Characterization of Inert Gas RF Plasma-Treated Indium Tin Oxide Thin Films Deposited Via Pulsed DC Magnetron Sputtering

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science

By

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY Amber Nicole Reed ENTITLED Characterization of Inert Gas RF Plasma-Treated Indium Tin Oxide Thin Films Deposited Via Pulsed DC Magnetron Sputtering BE ACCEPTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF Master of Science.

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In this work, the effects of a post-deposition RF plasma treatment on indium tin oxide (ITO) thin films prepared with pulsed DC magnetron sputtering in argon were investigated. The parameters of the post-deposition were studied to determine what RF power and gas pressure resulted in the greatest reduction in resistivity in the films while producing the smallest increase in substrate temperature for treatments with both argon and oxygen plasmas. The as-deposited (untreated) films and the treated films were characterized using Raman spectroscopy and X-ray diffraction to determine the effects of the post-deposition treatment on the degree of film crystallization. XPS was used to analyze the chemical composition of the films’ surface. SEM images were taken to observe surface features of the films. The resistivity of the films reached $1.66 \times 10^{-5} \, \Omega \, m$ as-deposited and $6.74 \times 10^{-6} \, \Omega \, m$ after treatment.
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Chapter 1

Introduction

With the advances in electronic devices, there is a demand for thin films that are electrically conductive and optically transparent. There are only a few categories of these materials and one group is the transparent conductive oxides (abbreviated TCO). One of the most common TCOs is indium tin oxide (ITO).

Because of its optical and electrical properties ITO film is commonly used in display applications such as, flat panel displays\(^1\), liquid crystal displays\(^2\), and solar cells\(^3\). ITO also has potential in organic light emitting diodes\(^4\) and antistatic coatings\(^5\). ITO can be used in heat shield applications because of its capability to reflect infrared radiation efficiently\(^6\). Another application for ITO is as a conduction film on aircraft canopies. Canopies need a conductive outer surface to shield the pilot and interior equipment from charge build up without impairing visibility.

ITO is a sesquioxide, a molecule that contains three oxygen atoms bonded to two atoms of another element, in this case two indium atoms. ITO is a vacancy defect oxide, and an n-type degenerate semiconductor with a reported energy gap of 3.5-4.0eV\(^7\). ITO has a melting point of 1800 Kelvin with a density of 1.712*10\(^4\) kg/m\(^3\) at room temperature. The optical transparency and electrical conductivity of ITO varies depending on the deposition process and parameters. Variations in these parameters can affect the crystal structure of the indium oxide and the doping of tin in the film. The
crystal structure of ITO will be discussed in chapter two along with the material’s optical and electrical properties.

ITO thin films can be deposited via a variety of methods such as: magnetron sputtering (RF sputtering\(^8\), DC sputtering\(^9\), and RF-superimposed DC sputtering\(^{10}\)), electron beam evaporation\(^{11}\), spray pyrolysis\(^{12}\) and sol-gel\(^{13}\). Each method has applications for which they are better suited. One of the most common and versatile methods for depositing ITO is magnetron sputtering.

ITO films produced by sputtering tend to be amorphous and require deposition to be done either on a heated substrate\(^{14}\) or with a post-deposition treatment to achieve crystallization. Annealing is a post deposition process that promotes crystallization through a heat treatment of the film\(^{15}\). Another post-deposition process that is being investigated is a plasma treatment\(^{16}\). These treatments will be discussed in more detail in section 2.2.

The purpose of this work was to determine the effects of a post deposition RF plasma treatment on the degree of film crystallization and the electrical resistivity of ITO films grown by pulsed DC magnetron sputtering in argon. Chapter 3 will describe the equipment used, the deposition process, the post-deposition treatment and characterization techniques used to analyze the films. Chapter 4 will contain a discussion of the optimization of the gas pressure and flow rate for the deposition process, as well as the optimization of the post-deposition plasma treatment. Chapter 4 will also discuss the results from the Raman, SEM, XPS, XRD and optical measurements taken for the as-deposited and treated films. Chapter 5 will summarize the results from this work.
Chapter 2

Background

2.1 Properties of ITO

2.1.1 Structure

ITO exists in two different states, amorphous and crystalline. In crystalline ITO, the atoms are arranged in a repeating pattern throughout the film. Amorphous ITO lacks the structural organization found in crystalline ITO. The atoms are arranged in a random fashion. An ITO thin film will be amorphous or crystalline depending on the conditions under which the film was grown or deposited.

Indium oxide crystallizes as a C-Type rare earth sesquioxide structure; commonly referred to as a bixbyite structure. The bixbyite structure is named after the mineral bixbyite, $\beta$-Mn$_2$O$_3$, which is illustrated in Figure 2.1. The bixbyite structure can be described in terms of a Bravais unit cell with a cubic Ia3 space group.

![Figure 2.1: Unit Cell of a Bixbyite Crystal](image)
The following discussion of the bixbyite structure is adapted from *Layered Atom Arrangements in Complex Materials* by Sickafus *et al.*\textsuperscript{19}. The bixbyite structure is described in terms of a modified hexagonal unit cell. This structure adopts a modified MOO layer stacking motif, where M represents a metal cation and the O’s represent oxygen anions. In Figure 2.1 the darker spheres represent the metal atoms while the lighter ones the oxygen. Table 2.1 outlines the atom arrangement in this layer stacking sequence. The first column in the table lists the layer height, $z$, which represents the layer’s location in the unit cell. The last entry in the table (layer 0/12) represents the bottom of the unit cell. The table can then be read upward adding on layers until reaching 12/12; the topmost layer. The number in parentheses in the first column is the fraction of the unit cell that has been described. The A, B, and C registry in the second column refers to lateral translation between adjacent layers. These translations are imposed by nature and repeat themselves every three anion or cation layers, hence the A, B and C notation. The subscripts in this column represent a change in the registry. The third column, Ideal Atom Arrangement, describes the shape of each layer. The fourth column of the table tells the equipoints for the atoms in each layer. The number in parentheses is the number of atoms at each equipoint. The A in this column stands for a metal cation, the O for an oxygen atom and the V for a vacancy.

