Preparation, Characterization and Applications of ITO Thin Film
——Material Study of Plasmonic EOM Modulators

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B.S. in Opto-Electronics Information Science and Engineering, June 2017, Anhui University

A Thesis submitted to

The Faculty of
The School of Engineering and Applied Science of the George Washington University
in partial fulfillment of the requirements for the degree of Master of Science

August 31th, 2019

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Acknowledgments

The researcher would like to express the deepest gratitude to the following for their help.

First and foremost, I would like to thank my thesis advisor, Prof. Volker J. Sorger of the Department of Electrical and Computer engineering at George Washington University. I am extremely grateful for his expert and valuable constant guidance throughout the project.

I would like to acknowledge Prof. Gina Adam and Prof. Ahmadi at George Washington University as the committee members of this thesis, and I am gratefully indebted to them for their very comprehensive comments and supports on this thesis.

I would also like to thank researchers in Sorger group especially Dr. Mohammad Tahersima, Dr. Mario Miscuglio, and Doctoral candidate Zhizheng Ma. They help me a lot during my thesis project.

Finally, I must express my very profound gratitude to my boyfriend, Jiawei. He is supportive of my research and life. When I didn’t have a driving license, he drove me to NIST and wait for me on the campus for 4-5 hours.

I’m so lucky to have you!

Thank you very much!
Abstract of Thesis

Preparation, Characterization, and Applications of ITO Thin Film
——Material Study of Plasmonic EOM Modulators

The class of transparent conductive oxides includes the material indium tin oxide (ITO) which has become a widely used material in modern every-day life. It is currently used in touch screens of smartphones and watches, but also used as an optically transparent low electrically resistive contact in the photovoltaics industry. This thesis focused on i) a general overview of ITO characteristics and ii) potential applications of ITO thin films. iii) the main contributions are the development of a comprehensive method and repeatable ellipsometry analysis were reported based on carefully calibrating the sputtering deposition process and rapid thermal annealing process. iv) Future directions are discussed in the last chapter. The thesis is structured in the following way;

An introduction to the topic which provides the context to my research is described in chapter 1. In chapter 2, the preparation and characterization of ITO thin film were shown together with the literature review result. Besides, the useful tool, spectroscopic ellipsometry was introduced in chapter 3. In chapter 4, the theory and idea of the Nano-optics circuit were discussed. Some further applications and ideas were shown in chapter 5. Finally, there comes the conclusion.
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Chapter 1 – Study of ITO EOM

Electro-optic modulator (EOM) is a device that is used to modulate a light beam propagating either in free space or in an optical waveguide with an electrical gate as an input (e.g. for data). An EOM usually consists of tunable materials altering propagating waves, such as the silicon waveguide in Silicon photonic integrated circuits (Si-PIC). However, silicon cannot realize proper light emitters and modulators due to the indirect nature of its bandgap. Light-Matter Interaction (LMI) is weak and different EO-active material can be heterogeneously integrated into Si-PIC technology. The latter method using ITO as tunable material is followed in this thesis. To increase the light-matter interaction the EOM are usually based on plasmonic interactions with tunable materials. Plasmons are highly confined, to a subwavelength scale, electromagnetic modes which travel along the surface of a dielectric-metal interface and therefore very sensitive to an active change of environment, such as carrier density or phase change modulation of the surrounding dielectric. However, plasmonic also has high optical losses thus limiting the applications to hybridization where active devices are plasmonic but passive structures (e.g. routers, spitters, waveguides, etc.) are silicon or silicon nitride (SiN) based [1].
Chapter 2: Material Study of ITO

Indium tin oxide is one of most popular tuning materials in EOM modulator. So, it is vital to study and control the quality of ITO thin films. We initially focus on defining a consistent and tunable ITO deposition process using RF sputtering and post-annealing process using Rapid Thermal Annealing System, which allow for adjusting the electrical and optical properties of the film. The purpose of our study is ultimately to engineer ITO film properties to deliver well-defined control over critical parameters for obtaining films that could enhance fabricated device properties.

2.1 Introduction of Indium Tin Oxide

2.1.1 Composition and Structure of ITO

![Figure 1 Structure of ITO](image)

Indium tin oxide (ITO) is a ternary composition of indium, tin, and oxygen in varying proportions. Depending on the oxygen content, it can either be described as a ceramic or alloy. Indium tin oxide is typically encountered as an oxygen saturated composition with a formulation of 74% In, 18% O2, and 8% Sn by weight. Indium oxide and ITO has cubic
bixbyite structure which is also known as the c-type rare earth sesquioxide structure. The structure can be amorphous, crystalline or mixed, depending on the deposition temperature and atmosphere.

