INDIUM ZINC OXIDE THIN FILMS:
A NOVEL FAMILY OF TRANSPARENT CONDUCTING OXIDES

by
Matthew P. Taylor
A thesis submitted to the Faculty and Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Doctor of Philosophy (Materials Science).

Golden, Colorado

Date 11/3/05

Signed: Matthew P. Taylor
Matthew P. Taylor

Approved: Dr. Dennis W. Reaney
Thesis Advisor

Golden, Colorado

Date 11/3/05

Dr. John J. Moore
Professor and Head
Department of Materials Science
ABSTRACT

Transparent conducting oxides (TCOs) are a unique class of wide band gap semiconductors, which exhibit metallic-like conductivity and high (>80%) optical transmission. These materials are widely used in opto-electronic applications such as solar cells and flat panel displays. The growth of these industries and the advent of polymer-based devices has instigated the development of “low temperature” TCOs that can be deposited below 100°C.

The indium zinc oxide (IZO) composition system was examined using high-throughput, combinatorial techniques, which enabled this vast composition range to be explored in an efficient and effective manner. Compositionally graded “libraries” were deposited by d.c. magnetron sputtering on glass substrates at 100°C using argon. The electrical, optical and structural properties were analyzed as a function of composition. A peak in conductivity with $\sigma > 3,000(\Omega \cdot \text{cm})^{-1}$ was observed at an indium content of ~70%. The mobility ($\mu$) exceeded 30cm$^2$/V$\cdot$s and the carrier concentrations (N) were greater than 8x10$^{20}$/cm$^3$. Crystalline phases were observed for In concentrations less than 45% and greater than 80% with an intermediate amorphous region. All films showed high optical transparency with the transmission >80% across the visible spectrum. The libraries were annealed up to 600°C in air and argon and the amorphous films showed excellent structural and functional stability. The maximum conductivity following the air and argon anneal at 600°C was ~200 and 1,350(\Omega \cdot \text{cm})^{-1}$, respectively.

Films were deposited at room temperature on glass substrates from a two-phase IZO target (70%In:30%Zn) using Ar, Ar + O$_2$ and Ar + H$_2$. A transparent (T>85% in the visible), smooth (rms roughness ~0.13nm) film with a maximum
conductivity of $\sim 2000 (\Omega \cdot \text{cm})^{-1}$ was achieved with $N = 3.3 \times 10^{19} / \text{cm}^3$ and $\mu = 33.0 \text{cm}^2 / \text{V} \cdot \text{s}$ when depositing in Ar. As oxygen was increased up to 6%, $N$ decreased to $4 \times 10^{16} / \text{cm}^3$ while $\mu$ remained largely unaffected. The introduction of $H_2$ did little to increase $N$, but at 4% $H_2$, the optical properties were significantly degraded to a transmission of only $\sim 55\%$ in the visible. The direct band gap of $\text{In}_{0.30} \text{Zn}_{0.30} \text{O}_2$ was 3.23 eV and was found to vary linearly with $N^{2/3}$. The combination of conductivity, optical transmission and surface smoothness at low temperature makes amorphous IZO an excellent material for many applications.
TABLE OF CONTENTS

ABSTRACT ........................................................................................................................................... iii

LIST OF FIGURES ............................................................................................................................ ix

LIST OF TABLES ............................................................................................................................... xviii

ACKNOWLEDGEMENTS .................................................................................................................. xx

CHAPTER 1 INTRODUCTION ........................................................................................................... 1

1.1 Introduction to TCOs ................................................................................................................. 1
1.2 Historical Development ............................................................................................................. 2
1.3 Motivation for Research ........................................................................................................... 9
1.4 Research Objectives .................................................................................................................. 9
1.5 Thesis Organization ................................................................................................................ 10

CHAPTER 2 THEORETICAL BACKGROUND .................................................................................. 11

2.1 Introduction ............................................................................................................................. 11
2.2 Electrical Properties ............................................................................................................... 11
2.3 Optical Properties .................................................................................................................. 17
2.4 Crystal Structure .................................................................................................................... 30
2.5 Band Structure ....................................................................................................................... 33
CHAPTER 3 PREVIOUS EXPERIMENTAL WORK ........................................... 37