Figure 2.2 shows the layers described in Table 2.1. The red circles represent the oxygen ions. The red squares represent anion vacancies and the black circles represent the metal cation.
<table>
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<tr>
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<th>Registry (A, B, or C)</th>
<th>Subscripts indicate changes in registry for the wishbone vacancy complexes in the O layers.</th>
<th>Ideal Atom Arrangements</th>
<th>Equipoints for atoms residing in each layer. Subscripts represent the number of atoms (or vacancies) contributed to each hexcell by a given equipoint.</th>
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<tr>
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</tr>
<tr>
<td>$\frac{1}{12}$</td>
<td>$C_1$</td>
<td>$\frac{3}{4}$ wishbone kagome lattice</td>
<td>O(1)$_2$ O(2)$_2$ O(3)$_3$ O(4)$_3$ V(1)$_3$ V(2)$_1$</td>
<td></td>
</tr>
<tr>
<td>$\frac{0}{12}$ ($0$)</td>
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<td></td>
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Table 2.1: Layers of Bixbyite structure from *Layered Atom Arrangements in Complex Materials*\(^{19}\).
Figure 2.2: MOO layer stacking motif for bixbyite structures from *Layered Atom Arrangements in Complex Materials*. 
In the MOO stacking motif vacancies normally form a Star of David kagome lattice; in the bixbyite structure, however, the vacancies take the form of a wishbone of kagome lattice. This wishbone pattern is shown in Figure 2.3.

Figure 2.3: Wishbone pattern of vacancies in oxygen layers of the bixbyite structure from *Layered Atom Arrangements in Complex Materials*.

The unit cell of indium oxide consists of 80 atoms arranged in a layered stack MOO motif described above with indium being the metal cation. The unit cell of an indium oxide crystal has a lattice parameter of 1.0117 nm. In ITO films the crystal is doped with tin atoms. The lattice parameter increases to 1.0125 nm with doping. These dopants are located at oxygen vacancy sites or sites normally occupied by indium atoms. The effects of this dopant on the film’s properties will be discussed in the next section.
Whether an ITO film is crystalline or amorphous depends on several factors. One factor that affects whether an ITO film is crystalline is the film’s thickness\textsuperscript{21}. Films less than 90 nm thick tend to be completely amorphous. Shigesato \textit{et al.} studied the x-ray diffraction peaks of films of varying thickness. In their work films less than 90 nm thick showed no x-ray diffraction (XRD) peaks and they concluded that these films are completely amorphous. Films 170 nm thick showed distinct XRD peaks corresponding to the (222), (400) and (400) planes. This group concluded that films thicker than 90 nm will be partly amorphous and partly crystalline\textsuperscript{21}.

### 2.1.2 Tin Doping

The crystal structure of materials can be modified by doping, in which additional elements are added to the lattice as impurities. These impurities are added to increase the concentration of either electrons or holes in the material to improve one or more of the material’s physical properties such as optical transparency and electrical conductivity. The dopants can be either acceptors or donors based upon their energy levels. Acceptors are able to receive additional electrons from the valence band of the material because the acceptor has energy levels slightly above the material valence band. This results in the dopant becoming a negatively charged ion and creates a hole. Donors become positively charged ions by donating an electron to the conduction band of the material. A donor can do this because it has energy levels slightly below the material’s conduction band.

In ITO the indium oxide is doped with tin. The tin dopants act as electron donors in the film, increasing the electron or free carrier concentration\textsuperscript{22}. The tin donates
electrons to the conduction band of the In$_2$O$_3$ which in ITO is dominated by the In-5s state. The valence band is dominated by the O-2p state\textsuperscript{23}.

2.1.3 Electrical Properties

The resistivities of ITO films vary depending on the deposition process and parameters, and on the film’s thickness. Reported conductivity values in literature for ITO are on the range of 1-3×10$^{-4}$ Ω cm for films approximately 100-200 nm thick deposited via magnetron sputtering. The resistivity, $\rho$, of film can be calculated from the following equation:

$$\rho = R_s \ast t$$

where $R_s$ is the sheet resistance of the film and $t$ is the film’s thickness. Both of these values can be measured in the lab. The sheet resistance of a material is a measure of that material’s resistance to electron flow in two dimensions, or across the surface.

The conductivity of a film is a measure of the ease in which electrons can travel through the film. The conductivity is the inverse of resistivity and can be expressed in terms of the conduction of electrons by

$$\sigma = \frac{1}{\rho} = \frac{N e^2 \tau}{m^*}$$

where $N$ is the electron concentration, $e$ is the elementary charge, $\tau$ is a constant referred to as the collision time and $m^*$ is the effective mass of an electron. The collision time is dependent upon the physical properties of the material.

The electrical conductivity of an ITO film is affected by several factors. These factors can be dependent upon each other. The most important of these factors are:
(1) Film Thickness

The conductivity of a film increases with film thickness. This is in part because of the relationship between film thickness and degree of crystallinity discussed in the previous section.

(2) Relaxation of Structure

Relaxation of structure occurs when there is a realignment of the In-O bonds which generates a locally ordered structure. This locally ordered structure occurs on a smaller scale than a unit cell for an ITO crystal but allows oxygen vacancies to be created. According to Paine et al. the kinetics of this system obey the chemical kinetic law:

\[
\frac{dX_a^r}{dt} = kX_a^m a
\]

Where \( na \) is the order of the reaction, \( k \) is the rate constant and \( X_a^r \), the volume of relaxed amorphous material, is:

\[
X_a^r = 1 - e^{-\frac{L}{t_{oa}}}
\]

with \( t_{oa} \) being the characteristic time for transformation. The resistivity of an amorphous film will vary linearly depending on the degree of relaxation in the film. Paine et al. relates the variation in resistivity as

\[
\rho_{amorphous} = (1 - X_a^r)\rho_{initial \ film} + X_a^r'\rho_{amorph}
\]

where \( \rho_{initial} \) is the resistivity of the as-deposited film and \( \rho_{amorph} \) is the resistivity of the relaxed material. The larger the fraction of material that is relaxed the lower the film’s resistivity.
Carrier Concentration