2.1.2 ITO Bandgap

The electronic band structure is one of the most critical factors for understanding the unique interplay between optical absorption and conductivity in TCO materials.

Fan and Goodenough [2] proposed a schematic energy band model (Fig 2) for pure and doped In$_2$O$_3$ by electron spectroscopy for chemical analysis (ESCA) measurements. The energy band model developed by Fan and Good still represents a good starting description for describing the electronic structure of both the pure and doped materials. The direct semiconductor bandgap is 3.75 eV.
Hamberg et al. [3] have reported the results of the analysis of the optical and transport properties for a one-dimensional model of the electronic structure, with effective masses taken from measurements (Fig 3). When tin doping is carried out, the valence band is shifted upwards, and the conduction band is moved downwards. One of the reasons is that the shapes of the valence and the conduction bands may not be accounted for by the same effective masses as in the undoped material.

2.2 Preparation of ITO Thin Film

2.2.1 Introduction of Preparation Methods

Many technologies can be used to prepare the ITO thin film, sputter, chemical vapor deposition (CVD), evaporation and sol-gel [4,5].

ITO films can be Sputtered using three ways, DC-Sputter, RF-Sputter, and Ion Beam Sputter. The most popular method in the industry is using DC-Magnetron Sputter. However, when preparing thin films with low conductivities, many positive ions will be produced within the chamber, accumulate on the surface of the thin film and prevent thin films from growing. This problem can be avoided by using RF-Sputter. Ion Beam
Sputter has the advantage that it can deposit dense and smooth films without radiation damage, but with less contamination by operating at the lower pressure. However low growth rate and high cost prevent it from being used in industry.

Evaporation can be subdivided into Vacuum Evaporation, Electron Beam Evaporation, Ion-Beam-Assisted Deposition, and Pulsed Laser Deposition. Electron-Beam Physical Vapor Deposition (EBPVD) is a form of physical vapor deposition in which a target anode is bombarded with an electron beam given off by a charged tungsten filament under high vacuum. The electron beam causes atoms from the target to transform into the gaseous phase. These atoms then precipitate into solid form, coating everything in the vacuum chamber (within line of sight) with a thin layer of the anode material. The material utilization efficiency of electron beam evaporation is high relative to other methods, and the process offers structural and morphological control of films. When electron beam evaporator is equipped with ion sources, it is called ion-beam assisted deposition. Ion bombardment also increases the density of the film, changes the grain size and modifies amorphous films to polycrystalline films. Low-energy ions are used for the surfaces of semiconductor films. It’s pulsed laser deposition when a high-power pulsed laser beam is focused inside a vacuum evaporation chamber to strike a target of the material that is to be deposited.

Chemical vapor deposition (CVD) technique has many merits. For an instance, it does not require high vacuum, and it is easier to produce films over large areas. However, this technology has a few drawbacks. For example, the CVD precursors can be highly toxic (Ni (CO)₄), explosive (B₂H₆), or corrosive (SiCl₄) and the byproducts of CVD reactions can be hazardous (CO, H₂, or HF).[6]
The sol-gel process is a method for producing solid materials from small molecules. The method is used for the fabrication of metal oxides. The process involves the conversion of monomers into a colloidal solution (sol) that acts as the precursor for an integrated network (or gel) of either discrete particles or network polymers.

For our case, as-deposited ITO thin films were of low conductivities. Although DC sputter is the most popular way in the industry, the positive ions will accumulate on the surface of target when using it to prepare ITO thin film. So, RF sputter was used to prepare ITO thin films in our study. What’s more, RF sputter is one of the most economical ways to prepare high-quality thin films.

2.2.2 Preparation Details

![Figure 4 Image of the 1x1 cm² ITO films on SiO₂/Si substrate for different oxygen flowrate, before and after annealing.](image)