3.1 Introduction ...................................................................................... 37
3.2 Phase Regions and Conductivity ..................................................... 37
3.3 IZO Annealing Studies ................................................................... 41
3.4 Other Amorphous TCOs ................................................................. 47

CHAPTER 4 FILM DEPOSITION AND CHARACTERIZATION ..................... 49

4.1 Introduction ...................................................................................... 49
4.2 Film Deposition: DC Magnetron Sputtering ..................................... 49
4.3 Chemical Analysis ........................................................................... 55
4.4 Electrical Measurements ................................................................. 57
4.5 Optical Measurements ..................................................................... 62
4.6 Structural Analysis .......................................................................... 63
4.7 Morphology .................................................................................... 67
4.8 Method of 4 Coefficients ................................................................. 67
4.9 Auger Electron Spectroscopy ............................................................ 70

CHAPTER 5 PRIMARY RESULTS .............................................................. 71

5.1 Introduction ...................................................................................... 71
5.2 “The Electrical, Optical and Structural Properties of In_xZn_{1-x}O_y (0 \leq x \leq 1) Thin Films by Combinatorial Techniques”, Measurement Science and Technology, Matthew P. Taylor, Dennis W. Ready, Maikel F.A.M. van Hest, Charles W. Teplin, Jeff L. Alleman, Matthew S. Dabney, Lynn M. Gedvilas, Brian M. Keyes, Bobby To, John D. Perkins, David S. Ginley, 16 (2005) 90-94. .............................................. 71
5.2.1 Introduction .................................................................................. 72
6.2.5 Annealing Profiles .................................................. 140
6.2.6 Unidentified Crystalline Phase ................................... 141
6.3 Single Composition IZO .............................................. 144
  6.3.1 Target Preparation, Analysis and Composition ............... 144
  6.3.2 Chemical Analysis: EPMA, TEM, AES .......................... 146
  6.3.3 Method of 4 Coefficients ....................................... 147
  6.3.4 Auger Spectroscopy ............................................ 152
6.4 Optical Modeling .................................................... 153
6.5 Undoped ZnO and In₂O₃ .............................................. 159
6.6 Plasma Wavelength Characterization ............................... 169

CHAPTER 7 CONCLUSIONS AND RECOMMENDATIONS .................. 171

  7.1 Introduction .................................................................. 171
  7.2 Combinatorial Study .................................................. 171
  7.3 Annealing Study ...................................................... 172
  7.4 Single Composition IZO ............................................ 172
  7.5 Recommendations for Future Work ............................... 173

CHAPTER 8 REFERENCES .................................................. 175

APPENDIX A .................................................................. 185

APPENDIX B .................................................................. 191
LIST OF FIGURES

Figure 1.1 Sales in megawatts of photovoltaic devices.\textsuperscript{[9]} ........................................... 4
Figure 1.2 Sales trend for flat panel displays.\textsuperscript{[10]} .......................................................... 6
Figure 1.3 Change in resistivity for In\textsubscript{2}O\textsubscript{3}, SnO\textsubscript{2} and ZnO from 1970 to 2000.\textsuperscript{[20]} ...... 8
Figure 1.4 TCO composition space in which novel materials may be found.\textsuperscript{[1]} ................. 8