Free carriers, electrons or holes, in a material carry electrical currents. There are two principal free carrier donors in an ITO film. One free carrier donor is provided by the substitution of four valence tin atoms for indium atoms. The tin substitution increases the carrier concentration by releasing electrons into the conduction band as described in the previous section. The concentration of the dopant is proportional to the concentration of free carriers in the film up to a doping of 5 wt% tin after which the proportionality rate decreases. This occurs because of a reduction in the electron activation efficiency of the tin due to the possible formation of tin based complexes in the material. These complexes can cause an increase in electron scattering in the film which increases the film’s resistivity. For high conductance applications, ITO films must be crystalline because the tin atoms will only contribute to the carrier concentration in a crystalline film.

Free carriers are also supplied by doubly charged oxygen vacancies. These vacancies are located in the kagome wishbone lattices discussed in section 2.1.

Mobility

The mobility of a material is defined as a measure of the ease of movement of an electron through an electric field and can be expressed as

\[ \mu_e = \frac{e \tau_e}{m_e} \]

where \( e \) is the elementary charge, \( \tau_e \) is the lifetime of an electron, and \( m_e \) is the effective mass of an electron. This definition comes from the ratio \( v_e/E \), where \( v_e \) is the electron drift velocity and \( E \) is the electric field strength. The electron drift velocity is expressed as
The mobility of electrons through the film increases after crystallization, due to a decrease in electron scattering\textsuperscript{27}. The electron scattering at the grain boundaries cause a decrease in the electron drift velocity.

(5) Crystallization

The degree of crystallization of a film influences most of the factors discussed in the preceding paragraphs. Crystallization in a film is necessary to activate the tin dopants in the film. The tin in an amorphous ITO film is inactive and does not contribute to increasing the carrier concentration in a film\textsuperscript{28}. An ITO film must be crystalline for the oxygen vacancies to form a wishbone-shaped kagome lattice.

2.1.4 Optical Properties

The optical properties of an ITO film are dependent on many of the same factors that affect the films electrical properties. Deposition method and process parameters, film thickness, degree of crystallinity and dopant concentration can influence a film’s transmittance, reflectance and index of refraction\textsuperscript{29}. ITO has a high optical transparency in the visible regime of the electromagnetic spectrum. The values for transmittance in this region can vary from between 60-90\% depending on other properties of the film. ITO tends to transmit wavelengths in the visible and near-IR regions and reflect wavelengths in the IR region. The transmittance in the visible and near-IR regions is a result of ITO’s wide band gap, while free-electron oscillations cause ITO to reflect wavelengths in the IR region. The transition between regions of transmittance and

\[
\nu_e = -\frac{e \tau_e E}{m_e}.
\]
reflectance occurs at $\lambda_p$, a wavelength called the plasma reflection edge. $\lambda_p$ depends on the concentration of free electrons, $n^3$. The reflectivity of an ITO film is partially dependent on the carrier concentration, $n$. Band to band transitions cause ITO films to absorb wavelengths in the UV region.

Important properties of ITO can be calculated or modeled using data from transmittance and reflectance measurements. Bhagwat et al. used their measured values for reflectance as well as the known refractive index of their substrate to calculate the refractive index of the ITO film:

$$n_{film} = \sqrt{n_{air} n_{sub}} \left( \frac{1 + \sqrt{R_{max}}}{1 - \sqrt{R_{min}}} \right)$$

where $R_{max}$ is the maximum reflectance and $R_{min}$ is the minimum reflectance$^3$. The reflectance was also used with the transmittance data to calculate the band gap from the following equation

$$T - R = e^{(hv - E_g)^{1/2}}$$

where $T$ is the film’s transmittance, $R$ is the reflectance, $hv$ is the energy of the photons and $E_g$ is the energy gap of the material$^3$.

Bender et al. obtained the dielectric function for ITO by fitting their measured data for transmittance and reflectance to physical models. The Drude theory for free carriers was applied to the long wavelength region ($\lambda > 1000$ nm) because the absorption by free electrons dominates the optical behavior$^2$. The Drude theory for free carriers uses kinetic theory to describe the transport properties of electrons in a material. This model assumes the electrons in the material are non-interacting and that the positive ions in the material are immobile. This theory produces the relationship:
\[ \omega_p = \frac{n - e^2}{\varepsilon_0 \varepsilon_{\infty} m_{\text{eff}}} \]

where \( \omega_p \) is the plasma frequency, \( n \) is the carrier concentration, \( \varepsilon_0 \) is the vacuum permittivity, \( \varepsilon_{\infty} \) is the relative permittivity as \( \omega \to \infty \), and \( m_{\text{eff}} \) is the effective mass of an electron. A model developed by Forouhi and Bloomer\(^{33}\) was used on the short wavelength region (\( \lambda < 350 \text{ nm} \)) where absorptions by valence electrons become important\(^{32}\).

### 2.2 Post-Deposition Treatments

#### 2.2.1 Annealing

Annealing is a post-deposition crystallization treatment that promotes crystallization\(^{34}\) by heating and then cooling the film. The effect of annealing of an ITO film depends on the conditions under which the annealing is performed\(^{35}\). These conditions include: background pressure, gas species present, temperature range, annealing time, cooling process and cooling time.