In our experiments, films are deposited on 1x1 cm² Si/SiO₂ substrates (Fig. 4), utilizing reactive RF sputtering (Denton Vacuum Discovery 550 Sputtering System). As reported by [7], temperature sensitive substrate is the prerequisite of preparation of high-quality ITO thin film, so we choose Si/SiO₂ substrates. ITO sputtering targets for my case consist of 10% SnO₂ to 90% In₂O₃ by weight. Four replicated samples are produced for
each oxygen flow-rate condition (0, 5, 10, 20, 30 sccm) and sputtering time (500,1000,1500,2000 s), for 40 sccm Argon flow rate (50 sccm Ar flow rate study is presented in SI). For each condition, represented by a single data-point, this study is repeated four times for statistical purpose and repeatability. Conducive to promote crystallinity and study the charge carrier activation mechanisms, a sub-group of deposited films are subjected to a thermal treatment at 350°C in the inert atmosphere (a mixture of H₂ and N₂) for 15 minutes. The recipe was chosen because that annealing the films under N₂/H₂ mixture is found to improve the transmittance of the films up to an annealing temperature of 300°C and a drastic decrease in transmittance was observed at 400°C. However, air annealing at 400°C improved the transmission of the darkened film because of the incorporation of oxygen into the ITO polycrystalline film.[8]

2.3 ITO Characterization

For assessing the quality of our process and determining its reliability, direct and indirect measurements are used as rigorous cross-validation tools (Fig 5). The resistivity of the thin film is indirectly obtained via ellipsometry and, directly, through 4-probe station (Four Dimensions 280DI) and Hall effect measurement system (HMS-5500). Hall measurement also gives information on the carrier type (n-doped) and concentration as well as mobility.
KLA-Tencor Profilometer

The first tool that should be used is *KLA-Tencor* Profilometer. Profilometry is used to measure the height difference with a sensitive needle. So, a small part of chip was covered with tape before deposition, and after deposition the tapes were removed so that we can have height difference. And the height difference is the thin film thickness It’s vital for us to measure the thickness using profilometer first since only when thickness is known can Hall measurement system work.

Ecopia Hall Effect Measurement System

The basic physical principle underlying the Hall effect is the Lorentz force which is a combination of two separate forces: the electric force and the magnetic force. The sheet resistance $R_s$, mobility $\mu$ and the sheet carrier density $N_s$ can be determined using Hall effect measurement system. The bulk electrical resistivity $\rho$ can be calculated using $\rho = R_s \times t$. Where $t$ represents thicknesses of the thin films.

J. A. Woollam M-2000 DI Spectroscopic Ellipsometer
Then using the thicknesses from profilometer and bulk resistivity as reference values, measure and analyze the characteristics by using Spectroscopic Ellipsometry. Thickness, resistivity, scattering time and optical constants can be extracted from the fitting result. Since ellipsometry data fitting is a complex task, I will explain in detail in the next part. Mobility and carrier concentration can be obtained from resistivity $\rho$ and scattering time $\tau$ by using $\mu = \tau q/m^*$ and $N = m^*/\tau q^2$. $m^*$ is effective mass. Here $m^*$ is 0.35 m.

2.4 Results Analysis

2.4.1 Effects of the Oxygen flow rate and thermal treatment on dispersion and absorption

![Graph showing the effects of Oxygen flowrate and deposition heating treatment on ITO film thickness](image)

*Figure 6* Oxygen flowrate and post deposition heating treatment effects: ITO film Thickness as function of the Oxygen flowrate (0,5,10,20,30) for different deposition time (500s, 1000s, 1500s, 2000s).

To establish baselines control over ITO films, we aim to understand the thickness-related or time-related influence on material parameters. We find that thinner films are obtained for higher oxygen concentration as a result of reduced sputter material deposition rate (Fig. 6). Quantitatively we find that for a fixed deposition time the ITO film thickness decreases by $t = ae^{bx}$ being $t$ the thickness, $a=509$nm the y-intercept and $b=0.047$scm, 1 the decay constant (RMS 97%). The deposition conditions, summarized in the method
section, enable precise control of the thickness, with repeatability within 10 nm (see SI) for the thickest film deposition (0 sccm, 2000 s). The films show a maximum roughness of around 3 nm. Thicknesses measured using ellipsometry and profilometer has a consistent level within a 95% agreement. No substantial variation of the thickness is observed for thermally treated and untreated samples. In the interest of simplicity, we focus our discussion for the remainder of this paper on films evaporated for 1500 s. Nevertheless, our findings are equally valid for other deposition times, which are summarized in the supplementary information, where an overall summary is provided.

The stark contrast in obtainable ITO material properties discussed further below can even be seen visually (Fig. 4) and hints towards a strong ability to engineer the material properties. Four replicated samples are deposited for each experimental condition (i.e., Oxygen flowrate, deposition time). The repeatability of the process is ensured by the concurrent low variability of the thickness and optical constants (well below 5%). A qualitative analysis on the film colorizations actually provides first insights on the doping type of the material [9]; a tendency to a brown color (Fig. 4 i,ii) indicates a higher Sn-In doping while a green-yellow colorization corresponds to the presence of oxygen vacancies (Fig. 4 iv,v).

