INFLUENCE OF DEPOSITION PRESSURE ON THE OPTICAL PROPERTIES OF DC-MAGNETRON SPUTTERED INDUM TIN OXIDE (ITO) THIN FILMS

By

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B. Ed. Sc. (Hons)

A thesis submitted in partial fulfilment of the requirements for the award of the degree of Master of Science in the School of Pure and Applied Sciences of Kenyatta University.

February 2006
Declaration

This thesis is my original work and has not been presented for the award of a degree in any other University or any other award.

All sources of information have particularly been acknowledged by means of references.

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We confirm that the candidate, under our supervision, carried out the work reported in this thesis.

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To my mum, Nancy, who taught me how to eat, smile and walk, and my dad, Elijah, who introduced me to the intrigues of holding and using a pen.
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Abstract

Indium tin oxide (ITO) has continued to attract great interest in the research and technological world because it bears a valuable compromise of both high optical transparency and high electrical conductivity. These twin properties make it very useful in architectural glass applications and in numerous optoelectronic devices such as front electrodes for solar cells, liquid crystal and gas discharge displays, photodiodes, image sensors and organic light-emitting devices. Magnetron sputtering, especially its reactive version, is the preferred method of preparing thin films of ITO. However, 'target poisoning' remains a major drawback in preparing films with optimal characteristics. In this work, ITO films have been prepared by DC magnetron sputtering of a ceramic ITO (90% In$_2$O$_3$, 10% SnO$_2$) target, without the use of oxygen gas. By varying the deposition pressure (0.5-3.0 Pa) due to argon gas, films of thickness 300-375 nm have been obtained, and their optical behaviour studied by optical spectroscopy. The optical analysis showed that the refractive index decreases while the optical band gap increases (3.24-3.33 eV) with increasing deposition pressure. This variation in the refractive index has been related to the increase in film porosity, and the change in porosity calculated using Bruggeman’s and Maxwell Garnett’s effective medium theories. The shift in the optical band gap can be explained by the Moss rule. Films deposited at an argon pressure of 2.5-3.0 Pa have shown an optical transmittance of 85 % averaged over the visible region.
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A Absorptance
BOC British Overseas Company
DC Direct Current
DOS Density of States
E Emittance
E_g Energy gap
EM Electromagnetic
IR Infra Red
ITO Indium Tin Oxide
JDOS Joint Density of States
k Extinction Coefficient
KKR Kramers-Kronig Relation
MFP Mean Free Path
n Refractive Index
OJL O'Leary, S.K., Johnson, S.R., Lim, P.K. (1997)-see list of References
PMT Photomultiplier
R Reflectance
RF Radio Frequency
SEM Scanning Electron Microscopy
STM photon-Scanning Tunneling Microscopy
T Transmittance
TCO Transparent Conducting Oxide
TEM Transmission Electron Microscopy
UV Ultra violet
Vis Visible Spectrum
XRD X-Ray Diffraction
CHAPTER ONE
INTRODUCTION

1.1 Introduction

This thesis gives a detailed report on the investigation of the influence of the deposition pressure on indium tin oxide thin films prepared by DC magnetron sputtering and deposited on ordinary glass substrates.

The thesis is organized as follows: Chapter One carries an introduction to the importance of transparent conducting materials in experimental and technological applications. A brief analysis of the trend of studies on indium tin oxide thin films is given. Chapter Two provides the theory with which the results are interpreted, while the experimental procedures constitute Chapter Three. The results and their discussions make up Chapter Four, and conclusions and recommendations for further research work are given in Chapter Five.

Badeker (1907) published the very first report on a transparent conducting oxide (TCO). He observed that thin films of cadmium metal deposited in a glow discharge chamber could be oxidized to become transparent in the visible region, while at the same time passing electric current. Ever since, the commercial value of these films has been recognized, and many other TCOs discovered. These include the oxides of tin, indium, cadmium, gallium, copper and zinc, and their blends. The most widely used TCO for optoelectronic device applications is tin-doped indium oxide. At present, and very likely into the foreseeable future, this material offers the best
available performance in terms of conductivity and transmissivity, combined with excellent environmental stability, reproducibility, and good surface morphology. Today, ITO films find various applications in optoelectronic devices such as front electrodes for solar cells (Gan & Zhang, 2002, Wamsler et al., 2002), liquid crystal and gas discharge displays (Sohn et al., 2003, Lee et al., 2002), photodiodes (Warmsingh et al., 2003), image sensors and organic light-emitting devices (Kim et al., 1999a, Kim et al., 1999b, Song et al., 2001, Wu et al., 1997). Other typical applications include touch panel contacts (Frach et al., 2003, Craciun et al., 2000), antistatic coatings for energy conserving architectural windows (Warmsingh et al., 2003), infra-red (heat) reflectors (Lewis & Paine, 2000), and heating stages for optical microscopes (Babu et al., 2004).

For optoelectronic applications, the transparent conductor must be carefully processed to maximize optical transmittance in the visible regime, while maintaining minimum electrical resistivity. Optimization of these properties will depend on the specific application, but in general, achieving the required performance in the as-deposited condition demands careful process control. The main goals of process control are: the minimization of microstructural features and impurities that lead to reduced carrier mobility, the maximization of activated substitutional Sn and the creation of optimal oxygen substoichiometry (Kim et al., 1999b). The oxygen stoichiometry is critical to the minimization of resistivity, since each doubly charged oxygen vacancy contributes two electrons. The presence of doubly charged vacancies and substitutional Sn creates an impurity band that overlaps the conduction band. An excess of charged defects, however, in the form of compositional impurities, singly charged Sn on an In site, or
doubly charged oxygen vacancies, leads to charged impurity scattering and a decrease in charge carrier mobility (Gan & Zhang, 2002).

During film deposition by sputtering, momentum transfer from gas molecules to the container walls gives rise to the forces that sustain the pressure in the system. This pressure determines the mean distance traveled by molecules between successive collisions, commonly referred to as the mean-free path of the molecules. The mean-free path consequently determines the energy with which the gas molecules impinge on the substrate and therefore influences the properties of the resulting films. A study of pressure as a process control tool is therefore necessary. There is need to carry out an explicit study on pressure variation that will show how this variation would affect the optical properties of the resulting indium tin oxide thin films. In this work, a report is given of the optical properties of ITO thin films produced at different chamber pressures.

There are plenty of methods of preparing thin films. Sputtering, the method used in this work is only one of them. Sputtering is the ejection of atoms from a surface of a material, known as the target, by bombardment with energetic particles. The ejected or sputtered particles can be condensed on a substrate to form a thin film. Sputtering is essentially a vacuum process; a low-pressure inert gas, typically argon, is first introduced in the coating chamber. By applying a sufficiently large voltage between the target and the substrate, a glow discharge is set up in such a way that energetic ions bombard the surface of the target and knock out atoms, which are then transported, because of the bias, to the substrate, thus forming the film. The sputtering technique is discussed in Section 2.5.
Sputtering stands out as a superior coating technique over other means such as thermal evaporation and electron beam evaporation. This is because these techniques show certain limitations: in particular, alloys and refractory metals cause problems given the differences in the alloy constituent vapour pressures and their high melting points, which demand for the need to run the sources at very elevated temperatures thereby affecting the coated articles. In addition, compounds can dissociate into their chemical constituents at the low evaporation pressures used. Sputtering overcomes these problems and has other advantages such as high deposition rates; ease of sputtering any metal, alloy or compound; possibility of producing multi-layer films; high purity films; extremely high adhesion of films; excellent coverage of steps and small features, thus allowing of production of films of certain required unique topographies; ability to coat heat-sensitive substrates; ease of automation; and excellent uniformity on large-scale substrates like architectural glass.

1.2 Literature Review

There exists an interesting class of materials, which falls somewhere between metals and dielectrics, known as transparent conductors because they exhibit a useful compromise of both high transparency and conductivity. Transparent conducting films consist either of very thin metals or semiconducting oxides. Examples of metals that have been used as transparent conductors include gold, platinum, rhodium, silver, copper, iron and nickel. Their first widespread use was for transparent electrical heaters in aircraft windshield de-icing application during World War II (Holden, 1989).
Simultaneous optimization of conductivity and transparency presents a considerable challenge to film deposition. At one extreme end are discontinuous islands of considerable transparency but high resistivity; at the other end are films that coalesce early and are continuous, possessing high conductivity but low transparency (Ohring, 1992). For these reasons, the semiconducting oxides of tin, indium, cadmium, and more commonly, their alloys (e.g. indium tin oxide), doped indium oxide (with tin, antimony, zinc, etc) and doped tin oxide (with fluorine, chlorine, molybdenum, etc) are used (Lewis & Paine, 2000).

