4$ buffers and carrier concentration tuning from $N_1$ to $N_4$ would be preferred. These conditions enable a maximum $\Delta \alpha$ while $\alpha_{ON}$ is only 0.9 dB$\mu$m$^{-1}$ at this wavelength. If the modulator is designed to work at the wavelength of 1.55 $\mu$m, then maintaining a low $\alpha_{ON}$ is an important consideration since the absorption loss increases for increasing wavelength.

**Figure 7.4:** Modulator performance with different buffer materials and thickness [14].
7.4 Integration of Slot-Waveguide Modulator with Si Strip Waveguides

In this section, we discuss two ways to integrate the ITO modulator with conventional Si strip waveguides. First, HongWei proposes a butt-coupled scheme with polarization rotators connecting the TE-loaded Si waveguide and the TM-mode slot-waveguide modulator (1-µm device length) section. This scheme works well for a wide optical band: from 1.28 µm to 1.60 µm by choosing suitable carrier concentrations. Second, the evanescent-coupling scheme has also been presented at the wavelength of 1.31 µm.

7.4.1 Butt-Coupled Scheme

For on-chip optical interconnects, the compact and efficient electro-absorption modulators proposed should be integrated with Si strip waveguides in the Si-on-Insulator (SOI) platform since these waveguides exhibit low propagation and bend loss. Based on the mode analysis presented, the optical loss of the TM₀ mode of the slot-waveguide modulator is efficiently modulated by tuning the carrier concentration in the active ITO layer. Therefore, it is critical to optimize the coupling efficiency (η) from the Si strip waveguides to the TM₀ mode of the slot-waveguide modulator.

Figure 7.5 shows a 3D schematic diagram of the proposed slot-waveguide modulator butt coupled to low-loss Si strip waveguides. Here, the dielectric buffers are 7-nm thick Si₃N₄ layers. In such a 3D structure, the total propagation loss depends on the modal loss (αₘ) and the coupling efficiency (η) from the strip waveguide to the slot.
waveguide. The modulator performance is given by the insertion loss (IL) and the extinction ratio (ER) where:

\[
IL = 10 \log \left( \frac{I_{in}}{I_{out(N_1)}} \right)
\] (7.5)

\[
ER = 10 \log \left( \frac{I_{out(N_i)}}{I_{out(N_i)}} \right) (i = 2, 3, 4)
\] (7.6)

Figure 7.5: 3D schematics of slot-waveguide modulator (with 7 nm thick Si₃N₄ buffers) butt coupled to Si strip waveguides [14].

At the input, the horizontal Si strip waveguide is 220 nm thick and 380 nm wide, which is designed for single mode operation. The fundamental TE mode (TE₀) is launched in the horizontal Si strip waveguide, then converted to the TM₀ mode through a polarization rotator [137]. The polarization rotator consists of two vertically stacked linear width tapers (9 µm in length). The end of the polarization rotator connects to a vertical strip waveguide (380 nm thick and 220 nm wide). The resulting TM₀ mode of the vertical strip waveguide is then coupled to the TM₀ mode of the slot-waveguide modulator. The
modulator length $L_m$ is only 1 $\mu$m for this design. Following propagation in the modulation region, the light is coupled to the TM$_0$ mode of a strip waveguide and then rotated back to the TE$_0$ strip mode through the output rotator.

A 3D FDTD simulation tool was employed to further evaluate the performance of the ITO-based Si modulators. Figure 7.6 shows the modulator performance when the carrier concentration is tuned from $N_1$ to $N_2$, $N_j$ to $N_3$ and $N_j$ to $N_4$, respectively. For a wavelength range from 1.53 $\mu$m to 1.64 $\mu$m, the ER is greater than 5 dB while the IL is less than 2.7 dB when the carrier concentration tuned from $N_1$ to $N_2$. At 1.55 $\mu$m, the ER and IL are 5.8 dB and 2.0 dB, respectively. If the 7-nm thick Si$_3$N$_4$ buffers are replaced by 10-nm thick SiO$_2$ buffers, the IL can be further reduced. When the carrier concentration is tuned from $N_j$ to $N_4$, the ER is greater than 6.0 dB while the IL is less than 1.3 dB for a wavelength range from 1.25 $\mu$m to 1.42 $\mu$m. Especially, at 1.31-$\mu$m wavelength, the IL is 0.93 dB, only slightly higher than the mode absorption loss $\alpha_m(N_1) = 0.86$ dB. This indicates an efficient coupling from the TE$_0$ mode of the Si strip waveguide to the TM$_0$ mode of the slot waveguide modulator for the ON state. The corresponding ER here is 11.75 dB.
Figure 7.6: The modulator performance of the butt-coupled structure (1.0 µm modulator length) with the carrier concentration tuned from $N_1$ to $N_2$, $N_1$ to $N_3$ and $N_1$ to $N_4$, respectively [14].