Figure 7 Spectral behavior of the real (black) and imaginary (red) part of the refractive index of films sputtered using different oxygen flowrate and effects of the post-deposition heat treatment process (dashed lines)
However, in order to quantitative analyze the optical constants, spectroscopic ellipsometry studies are reported in Fig. 7 for 1500 s deposition time. Beside 0 sccm, it appears that ITO films not subjected to an annealing process, films are predominantly not absorptive above 500 nm. In the wavelength range from 500 nm to 1680 nm, values of extinction coefficient are, in fact, below hundredths. A major effect attributed to thermal annealing is the activation of the carrier [10], which is responsible for the optical absorption. Because of that, films with 0 sccm (Fig 7 i) appear to be strongly absorptive in this region, due to the higher oxygen vacancies and consequent higher carrier concentration. Films deposited with this oxygen flowrate could be embedded in NIR metamaterial perfect absorbers [11] or as a building block in metasurface [12]. Consistently, for all the different oxygen flowrates tested, after annealing, ITO thin films appear to be more absorptive. The value of $\kappa$, the imaginary part of the refractive index, of annealed samples substantially increases as a function of the wavelength in the IR region, compared to not-annealed samples, thus producing a shift in the plasma frequency and an overall variation of the refractive index, being $n(\omega)$ and $\kappa(\omega)$ in Kramer-Kronig relation. The filling of the oxygen vacancies at 5 and 10 sccm (Fig 7 iii-iv) induces the sputtered ITO films to show the lowest $\kappa$ among the other groups and, they might be a viable option for low-loss conductive transport layer in optoelectronic devices or as a sensing platform [13]. For higher oxygen flow rate (20, 30 sccm) the films become more absorptive in the IR.
Figure 8 The complex refractive index and resistivity depth profile a-c Real (left y-axis) and imaginary part (right y-axis) of the refractive index spectral response investigated by ellipsometry. Different curves (red to green) represent different depth profile

Post-deposition annealing profoundly changes the structural and optical properties of ITO thin films, as previously discussed in the optical characterization. This process represents an effective way to promote crystallinity and modify the physical features of ITO films, such as roughness, but also it contributes to drastically altering the carrier distribution.

Our ellipsometry studies use a fitting approach which contemporary minimize the error (RMS) computed in the fitting and considered a graded variation of optical/electrical parameters. This approach is essential for quantitatively pointing out that the resistivity, for annealed samples, is a function of the film depth as discussed below, which confirms that the thermal processes can favor the redistribution of carriers, homogenizing them throughout the sample, as illustrated by Buchanan et al. [14]. Another effect, which can be ascribed to thermal heating, is related to optical absorption. Moreover, for oxygen flowrates above 0 sccm, the absorption significantly increases in the IR region. As an obvious influence on the resistivity, this type of films displays an exponential decaying
resistivity within the film depth (Fig. 8 b-c). Interestingly, the absorption and resistivity trend for film sputtered with a null Oxygen flow-rate (Fig. 8 a) have the highest value confined in the film core, and it is significantly smaller (1 order of magnitude) than highest resistivity recorded for the ITO film sputtered at 10 sccm oxygen flow-rate [15]. We can speculate that thin film of 10 sccm oxygen flow rate has the thickest (approx. 600 nm) among the studied groups and the annealing time is not sufficient to completely redistribute the carriers throughout its depth.

![Figure 9](image)

*Figure 9* Resistivity measured with different techniques (Ellipsometer, 4-Probe and Hall Measurement) as a function of the Oxygen flowrate thermally untreated (a) and treated (b) samples. Mobility and carrier concentration for treated and untreated samples validated through direct (Hall Effect) and indirect (Ellipsometer) measurement.