Indium tin oxide is (ITO) useful in technologies that require both large-area electrical contact and optical access in the visible portion of the light spectrum. Selecting a wide-bandgap oxide and introducing native or substitutional dopants achieves high transparency combined with useful electrical conductivity. The transparency of ITO is related to its conductivity: if the TCO is too conductive, then there are too many electrons and transparency will be reduced because the "electron gas" reflects/absorbs light (Deng et al., 2001). In order for the TCO to be transparent in the visible wavelength range of light, the band gap must be greater than \(-3\) eV (\(-380\) nm). This is above the energy range of visible light. Carriers can be excited by light above and below the energy range of visible light and still remain transparent in the visible part of the spectrum. In other words, there is a transparent window in the visible regime between the band edge (> 3 eV) and the plasma edge (<1.7 eV). This window corresponds to the 380 to 780 nm wavelength of light. The infrared (IR) end of the transparency window is defined by the plasma-absorption frequency, which also depends on the carrier density and the effective mass of the carrier. Film deposition and post-deposition process control will therefore determine the transport and optical
properties of the resulting ITO material. Oxidizing or reducing conditions, for instance, will modify the oxygen-vacancy concentration and hence the carrier density (Craciun et al., 2000).

As already pointed out, the properties of ITO films are highly dependent on the deposition parameters, the composition of evaporation or target material used, and post-deposition treatment. The deposited film layer must contain a high density of charge carriers for it to conduct. These carriers comprise of both substitutional tin and oxygen vacancies, created either during film deposition or by post-deposition annealing in a reducing atmosphere, resulting in a material that can be represented as $\text{In}_{2-x}\text{Sn}_x\text{O}_{3-x}$ (Screenivas et al., 1985). An excessive population of these carriers produces absorption (Craciun et al., 2000). High conductivity (or low sheet resistance) must be balanced against high transmission in the visible region. For instance, sheet resistance can be less than 10 $\Omega$/sq with a visible transmission of more than 80%. To obtain transmission near 90%, sheet resistance must be greater than 100 $\Omega$/sq (Craciun et al., 2003). ITO films behave like metals to long wavelength because of the presence of a plasma wavelength in the near IR (Craciun et al., 2000). At longer wavelengths, the films become reflecting, and the IR reflectance is related to the sheet resistance of the film.

The preparation of ITO in a manufacturing environment is typically by means of DC sputtering. The variables that are adjustable during process optimization, and have been studied, include oxygen partial pressure (Jeong et al., 2001), substrate temperature (Shanthi et al., 1982, Screenivas et al., 1985, Craciun et al., 2003, Liu et al., 2003), plasma current (Wu et al., 1997, Song et al., 2001) source-substrate distance (Mansingh & Kumar, 1989) and film thickness (Kim et al., 1999a, Gan &
Zhang, 2002). One has to aim at the creation of optimal oxygen substoichiometry, maximization of activated substitutional tin sites and minimization of microstructural features and impurities that effectively reduce carrier mobility (Kim et al., 1999b).

Morales-Paliza et al., (2002) have hypothesized a picture of low-temperature formation of ITO films after studying the effect on oxygen pressure on film formation. They observe that at low pressures (< 0.5 Pa), the film formation is highly nonstoichiometric and probably contains free In and Sn which cannot be described as an indium-tin-oxide semiconductor. At pressures just greater than 0.5 Pa, the material begins to display semiconductor behaviour, with an optimum carrier concentration at 1.2 Pa. Above 1.3 Pa, the number of oxygen vacancies decrease, and correspondingly, the carrier mobility increases. However, beyond 4 Pa, the gas “thickness” is so great that many target species cannot reach the substrate.

Deng et al., (2001) have investigated the effect of oxygen flow rate (1 to 5 sccm) on the optical transmission and resistivity of as-deposited and annealed rf-sputtered ITO films. They report an increase in both transmittance and resistivity with oxygen flow rate and explain it in terms of two competing effects: increase in oxygen flow rate enhances the growth of crystalline phases which leads to higher mobility of carriers. On the other hand increased oxygen flow rate decreases the carrier density. The good electrical conductivity of ITO films depends on doping with Sn⁺⁺ at In⁺⁺ sites in the In₂O₃ lattice. Oxygen-hole defects generate two electrons as carriers and one electron is generated when Sn⁺⁺ substitutes In⁺⁺.
It is clear from the foregoing review that studies involving a pressure variation have concentrated on the effect of the oxygen gas. There is need, therefore, to study the influence of total chamber pressure due to argon gas alone in a non-reactive process. This is necessary because, although reactive sputtering has many advantages, its major setback lies in the hysteresis loop (Swann, 1988b) formed upon increasing and decreasing the reactive gas flow rate.

Films for this study were therefore prepared from an alloy target of standard composition: 90 wt. % In$_2$O$_3$ and 10 wt. % SnO$_2$ without the use of oxygen gas. The deposition pressure due to argon gas alone was then the variable of study. The optical behaviour of the resulting films was investigated, with a view to gaining an insight into the influence of the chamber pressure due to argon gas on the ITO films produced.

1.3 Statement of the Problem

Preparation of indium tin oxide films by reactive sputtering suffers the practical limitation imposed by target poisoning: as the oxygen gas flow rate is increased, a sudden transition occurs where the oxide forms on the surface of the metal target. The sputtering rate drops and the partial pressure of the reactive gas increases ensuring even further target "poisoning". Frequently, then, the process is carried out in an essentially unstable condition.
1.4 Objectives

The aim of this work is to produce thin films of indium tin oxide (ITO) at different deposition pressures and to study the effect of varying this deposition pressure due to argon gas on optical properties of the films. The specific objectives can be summarized as follows:

(i) To prepare indium tin oxide thin films at different pressures by DC magnetron sputtering, and

(ii) To characterize the optical behaviour of the resulting films

1.5 Rationale

Transparent conducting oxides continue to attract major attention because of their versatile technological applicability. The exceptional properties of ITO are being exploited in numerous applications in optical electronic devices such as solar cells, photodiodes, image sensors, liquid crystal displays, charge-coupled devices, among others. Novel uses are also emerging, for instance, the application of ITO as a coating on an optical fibre tip for photon-scanning tunneling microscopy (STM) imaging. The quality of the prepared films is very sensitive to the type of target used, whether or not a reactive gas is introduced, technique of deposition, deposition parameters such as substrate temperature, oxygen partial pressure, substrate-source separation, and post-deposition heat-treatment, and hence plays a crucial role in producing films of adequate stoichiometry. Reactive sputtering is the preferred method of preparing ITO thin films because of its many advantages. However, reactive sputtering of most metal oxides suffers from the problem of target poisoning, which results in the hysteresis loops observed in the deposition rate, oxygen partial pressure and cathode potential as the oxygen gas is increased and decreased (Mohamed, et al. 2003, Ngaruiya, et al.,
There is therefore need to study and develop sputtering versions that do not suffer this limitation.

Correlation of film properties with deposition conditions provides important guidance for optimization of the ITO material to meet a given application. The continued demand for transparent conducting oxides requires that an exhaustive database for the properties of ITO be established. The optical behaviour of these films prepared in pure argon ambient should therefore be understood, for the benefit of materials science, and for large-scale technological applications.
CHAPTER TWO

THEORY

2.1 Introduction

This chapter carries the basic physics principles on which the results of this work are interpreted. The basic theory of the interaction of radiation with matter is given and the concept of spectral selectivity explored. The optics of thin films, which give the necessary theory for the exploitation of spectral selectivity using materials in thin film form, is discussed. In addition, an overview is given of some physical models that describe the behaviour of electrons in a conductor, and the mechanics of interband transitions in semiconductors. Finally, the theory of thin film production is discussed, with particular focus on sputtering, which is the technique used to fabricate films for this study.