Figure 7.7 shows the light propagation from the front end to the back end (including the polarization rotators on both sides) at 1.31 µm with carrier concentrations of $N_1$ to $N_4$, respectively. The normalized transmissions at the output are 81.4 % in Figure 7.7(a) and 5.4 % in Figure 7.7(b).
Figure 7.7: The light propagation from the front to the back end in butt-coupled scheme at $\lambda=1.31$ $\mu$m when (a) $N = N_1$; (b) $N = N_4$ [14].

Figure 7.8: 3D schematics of slot-waveguide modulator (with 7 nm thick SiO$_2$ buffers) evanescently coupled to Si strip waveguides [14].
7.4.2 Evanescent-Coupled Scheme

In the previous section, by incorporating polarization rotators, the slot-waveguide modulator can be connected with TE-loaded Si strip waveguides and other passive/active components that function for TE-polarized light. Alternatively, the slot-waveguide modulator can be evanescently coupled to TM loaded Si strip waveguides, therefore we investigate such a structure as well. As shown in Figure 7.8, the ITO-based modulator layers are positioned on top of a Si strip waveguide (220 nm thick and 400 nm wide). Compared with butt coupling evanescent coupling is less efficient, however, it simplifies the fabrication.

Figure 7.9 shows the performance of the slot-waveguide modulator with 10-nm thick SiO$_2$ buffers as a function of the device length ($L_m$) for a wavelength of 1.31 $\mu$m. In this case, the carrier concentration is tuned from $N_1$ to $N_4$. When the device length increases, the ER increases gradually while the IL experiences periodic variation. To achieve a high ER and a low IL, we set $L_m = 1.5$ $\mu$m. For a wavelength of 1.31 $\mu$m, the ER and IL are 10.18 dB and 1.4 dB, respectively. The performance of the modulator with $L_m = 1.5$ $\mu$m over a broad wavelength range is shown in Figure 7.9(b). The ER is greater than 6.0 dB while the IL is less than 1.7 dB for a wavelength range from 1.25 $\mu$m to 1.39 $\mu$m.
Figure 7.9: (a) Extinction ratio (ER) and insertion loss (IL) versus modulator length ($L_m$) at 1.31 µm wavelength in the evanescent-coupled scheme; (b) modulator performance with $L_m = 1.5$ µm for wavelength range from 1.25 µm to 1.65 µm [14].

7.5 Conclusion

Compact broadband modulator designs based on engineered ENZ ITO materials has been presented. By electrically controlling the carrier concentration of the active ITO layer, the optical loss of the slot-waveguide modulator is modulated with high efficiency.
Using a butt-coupled scheme (1.0-µm device length), the modulator demonstrates a high ER of greater than 6.0 dB while the IL is less than 1.3 dB for a wavelength range from 1.25 µm to 1.42 µm. By adjusting the carrier concentration, broadband modulation can also be achieved around a 1.55-µm wavelength. In the case of the evanescent coupling (1.5-µm device length), for a wavelength range from 1.25 µm to 1.39 µm, an ER greater than 6.0 dB is achieved while the IL is less than 1.7 dB.
Chapter 8

8 Indium Tin Oxide for Mid-Infrared Plasmonics

This chapter provides the optical characterization of ITO thin films using Spectroscopic Ellipsometry (SE) and Fourier Transform Infrared Spectroscopy (FTIR) for mid-infrared applications. Firstly, in collaboration with Prof. NanFang Yu’s group, the optical dispersion of as deposited and annealed thin films are characterized by FTIR to obtain its optical permittivity, \( \lambda_{\text{ENZ}} \) and optical loss \( \varepsilon_2 \). Subsequently, we fabricate 2D-periodic ITO arrays and characterize the plasmonic properties of the materials. Tunable plasmonic resonance in mid-infrared from 4.0 \( \mu \text{m} \) to 10 \( \mu \text{m} \) has been observed. The tunability and control of the optical properties in mid-infrared of ITO can be used to tailor optical resonant responses for various device applications to plasmonics, metamaterials and transformation-optics.