2.4.2 Effects of the Oxygen flow rate and thermal treatment on the electrical properties

Electrical properties, carrier concentration and mobility of ITO have been found previously to vary for different deposition techniques, but also different process
conditions for the deposition such as power, oxygen flow, and annealing temperature [10, 16, 17, 18]. In this section, we focus on the impact of the oxygen flowrate and thermal post-deposition treatment on the electrical properties of ITO. Figure 9 summarizes the electrical properties of the ITO films sputtered with different oxygen flow rate (the 1500s), for thermally untreated (a) and treated samples (b), measured using three different methods, i.e., Hall measurement, 4-probe, and spectroscopic ellipsometry. It is worth noticing that the measurements (direct and indirect) are in quasi-perfect agreement (>90% correlation). Only in case of the 4-probe measurement of non-annealed samples, the resistivity has a different trend. This has to be attributed to the instability of the contacts-film junction, due to the rather soft upper layer of the samples, which are not thermally treated. It is evident that not annealed thin films are less conductive, displaying one order of magnitude higher resistivity (a-b), an overall slightly higher mobility (c), lower carrier concentration (d) compared to the annealed samples. Therefore, annealed films are generally more suitable for the implementation of capacitive sensors, and promote the absorption in the optical telecom wavelength, enabling the fabrication of efficient electro-absorption modulators based on ITO films. As previously mentioned, for ITO, electrons are the majority carriers, and they are originating mainly from the doping donor Sn and oxygen vacancies. For our sputtering conditions, we show that increasing oxygen flowrate produces an initial increase of the resistivity, induced by a lower carrier concentration. The lower carrier concentration is reached for Oxygen flow rate within 5-20 sccm. Therefore, increasing the oxygen flow rate replenishes the oxygen vacancies up to 10 sccm. For higher oxygen flowrates the sputtered particles from the target cannot
oxidize sufficiently. Hence the ITO films are anoxic, and sub-oxides such as InOx and SnOx are present in the films [19].

For annealed sample both the carrier concentrations and overall mobility decrease by increasing oxygen flow rates [20]. This can be attributed to the concurrent filling of the oxygen vacancies and the deactivation of the Sn donor by the overflowing oxygen. It can be said that 10 sccm of oxygen flow rate can be an optimum flow rate for obtaining high resistivity (low carrier concentration) and as previously shown low absorption.

The mobility on the effect of annealing is within the same order of magnitude, although the trend is rather different. The mobility in non-annealed films is higher for lower carrier concentrations, while the opposite trend is visible for annealed films.

Figure 10 Experimental (interpolated) data of ITO film loss and ENZ-position as a function of oxygen process flowrate. a) Measured ENZ wavelength as a function of the deposition time and oxygen flow-rate b) Measured damping ($\varepsilon''$) function of the deposition time and oxygen flow-rate c) Scattering Time $\tau$ as function of the deposition time and oxygen flowrate. d) ENZ wavelength (black solid line, left-axis) as function of the Oxygen flowrate and corresponding damping ($\varepsilon''$) (red solid line, right-axis) for ITO film deposited for 1500 s.
Afterwards, for annealed samples, we investigate the variation of spectral response of the real part of the permittivity ($\varepsilon'$) for different oxygen flow-rate and deposition time. The x-intercept of the curve reveals the wavelength where $\varepsilon_1 = 0$. The trend of ENZ position as function of the oxygen flowrate is strongly inherited from the resistivity response (Fig. 10 b), displaying a 96% cross correlation. This is further illustrated by the difference scattering time $t$ which has complementary trend with respect to the $\varepsilon''$ as a function of deposition time and oxygen flowrate. Our ability, to methodically tune ENZ position for a broad range of wavelength spacing from the E- to L-bands (1400 to 2500 nm) offers to engineer precise ENZ-based devices at targeted wavelengths (Fig.10 d). Considering 1500s deposition time, the longest wavelength reached is for 10 sccm, which corresponds to lower absorption, as well as higher resistivity. As a matter of fact, this further degree of freedom in setting the ENZ position could for instance enable the realization of sub-wavelength electro-optic modulators based on ITO films embedded in integrated photonics circuit [20]. Through this study, RF-sputtered ITO films with crafty ENZ positioning in the optical telecom range can be deposited, thus lowering the energy required to switch from ENZ (high absorption) and epsilon-far-from-zero (low absorption) [21].
2.4.3 Effects of Rapid Thermal Annealing Time

Five samples were prepared at the same time (1000s) and recipe (40 Argon, 40 Oxygen, 100 bias voltages). But they were annealed for different time (0, 1, 5, 30, 35 mins) using Rapid Thermal Annealing System. As shown in Fig.11, ENZ point move towards the short wavelength with increasing annealing time but the $k$ at ENZ wavelength remains almost the same. They are 0.728, 0.726, 0.788 and 0.778.
Chapter 3: Spectroscopic Ellipsometry

3.1 Spectroscopic Ellipsometry Introduction

Spectroscopic ellipsometry (SE) [22] is commonly used to measure the optical constants of thin films and bulk materials using dispersion relation.