2.2 Spectral Selectivity

The concept of spectral selectivity is best understood from the properties of ambient radiation in our natural environment. Solar radiation is a form of electromagnetic (EM) waves whose spectrum lies almost entirely within the wavelength range $300 < \lambda < 3000$ nm with a peak at about 475 nm. This solar spectrum is therefore only a small component of EM waves whose spectrum lies in the range $10^{-11} < \lambda < 10^{19}$ nm. The visible part of the solar spectrum is much smaller, lying in the range $380 < \lambda < 780$ nm. This radiation is best understood by starting from an ideal blackbody whose
emitted spectrum, referred to as the Planck’s spectrum, is uniquely defined by equation (1).

\[ q = \frac{c_1 \lambda^4}{e^{c_2 / \lambda} - 1} \]  

(1)

where \( q \) is the monochromatic emission at wavelength \( \lambda \) and of units Wm\(^{-3}\). \( T \) is the absolute temperature and \( c_1 \) and \( c_2 \) are constants.

**Figure 2.1**: Spectra for relative sensitivity of the human eye, blackbody radiation at two temperatures, and solar radiation that has passed through the earth’s atmosphere (Grangvist, 1991).

Fig. 2.1 shows Planck spectra for two temperatures close to room temperature. The spectra are bell-shaped as a consequence of Planck’s law, and they are confined to the range 2000 < \( \lambda < 10^4 \) nm, where \( \lambda \) is the wavelength. Due to Wien’s displacement law (equation 2), the peaks of the spectra lie at different wavelengths.
\[ \lambda_{\text{max}} = \frac{0.2898}{T} \] 

(2)

where \( \lambda_{\text{max}} \) is the peak value for the expression of \( q_k \) and \( T \) is the absolute temperature. The constant has units of cmK.

The higher the temperature of the blackbody, the shorter the wavelength for the peak of the curve. From Fig. 2.1, it is observed that there's almost no overlap between the spectra for thermal radiation and of the sun. The existence of this demarcation makes it possible to tailor spectrally selective surfaces, so that a material can be found or fabricated to differentiate in their absorption, reflection or transmission characteristics of radiation.

Thus the radiative properties comprise of transmittance (T), emittance (E), absorptance (A) and reflectance (R), each signifying a certain fraction of incident or maximum emitted radiative power. Energy conservation demands that at each wavelength, one has

\[ T(\lambda) + E(\lambda) + A(\lambda) + R(\lambda) = 1 \] 

(3)

and from Kirchoff's law for thermodynamic equilibrium,

\[ E(\lambda) = A(\lambda) \] 

(4)

Wavelength-averaged radiative properties can be defined by integrating over the eye’s sensitive curve, solar spectrum or thermal spectrum, which give the luminous (lum), solar (sol) or thermal (therm) performances, respectively. Quantitative data can be obtained from the general relation (Grangvist, 1991):
where $\chi$ is A, R, T or E; $\theta$ is the angle from the normal for the incident or emitted radiation; and $\gamma$ denotes lum, sol or therm. In principle, angle-averaged properties can be specified by integration over $\theta$.

2.3 Optics

2.3.1 Thin Film Optics

When an EM wave is incident upon the interface between two media of different optical properties, the wave is split into two: a transmitted wave that proceeds into the second medium and a reflected wave propagating back into the first medium. The electric vector $E$ and the magnetic induction vector $B$ are used to represent an EM field. The description of the effect of this EM field on material objects demands the introduction of another set of vectors namely: the electric current density $j = \sigma E$, the electric displacement $D = \varepsilon E$ and the magnetic vector $H = B/\mu$ where $\sigma$, $\varepsilon$ and $\mu$ are the electrical conductivity, the electric permittivity and the magnetic permeability, respectively. The space and time derivatives of the five quantities above are related by Maxwell’s equations (Born & Wolf, 1980), which are valid at every point in whose neighbourhood the physical properties are continuous. Therefore Maxwell’s equations completely describe EM propagation in a homogeneous medium.

The study of the optical properties of a given material often has greater interest in its transmission (T) and reflection (R) behaviour. Where the determination of the optical
constants is important, the incident radiation intensity as well as the state of polarization are considered too. The R and T properties of a given material are related to the magnetic and dielectric permeabilities.

By applying boundary conditions to the solutions of Maxwell's equations, one is able to solve the problem of determining the light transmitted and reflected at a boundary separating two optically different media (Lorrain and Corson, 1970). The reflectance and transmittance of a thin film on a substrate can be used to derive the complex dielectric function of the film. This function is the fundamental material property that describes the optical behaviour of the film. The dielectric function, or the permeability, $\varepsilon = \varepsilon_1 - i\varepsilon_2$, is related to the complex refractive index by the equations:

\begin{align}
N &= n - ik \\
\varepsilon &= N^2
\end{align}

which result in

\begin{align}
\varepsilon_1 &= n^2 - k^2 \\
\varepsilon_2 &= 2nk
\end{align}

Either the set of ($\varepsilon_1$, $\varepsilon_2$) or ($n$, $k$) are referred to as optical constants. These constants are properties dependent on the wavelength of the probing radiation. $\varepsilon_1$ is related to the polarizability and $\varepsilon_2$ is the true optical absorption. $n$ is the refractive index while $k$ is the absorption or extinction coefficient. Born & Wolf (1980) have provided a
theoretical treatment of the optical properties of thin films on a substrate, which
determine the above quantities. A brief review of this theory is explored here.

For the ultraviolet, visible and infrared spectral regions, the EM radiation is
considered to be propagating as plane waves. Plane waves incident on a specimen of
one or several homogeneous phases, separated by specular surfaces are considered.
The amount and degree of refraction, reflection and transmission are direct measures
of material parameters.

Consider an interface between two media denoted by i and j. The amplitude ratios for
transmitted and reflected light are denoted by \( t^{ij} \) and \( r^{ij} \), respectively. The dielectric
permeabilities of the two media are \( \varepsilon_i \) and \( \varepsilon_j \), respectively. The light is incident from
medium i with an angle \( \theta_i \) as sketched below in Fig. 2.2.

The Fresnel relations give the amplitude ratios:

\[
\begin{align*}
\frac{r_s^{ij}}{r_p^{ij}} &= \frac{(\varepsilon)^{1/2} \cos \theta_i - (\varepsilon_j - \varepsilon_i \sin^2 \theta_i)^{1/2}}{(\varepsilon_i)^{1/2} \cos \theta_i + (\varepsilon_j - \varepsilon_i \sin^2 \theta_i)^{1/2}}, \\
\frac{r_p^{ij}}{r_s^{ij}} &= \frac{(\varepsilon)^{1/2} (\varepsilon_j - \varepsilon_i \sin^2 \theta_i)^{1/2} - \varepsilon_j \cos \theta_i}{(\varepsilon_i)^{1/2} (\varepsilon_j - \varepsilon_i \sin^2 \theta_i)^{1/2} + \varepsilon_j \cos \theta_i}, \\
t_s^{ij} &= \frac{2(\varepsilon_i)^{1/2} \cos \theta_i}{(\varepsilon_i)^{1/2} \cos \theta_i + (\varepsilon_j - \varepsilon_i \sin^2 \theta_i)^{1/2}}, \\
t_p^{ij} &= \frac{2(\varepsilon, \varepsilon_i)^{1/2} \cos \theta_i}{(\varepsilon_i)^{1/2} (\varepsilon_j - \varepsilon_i \sin^2 \theta_i)^{1/2} + \varepsilon_j \cos \theta_i},
\end{align*}
\]

where \( s \) and \( p \) denote s- and p-polarization, respectively.
If consideration is made of a thin homogeneous film on a transparent substrate, the above equations can be used to describe the amplitude of the reflected and transmitted vectors at each surface. The full reflection and transmission of the film must be calculated including phase factors. The phase change $\delta$ of the beam when traversing the film of thickness $d$ is given by

$$\delta = \frac{2\pi t (s - \sin^2 \theta)}{\lambda}$$  \hspace{1cm} (14)$$

Neglecting the backside of the substrate, the following expressions are obtained for the reflectance and transmittance of a thin film with the geometry shown in Fig. 2.3.

$$r_{1s,p}^f = \frac{r_{1s,p}^{12} + r_{1s,p}^{23} e^{2\delta}}{1 + r_{1s,p}^{12} r_{1s,p}^{23} e^{2\delta}}$$  \hspace{1cm} (15)$$
Figure 2.3: The geometry for the interfaces in a thin film (2). \( f \) and \( b \) denote light incident from the front and back respectively. Symbol \( s \) denotes s-polarized.

\[
R^f_{2s} = |r^f_{2s}|^2, R^f_{2p} = |r^f_{2p}|^2
\]

\[
T^f_{2s} = |t^f_{2s}|^2, T^f_{2p} = |t^f_{2p}|^2
\]