8.1 Optical Properties of ITO in Mid-Infrared

In the present work, by using post-deposition annealing treatments in oxygen (O2) atmosphere, we characterize the dispersion properties of fabricated ITO thin films using FTIR, and demonstrate that the tunability of optical properties of ITO with significant reduction of optical losses can be expanded to mid-infrared spectral ranges.

ITO thin films were deposited using RF magnetron sputtering in a Denton Discovery 18 confocal-target system, with ITO (99.99% purity) target in Ar atmosphere at room temperature. The sputtering power for ITO thin films varied from 40 W to 200 W.
The base pressure was $1.0 \times 10^{-7}$ Torr and the Ar gas flow was kept at 12 sccm. The thicknesses of all fabricated ITOs were fixed at 209 nm, irrespective of the deposition conditions.

We performed the post-deposition annealing using a Mellen thermal furnace, which resulted in a large tunability of the measured optical dispersion for ITO in the near-IR and mid-IR spectrum. After annealing, the film thickness remains almost constant (thickness error: ± 5 nm), as independently verified by spectroscopic ellipsometry and surface profilometry.). Annealing processes were performed in Ar and O$_2$ gas atmosphere at temperatures between 350 and 750 °C for 1 hour. Table 8.1 summarizes the sputtering power and annealing conditions of all fabricated ITO samples.

**Table 8.1:** Sputtering and annealing parameters of ITO thin films on Si substrate

<table>
<thead>
<tr>
<th>Sputtering Power (W)</th>
<th>Thickness(nm)</th>
<th>$\lambda_{\text{ENZ}}$ (nm)</th>
<th>$\varepsilon_2 @ \lambda_{\text{ENZ}}$</th>
<th>Annealing Temp. (°C)</th>
<th>Annealing gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>209</td>
<td>1830</td>
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<td>209</td>
<td>1150</td>
<td>0.33</td>
<td>750</td>
<td>Ar</td>
</tr>
<tr>
<td>200</td>
<td>209</td>
<td>3001</td>
<td>1.47</td>
<td>750</td>
<td>O$_2$</td>
</tr>
<tr>
<td>100</td>
<td>209</td>
<td>3230</td>
<td>1.18</td>
<td>750</td>
<td>O$_2$</td>
</tr>
<tr>
<td>80</td>
<td>209</td>
<td>3430</td>
<td>2.05</td>
<td>750</td>
<td>O$_2$</td>
</tr>
<tr>
<td>60</td>
<td>209</td>
<td>3700</td>
<td>2.94</td>
<td>750</td>
<td>O$_2$</td>
</tr>
<tr>
<td>40</td>
<td>209</td>
<td>4270</td>
<td>2.96</td>
<td>750</td>
<td>O$_2$</td>
</tr>
</tbody>
</table>

In collaboration with Prof. NanFang Yu’s group, the infrared optical properties of the ITO films were obtained using Fourier Transform Infrared Spectroscopy (FTIR). The FTIR instrument is a Bruker Scientific Vertex 70v model, covering a wavelength range from 1 μm to 16 μm with a combination of a TE cooled InGaAs detector (1 μm to 2.5 μm) and a liquid nitrogen cooled MCT detector (2.5 μm to 16 μm). Light sources were a
Tungsten lamp for the near infrared, and a globar for the mid infrared. The reflectance of the thin films was measured using a silver mirror as a reference. The measured data were fitted with a combination of a thin film interference model and a Drude model (see Equation 2.25 in Chapter 2) [138]. The film thickness was taken from spectroscopic ellipsometry measurements as 209 nm, leaving the fitting parameters to be (1) the background permittivity, $\epsilon_\infty$, (2) the plasma frequency, $\omega_p$ and (3) the scattering rate, $\gamma$. Figure 8.1 shows an example of fitting using reflectance measurements of FTIR.

![Reflectance measurements and fits](image)

**Figure 8.1:** Example of FTIR reflectance measurement (solid) and fit (dashed), for the as deposited sample (grey), 350 °C 1h annealed sample (red), 550 °C 1h annealed sample (green) and 750 °C 1h annealed sample (blue).
8.1.1 Effect of Sputtering Power

In order to investigate the effect of the sputtering power for the tunability of dispersion properties of ITO thin films in mid-IR spectrum, we measured optical permittivity for ITO samples deposited at different sputtering power. Upon deposition, all ITO samples were annealed at 750 °C in O₂ for 1 hour. The sputtering conditions are listed in Table 8.2.