Light is an electromagnetic wave and has the electric and magnetic field components. In the figure 12, only the electric field component is shown. The light waves are polarized and be classified into p- and s- polarization in this measurement process. \( \theta \) is the incident angle. As shown in figure 12, the direction of P-polarizations is parallel to the incident plane, while that of the s-polarization is perpendicular. The incident s-polarization waves and p-polarization waves are in the same phase. However, the reflected waves have a phase difference because of their different Fresnel reflection coefficients. Ellipsometry measures the amplitude ratio, phi, and the phase difference, delta, between S- and P-polarizations. Then physical models and mathematical models are applied to analyze and abstract parameters from the measured data.
Generally speaking, if the wavelength range of interest is located in the transparent region which \( k = 0 \), the Cauchy model is the best choice to fit the data while the wavelength range of interest is located in absorptive wavelength region or both transparent and absorptive wavelength region, either the \( b \)-spline model or GenOsc model can be used. \( B \)-spline model is a mathematical model while the GenOsc model is a physical one. \( B \)-spline is suitable for a quick fit. And Kramer-Kronig relation can be applied to restrict the fitting result and make it more reasonable. However, ITO has complicated optical behaviors. The window of transparency in ITO extends from the bandgap on the UV end to the plasma-absorption frequency at the IR end. In the ultraviolet region, the absorption
is strong due to excitations across the fundamental bandgap. It is common to use the GenOsc model for ITO thin film characterization. GenOsc model is a combination of different oscillators and oscillators describe how dipoles behaviors affect the dielectric function. Usually, for ITO thin film, the GenOsc model consists of Drude oscillator, which is used to describe the free-carrier absorption, Lorentz oscillators used to describe the optical functions near the bandgap energy or Gaussian oscillators used to describe the effects of electronic transitions.

3.2 Ellipsometry Fitting Method

In the following section, I provide an accurate description of the software (CompleteEASE) and process used for fitting the ellipsometry data using a model (Cauchy, Drude, Lorentz, and Cody-Lorentz), suitable algorithm and figure of merit, which allowed to determine fundamental parameters of the investigated film, optimizing the goodness of the fit.
Here we choose the recipe that ellipsometry can measure the result and collect the data from three different angles: 65°, 70°, 75°. After placing the target in the middle of the stage, click measure. The ellipsometry will do stage alignment and data acquisition automatically.

The interface of analysis is consisting of four parts: the raw data, the fitting model, fitting result and output figures. After acquiring the data of Psi and Delta, we start our analysis from building physical model of the sample. ITO thin films of our study were prepared on commercial SiO2/Si substrates. The thicknesses of SiO2 were about 320nm. The thickness of ITO thin film shown in fig. is about 280nm which is obtained from profilometer.

✓ Cauchy model

In our work, we first use the Cauchy model to fit the transparent region and find out the accurate thickness of the thin film according to the following:
\[ n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} \]

where A, B, C are adjusted to fit the refractive index for this region. Since the Cauchy model is not constrained by the Kramer-Kronig relation, the un-physical shape should be neglected. The advantage of the Cauchy model is that it has only 2-3 free parameters are needed to achieve a proper fitting result with low Mean Square Error (MSE). But the limitation is that it can only be used in the transparent region.

✓ B-spline

Then we used the B-spline to expand the fitting wavelength. This kind of fitting was unrelated to the physics involved and exploited an \( n \)th degree polynomial:

\[ P_m(x) = a_m x^m + a_{m-1} x^{(m-1)} + \cdots + a_1 x + a_0 \]

B-spline is designed to best match the known shape of an optical constant in the whole range, while the Cauchy model can only describe the transparent region. Comparing with GenOsc model, B-spline can describe more optical function shapes.

✓ GenOsc model

![Figure 16 Analysis model](image)

For addressing peaks in absorption at resonant frequencies where the material is most likely to absorb the incoming light of that wavelength, we use Genosc model. In GenOsc
model, oscillator equations are used to describe resonant absorption. The permittivity function can be described as:

$$\Im(\varepsilon(f)) = \Im(\varepsilon_{\text{Drude}}) + \Im(\varepsilon_{\text{Lorentz}}) + \Im(\varepsilon_{\text{Cody-Lorentz}})$$

which consists of the summation of the imaginary part of a Drude oscillator function, matching the lower frequency, the Lorentz oscillator function and two Cody Lorentz oscillator functions matching the higher frequency peak.

– Drude oscillator.