Interchanging indices 1 and 3 gives the relations for light incident from the backside i.e. from the substrate. The intensities are proportional to \(|r^f_2|^2\) and \(|t^f_2|^2\), and are denoted by upper cases, \(R_2\) and \(T_2\). In the case of a metallic substrate, where transmittance is zero, the only quantity of interest is the reflectance.
If the backside of a transparent substrate is now included, a more complicated situation arises, and the multiple reflections in the substrate must be accounted for. The reflections are incoherent for large substrate thickness and are included through the addition of the intensities of the multiply reflected beams. The final expressions for the reflectance and the transmittance are

\[
R_s = \frac{R_{2s}^f + T_{2s}^f T_{3s}^b R_{3s}}{1 - R_{2s}^f R_{3s}} \quad (19)
\]

\[
T_s = \frac{T_{2s}^f T_{3s}}{1 - R_{2s}^f R_{3s}} \quad (20)
\]

where \( R_{3s,p} = |r_{3s,p}|^2 \), \( T_{3s,p} = |t_{3s,p}|^2 \). \( R_{3s,p} \) and \( T_{3s,p} \) are the reflectance and transmittance expressions for the backside of the substrate. Analogous expressions are obtained for the \( p \)-components.

2.3.2 Optical Behaviour in Semiconductors

When light is emitted from or absorbed in a semiconductor, energy as well as momentum must be conserved. In a direct band-gap semiconductor, the carrier transitions between the valence and the conduction bands occur without change in momentum of the two states involved. Here the emission of light occurs by a vertical electron descent from the minimum conduction band energy level to the maximum energy level in the valence band. However, in indirect band-gap semiconductors, the transition occurs with a change in momentum that is essentially accommodated by excitation of lattice vibrations and heating of the lattice. This makes direct electron-hole recombination with photon emission unlikely. Another implication of the
distinction between direct and indirect semiconductors is the variation of the absorption coefficient, $\alpha$, as a function of photon energy. The ratio of the photon intensity at a depth $x$ below the surface, $I(x)$, to that incident on it, $I_0$, is described by

$$I(x) = I_0 \exp(-\alpha x)$$

(21)

In all semiconductors, $\alpha$ becomes negligible once the wavelength exceeds the cut-off wavelength. This critical wavelength $\lambda_c$ is related to the band gap energy $E_g$ by the well-known equation $E_g = h\nu / \lambda_c$. For direct band-gap semiconductors the value of $\alpha$ becomes large in the short wavelength side of $\lambda_c$, meaning that light is absorbed very close to the surface. For wavelengths larger than $\lambda_c$, semiconductors are essentially transparent because no mechanisms exist to excite electron transitions. However, for wavelengths shorter than $\lambda_c$, electrons can be stimulated into the conduction band. Moreover the generated free carriers can now absorb quanta of energy and occupy excited levels in the continuum of conduction-band states (Longhurst, 1973). Semiconductors then behave like metals and are highly reflective.
2.4 Physical Models

2.4.1 Introduction

The aim of optical spectroscopy is often the determination of microscopic quantities such as resonance frequencies of oscillating atoms, impurity concentrations or thin film thicknesses from macroscopic experiments. This is possible if the microscopic phenomena are coupled to the electric fields of the probing radiation. The key property of a material representing this connection is the dielectric function or its square root, the complex refractive index. In the case of layered systems a very powerful technique to interpret optical spectra is given by a simulation of the experiment (based on a physical model) and adjustment of the model parameters to fit the measured data. Fortunately, rather simple models of dielectric functions lead to a realistic simulation of optical spectra. This enables quick parameter fits from which the wanted information can be obtained. The so-called OJL (O"Leary et al., 1997) model has been employed to describe interband transitions in amorphous materials, and the Drude Model (reviewed by Kachhava, 1990) to account for the movement of free electrons in a conductor.

2.4.2 The OJL Interband Transition Model

The OJL model for interband transitions gives expressions for the density of states (DOS) for the optical transition from the valence band to the conduction band. Parabolic bands are assumed with tail states exponentially decaying into the band gap (Fig. 2.4).
The original parameters of the OJL density of states model are the energies $E_v$ and $E_c$, the 'damping constants' of the valence and conduction band $\gamma_v$ and $\gamma_c$, respectively, as well as the masses of the valence and conduction band $m_v$ and $m_c$. The expressions

$$E_{M,v} = E_v - \frac{1}{2} \gamma_v$$

and

$$E_{M,c} = E_c + \frac{1}{2} \gamma_c$$

denote the mobility edges of the valence and conduction band, respectively. The mobility gap, $E_o$, in the OJL model is therefore given by

$$E_c + \frac{1}{2} \gamma_c - \left( E_v - \frac{1}{2} \gamma_v \right) = E_o$$
The meaning of the term 'mass' in this context is the following: Consider the band structure of a crystal (here, silicon) as shown in Fig. 2.5:

\[ E = a(k + k_0)^2 + b \]  \hspace{1cm} (25)

The coefficient \( a \) determines the curvature of the conduction band and can be associated with the inverse mass of a classical particle, which is said to represent an electron in that conduction band:

\[ a = \frac{\hbar^2}{2m} \Rightarrow m = \frac{\hbar^2}{2a} \]  \hspace{1cm} (26)
A small mass therefore corresponds to a large increase of energy with $k$, i.e. large slopes in the band structure, while on the other hand, a large mass stands for a flat band. For the optical properties only the joint density of states (JDOS), denoted here as $J$, is important and it can be expressed as a certain combination of the density of states of the valence band (vb) and conduction band (cb):

$$J(h\omega) = \int N_{cb}(E)N_{vb}(E - h\omega)dE$$  \hspace{1cm} (27)$$

The integration collects all possible transitions from the valence band to the conduction band with energy separation equal to the energy of the absorbed photon. It is shown by O’Leary et al., (1997) that $J$ can be written as a product of a function which is independent of the masses and a pre-factor (called $M$ here) which contains the masses of the conduction and valence bands besides some constant factors:

$$M \sim \sqrt{\frac{m_v^3}{m_c^3}}$$  \hspace{1cm} (28)$$

2.5  Sputtering

2.5.1  The Sputtering Process

Sputtering is the process whereby atoms or molecules of a material are ejected from a target by the bombardment of high-energy particles. In particular, the cathodic sputtering used in this work, is one where the bombardment is by positive ions derived from an electrical discharge in a gas. Other variants of the sputtering physical process include diode sputtering, RF or DC sputtering, ion-beam sputtering, reactive sputtering, or a hybrid of several of these methods.
Figure 2.6: A schematic representation of the principle of sputtering (Hansjoerg Weis, Phys. Inst. RWTH-Aachen).

Sputtering can be explained to follow the following criteria: Firstly, ions of sufficient energy must be created and directed towards the surface of a target to eject atoms from the material (Fig. 2.6). Secondly, ejected atoms must be able to move freely towards the substrate with as little impedance as possible to their movement. This explains why sputtering is a vacuum process; low pressures are required to maintain
high ion energies and to prevent too many atom-gas collisions after ejection from the target.

The concept of mean free path (MFP) is an important one in a sputtering process. This is the average distance that an atom can travel before colliding with another gas atom. Figure 2.7 shows how MFP varies with pressure (Swann, 1988b). It can be seen that in order to attain fairly unimpeded travel through a gas, it is necessary to operate at pressures of 1.0 Pa \((10^{-2} \text{ mbar})\) or better. Above this pressure, the ejected atom undergoes many gas collisions and deposition rates are very low. The atom can also be deflected straight back onto the target and this reduces deposition rates further (Swann, 1988b). Unfortunately, the need to operate at low-pressure contrasts with the process required to produce the bombarding ions, namely that of plasma generation. All cathodic processes require a plasma or glow discharge in order to work. This plasma may be generated by DC (like in this work) or RF power.

This problem demands a method of producing more efficient ionization at these lower pressures. The magnetron design is the apt solution. The magnetron uses the principle of applying a specially shaped magnetic field to a diode-sputtering target. The principle then is that the cathode surface is immersed in a magnetic field such that electron traps are created so that \(\vec{E} \times \vec{B}\) drift currents close in on themselves. In essence, the operation of a magnetron source relies on the fact that primary and secondary electrons are trapped in a localized region close to the cathode into an endless ‘racetrack’ (Ohring, 1992). In this manner their chance of experiencing an ionizing collision with an atom is vastly increased and so the ionization efficiency is increased too. This causes the impedance of the plasma and the magnetron source
operates at much lower voltages (500-600 V) than diode systems (several kV). This greater ionization efficiency leads directly to an increase in ion current density onto the target, which is proportional to the erosion rate of the target.