Table 8.2: Effect of sputtering power of ITO thin films on Si substrate

<table>
<thead>
<tr>
<th>Sputtering Power (W)</th>
<th>Thickness(nm)</th>
<th>λ₁ENZ (nm)</th>
<th>ε₂ @ λ₁ENZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>209</td>
<td>3001</td>
<td>1.47</td>
</tr>
<tr>
<td>100</td>
<td>209</td>
<td>3230</td>
<td>1.18</td>
</tr>
<tr>
<td>80</td>
<td>209</td>
<td>3430</td>
<td>2.05</td>
</tr>
<tr>
<td>60</td>
<td>209</td>
<td>3700</td>
<td>2.94</td>
</tr>
<tr>
<td>40</td>
<td>209</td>
<td>4270</td>
<td>2.96</td>
</tr>
</tbody>
</table>

Figure 8.2 shows the experimentally measured optical permittivity data for ITO samples annealed in O₂, which display the effect of sputtering power on the real (ε₁) and imaginary (ε₂) parts of the complex permittivity. The conduction mechanism was explained in our previous paper [60], the annealing of ITO in O₂ will strongly increase O₂ vacancies and reduce free-carriers inside the ITO, which moves the λ₁ENZ from near-IR (when annealed in Ar/N₂) into mid-IR spectrum. Our data demonstrates that the λ₁ENZ of all the ITO samples can be largely tuned in the range of mid-IR (3000 – 4300 nm for ITO) depending on the sputtering power conditions. As the sputtering power is decreased, the λ₁ENZ is increased, which provides another tool to tailor the dispersion properties of ITO in mid-IR beyond annealing in O₂.
Figure 8.2: Real (a) and imaginary (b) part of permittivity of ITO samples on Si substrate sputtered at different power: 200 W (green), 100 W (blue), 80 W (cyan), 60 W (magenta), 40 W (dark yellow). All samples are annealed at 750 °C in O₂ for 1h.

Figure 8.3 presents the $\lambda_{\text{ENZ}}$ and $\varepsilon_2$ as a function of sputtering power for ITO samples, it clearly visualizes the effect of the post-deposition annealing on the thin film optical properties. The data indicates that as the sputtering power is increased, both the $\lambda_{\text{ENZ}}$ and $\varepsilon_2$ are decreased. We note that the imaginary part of the permittivity $\varepsilon_2$ assumes at $\lambda_{\text{ENZ}}$ values in the range 1.18–2.96 for ITO (see Table 8.1), which is larger than the $\varepsilon_2$ of ITO samples annealed in Ar/N₂. We ascribe this difference to the improved crystallinity degree of the ITO samples annealed Ar/N₂ compared with those annealed in O₂.
Figure 8.3: $\lambda_{\text{ENZ}}$ (black curves on left axis) and $\varepsilon_2$ (blue curves on right axis) as a function of the sputtering power. All samples are annealed at 750 °C in O$_2$ for 1h.

8.1.2 Tunability of $\lambda_{\text{ENZ}}$ of ITO from Near-IR to Mid-IR Spectral Ranges

In order to demonstrate the tunability of $\lambda_{\text{ENZ}}$ of ITO thin films from near-IR to mid-IR spectrum, the permittivity of ITO samples deposited and annealed at different sputtering power and ambient gas are shown in Figure 8.4. These samples feature a $\lambda_{\text{ENZ}}$ in the range between 1150 nm to 4270 nm, demonstrating that the ENZ condition can be largely tailored with post-deposition annealing process. In particular, for as deposited and 750 °C Ar 1h annealed samples, they show ENZ condition in near-IR range (1150–2000 nm). On the contrary, samples annealed at 750°C O$_2$ 1h with different sputtering powers demonstrate ENZ condition in mid-IR range ((3000 – 4300 nm). All the sputtering and annealing conditions of ITO samples in Figure 8.4 can be found in Table 8.1.
Figure 8.4: Real (a) and imaginary (b) part of permittivity of ITO samples on Si substrate with annealing conditions and sputtering powers: As Dep_200 W (black), 750 °C Ar 1h_200 W (red), 750 °C O₂ 1h_200 W (green), 750 °C O₂ 1h_100 W (blue), 750 °C O₂ 1h_80 W (cyan), 750 °C O₂ 1h_60 W (magenta), 750 °C O₂ 1h_40 W (dark yellow).