#### 2.2.2 Plasma treatments

Ohsaki \textit{et al.} have investigated room temperature crystallization of ITO on PET (polyethylene terephthalate) substrates. The films were crystallized using a two minute RF-argon plasma at varying background pressures after magnetron sputtering deposition. Films were characterized using XRD. A noticeable change in the intensity of the diffraction peak for the (222) plane was observed after the plasma treatment. The most noticeable increase in peak intensity occurred when the film was treated with 7.50 Torr
plasma gas pressure for the argon plasma. The resistivity of the as-deposited film versus that of the treated film was compared. A reduction in the resistivity of the ITO films post-treatment was achieved. The largest decrease in resistivity occurred with a plasma gas pressure of 5.93 Torr argon plasma with a change from $3.6 \times 10^{-6}$ Ω m to $1.7 \times 10^{-6}$ Ω m. The parameters that yielded the largest increase in the intensity of the diffraction peaks did not yield the largest decrease in resistivity$^{16}$.
Chapter 3

Experiment Details

3.1 Equipment

Depositions and post-deposition treatments were carried out in a 16” wide, 26” long and 16” high PVD Products vacuum chamber. Figure 3.1 is a schematic of the chamber’s interior. The chamber was equipped with two 2” diameter magnetron guns. The magnetron guns were 4” away from the substrate stage. The guns were cooled during the deposition process by a chilled water line. The chamber was equipped with a translational substrate stage that was wired to allow a bias to be applied. The translation stage slowly oscillated horizontally to allow for uniform deposition on substrates larger than 2 inches. The substrate stage had a heater to allow the samples to be heated before or during deposition, as well as a temperature sensor to allow changes in the stage temperature to be monitored. The chamber had a removable shutter 4 cm above the substrate stage.
Figure 3.1: Schematic of interior of vacuum chamber for deposition and treatment.

The chamber was equipped with a Granville-Phillips 307 vacuum gauge controller, and a VAT adaptive pressure controller. Argon, oxygen and high purity nitrogen gas lines were connected to the chamber and the flow was controlled with a MKS instruments multi-gas controller 647B. The gas flow rate and chamber pressure were controlled using LabVIEW.

A 1/8” thick In$_2$O$_3$ target doped with 10%, wt% SnO$_2$ with 99.99% purity was attached to magnetron gun 1. The target material was mounted to a copper backing plate with heat resistant silver paste. The backing plate allowed the target to be magnetically held to the sputtering gun. Magnetron 2 was not used during this work.

For film deposition an Advanced Energy MDX 500 power supply was connected to the substrate stage to apply a bias voltage to assist in attracting the target material to the substrate. An Advanced Energy DC Pinnacle Plus DC pulsed power supply was connected to magnetron gun 1. This power supply switches the voltage applied to the magnetron on and off at a set frequency with a fixed duty cycle that determined duration the power was turned on. This pulsing voltage, with a reverse pulse to prevent charging,
helped to minimize problems with arcing or charging at the target and maintains a desired power set point by automatically adjusting the applied voltage. The control panel of the supply had a read-out for the discharge voltage and current.

The post-deposition plasma treatment was performed in the same chamber in which deposition was done. Prior to treatment a steel shutter was moved into position over the substrate, which placed the sample between two conductive surfaces allowed the sample to be exposed to the plasma. The Advanced Energy MDX 500 power supply was disconnected from the substrate stage and a US Gun II RF supply was connected. This supply was used to apply the RF power to the stage. The supply had read-outs for the forward power, reflected power and the DC bias voltage.

3.2 Deposition Process

The films were deposited on glass microscope slides and extruded acrylic. The substrates were cut into one inch squares and cleaned with methanol. A small strip of Kapton tape was adhered to the surface of each slide to allow thickness measurements. The substrates were then placed on the substrate stage and the chamber was pumped down to a pressure on the order of $10^{-6}$-$10^{-7}$ Torr.

Tests were run to determine optimal parameters for deposition. All depositions were done with 30 W supplied to the magnetron at a frequency of 100 kHz and a reverse time of 1.0 $\mu$s. The pressure and flow rate were adjusted to determine the settings to achieve the largest deposition rate. The discharge voltage was used as a metric to optimize for the highest deposition rate.
3.3 Post Deposition Plasma Treatment

After the as-deposited films were characterized, the samples were placed back in the chamber and the steel shutter was closed over the sample. The cable connecting the stage to the DC bias was removed and the stage was connected to the RF power supply. The chamber was then filled with 0.5-3.0 Torr of pure oxygen or argon. The RF power applied to the substrate stage was varied between 30 W and 200 W. The DC bias and reflected power was recorded as well as any changes in temperature at the level of the substrate stage. The temperature of the substrate stage was observed and recorded in two minute intervals during the treatment process to insure that the temperature did not exceed 100°C.

When the power was applied to the substrate stage a plasma was formed between the substrate stage and the shutter. Figure 3.2 is a photo of oxygen plasma of 2.5 Torr with a forward power of 148 W, 16 W reflected power. Dense white plasma is seen concentrated between the metal shutter and the substrate stage. The sample was completely surrounded by the plasma.

Figure 3.5: Image of 2.5 Torr with 148 W Oxygen plasma for post-deposition treatment of ITO film.
3.4 Characterization

Thickness measurements were performed using a KLA Tencor P-15 stylus profiler. Only samples deposited on glass substrates were measured; the variation in the surface of the extruded acrylic was on the same order as the film thickness making it impossible to use the stylus profiler to measure the film’s thickness.

A small area of the glass substrate was marked with Kapton tape before the film was deposited. After deposition the Kapton tape was removed revealing an uncoated portion of the substrate. Figure 3.3 shows a diagram of the profiler and a film on a marked substrate. The coated substrate was placed on the profiler’s stage. A motor then lowered a needle (stylus), with a tip radius of 2.00 μm, so that it touched the films surface with an applied force from a mass of 1.0 μg. The stylus moved across the surface at 50 μm/s recording any changes in the needle’s vertical position. When the stylus reached the point where the Kapton tape was removed it lowered until it touched the surface of the substrate. The sampling rate was set to 200 Hz and the length of the scan was approximately 1.5 mm.

![Figure 3.3: Schematic of Stylus Profiler and sample with film.](image-url)
The profiler then produced a two dimensional plot of the surface of the sample. The thickness of the film could be determined by measuring the step down from the film’s surface to the uncoated substrate. The film thickness was used to calculate the film’s resistivity.