![Figure 2.7: Typical variation of mean free path (MFP) with pressure (Swann, 1988b).](image)

There are several types of magnetron designs possible, including post-magnetrons, planar magnetrons, S guns etc, but these are only geometric variants of the same physical principle. The common feature is that electron drift is controlled and electrons are trapped.
2.5.2 Sputtering Yield

The average number of atoms ejected from the target by an incident ion is known as the sputtering yield. The sputtering yield increases with increasing energy of ions and their mass, relative to the atomic weight of the target. A sputtering threshold exists between 5-25 eV for most metals (Ohring, 1992), the lower limit being set by the sublimation energy. The yield increases rapidly for energies greater than threshold, and then shows a small region of linear proportionality, before finally approaching saturation. The heavier the bombardment particle, the higher the energy region at which the saturation will occur. In addition, at very high energies, the yield decreases because of the increasing penetration depth, which leads to considerable energy losses below the surface as a result of which not all ejected atoms are able to reach the surface to escape. The sputtering yield also depends on the angle of incidence. Various results (Kivaisi 2000) show that it increases approximately as \( 1/ (\cos \theta) \), where \( \theta \) is the angle between the line of travel of the ion and the normal to the target surface.
CHAPTER THREE
MATERIALS AND METHODS

3.1 Introduction
This chapter gives a detailed account of the experimental procedures employed in this work. The basic properties of the material of study are given and the method used to prepare indium tin oxide (ITO) thin films is outlined. A brief description of the sputtering system, the gases control mechanism, as well as a report on the substrates cleaning process is provided. Finally, the procedure for optical analysis of the thin films is given.

3.2 Material of Study: Indium Tin Oxide
The solid indium tin oxide (ITO) material has a molecular weight that varies with composition, a melting point of about 1900 °C and a crystal density of ~1.7 g/cc while its colour varies from yellow to gray depending on the degree of oxidation (AIP, 1993). ITO is a degenerate n-type semiconductor (Akkad, et al., 2000) with high electrical conductivity and high transparency in the visible region of the spectrum, and exhibiting a high reflectance in the infrared region. Owing to this unusual combination of electrical and optical properties, this material is widely applied in optoelectronic devices. The association of these properties in a single material explains the vast domain of its continued applicability and the diverse
production methods that have emerged, and hence the need to explore its thin film properties.

3.3 Thin Films Production

3.3.1 Magnetron Sputtering

Magnetron sputtering is a high rate vacuum coating technique for depositing metals, alloys and compounds of a wide range of materials. It exhibits several important advantages over other vacuum coating techniques and this has led to the development of a number of commercial applications ranging from microelectronics through to simple aesthetic coatings. Magnetron sputtering has emerged to complement other vacuum coating techniques such as thermal evaporation and electron-beam evaporation. However, these techniques show certain disadvantages. In particular, alloys and refractory metals cause problems because of differences in alloy constituent vapour pressures and their high melting points, which demand that sources be run at elevated temperatures, and hence affect the coated articles. Furthermore, compounds can dissociate into their chemical constituents at the low evaporation pressures used. Magnetron sputtering overcomes these limitations and has many other advantages such as high evaporation rates; ease of sputtering any metal, alloy or compound; high purity films; extremely high adhesion of films onto substrates; excellent coverage of steps and small features; ability to coat heat-sensitive substrates; ease of automation, and excellent uniformity on large area substrates like architectural glass (Swann, 1988a).

In its simplest applications, the magnetron is used to deposit metallic materials by DC sputtering. In the DC mode, the target is directly conducting electricity and is subject
to $FR$ losses and may be operated up to currents of perhaps $70 \ W \ cm^2$ averaged over the target. Examples of applications where the DC version of the magnetron is used include: metallising for microelectronic circuits and chip carriers; electrical resistance films, e.g. Ni-Cr for strain gauges; magnetic films for general magnetic storage devices, floppy discs, tapes and thin-film magnetic heads; opto-storage devices, e.g. compact discs and video discs; corrosion-resistant films (Cr-Ni); and bonding layers for various purposes (Ohring, 1992).

3.3.2 Fabrication of ITO Films.

Indium tin oxide films were produced in an Edwards Auto 306 Sputtering System (see Fig. 3.1 and Appendix I) by dc magnetron sputtering of 99.99% pure ITO target whose $In_2O_3: SnO_2$ ratio is 9:1. The target measuring 75 mm in diameter and 6 mm thick was sourced from the Edwards High Vacuum Part of BOC Ltd., Crawley Sussex, England. The sputtering gas was argon (99.999 % pure). Nitrogen gas was used for venting the vacuum chamber. Both gases were supplied by the BOC (K) Ltd. The Sputtering System has both turbomolecular and diffusion pumps, which can pump down to pressures in the order of $10^{-6} \ mbar$. The System has a recommended working pressure range of $5 \times 10^{-3}$ to $20 \times 10^{-3} \ mbar$ for DC sputtering.

The sputtering system accommodates a rotatable substrates holder, rf and DC power supplies, a quartz crystal thickness monitor and gas regulating valves for reactive and sputtering gases. The fact that the substrates holder is rotatable ensures the capability of producing uniform thin films. This is an important feature of this equipment since non-uniformity of films is normally a major problem. Other amenities include, a
Figure 3.1: A cross-section of the vacuum chamber of the Edwards Auto 306 Magnetron Sputtering System.
power control unit, an improvised shutter for purposes of presputtering, a window for plasma viewing, a cooling system anchored on a chiller (Haake UWK 45) and an exhaust-extraction system.

Ordinary glass slides measuring 76.2 × 25.4 × 1.2 mm were used as substrates. These were cleaned as follows: First, the slides were soaked in soap solution for 20 minutes before rinsing with distilled water. Then they were rinsed in ethanol and stack in a rack to allow for complete drying.

The substrates holder was loaded with clean slides, 150 mm above the target and the chamber then pumped down to 2.0 × 10^{-6} mbar in about 2 hours. The quartz crystal monitor was used to control film thickness during depositing, and actual thickness obtained from optical spectroscopy measurements.

To begin with, the sputtering gas, argon, was let in with such a flow as to attain a chamber pressure of 8.0 × 10^{-3} mbar. Presputtering of the ITO target was then carried out for 15 minutes with a DC power of 400 W with the manual shutter closed. This step ensured that surface impurities, such as vacuum grease, were removed from the target's surface and deposited on the shutter. The power was then adjusted to 200 W. The chamber pressure was then set at particular values in the range 5.0-30 × 10^{-3} mbar and the shutter then opened to allow for film deposition on the glass substrates. By varying the base chamber pressure from 0.5 to 3.0 Pa, film samples were produced for this study. Table 3.1 provides a summary of the deposition parameters used in preparing the film samples.
Table 3.1  
Sputtering parameters for deposition of ITO films.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power on ITO target</td>
<td>200 W</td>
</tr>
<tr>
<td>Target-substrate separation</td>
<td>150 mm</td>
</tr>
<tr>
<td>Argon gas pressure</td>
<td>0.5-3.0 Pa</td>
</tr>
<tr>
<td>Substrate temperature</td>
<td>No deliberate heating</td>
</tr>
<tr>
<td>Target composition</td>
<td>90% wt. In$_2$O$_3$, 10% wt. SnO$_2$</td>
</tr>
<tr>
<td>Rotation speed of substrate holder</td>
<td>40 rev/min</td>
</tr>
</tbody>
</table>

3.4 Sputter Equipment Modification

3.4.1 Gases Flow Control

Because of the unavailability of standard mass flow meters, available rotameters (TA Instruments) were simply used as control valves (see Fig. 3.2). First, the inlet valve into the sputtering chamber and the rotameter’s knob were kept closed before opening the gas cylinder. Then the rotameter’s knob would be adjusted to allow gas to pass. Finally, using the chamber’s inlet valve, the amount of argon gas getting in was controlled to get particular desired base pressures for making our various samples. The Edwards Auto 306 Sputtering System is equipped with a pressure gauge, and the chamber pressure is shown, and can be read off, on the Controller Display in millibars.
3.4.2 Provision for Presputtering