8.1.3 Effect of Annealing Temperature

ITO has been demonstrated to have tunable optical dispersion by controlled deposition temperature [15,19]. In order to understand the role of annealing temperature to engineer optical dispersion properties of ITO, we performed post-deposition annealing in O₂ atmosphere between 350 and 750 °C for 1 hour, as detailed in Table 8.3.
Table 8.3: Effect of annealing temperature of ITO thin films on Si substrate

<table>
<thead>
<tr>
<th>Sputtering Power (W)</th>
<th>Thickness(nm)</th>
<th>$\lambda_{ENZ}$ (nm)</th>
<th>$\varepsilon_2 @ \lambda_{ENZ}$</th>
<th>Annealing Temp. (°C)</th>
<th>Annealing gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>209</td>
<td>1866</td>
<td>0.61</td>
<td>As Dep</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>209</td>
<td>2505</td>
<td>4.11</td>
<td>350</td>
<td>O$_2$</td>
</tr>
<tr>
<td>100</td>
<td>209</td>
<td>2742</td>
<td>4</td>
<td>550</td>
<td>O$_2$</td>
</tr>
<tr>
<td>100</td>
<td>209</td>
<td>3230</td>
<td>1.18</td>
<td>750</td>
<td>O$_2$</td>
</tr>
</tbody>
</table>

Figure 8.5 shows the permittivity of ITO samples annealed at different temperature. As annealing temperature increases, the optical loss decreases, as shown in Figure 8.6.

Figure 8.5: Real (a) and imaginary (b) part of permittivity of ITO samples on Si substrate annealed at different temperatures: As deposited (black), 350 °C (red), 550 °C (green), 750 °C (blue). The annealing is performed in O$_2$ atmosphere for 1h for all samples.
8.2 Tunable Plasmonic Resonances of Nanopatterned ITO Arrays

In order to quantify the plasmonic resonances of our fabricated ITO samples in mid-IR, we fabricated 2D ITO disk arrays of 300 nm height with diameter range of 1–5 µm using the process flow described in Figure 8.7. Electron Beam Lithography (EBL, Zeiss SUPRA 40VP) was used to write periodic patterns and developed in MIBK. 30 nm Cr served as etch mask for ITO and was deposited using electron beam evaporator (CHA industries), then followed by lift-off process in acetone. ITO thin films were etched using reaction ion etching (RIE, Plasma-Therm, model 790) in a mixture of CH₄/H₂. After that, the ITO disk arrays were annealed at 750 °C in O₂ for 1 hour. Figure 8.8 presents the representative SEM images of the fabricated ITO arrays with diameter 2–5 µm.
Figure 8.7: Schematic configuration of process flow to fabricate ITO periodic arrays.
Figure 8.8: Representative SEM image of fabricated ITO disk arrays with diameter (a) 2 µm, (b) 3 µm, (c) 4 µm, (d) 5 µm.

Using FDTD simulation (Lumerical), we investigate the effects of disk diameter on the scattering efficiencies of ITO arrays. In the calculation, the optical properties of ITO were obtained from the fitting of FTIR measurement, as described earlier. As shown in Figure 8.9, as the disk diameter increases, the resonance red shifts from 4.0 to 10 µm and becomes stronger because it supports higher-order plasmonic modes.
Figure 8.9: FDTD calculations of the scattering of ITO disk arrays as a function of disk diameter: 1 µm (black), 2 µm (red), 3 µm (green), 4 µm (blue), 5 µm (cyan). All the ITO arrays have disk height as 300 nm.

The plasmonic resonances will be experimentally verified by the transmission measurements with FTIR, we will update the measurement results very soon.