Drude oscillator describes the interaction of time-varying electric fields with free carriers—electrons or “holes” [23]—which move freely in conductive materials. The form of the Drude oscillator is that of a Lorentz oscillator (5.17) with zero center energy (no restoring force). The Drude model portion of complex permittivity is:

$$\varepsilon_{\text{Drude, Ellipsometry}} = \frac{\hbar}{\varepsilon_0 \rho (\tau E^2 - i\hbar E)}$$

where \(\hbar\) is the reduced Planck’s constant, \(\varepsilon_0\) is the free space permittivity and \(E\) is light energy.

– Lorentz oscillator.

Lorentz oscillator is characterized by broad absorption, and it is suitable for describing metal. They are used to model excess absorption near the bulk plasma frequency besides the Drude model. The portion of Lorentz oscillator [24] can be described as:

$$\varepsilon_{\text{Lorentz, Ellipsometry}} = A_1 \frac{f_r f_c}{f_c^2 - f^2 - i f_r f}$$

where \(A_1\) is the unitless amplitude of the oscillator, \(f_r\) and \(f_c\) represent the broadening and central frequency of the oscillator.

– Cody-Lorentz oscillator [25]

Both Tauc-Lorentz and Cody-Lorentz can be used to describe UV region of ITO thin film. In this work, we use Cody-Lorentz. The portion of Cody Lorentz oscillator can be described as:

$$\varepsilon_2(E) = \frac{E_1}{E} e^{(E-E_\tau)/E_u}, \quad 0 < E \leq E_\tau$$
\[ \varepsilon_2(E) = G(E)L(E) = \frac{(E - E_g)^2}{(E - E_g)^2 + E_p^2} \frac{AE_0 \Gamma E}{(E^2 - E_0^2)^2 + \gamma^2 E^2}, \quad E > E_t \]

where \( E_1 = E_t G(E_t) L(E_t) \).
Chapter 4: ITO Application: Nano-Optical Circuit

An intriguing field that could greatly benefit from ITO material is metatronics, allowing the implementation of Nano-optical circuit entirely based on ITO film, wisely doped, using suitable process parameters. For illustrating the potentiality of this study, we with this demonstrate the possibility to finely tune RF sputtering parameters to achieve metatronics circuits based on ITO with opportunity tailored permittivity using the previously discussed process parameters. Therefore, we combine experimental data related to ENZ position with numerical approaches (Fig. 16). For a homogeneous thickness of ITO with tailored values of a real and imaginary part of the dielectric constant one can design optical lumped-circuit elements in an integrated system. For instance, using a similar approach proposed by Engheta et al. in [26], we design and analyze a nanophotonic circuit based on ITO film, whose permittivity is a function of the oxygen flowrate used for deposition. It is possible to use a sub-wavelength photonic circuit based on different ITO film, sputtered at different oxygen flowrate, for interacting with a propagating mode. A 1550 nm TE10 mode is launched in a Silicon waveguide with a permittivity of 12. A metatronic circuit entirely composed by ITO films is positioned in the center of the waveguide, in two possible configurations (parallel/series). The thickness, t, of the ITO films, is 50 nm. Thus, a lumped circuit model can be applied, being t << l. In the equivalent circuit, the film with real part of the permittivity (e’) larger than zero acts as a capacitor, whereas the film with the negative real part as an inductor. The films are also characterized by damping (e” > 0) which induces losses, modeled in the lumped model as a resistance. A capacitor-like ITO film can be sputtered adopting a null oxygen flowrate, obtaining an ENZ position shifted
towards red concerning the considered wavelength (1550 nm), while an inductor can be obtained using 20 sccm oxygen flow-rate, resulting into a blue shift of the ENZ position. When the films with $\varepsilon'$ with opposite signs are placed in a parallel configuration, there is a pronounced impedance mismatch, leading to a high reflection coefficient, which translates to a -12 dB transmission of the signal. Contrarily, for films placed in series the imaginary part of the permittivity becomes negligible and only insertion losses are present, achieving a transmission of -4dB.