Figure 3.3 below is a simplified representation of the coating chamber. It shows, among other things, an improvised manual shutter; the means used to allow for presputtering of the target. This provision was not catered for in the equipment design. Presputtering is a very necessary step, since sputtering onto the substrates should only commence after the target has been cleaned and required deposition conditions set, and terminated when required film thickness is achieved.
Key

A: Target shutter (our improvisation) [can be rotated]
B: Substrates' holder
C: direct current magnetron source
D: radio-frequency magnetron source
E: manual open-shut shutter control [operated from outside the chamber]
F: coating chamber

Figure 3.3: An illustration of the equipment modification for purposes of presputtering.
3.5 Optical Characterization

3.5.1 The Spectrophotometer

The spectrophotometer used in this work was the Spectro 320 Optical Spectrum Analyzer (Appendix II) supplied by Instrument Systems, Inc. The spectrophotometer has two detectors: a charge coupled device detector (photomultiplier [PMT]) for the UV/Vis region (190-880 nm) and an InGaAs semiconductor diode array detector for the near-infrared region (800-1700 nm). A 12V, 0.25A DC power lamp (Nippon Keiki Works (Japan) Ltd.) was used as the source of light. Fig. 3.4 is a schematic for the set up for spectral measurements. A working lamp power of 7W was used for all measurements. A lamp-detector separation of 20 mm was employed for transmittance measurements. Optical characterization was carried out by taking spectral measurements in the range $300 \leq \lambda \leq 1600$ nm.

3.5.2 Optical Transmission Measurements

The configuration employed to carry out optical transmission measurements is sketched in Fig. 3.5. The transmittance data was recorded at normal incidence in the spectral range from 300 to 1600 nm. First, a reference measurement was made with no sample placed between the lamp and the detector. Then, the film sample was placed between the light source and detector and measurements made.
Wooden box painted black on the inside

Figure 3.4: A schematic representation of the set up for optical measurements.

Figure 3.5: A schematic representation of the configuration for optical transmission measurements.
3.6 Spectral Data Analysis

3.6.1 Introduction

Relationships that exist between optically measurable macroscopic properties of a material and the material’s microscopic behaviour have been used. The dielectric function provides this important link. Therefore optical transmittance data obtained from the film samples was subsequently used as input for computer simulations, by the SCOUT_98 software, to determine both the thickness and dielectric function of the ITO films. Since the interest in ITO films is so much in the visible region, electronic transitions ought to be considered and adequately described. The model proposed by O’Leary et al., (1997) [OJL], which has been adapted by Theiss (2000) was employed. This model is particularly well suited to describe amorphous materials or crystalline phases with high defect density. Expressions for the joint density of states are given for optical transitions from the valence band to the conduction band. From this density of states, the imaginary part of the dielectric function is modeled and then the real part is calculated by fast Fourier transformation to satisfy causality (Kramers-Kronig relation [KKR]). Parabolic bands are assumed in this model with tail states decaying exponentially into the band-gap. These states are characteristic for the defects in the film. The model employs five parameters: the energy gap $E_g$ between the valence and conduction bands, a so-called mass factor $m$ for the strength of optical transition, gamma factors $\gamma_v$ and $\gamma_c$ for the exponential decay from the valence and conduction band, respectively, into the band-gap, related by the ratio $r = \gamma_c / \gamma_v$, and a decay factor which is introduced to force the imaginary part to zero at high frequencies.
In addition, the Drude model for free electrons was used in the simulations because ITO is a conductor. The two important parameters of this model are the damping constant $\Omega_r$ and the electron plasma frequency $\Omega_p$, from which the microscopic quantities carrier concentration $n$ and mobility $\mu$ can be calculated.

3.6.2 OJL Model Implementation

Since there is no easy way to determine the absorption coefficient of a material in a thin film system, the absorption coefficient is not a good 'interface quantity' between theory and experiment. Instead, a simulation approach is often recommended, which ends up in a prediction of optical spectra (reflectance and transmittance, usually) that can be compared directly to the measured data. A model parameter fit then adjusts the parameters of interest to the recorded spectra. To compute the transmittance spectra, the complex dielectric function of all materials in the system must be known. Unfortunately, in case of a known joint density of states only the imaginary part of the dielectric function can be computed, but not the real part. Fortunately, if the imaginary part is known for all frequencies, which is the case in a model, the real part can be constructed uniquely by employing the KKR between a real and imaginary part of a causal quantity. To do this, however, the imaginary part must approach zero for high frequencies, which is not the case in the O'Leary expressions. Hence a decay of the imaginary part is enforced by a term, which is introduced in addition to the OJL paper.
3.6.3 The OJL Model Parameters

The SCOUT_98 parameters for the OJL model are mass, gap energy, gamma valence band, ratio and decay. The mass is the coefficient $M$ mentioned in the previous section, which collects all constants and the square root of the third power of the valence and conduction band masses. The gap energy $E_0$ is the difference $E_c - E_v$, i.e. the band gap in the case of no disorder, which is realized when both $\gamma_v$ and $\gamma_c$ are zero. It is important to note here that the gap energy is different from the mobility gap which depends on the values of the disorder parameters $\gamma_v$ and $\gamma_c$. For traditional reasons, SCOUT_98 specifies the gap energy in wavenumbers. Conversion of wavenumbers given in reciprocal centimeters to electron volts, was simply done by just dividing by 8065, the conversion factor.

The gamma valence band is $\gamma_v$, while the ratio refers to the parameter $\gamma_v / \gamma_c$ which is used here because it simplifies working with a constant ratio of valence and conduction band exponential decays. Lastly, the parameter referred to as decay is the number that determines the way in which the imaginary part decays to zero for high frequencies.
CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Introduction

This chapter presents results of this research work and their discussion. These results are for as-deposited indium tin oxide films prepared at base chamber pressures in the range 0.5 to 3.0 Pa due to pure argon gas. The chapter carries a report of the optical analysis of these films. Optical spectroscopy is capable of giving microscopic quantities of a material such as resonance frequencies of oscillating atoms, carrier concentrations, carrier mobilities, optical band gap, and thin film thicknesses from macroscopic experiments. This is made possible because microscopic phenomena can be coupled to the electric fields of the probing radiation. The fundamental property of a material embodying this useful connection is the dielectric function, or its square root, the complex refractive index. In this work, the powerful tool of interpreting optical transmittance spectra by simulation of experimental data and adjustment of the model parameters to fit the measured data was put to use. Once a satisfactory fit was achieved, the required information could be obtained. This analysis was carried out in the spectral range $300 \leq \lambda \leq 1600$ nm.
The deposited films appeared yellowish green to the eye in transmitted light, characteristic of well-oxidized ITO thin films. The characteristic spectrum of the lamp available for our optical studies is given in Fig. 4.1.

4.2 The Lamp Spectrum

![Graph showing the intensity spectra of the lamp used for optical studies.](image)

**Figure 4.1:** The intensity spectra of the lamp used for our optical studies.

This lamp is clearly a VIS-IR light source; no study can therefore be done with this lamp in the ultra-violet region much as the available PMT detector is sensitive up to
The absorption peaks observed at 494 and 638 nm correspond to the atomic absorption spectra for neon (AIP, 1993), which is a component of the PMT detector.

4.3 Film Thickness Distribution

Film thickness distribution on the substrate depends on such factors as source design, its characteristic emission behaviour, the ambient pressure, source-to-substrate distance, substrate geometry and relative motions between source and substrate (Swann, 1988a). These parameters therefore affect the resultant uniformity of the films deposited from a magnetron source. Thickness uniformity bears a direct influence on the useable substrate size and overall process economics. A check was carried out on the uniformity of the films, having been produced from a planar magnetron source at a source-substrate separation of 150 mm, with the substrates held by a rotating holder. Film thickness measurements were carried out by optical spectroscopy means. Fig. 4.2 illustrates the spots at which these measurements were done on the film sample.

Figure 4.2: Positions on the film sample on a glass substrate at which thickness measurements were taken. The distance between two consecutive spots is 10 mm.
Simulated

---

Experiment

---

Thickness: 301.3 nm

Thickness: 301.5 nm

Thickness: 301.8 nm

Thickness: 302 nm
Figure 4.3: Both simulated and measured transmittance spectra for spots A, B, C, D, E, F and G (see Fig. 4.2). The film thickness obtained for each spot is indicated.
Fig. 4.4 shows the general distribution of the film thickness on the substrate as obtained from the simulations in Fig 4.3. It is observed that the film is thickest at the center (i.e. spot D) and tends to slightly decrease towards the ends of the substrate, similar to the work of Swann (1988a), on copper and silicon oxide thin films. These measurements show a difference of 0.7 nm between the thickest and thinnest regions on the substrate; hence these films are acceptably uniform. Thickness variations in a non-rotating substrate holder are normally so large in the range of 15 to 35 nm (Swann, 1988a).