8.3 Conclusion

In this chapter, we have demonstrated tunable optical properties of ITO thin films in mid-infrared spectrum. By fabricating 2D periodic arrays of ITO, we demonstrated wide tuning of plasmonic resonances of ITO nanostructure from 4 to 10 µm. The proposed ITO platform shows the critical importance of annealing treatments to provide wide tunability of optical properties of ITO from near-IR to mid-IR, thus providing promising method for the control and engineering of Si-based tunable plasmonic and metamaterial devices in the infrared spectrum.
Chapter 9

9 Broadband Absorption Enhancement of Light Using Non-Radiative Anapole Modes

This chapter provides preliminary results of novel approach to achieve absorption enhancement in Si nanostructures through engineering of anapole modes. My colleague Ren Wang designed and I experimentally demonstrated an anapole-driven Si nanostructures with strong suppression of far-field scattering close to the wavelength of anapole mode excitation.

We are currently working on realization of active anapole structures based on active light emitting materials (i.e. Er doped Silicon dioxide). Potential applications in active invisibility structures based on the cancellation of scattering will become possible.

9.1 Anapole Mode

The existence of non-radiating sources (NRs) has puzzled physicists since the foundation of electromagnetic theory [139]. During the past few years, people have shown the non-radiating anapole modes in dielectric nanoparticles [140–142]. In electromagnetics, circulating magnetic field produces toroidal dipole moment. Under certain conditions, anapole modes can be created by exciting electric dipole out-of-phase with toroidal dipole moment. This anapole mode is essentially radiationless because of the destructive interference between electric dipole and toroidal dipole moment, due to their similarity of far-field scattering patterns. Therefore, anapole modes will strongly
reduce the intensity of scattered field outside the structures for particular incident wave. Figure 9.1 shows the anapole mode excitation with the electric and toroidal dipole moment.

**Figure 9.1:** The excitation of anapole mode. Anapole mode is excited when the toroidal dipole moment destructively interferes with electric dipole moment which leads to the cancellation of far-field with non-zero near-field excitation [140].

Electric dipole moment inside a nanoparticle \( P_{\text{car}} \) can be represented by integration of induced current over the volume (in Cartesian coordinates)

\[
P_{\text{car}} = \frac{i}{\omega} \int J dr
\] (9.1)

\[
J = -i\omega\varepsilon_0[n^2 - 1]E
\] (9.2)

Where \( J \) is the current distribution function. By expressing the scattering coefficients with Cartesian multiple coefficients [140], we can calculate the toroidal dipole moment via induced current as

\[
T_{\text{car}} = \frac{1}{10c} \int [(r \cdot J)r - 2r^2 J] dr
\] (9.3)
And the total contribution to the far-field scattering is given by

\[ E_{sca} \sim \frac{k^2}{4\pi\varepsilon_0} \{ \mathbf{n} \times \mathbf{P}_{\text{car}} \times \mathbf{n} + i k \mathbf{n} \times \mathbf{T}_{\text{car}} \times \mathbf{n} \} \] (9.4)

Therefore, the far-field radiation will vanish when the contributions of electric and toroidal dipole to the far-field scattering are out of phase, this condition of destructive interference for radiationless anapole mode is given by

\[ \mathbf{P}_{\text{car}} = -i k \mathbf{T}_{\text{car}} \] (9.5)

Figure 9.2 shows the experimental demonstration of anapole mode in silicon nanodisk. Figure 9.2(a) demonstrates the red shift of scattering dip (anapole mode) as a function of increased diameter of silicon nanodisk. It clearly demonstrates that by properly designing the silicon nanodisks, the anapole mode can be excited in the visible spectrum. Figure 9.2(c) illustrates the near-field distribution of electric field around the nanodisk using near-field scanning optical microscope (NSOM). When wavelength approaches 640nm, which is the anapole mode excitation wavelength, the near-field hotspot starts to appear in the middle of the disk. Besides, its intensity increases with wavelength. The result has good agreement with theoretical results, as shown in Figure 9.2(c) middle and bottom rows.
Figure 9.2: Experimental demonstration of anapole mode in silicon nanodisks. (a) Dark-field scattering measurement of silicon nanodisks with different diameter from 160 to 310 nm. (b) Representative SEM images of nanodisks with diameter of 310 nm (top) and 285 nm (bottom). (c) Near-field electric field distribution around the nanodisks with diameter 310 nm. Top row represents the experimental results of NSOM measurements, where middle and bottom rows show the simulated transverse electric and magnetic near-field, respectively. (d) Schematic setup of NSOM measurement [140].