The films’ sheet resistances were measured and the resistivity calculated from sheet resistance and thickness. The film was then analyzed using x-ray photo-electron spectroscopy (XPS), x-ray diffraction (XRD), Raman spectroscopy and scanning electron microscopy (SEM). These characterizations were done on the as-deposited film and again on the treated film.
Chapter 4

Results and Discussion

4.1 Optimization of Flow Rate and Pressure

The chamber pressure was varied from 8-30 mTorr with flow rates of 5-15 standard cubic centimeters per minute (sccm). The frequency of the pulse was 100kHz with a reverse time of 1.0 μs. The variation in flow rate yielded a discharge voltage of 230-280V and a discharge current of 0.11-0.13A. The different variations in parameters were examined to determine which combination would provide the fastest deposition rate.

The power supplied to the magnetron was set at 30 W with a reverse time of 1.0 μs and a frequency of 100 kHz. Films were deposited for 30 minutes at varying argon pressures. The films’ thickness was then measured to determine which pressure provided the highest deposition rate. Figure 4.1 shows the largest deposition rate being when the pressure was 10 mTorr.

![Graph showing deposition rate versus argon pressure](image)

*Figure 4.1: Deposition rate versus argon pressure for film’s deposited for 30 minutes at 30W DC, a flow rate of 15 sccm, reserve time of 1.0 μs, and a frequency 100 kHz.*
The glow discharge’s discharge voltage was recorded for different flow rates of argon. Figure 4.2 shows the discharge voltage plotted against the argon flow rate as well as the best-fit curve for the data. The highest discharge voltage of 273 V was measured at a flow rate of 15 sccm.

![Figure 4.2: Plot of discharge voltage versus argon flow rate for glow discharge with 30W pulsed at a frequency of 100kHz and a reverse time of 1.0µs. The argon pressure was 10mTorr and the discharge current remained 0.11A.](image)

### 4.2 X-Ray Photo-electron Spectroscopy (XPS)

A SSI XPS was used to analyze the films’ surface chemical composition. Before each scan the film surface was sputtered for two minutes in 2.0*10^{-7} Torr argon to remove any surface contaminants that may have settled on the film during handling. Table 4.1 lists the settings used for the XPS scans.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Setting</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glassman High Voltage</td>
<td>10 kV</td>
</tr>
<tr>
<td>Spot size</td>
<td>remote</td>
</tr>
<tr>
<td># scans</td>
<td>10</td>
</tr>
</tbody>
</table>

Table 4.1: XPS scan parameters.
The XPS capture software, ESCA Capture, plots an arbitrary intensity count versus the binding energy of the electrons. Figure 4.3 is the XPS plot for an untreated ITO film that was deposited on silicon glass. This deposition was done in 10mTorr Ar with a flow rate of 15 sccm. The frequency of the DC pulse for this deposition was 100 kHz with a reverse time of 1.0μs. It can be seen from Figure 4.3 that there is no surface contamination of the ITO based on the following discussion.

![XPS Data for untreated ITO film deposited on silicon glass with 10mTorr Ar at 15sccm with a pulsed DC power frequency of 100 kHz and a reverse time of 1.0μs.](image)

Figure 4.3.: XPS Data for untreated ITO film deposited on silicon glass with 10mTorr Ar at 15sccm with a pulsed DC power frequency of 100 kHz and a reverse time of 1.0μs.
The software CasaXPS was used to identify the peaks in Figure 4.3. The software contains a database of binding energies for electrons of different spins in different orbits for all the elements. Table 4.2 contains the identification for the different peaks found in Figure 4.3. The 3d$_{5/2}$ electron in In$_2$O$_3$ has a shifted binding energy of 444 eV$^{34}$, the value for the 3d$_{5/2}$ In electron from the XPS data agrees with this value confirming that the compound in the film is In$_2$O$_3$.

The peak found at 485.0 eV corresponds to the 3d$_{5/2}$ electron in tin that is not bonded to any other elements. This suggests that even though the target used had a dopant concentration above 5% tin there was no formation of tin-based complexes. The small peak at 974 eV corresponds to the Auger oxygen electron emitted. This electron is identified as O KLL. The initial vacancy occurred in the K shell; the final double vacancy occurred in the L shell of an oxygen atom.

<table>
<thead>
<tr>
<th>Binding Energy (eV)</th>
<th>element</th>
<th>orbit</th>
<th>spin</th>
</tr>
</thead>
<tbody>
<tr>
<td>825</td>
<td>In</td>
<td>3s</td>
<td>1</td>
</tr>
<tr>
<td>756</td>
<td>Sn</td>
<td>3p</td>
<td>1/2</td>
</tr>
<tr>
<td>716</td>
<td>Sn</td>
<td>3p</td>
<td>3/2</td>
</tr>
<tr>
<td>702</td>
<td>In</td>
<td>3p</td>
<td>1/2</td>
</tr>
<tr>
<td>665</td>
<td>In</td>
<td>3p</td>
<td>3/2</td>
</tr>
<tr>
<td>533</td>
<td>O</td>
<td>1s</td>
<td>1</td>
</tr>
<tr>
<td>495</td>
<td>Sn</td>
<td>3d</td>
<td>3/2</td>
</tr>
<tr>
<td>485</td>
<td>Sn</td>
<td>3d</td>
<td>5/2</td>
</tr>
<tr>
<td>452</td>
<td>In</td>
<td>3d</td>
<td>3/2</td>
</tr>
<tr>
<td>444</td>
<td>In</td>
<td>3d</td>
<td>5/2</td>
</tr>
<tr>
<td>138</td>
<td>Sn</td>
<td>4s</td>
<td>1</td>
</tr>
<tr>
<td>121</td>
<td>In</td>
<td>4s</td>
<td>1</td>
</tr>
<tr>
<td>90</td>
<td>Sn</td>
<td>4p</td>
<td>3/2, 5/5</td>
</tr>
</tbody>
</table>

Table 4.2 Information for peaks in Figure 4.3.
4.3 Optimization of Post-deposition Treatment

4.3.1 Substrate Temperature during Post-deposition Treatment

The parameters for the post-deposition plasma treatment were chosen to produce the greatest reduction in film resistivity with the smallest increase in substrate temperature.