This kind of film thickness distribution can be attributed to the manner in which a circular magnetron source erodes in the course of ion-bombardment and the geometry
of the sputtering chamber. An erosion groove (Fig. 4.5) is formed on the target due to the magnetic confinement of electrons into a toroid above the target surface. This groove shape is so much dependent on the magnetic field strength, magnetic field shape and target material and is controlled primarily by the magnetron design. The position and shape of this groove directly affects the film thickness distribution on the substrate.

![Figure 4.5: The erosion groove shape formed on an ITO target in the course of film deposition.](image)

Swann, *et al.*, (1989) have developed a mathematical model to predict film distribution. They have shown that for an off-axis geometry with a static circular source and a rotating workholder (as is the case for the Sputtering Unit design used in this work, [see Fig. 4.6]), film thickness, \( t \), can be predicted by equation (29):
Figure 4.6: Geometry of offset source/workholder system.

\[
t(A) = \frac{m h^2}{\rho \pi^2} \int_0^{2\pi} \frac{h^2 + A^2 + d^2 + r^2 + 2dr \cos \theta}{\left[h^2 + A^2 + d^2 + r^2 + 2dr \cos \theta + 2A(d^2 + r^2 + 2dr \cos \theta)^{1/2}\right]^{3/2}} d\theta
\]

where \( A \) is the radial distance from workholder axis, \( m \) is the total ejected mass, \( h \) is the axial distance between source and workholder, \( r \) is radius of the source, \( \rho \) is
source mass density, \( d \) is source offset, \( R \), given by \( R^2 = d^2 + r^2 + 2drcos\theta \), is the horizontal distance from workholder axis to a point on the source and \( \theta \) is the angle between the source point with maximum \( R \) value and the source point in question. From equation (29), it can be seen that \( t \) falls with increasing \( A \) just as observed for our films as shown in Fig. 4.4.

### 4.4 Thin Film Deposition Rate

Fig. 4.7 shows the growth rate of indium tin oxide thin films as a function of total chamber pressure. The data points for increasing and decreasing chamber pressure show no hysteresis. The fact that no oxygen gas was used in preparing our films explains this absence of hysteresis. Hysteresis loops are often observed when sputtering metal targets in a reactive atmosphere; when oxygen is used as the reactive gas, upon increase in oxygen pressure (flow), there's adsorption of oxygen on the target's surface, resulting in the consumption of oxygen. For a decrease on oxygen pressure, an oxide layer with low sputtering yield already covers the surface, and therefore the target needs time to become metallic and the consumption of oxygen will be low (Mohamed, et al., 2003).

The deposition rate decreases exponentially with increasing deposition pressure. The fall in film growth rate with total pressure can be explained by the fact that as the deposition pressure increases, the mean free path of the atoms decreases, hence reducing the sputtering yield. Further, it is observed that the growth behaviour seen here follows the prediction by the Keller-Simons relation (reviewed in Drusedan et
The phenomenon of resputtering at low pressures as observed in some other oxides, like zinc oxide (Kappertz et al., 2002) and tungsten oxide (Bechinger et al., 1996) does not occur in the pressure range studied.

![Deposition Pressure vs Sputter Rate](image.png)

**Figure 4.7:** ITO thin film growth rate as a function of the deposition pressure. The closed squares indicate the trend upon increasing pressure while the star symbols show the trend for decreasing pressure. The Keller-Simons' prediction is superimposed.
4.5 Transmittance Spectra

Fig. 4.8 shows the superimposed spectra of the optical transmittance behaviour of the ITO film samples. It can be observed that the optical transmittance of the films increases with increasing base deposition pressure, as best illustrated by a depiction of the trend at 500 and 800 nm, in Fig. 4.9.

![Transmittance Spectra Diagram]

**Figure 4.8:** Transmittance as a function of wavelength for ITO film samples prepared at different base chamber pressures. The transmittance of an uncoated glass substrate is also shown.
This increase of the optical transmittance is attributed to an increase in film porosity with deposition pressure, and is explained in section 4.5. Fig. 4.10 (a)-(f) shows the simulation of each of the transmittance spectra depicted in Fig. 4.8. There's good agreement between the experimental data and the simulation, showing that the models used for these simulations adequately describe the optical behaviour. The values of film thickness, optical band gap and respective deposition pressure are indicated on each of the graphs. From these fits, values of the refractive index and absorption coefficients of the films, and the band gap, have been found and discussed in sections 4.6 and 4.7 respectively.
Figure 4.10(a): Simulation of experimental data for the film sample prepared at 0.5 Pa.
Deposition Pressure: 1.0 Pa
Film thickness: 302.4 nm
Band gap: 3.27 eV

Figure 4.10(b): Simulation of experimental data for the film sample prepared at 1.0 Pa.
Figure 4.10(c): Simulation of experimental data for the film sample prepared at 1.5 Pa.
Figure 4.10(d): Simulation of experimental data for the film sample prepared at 2.0 Pa.
Figure 4.10(e): Simulation of experimental data for the film sample prepared at 2.5 Pa.

Deposition Pressure: 2.5 Pa
Film thickness: 311.1 nm
Band gap: 3.30 eV
Figure 4.10(f): Simulation of experimental data for the film sample prepared at 3.0 Pa.
4.6 Optical Constants

The extinction coefficient, \( k \), and the refractive index, \( n \), for ITO films formed at different chamber pressures are shown in Fig. 4.11.

![Figure 4.11: Variation of (a) refractive index \( n \) and (b) extinction coefficient \( k \) of ITO films prepared under various deposition pressures.](image-url)
The extinction coefficients have values less than 0.10 at photon energies below 3 eV, indicating that these films hardly absorb light in the visible region. For each deposition pressure, the value of the refractive index increases significantly with photon energy (see table 4.1). In the visible region, the value of the refractive index decreases with increasing deposition pressure. This is attributed to the decrease in film density upon increasing deposition pressure as shown in Fig. 4.12.

**Table 4.1**

*Properties of an ITO film prepared at 2.5 Pa*

<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>Wavelength (nm)</th>
<th>Refractive index</th>
<th>Extinction coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>311.1</td>
<td>1240</td>
<td>1.67</td>
<td>0.03</td>
</tr>
<tr>
<td>620</td>
<td>1.67</td>
<td>1.96</td>
<td>0.01</td>
</tr>
<tr>
<td>410</td>
<td>2.13</td>
<td>0.09</td>
<td></td>
</tr>
<tr>
<td>310</td>
<td>2.27</td>
<td>0.43</td>
<td></td>
</tr>
<tr>
<td>250</td>
<td>2.32</td>
<td>0.44</td>
<td></td>
</tr>
<tr>
<td>205</td>
<td>2.33</td>
<td>0.69</td>
<td></td>
</tr>
</tbody>
</table>

This change in film density is related to a variation of the film porosity whose values can be derived from the refractive index by employing effective medium theories (Mohamed *et al.*, 2003). Values of the porosity were calculated by using the effective medium theories suggested by Bruggeman and Maxwell Garnett (discussed by Kong, 1986). The expressions given by these theories are given, respectively, as
\[ f_i \frac{\varepsilon_i - \varepsilon}{\varepsilon_i + 2\varepsilon} + f_m \frac{\varepsilon_m - \varepsilon}{\varepsilon_m + 2\varepsilon} = 0 \]  

(30)

\[ \varepsilon - \varepsilon_m = f_i \frac{\varepsilon_i - \varepsilon_m}{\varepsilon_i + 2\varepsilon_m} \]  

(31)

In these equations, \( f \) is the volume fraction of the component, subscripts \( i \) and \( m \) indicate inclusions (the included substance), and matrix (the surrounding substance).

**Figure 4.12:** ITO film density as a function of the deposition pressure
respectively, and \( \varepsilon \) without a subscript is the dielectric constant of the mixture. The formulae are written in terms of the complex dielectric constant 
\( \varepsilon = (n^2 - k^2) + i(2nk) \). For a non-absorbing media, where \( k = 0 \), the complex dielectric constant can be written as \( \varepsilon = n^2 \). For pores or voids filled with air, \( \varepsilon_i = 1 \).