Figure 17 3D view of the numerical simulation of a metatronics parallel and series setup. A TE10 incident mode is propagating in a waveguide ($e = 12$). Two ITO film in parallel a and series b configuration are placed in between of the waveguide. Colour map of the simulation results for the normalized electric field intensity distributions for the series (a) and parallel (b). The transmission coefficients ($S_{21}$) along with the equivalent circuit model and the process parameters used for obtaining specific permittivity values are reported on the right side.
Chapter 5: Further Directions

5.1 Short-Term Plan

5.1.1 study of ITO material (1.5 version) optimize the characterization of ITO thin film

For my previous study, the microstructures of different ITO thin films have not been studied. The electro-optical properties are a function of the crystallinity of the material. In general, ITO deposited at room temperature is amorphous, and ITO deposited at higher temperatures is crystalline. For our case the as-deposited ITO thin film is thought to be amorphous because of its poor conductivity. For our annealed thin film, gradient structure has been found. As reported by [28], sintering and/or recrystallization took place during annealing. We need to know: i) the difference between the crystalline of the upper layer and that of the bottom layer of thin film; ii) how do heat and H2 contribute to the sintering and/or recrystallization if we study both as deposited and annealed structure. For further discussion, AFM (atom force microscope) can be used to see the roughness and the grain size of the thin film surface. FIB (focus ion beam) can be used to see the cross-section. These experiments can be conducted using the existing thin film. Moreover, transmission line measurement can be used to obtain the contact resistance if needed.

5.1.2 Study of ITO material (2.0 version) Optical Constant of Biased ITO Thin Film

For ITO modulators, the ITO thin films functions as the electro-optical tunable material under bias. To obtain the optical constant of biased ITO thin films, we have an idea that constructs a capacitor structure, applied bias on them using the power supply. It would be convincing for simulating the behavior in the device since the electrons will be distributed
uniformly in the surface of the capacitor, the active part of the modulator. Note that when performing the experiment, the ITO thin film annealing treatment should strictly follow the same process that was used in the device fabrication. For our previous ITO study, the annealing recipe is at 350°C in the atmosphere of H2 and N2. However, sometimes we anneal the ITO thin film at 180°C in air. As reported by A. R. Patel at el. [29], in the thermal oxidation of tin in the air only SnO is formed below 200 °C with SnO2 after that. So, the components of the thin film would be different, and it will result in deviations if the strictly same treatment process cannot be followed. Lastly, we need to make a small voltage source using a power supply and control the voltage precisely.

5.1.3 Nano-Optical Circuit
The next step of the experiment is to inject light in parallel and series ITO thin films and analyze the transmittance. It is easy to measure the transmittance of the series ITO thin film in the free space while it is a challenge to measure parallel ITO thin film. The parallel ITO thin films were prepared using an alignment mask. TE01 mode laser is used as a source. However, the laser spots are too small to be in the right middle manually.
5.1.4 Optical Limiter

Fabricate ITO thin film with ENZ located in the wavelength of 1550nm. According to by M. Zahirul Alam el. [27], ITO thin films have large optical nonlinearity in ENZ region. Then carry out the transmittance measurement. Pulsed laser beam other than the continuous laser beam is used in this experiment to protect the films from overheating. There some concerns about i) high power intensity. Lenses with different magnification are used in the experiment to reduce the size of laser spot and get higher power intensities. However, the exact focus area in the detector is unknown. ii) phenomenon control. Transmittance will gradually flatten with increasing power density. The mechanism behind the phenomenon and the way to control the phenomenon still needs to explore.

5.2 Long-Term Plan

5.2.1 A Cavity-Enhanced ITO-Based ENZ Optical Limiter

ENZ Optical limiter is a device that can constrain the transmission rate of large-scale incident light. Cavity-enhanced one can change the saturate transmission rate of intensive light based on different design.

5.2.2 Optical Antenna

Optical antennas [30] are devices that convert freely propagating optical radiation into localized energy and vice versa. They enable the control and manipulation of optical fields at the nanometer scale and hold promise for enhancing the performance and efficiency of photodetection, light emission, and sensing. Although many of the properties and parameters of optical antennas are similar to their radio wave and microwave counterparts, they have important differences resulting from their small size and the resonant properties of metal nanostructures.
5.2.3 Impedance Measurement and Impedance Match

Impedance match should be taken into consideration in the integrated optical system. Otherwise, the power loss would be remarkable. How to measure the impedance and how to control impedance in the fabrication level are still unknown.
Conclusion:

In this thesis, introduction of EOM and material study of ITO thin films were shown. What’s more, the detailed data analysis process is present and explained. A series of self-consistent methods were developed to characterize the ITO thin films. And these methods can also be applied to other materials, such as monolayer graphene. For two-year research study, I have deep understanding of Nano-photonic devises and learn to use several technologies to deposit, pattern, etch and characterize. What’s more, I learned to run simulations using FDTD and measure the breakdown voltage of Aluminum oxide deposited by Atom Layer Deposition. Those technique abilities are benefit to my future study.
Reference