Figure 4.4 is a plot of stage temperature versus time. The trial this data is from was done without venting the chamber; resistance measurements were done in-situ as described in the next section. The initial temperature after deposition was 28°C. The temperature increased gradually during the treatment but the stage never reached temperatures that would be damaging to an acrylic substrate.

![Temperature vs Time for ITO film treated with a 2.5 Torr oxygen plasma with 198 W forward power.](image)

The process was repeated with lower RF powers. It was determined that 27 W was the lowest RF power that allowed the creation of plasma at the desired pressures and resulted in lower temperature increases. At 30 W the temperature change at the substrate stage did not exceed 2-4°C.
4.3.2 Resistance, Resistivity and Conductivity

Two different methods for measuring change in conductivity of the films were tried. In one method the resistance was measured in-situ in two minute intervals during the treatment process, while in the other the sheet resistance was measured after deposition and again after the treatment.

The in-situ resistance measurements were done by attaching two wires to opposite ends of the glass substrate (approximately an inch apart) with carbon sticky dots before deposition. The two wires were then fed through a feed-through flange. A Fluke 87V multimeter was connected to the flange to allow resistance measurements to be taken without venting and opening the chamber. When the ITO was deposited it formed a closed loop with the two wires. The sputtering argon was pumped out of the chamber and the chamber was brought to the desired pressure of oxygen or argon. The post-deposition plasma treatment was performed for two minutes. A resistance measurement was taken with the multimeter and then multimeter was disconnected from the chamber to prevent damage to the multimeter. This was repeated in two minute intervals for a total of 10 minutes or until the resistance was too high for the measuring range of the multimeter, which meant that either the probe contact had been ablated off the substrate or the wires had become disconnected from the film. Figure 4.5 is a plot of resistance versus time. The resistance of the film decreased over time. The plasma treatment decreased the resistance as desired.
There were several disadvantages to this method of in-situ resistance measurement. One disadvantage was that the measurements made were of the surface resistance of the film only where the multimeter probe made contact, as opposed to a measurement of resistance across the film. The measurement was also dependent how well the wires, carbon sticky dots and film were in contact with each other. This method was only used to get a relative resistance to determine if the value was decreasing. The wires, carbon dots and multimeter probes all had internal resistance that increased the reading.

The other method used was to measure the sheet resistance of each film as-deposited and then again after the post-treatment using a Loresta EP four-point probe. The probe had four pins spaced 5.0 mm apart. The resistivity and conductivity of the films were then calculated using the sheet resistance and film thickness.

Table 4.3 shows the as-deposited films’ resistivity compared to the resistivity after a ten minute plasma treatment in argon. The RF power for all the treatments was
The films were all deposited at the same time but the post-treatments were performed separately with different gas pressures. The variation in the film thicknesses was due to the substrates’ placement on the stage. The differences in film thickness caused the variation in the as-deposited resistivity. All the films experienced a decrease in resistivity with the exception of the film treated with 1.0 Torr the resistivity of this film increased. The film treated with 1.5 Torr argon had the greatest change in resistivity with a reduction of about 40%.

<table>
<thead>
<tr>
<th>Gas Plasma Argon Pressure</th>
<th>Thickness (nm)</th>
<th>As-Deposited Resistivity (Ωm)</th>
<th>Post-Treatment Resistivity (Ωm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 Torr</td>
<td>98.4</td>
<td>4.91E-05</td>
<td>3.69E-05</td>
</tr>
<tr>
<td>1.0 Torr</td>
<td>357.1</td>
<td>5.57E-05</td>
<td>7.01E-05</td>
</tr>
<tr>
<td>1.5 Torr</td>
<td>333.2</td>
<td>3.25E-05</td>
<td>1.89E-05</td>
</tr>
<tr>
<td>2.0 Torr</td>
<td>169.9</td>
<td>9.38E-05</td>
<td>8.01E-05</td>
</tr>
</tbody>
</table>

Table 4.3: Resistivities of as-deposited ITO film on glass and resistivities of ITO after treatment with 27 W RF argon plasma of varying pressures.

Table 4.4 shows the as-deposited films’ resistivity compared to the resistivity after a ten minute plasma treatment in oxygen. The films were once again deposited simultaneously and treated separately with a RF power of 27 W and different oxygen pressures. The variation in the films’ thicknesses was due to the substrates’ placement on the stage. The differences in film thickness caused the variation in the as-deposited resistivity. The treatment done with 1.0 Torr oxygen produced the greatest reduction in
film resistivity with a reduction of 60%. This reduction is greater than that which occurred during the argon plasma treatment.

<table>
<thead>
<tr>
<th>Gas Plasma Oxygen Pressure</th>
<th>Thickness (nm)</th>
<th>As-Deposited Resistivity (Ωm)</th>
<th>Post-Treatment Resistivity (Ωm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 Torr</td>
<td>240.2</td>
<td>5.96E-05</td>
<td>1.27E-04</td>
</tr>
<tr>
<td>1.0 Torr</td>
<td>297.0</td>
<td>1.66E-05</td>
<td>6.74E-06</td>
</tr>
<tr>
<td>2.0 Torr</td>
<td>180.5</td>
<td>1.69E-05</td>
<td>1.92E-05</td>
</tr>
</tbody>
</table>

Table 4.4: Resistivities of as-deposited ITO film on glass and resistivities of ITO after treatment with 27 W RF oxygen plasma of varying pressures.