By substituting the square of the refractive index into the dielectric constant and replacing the volume fraction with porosity \( P \), equations (30) and (31), respectively become

\[
\frac{p}{1 - n^2_{\text{eff}}} + \frac{(1 - P)}{n^2_{\text{eff}} + 2n^2_{\text{eff}}} = 0 \tag{32}
\]

\[
\frac{n^2_{\text{eff}} - n^2_{\text{ITO}}}{n^2_{\text{eff}} + 2n^2_{\text{ITO}}} = p \cdot \frac{1 - n^2_{\text{ITO}}}{1 + 2n^2_{\text{ITO}}} \tag{33}
\]

To detect the change in porosity upon increasing deposition pressure, it was assumed that the film prepared at 0.5 Pa, which has the highest density, has very few or no pores. Thus \( n_{\text{ITO}} \) was replaced by 2.00 (Table 4.2). Therefore the change in porosity was obtained using, respectively, the equations (34) and (35) and by replacing \( n^2_{\text{eff}} \) by the values of \( n \) from Table 4.2.

\[
p = 2.00^2 - n^2_{\text{eff}} \left/ \left( \frac{2.00^2 - n^2_{\text{eff}}}{2.00^2 + 2n^2_{\text{eff}}} \cdot \frac{1 - n^2_{\text{eff}}}{1 + 2n^2_{\text{eff}}} \right) \right. \tag{34}
\]
\[ P = \frac{n_{\text{eff}}^2 - 2.00^2}{n_{\text{eff}}^2 + 2 \times 2.00^2} / \frac{1 - 2.00^2}{1 + 2 \times 2.00^2} \] (35)

Table 4.2

Film density, film thickness, band gap and refractive index of ITO films produced at various deposition pressures.

<table>
<thead>
<tr>
<th>Deposition pressure [Pa]</th>
<th>Density [g/cm²]</th>
<th>Film thickness [nm]</th>
<th>Band gap [eV]</th>
<th>Refractive index at 685 nm [1.81 eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>1.661</td>
<td>300.8</td>
<td>3.24</td>
<td>2.00</td>
</tr>
<tr>
<td>1.0</td>
<td>1.641</td>
<td>302.4</td>
<td>3.27</td>
<td>1.98</td>
</tr>
<tr>
<td>1.5</td>
<td>1.636</td>
<td>372.0</td>
<td>3.26</td>
<td>1.97</td>
</tr>
<tr>
<td>2.0</td>
<td>1.612</td>
<td>358.0</td>
<td>3.29</td>
<td>1.95</td>
</tr>
<tr>
<td>2.5</td>
<td>1.594</td>
<td>311.1</td>
<td>3.30</td>
<td>1.92</td>
</tr>
<tr>
<td>3.0</td>
<td>1.591</td>
<td>314.3</td>
<td>3.33</td>
<td>1.85</td>
</tr>
</tbody>
</table>

The determined values of the porosity are plotted in Fig. 4.13. It is easy to see from this plot that ITO film porosity increases with increasing deposition pressure. As the number of pores increases, the carrier concentration is reduced and this is responsible for the decrease in the value of the refractive index and hence the increase in optical transmittance with deposition pressure as earlier observed in Fig. 4.8.
Figure 4.13: Change in film porosity with deposition pressure as calculated from the Bruggeman and Maxwell Garnett effective medium expressions.

4.7 The Optical Band Gap Shift

In Fig. 4.14, the band gap is plotted as a function of deposition pressure. It is seen that the band gap widens from 3.24 to 3.33 eV at 0.5 and 3.0 Pa respectively. This shift of the band gap has a direct bearing on the changing optical properties. The reason for this phenomenon is not completely clear, but it can be explained using the Moss rule (Moss, 1950), which is the result of an analytical study that gives the relationship between the refractive index \( n \) and band gap \( E_g \) as:

\[
\frac{n^4}{E_g} = \text{const.}
\]  

(36)
The Moss rule is a scaling of energy states due to imperfection and voids in the formed films. At higher process pressure, there is increased collision between the target species and the gas molecules. As a result, the growing film is not bombarded with energetic particles for any structural re-arrangement leading to voids and defects and thus a wider band gap.

![Figure 4.14: The evolution of the band gap with increasing deposition pressure.](image)

The values of the optical band gap (3.24-3.33 eV) obtained in this study compare well with that reported by Stoica, et al., (2004) [3.3 eV] who have also studied amorphous films. However, our values are slightly lower than those reported by Mansingh & Kumar (1989) [3.5-3.7 eV] and Kammler et al., (2001) [3.5-3.65 eV]. Differences in the number of electronic states formed in the forbidden band gap due to the variety of prevailing deposition conditions, may be responsible for these different values of the band gap.
CHAPTER FIVE
CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The preceding chapters have given a report of the optical analysis of indium-tin-oxide thin films prepared with chamber pressures, due to argon gas alone, in the range 0.5 to 3.0 Pa. These films were fabricated by DC magnetron sputtering because of its excellent large area capability, ease of automation and production of high-purity films. In addition, the method is suitable for fabrication processes where step coverage, compositional control, film uniformity, high film adhesion and high deposition rates are required. DC magnetron sputtering of compounds is a cheaper alternative to rf magnetron sputtering of compounds because DC power supplies and target materials are comparably cheaper.

The films were fabricated using a target power of 200 W. The source-substrate separation was kept constant at 150 mm and the rotation speed of the substrates holder set at 40-rev/min. Only the deposition pressure due to argon gas was varied from 0.5 to 3.0 Pa, and thus obtained the various samples studied in this work. The films were produced from an ITO target of standard composition: 90% wt. In_{2}O_{3}, 10% wt. SnO_{2} and the starting substrates temperature during film production was room temperature.
Films with a thickness in the range 300-375 nm were fabricated and studied. The thicknesses of these films were established from optical transmittance in conjunction with a theoretical simulation of optical properties. The films showed excellent uniformity on the glass substrates, a feature that is admirable for the ITO films in their technical applications, given the precisions demanded. In addition, the film deposition rate showed no hysteresis behaviour, as would be the case for reactive sputtering. This indicated that our method of film preparation is preferable since it overcomes the problem of target poisoning.

The refractive index of the films decreased with deposition pressure, implying an increase in optical transmittance with deposition pressure. This phenomenal behaviour was explained by characterizing the density of the films. It was shown that the film density decreased with deposition pressure, and that this trend is related to the formation of pores in the film. The effective medium theories put forward by Bruggeman and Maxwell Garnett were used to calculate the change in film porosity with deposition pressure.

The optical band gap of the ITO films showed a general trend of increasing with deposition pressure: from 3.24 to 3.33 eV in the pressure range studied. This evolution of the band gap may be explained by the Moss rule. Values of the band gap obtained in this work compare well with those reported elsewhere.
5.2 Recommendations for Further Work

The results obtained and reported in this work show a clear influence of the deposition pressure on the optical behaviour of ITO films. However, this study was confined to a narrow range of chamber pressures (0.5-3.0 Pa) because of limitations imposed by the Sputtering Unit used for film production. It is therefore suggested that these films be investigated for a wider range of chamber pressures, probably up to 9.0 Pa. This is possible with state-of-the-art sputtering systems, and would provide a complete picture of the influence of deposition pressure on the prepared films.

The exact microstructure of the films obtained as the deposition pressure is varied could lead to a better understanding of this material. It is therefore suggested that X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) analyses be performed. Further, some applications to which these films are put, such as the use of ITO coating on an optical fibre tip for photon-scanning tunneling microscopy, demand a test of their mechanical stability. Various methods exist for doing this, and therefore recommendation is made for mechanical stability tests of these films, say by the so-called diamond method and/or the Taber Scratch test. These are adequate to reconstruct practical results.

Heat treatment of films is known to reduce intrinsic stress and increase stoichiometry. This study did not involve annealing, and therefore a similar study with in-situ or ex-situ annealed films is suggested. In addition, films in this work were characterized immediately after production. It would be interesting to study the behaviour of these films upon aging to gauge their longevity in the case of large-scale commercial applications.
REFERENCES


Appendix I

A picture of the Edwards Auto 306 Magnetron Sputtering System used in this work.
A picture of the set up of the Spectro 320 Optical Spectrum Analyzer used for spectral analysis.