The anapole mode offers new revenues for engineering invisibility for lossless dielectric nanostructures. In particular, it is physically different from traditional scattering cancellation mechanism based on the destructive interference between the electric and magnetic dipole moments which cancel one another exactly only in the backward direction [143–145].
9.2 Engineer Si Nanodisks for Broadband Absorption Rate Enhancement of Light

In the following, I will provide preliminary results of anapole-mode excitation in silicon nanodisks for far-field scattering cancellation in the visible from 500 to 700 nm. With Ren Wang’s design, we will further explore anapole-induced absorption rate enhancement.

Silicon nanodisk arrays of 60 nm height with diameter of 300 nm, 380 nm and 430 nm on fused silica substrate have been fabricated using the process flow described in Figure 9.3. The 60 nm amorphous silicon layer (α-Si:H) is deposited with reactive sputtering of Si target in hydrogen and argon atmosphere. Table 9.1 lists the sputtering parameter of hydrogenated silicon thin film.

**Table 9.1**: Sputtering deposition parameter for α-Si:H films.

<table>
<thead>
<tr>
<th>Film</th>
<th>Gas 1 / Gas 2</th>
<th>Flow Rate 1/ Flow Rate 2 (sccm)</th>
<th>Cathode Power (W)</th>
<th>Base Pressure (Torr)</th>
<th>Deposition rate (nm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Si:H</td>
<td>H₂/Ar</td>
<td>3.2/10.1</td>
<td>350 (Si)</td>
<td>1.8E-07</td>
<td>14.5</td>
</tr>
</tbody>
</table>

Figure 9.3 illustrates the fabrication process of silicon nanodisks. Electron Beam Lithography (EBL, Zeiss SUPRA 40VP) was used to write periodic patterns and developed in MIBK. 30 nm Cr served as etch mask for Si and was deposited using electron beam evaporator (CHA industries), then followed by lift-off process in acetone. Si thin films were etched using reaction ion etching (RIE, Plasma-Therm, model 790) in a
mixture of SF$_6$/O$_2$. Figure 9.4 presents the SEM image of the fabricated silicon nanodisk arrays with different diameters.

**Figure 9.3:** Schematic configuration of process flow to fabricate silicon nanodisk arrays.
Figure 9.4: Representative SEM image of fabricated silicon nanodisk arrays with diameter of (a) 300 nm, (b) 380 nm and (c) 430 nm, respectively.

Figure 9.5 shows the dark-field scattering measurements of the silicon disks of 60 nm height with different diameter. For disk arrays with diameter of 300 nm, 380 nm and 430 nm, the scattering dip appears around 540 nm, 620 nm, and 680 nm, respectively. The experimental results match very well with our theoretical predictions, as shown by Ren Wang in Ref [146].
Figure 9.5: Dark-field scattering experiment of fabricated silicon nanodisks. The observed scattering dip around 540 nm, 620 nm, and 680 nm correspond to the disk arrays with diameter of 300 nm (black), 380 nm (red) and 430 nm (green), respectively.

For the next step, we will quantify the absorption rate enhancement of silicon nanodisks that are induced by anapole mode. The absorption rate enhancement is calculated by comparing the power absorbed by nanodisk array to that absorbed by a thin-film with the same thickness and excited volume [146]. Figure 9.6 shows the peak of absorption rate enhancement as a function of diameter D and height H of silicon nanodisks. Additionally, by combining active light emitting material (i.e. Er doped SiO₂) with high index dielectric, we will demonstrate the active anapole structures to enhance light-matter interaction.
Figure 9.6: (a) and (b) are the peaks of the anapole-induced absorption rate enhancement as a function of diameter D and height H of silicon nanodisks [146].

9.3 Conclusion

In this chapter, we have demonstrated the tunable anapole mode excitation, which is introduced by destructive interference of electric and toroidal dipole moment. Our preliminary results have shown scattering dip of silicon nanodisks arrays in the visible, which can be tuned by changing the aspect ratio of silicon nanodisks. In the near future, we will investigate the absorption rate enhancement of silicon nanodisks and active structures to demonstrate the absorption can be enhanced by anapole mode in the visible and near-IR spectrum. The proposed method of radiationless nanostructures can be potentially used for the engineering of broadband semiconductor photodetectors driven by the controllable anapole responses in high-index dielectrics.
Chapter 10