4.4. X-Ray Diffraction

The ITO target, the as-deposited films and the treated films were analyzed using x-ray diffraction. The diffraction patterns of the as-deposited and treated film were compared to determine if there was any change in the degree of crystallization of the films. Two different x-ray diffraction apparatuses were used; a Rigaku DMAX B was used for the glass substrates measurement and a Rigaku 2500 was used for the target and films. The measurements for the target and films were taken with 2θ/θ scans from 2θ = 10° to 2θ = 30°. Table 4.5 lists the parameters used during measurements.
Parameter Setting

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Setting</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tube Voltage</td>
<td>50 kV</td>
</tr>
<tr>
<td>Tube Current</td>
<td>300 mA</td>
</tr>
<tr>
<td>Divergence Slit</td>
<td>1°</td>
</tr>
<tr>
<td>Scatter Slit</td>
<td>1°</td>
</tr>
<tr>
<td>Divergence limiting Slit</td>
<td>10 mm</td>
</tr>
</tbody>
</table>

Table 4.5: Parameters for Rigaku 2500 XRD measurements.

Figure 4.6 is the x-ray diffraction pattern for the ITO target used for sputtering. The target is composed of crystalline ITO as seen by the presence of strong diffraction peaks. Table 4.6 outlines what planes, (hkl), the diffraction peaks correspond to.

![X-ray diffraction data for ITO target](image)
<table>
<thead>
<tr>
<th>2 Theta (°)</th>
<th>(hkl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>(211)</td>
</tr>
<tr>
<td>30</td>
<td>(222)</td>
</tr>
<tr>
<td>35</td>
<td>(400)</td>
</tr>
<tr>
<td>50</td>
<td>(440)</td>
</tr>
<tr>
<td>60</td>
<td>(622)</td>
</tr>
</tbody>
</table>

Table 4.6: Diffraction peaks and corresponding planes for ITO target.

The diffraction profile for the glass substrate was measured to identify any diffraction peaks from the substrate that might appear in the diffraction profiles for the films. The XRD spectra of the glass substrate, Figure 4.7, show a weak broad peak from 13° to 30°.

Figure 4.7: XRD data for glass substrate.
Figure 4.8 is the x-ray diffraction data for a 300 nm as-deposited film. Due to the thickness of this film it can be anticipated that it will be partially crystalline. The broad peak that was seen in the XRD data for the glass substrate is still present. Superimposed on this peak are smaller diffraction peaks corresponding to the (211) and (222) planes. There are no diffraction peaks for the higher Miller indices planes. This suggests that the as-deposited film is partially amorphous.

![Figure 4.8: XRD data for as-deposited ITO film on glass.](image)

Figure 4.9 is the XRD data for the same film after being subjected to a 10 minute 1.0 Torr oxygen plasma treatment with a forward RF power of 27 W, the treatment parameters which resulted in the greatest decrease in resistivity. The treated film exhibits the same peaks as the as-deposited film though the peaks were more intense. The diffraction peak corresponding to (211) has increased significantly in intensity while the
(222) peak’s intensity only increased by a few counts. It can be concluded that the film has a higher degree of crystallization than the as-deposited film.

![Graph showing XRD data for ITO film treated 10 minute 1.0 Torr oxygen plasma treatment with a forward RF power of 27 W.](image)

**Figure 4.9:** XRD data for ITO film treated 10 minute 1.0 Torr oxygen plasma treatment with a forward RF power of 27 W.

### 4.5 Raman Spectroscopy

A Renshaw inVia Raman Microscope, which used a 514 nm excitation laser and was capable of imaging the area from which the spectrum was taken, was used to take the Raman spectrum for the ITO target, the as-deposited films and the films after treatment. The spectra were then compared to identify any changes in the molecular bonding of the films after plasma treatment.
Figure 4.10 is the Raman spectrum for an as-deposited the 297nm thick ITO film analyzed in the previous sections. This Raman spectrum was compared to spectra reported by Chandrasekhar et al. (Figure 4.11) to identify the peaks present.

Chandrasekhar et al. measured the Raman spectra for a commercial ITO sample prepared with sputtering as well as the Raman spectra of ITO film deposited by electrostatic assisted vapour deposition (ESAVD)\(^3^6\). Chandrasekhar et al. located peaks at 585 cm\(^{-1}\), 1110 cm\(^{-1}\) and 1610 cm\(^{-1}\) on both samples. The Raman spectrum shown in Figure 4.10 has peaks at 581 cm\(^{-1}\) and 1107 cm\(^{-1}\).

![Figure 4.10: Raman spectrum of as-deposited ITO on glass.](image-url)
Figure 4.11: Raman spectra from Chandrasekhar et al. of a.) a commercial sputtered ITO sample b.) ITO sample prepared with ESAVD at 550°C.
Figure 4.12 is the Raman spectrum of the film in Figure 4.10 after being treated for 10 minutes with oxygen plasma at 1.0 Torr gas pressure and 27 W forward RF power. The peaks at 581 cm\(^{-1}\) and 1107 cm\(^{-1}\) seen in Figure 4.10 are still present in this spectrum. The intensity of the peaks is stronger in the treated film than it was in the as-deposited film. There are two peaks in the treated film that were not present in the as-deposited film. The peak at 1420 cm\(^{-1}\) was not present in Raman data from Chandrasekhar et al. The peak at 1592 cm\(^{-1}\) could correspond to the shoulder seen in Figure 4.11 at 1600 cm\(^{-1}\).

Figure 4.12: Raman spectrum of ITO after being treated with oxygen plasma with 1.0 Torr gas pressure and 27 W forward RF power.
4.6 Surface Features

The surface features of the as-deposited and treated films were examined using a FEI Sirion system. The surface features of a film treated with the post-deposition treatment parameters that resulted in the greatest decrease in resistivity will be compared to the surface features of the as-deposited film.

Figure 4.13 shows the surface of an as-deposited ITO film deposited with 10mTorr Ar and a thickness of 297nm. The magnification of this image is 80000x with an accelerating voltage of 5.00kV and a spot size of 3.0.

Figure 4.14 shows the film at the same magnification after being treated for 10 minutes with a 1.0 Torr oxygen plasma with a forward RF power of 27W. The grain size in the film after treatment appears the same as that of the as-deposited film.