Figure 2.1 The transmission, reflection and absorption characteristics of a typical TCO. ................................................. 18
Figure 2.2 Change in transmission spectra as the carrier concentration varies. The parameters, t, \( \mu \), \( \varepsilon_x \), and \( m^* \) were fixed (t=film thickness). The periodic variation at short wavelengths is due to constructive and destructive interference from reflections at the substrate-film and film-air interface. The index of the glass substrate was assumed to be 1.5. .............................................................. 21
Figure 2.3 Change in reflection spectra as the carrier concentration varies. The parameters, t, \( \mu \), \( \varepsilon_x \), and \( m^* \) were fixed. ............................................................... 22
Figure 2.4 Change in transmission spectra as the mobility varies. The parameters, t, N, \( \varepsilon_x \), and \( m^* \) were fixed. ............................................................... 23
Figure 2.5 Change in reflection spectra as the mobility varies. The parameters, t, N, \( \varepsilon_x \), and \( m^* \) were fixed. ............................................................... 23
Figure 2.6 Change in transmission as the thickness of the film varies. ................................................. 29
Figure 2.7 Change in reflection spectra as the thickness of the film varies. ................................................. 29
Figure 2.8 Crystal structure of In\textsubscript{2}O\textsubscript{3}, showing the two non-equivalent In cation sites. ........................................................................................................... 31
Figure 2.9 Crystal structure of ZnO. ................................................................................................. 31
Figure 2.10 Layered Zn\textsubscript{2}In\textsubscript{2}O\textsubscript{8} homologous compound along the [010] from Dupont et al.\textsuperscript{[43]} ........................................................................................................... 32
Figure 2.11 Band structure of a crystalline semiconductor showing an unfilled conduction band (left) and a filled conduction band (right). ................................................. 35
Figure 2.12 Density of states versus energy for an amorphous semiconductor.\textsuperscript{[60]} .......... 36
Figure 3.1 Phase regions as a function of composition for IZO films deposited by various techniques at different temperatures ................................................................. 40

Figure 3.2 XRD spectra for IZO (84% In) annealed in vacuum for 1 hour at each target temperature. The (222) peak evident at 600°C corresponds to the In₂O₃ phase. [75] .......................................................................................... 41

Figure 3.3 The variation in mobility, carrier concentration and resistivity for IZO(84% In) when annealed at 300°C for 1 hour under various environments. [75] .......................................................................................... 42

Figure 3.4 Change in the resistance of IZO(67% In) during annealing from room temperature (RT) to 650°C in vacuum for films deposited at RT with varying amounts of O₂ (panel a). Panel b shows the resistance for the films in panel a at RT, 650°C and again at RT following the anneal. [77] ................................................................. 43

Figure 3.5 Change in resistance of IZO(67% In) during annealing from RT to 650°C in air for films deposited at RT with varying amounts of O₂ (panel a). Panel b shows the resistance of the vacuum annealed films (Figure 3.4) when they were reannealed in air up to 650°C. [77] .................................................................................. 44

Figure 3.6 Variation in resistance for ZnO (a), In₂O₃ (b) and IZO(70% In) (c) films which were annealed at 500° for 1 hour in air. [69] .......................................................... 45

Figure 3.7 Change in resistivity with temperature in vacuum (•) and oxygen (O) environments for pure ZnO (——) and IZO(3% In) (---). [76] .................................................. 46

Figure 4.1 Schematic representation of the orientation of the substrate to the ZnO and In₂O₃ targets. The row and column designation is also shown and the solid circles represent the location of the combinatorial measurements ............... 50

Figure 4.2 Illustration of a magnetron showing the magnetic field and path of the electrons .................................................................................................................. 52

Figure 4.3 Plan view of the sputtering chamber showing the orientation of the targets and the substrate ........................................................................................................... 54

Figure 4.4 Generation of characteristic x-rays, adapted from Williams, et al. [93] ....... 56

Figure 4.5 Typical EPMA map of a 5cm x 5cm compositional library, where the contours indicate the atomic % In to Zn. The mapping was performed in a 4 row by 11 column format as illustrated in Figure 4.1. The contours were created by interpolating between the 44 measured data points, which are listed in Table 4.3. ........................................................................................................... 56
Figure 4.6 Schematic illustration of the 4-point probe technique. A constant current (I) is forced through the outer two probes and the voltage drop across the inner two probes is measured. ................................................................. 59

Figure 4.7 Typical sheet resistance map of a 5cm x 5cm compositional library where the contours indicate the sheet resistance (Ω/sq). The sheet resistance mapping was performed in a four row by 11 column format as shown in Figure 4.1. The measured data points corresponding to this map are listed in Table 4.4. ............ 59

Figure 4.8 Hall effect in a thin film, where the electrons are deflected to one side of the film due to the magnetic field, $B_y$. ................................................................. 61

Figure 4.9 Transmission and reflection of Corning 1737 glass substrates. ........... 63

Figure 4.10 Illustration of the Bragg condition................................................................. 64