10 Conclusions and Future Prospective

10.1 Summary of Results

In this thesis, alternative plasmonic materials of transparent nitrides and conductive oxides (TNCOs) including ITO, AZO and TiN, have been presented as a novel material platform with enhanced light-matter interaction over a broad spectral range for Si-compatible plasmonics and metamaterials applications. By using post-deposition annealing treatments, a systematic study of these material demonstrates the tunability of the optical and structural properties of ITO, AZO and TiN thin films, with significant reduction of their optical losses. In addition, the optical bandgap and grain size can be tuned very reliably based on the thermal annealing. In collaboration with Prof. NanFang Yu’s group, tunable optical properties of ITO thin films in mid-infrared spectrum have been recently demonstrated by thermal annealing in oxygen atmosphere. In particular, we have also observed plasmonic resonances of ITO nanostructures from 4 to 10 µm. The powerful material platform based on ITO can provide many opportunities for engineering Si-compatible tunable plasmonic and metamaterial devices in the infrared spectrum.

The modulation of optical properties in these material results in the modulation of epsilon-near-zero (ENZ) condition of ITO in the near-infrared, TiN in the visible spectra. ENZ condition with optical loss $\varepsilon^\prime < 1$ creates enhanced internal electric field at the ENZ wavelength, which will enhance the harmonic generation in these materials. It is shown
that SHG process in ITO is enhanced by approximately 4 orders of magnitude at ENZ. ITO nanolayers generate a comparable SHG signal with that of a crystalline quartz plate of thickness 0.5 mm, but TiN shows a much lower SHG intensity. Additionally, at ENZ wavelength, ITO nanolayers feature a THG efficiency that is ~600 times larger than that of crystalline Si.

In collaboration with Prof. Minoru Fujii’s group, the application of the TNCOs platform to hyperbolic metamaterial (HMM) has been investigated. It is shown that the TiN-based HMMs are a promising platform for LDOS engineering to enhance light-matter interactions in the visible spectrum. We experimentally performed wavelength dependent PL intensity and lifetime spectroscopy to demonstrate up to 1.6-times enhanced decay rate of QDs emission when coupled to the high-k modes of HMM compared with identical QDs deposited on a silica glass sample. Additionally, we have artificially reduced the optical loss in the TiN layers by a factor of two and theoretically show that no appreciable enhancement is noticed in the ratio of total decay rate, which highlights the point that high-k modes extraction in HMM is critical in order to greatly enhance light emission intensity.

In collaboration with Prof. Jonathan Klamkin’s group, the application of the TNCOs platform to electro-optical modulator has been numerically investigated. Compact broadband modulator based on ITO materials has been presented. Both butt coupling and evanescent coupling of the modulator have been investigated with high ER (>6.0 dB) and relatively low IL (<1.7 dB) over broadband spectra range in near-IR.

Lastly, silicon nanodisk arrays with different diameter have been fabricated and
experimentally demonstrated to achieve tunable anapole mode excitation in the visible spectrum. We will investigate its absorption spectra to demonstrate anapole-induced broadband absorption enhancement of light. This platform is promising for applications of broadband semiconductor photodetector driven by controllable anapole responses.

10.2 Future Prospective

This research presented in this thesis has revealed a number of results that can be potentially applied to future nanophotonic devices. Much of the efforts of this thesis focused on the engineering of material and nanostructures for the engineering of light-matter interaction to enhance LODS or absorption rate. In Chapter 6, we investigate the light emission of silicon quantum dots on TiN-based hyperbolic metamaterial (HMM). This device requires spinning coating of an active layer of quantum dots, which means the light emission is from the top of the device. Based on the findings of this thesis, an active hyperbolic metamaterial (HMM) of ITO/Er:ZnO has been proposed to potentially enhance light emission at 1.55 µm and nonlinearity in the visible spectrum. The effective permittivity of this HMM is shown in Figure 6.8 of Chapter 6.

Additionally, my colleague Ren Wang has demonstrated wide and controllable wavelength tunability of anapole-driven absorption enhancement in nanodisks. By systematically studying the effects of width D and height H of the nanostructures on the absorption enhancement spectra, we can achieve the excitation of anapole modes with optimal absorption enhancement [146].
As shown in Chapter 9, we have demonstrated tunable anapole mode excitation due to the destructive interference of electric and toroidal dipole moment. The next logical step of research is to study the absorption spectra of the fabricated silicon nanodisks. The engineering of the silicon nanostructures could be extended to other high index materials and geometries, which eventually allows the broadband absorption rate enhancement in the visible and near-infrared spectra.
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