![Figure 4.13](image1.png)  ![Figure 4.14](image2.png)

Figure 4.13: SEM images of 297nm thick as-deposited ITO film on glass.  Figure 4.14: SEM images of 297nm thick ITO film on glass after 10 minute treatment with 27 W 1.0 Torr oxygen plasma.
4.7 Optical Measurements

Optical characterization was done of the films’ transmission and reflectance for wavelengths from 250 nm to 900 nm. These optical measurements were done using a Perkin Elmer Lambda 9 Spectrometer. For the transmittance measurements the samples were placed in front of an entrance port and a Spectralon 99% reflector. The sample was wall-mounted and placed on a 3% Krylon ultra flat reflector for the reflectance measurements. The percentage of a wavelength absorbed by a film could be determined by \(100 - (T + R)\), where T is the percent transmitted and R is the percent reflected. In this section the optical measurements for one film treated with argon plasma and one film treated with oxygen plasma will be discussed.

Transmittance measurements were taken for a film treated with an argon plasma and a film treated with oxygen plasma with the gas pressures for each gas that resulted in the greatest reduction in resistivity. Figure 4.15 is a plot of the transmittance versus wavelength through those two films. The first measurement (the red line) is for a 333.2 nm thick ITO film on glass treated with an argon plasma with a gas pressure of 1.5 Torr, The film treated with argon had a resistivity of \(1.89 \times 10^{-5}\) Ω m. There is zero transmittance of wavelengths in the ultraviolet region of the spectrum. Wavelengths in the visible region of the spectrum (400 nm – 700 nm) have a transmittance between 48.83% for violet light (400 nm) and 81.74% for 700 nm. The film has the highest transmittance, 84%, at 748 nm which is just outside the visible region. The second measurement (the purple line) is the transmittance measurements through a 297 nm thick ITO film on glass treated with oxygen plasma with a gas pressure of 1.0 Torr. The film treated with oxygen had a post-treatment resistivity of \(6.74 \times 10^{-6}\) Ω m, the lowest value
for all the films in this work. Despite being thinner the film treated with oxygen had lower transmittance than the film treated with argon. Wavelengths in the ultra violet region of the spectrum were not transmitted through the film. The visible region had a transmittance of 23% to 63%. The wavelength with the highest transmittance was 658 nm.

Figure 4.15: Transmittance of 250 nm to 900 nm wavelengths through film treated ITO film on glass.
Reflectance measurements, seen in Figure 4.16, were then taken for the films. The film treated with argon (the red line) has about 20% reflectance in the ultraviolet region. The greatest amount of reflectance was in the visible region of the spectrum. There are no regions on the spectrum where the reflectance exceeds 25%. The film treated with oxygen (the purple line) had < 18% reflectance in the ultraviolet region. The greatest amount of reflectance was in the visible region of the spectrum particularly for wavelengths around 550 nm. There are no regions on the spectrum where the reflectance exceeds 23%.

Figure 4.16: Reflectance of 250 nm to 900 nm wavelengths through treated ITO films on glass.
Figure 4.17 is a plot of the films’ absorbance versus wavelength. The absorbance can be determined by 100% - (T + R), where T is the transmittance and R is the reflectance. The film treated with argon (the red line) had less absorbance in the visible region than the film treated with oxygen (the purple line). Both films show high absorbance in the ultraviolet region, between 70-84%.

Figure 4.17: Absorbance of 250 to 900 nm wavelengths through treated ITO films on glass.
Chapter 5

Conclusion

ITO films were prepared using pulsed DC magnetron sputtering in an argon background. Tests were run varying the argon pressure and flow rate to determine which settings resulted in the highest deposition rate when the magnetron was supplied with 30 W at a frequency of 100 kHz and a reverse time of 1.0 μs. The as-deposited films were characterized for resistivity, surface composition, surface features and degree of crystallinity.

The films were then treated with RF plasma to promote crystallization and decrease resistivity. Oxygen and argon plasmas were both investigated to determine which produced the greatest reduction in the films’ resistivity. The RF power and gas pressure were varied to determine which post-deposition treatment parameters yielded the greatest reduction in film resistivity and the least increase in substrate temperature. It was determined that 27 W RF power caused no significant change in the substrate temperature while resulting in a decrease in film resistivity in post-deposition treatments using both oxygen and argon plasma.

The treated films were characterized for resistivity, surface composition, surface features and degree of crystallinity. These properties were compared to those of the as-deposited films to study the effect of the post-deposition treatment of the films and determine which treatment parameters resulted in the largest decrease in resistivity. For treatments performed in argon the greatest reduction in resistivity occurred when the film
was treated with 1.5 Torr argon. The resistivity decreased from $3.25 \times 10^{-5} \, \Omega \, \text{m}$ to $1.89 \times 10^{-5} \, \Omega \, \text{m}$. For treatments performed in oxygen the greatest reduction in resistivity occurred when the film was treated with 1.0 Torr oxygen. The resistivity decreased from $1.66 \times 10^{-5} \, \Omega \, \text{m}$ to $6.74 \times 10^{-6} \, \Omega \, \text{m}$.

The post-deposition treatment with 1.0 Torr oxygen and 27 W RF power resulted in the greatest decrease in film resistivity. This film exhibited an increase in the x-ray diffraction peaks suggesting that the reduction in the film resistivity was linked to an increase in film crystallinity. The Raman spectrum of the treated film also showed an increase in peak intensity. SEM images of the as-deposited and treated films showed no distinct differences in the films’ surface features.

Optical measurements were performed to determine the transmittance and reflectance of the film treated with 1.5 Torr argon and the film treated with 1.0 Torr oxygen. Both films had no transmittance in the ultra violet region. The film treated with argon has a higher transmittance in the visible region. The film treated with oxygen was less transparent in the visible regime but had a lower resistivity. Determining which gas to use in the post-deposition treatment would depend on whether the film application requires a lower resistivity or higher transparency.

Suggested future work for this project would include further exploration in the mechanisms involved in the reduction in film resistivity during the plasma treatment. The influence of film thickness on the efficiency of the treatment should also be studied in greater detail. Another area of further study would be to calculate the carrier concentration in the as-deposited and treated films.
Bibliography