Figure 4.11 Illustration showing how diffracted x-rays in a textured, polycrystalline film are detected by changing the orientation (X) of the sample to the incident x-rays. Note: The x-ray source and detector are in the plane of page and the film extends out of the page................................................................. 65

Figure 4.12 Multiple scattering events occur as an electron beam impinges on a thin sample, which includes transmission of electrons.$^{[93]}$ ................................................................. 66

Figure 4.13 Illustration of the operation of an atomic force microscope.$^{[95]}$ ........... 67

Figure 4.14 Illustration of the Hall, Seebeck and Nernst effects in an n-type parabolic band material. The magnetic field, $B_y$, is directed out of the page and $V_{\text{drift}}$ and $V_{\text{diffusion}}$ are the electron drift and diffusion velocities, respectively.$^{[11]}$ ........................................ 69

Figure 4.15 Film configuration necessary for the method of 4 coefficients measurement.$^{[96]}$ ................................................................. 69

Figure 5.1 Conductivity as a function of indium content for the five IZO libraries... 76

Figure 5.2 Transmission and reflection characteristics of a typical film (top panel). Reflectance image plot with the estimated plasma wavelength overlaid for library 5 (bottom panel)........................................................................................................ 77

Figure 5.3 X-ray diffraction spectrum for the four libraries. The composite spectrum represents 11 data points from a single row of libraries 1 through 4. The inset shows the raw detector images for library 1, column 10 (A) and library 2, column 1 (B). ........................................................................................................ 79
Figure 5.4 FWHM (panel a) and the change in the (002) and (222) spacing (panel b) for libraries 1 through 4. The dotted line shows the c-axis interatomic spacing of the Zn$_k$In$_2$O$_{k+3}$ homologous compounds.\textsuperscript{[43]} ................................................................. 81

Figure 5.5 Conductivity (panel a), carrier concentration (panel b) and mobility (panel c) as measured by combinatorial tools (closed symbols) and discrete Hall measurements (open symbols). ................................................................. 82

Figure 5.6 Structural properties of as-deposited IZO. X-ray diffraction image intensity map for the 4 as-deposited libraries (L1-L4) shows both crystalline and amorphous regions. The insets show the raw detector images for 4\%, 69\% and 92\%In. The texturing of 4\%In is approximately normal to the substrate and that of 92\%In is toward the In$_2$O$_3$ gun. The different composition ranges were obtained by varying the sputtering conditions from the two targets. .................. 88

Figure 5.7 Analysis of the X-ray diffraction spectra. The full width at half maximum (FWHM) and calculated d-spacing for as deposited and 600°C Ar annealed libraries. The horizontal, dashed lines in the bottom panel indicate the d-spacing for ZnO (002) and In$_2$O$_3$ (222). Insets A and B show the structural transformations occurring at 4\% In and 92\% In, respectively. The vertical dashed lines in the insets show the 20 positions for ZnO (002) and In$_2$O$_3$ (222). The d-spacing for the amorphous region represents the nearest neighbor spacing for those compositions. The red, hour-glass shaped symbol in the bottom panel at 70\% In is the nearest neighbor spacing as determined by a TEM electron diffraction pattern and it agrees well with XRD data. The dotted line represents the d$_{002}$ of the Zn$_k$In$_2$O$_{k+3}$ homologous compounds.\textsuperscript{[42]} .................................................. 90

Figure 5.8 The conductivity, surface roughness and index of refraction for IZO deposited at 100°C. While the index of refraction varies slightly for all compositions, the conductivity shows a maximum and the roughness is at a minimum in the amorphous region, which is shown as the background color. .... 92

Figure 5.9 Optical properties of IZO films. Transmission image maps for the four compositional libraries in the as deposited, 600°C air and 600°C argon annealed conditions. The transmission spectrum shown at the top of each column is that of the highest conducting material in that group. The corresponding reflection data (black line) is also shown. The plasma wavelength is indicated by the black circles. The optical band gap of the material is shown at the right. .................. 94

Figure 5.10 Electrical and structural changes of IZO upon annealing. The conductivity of the IZO films is shown as function annealing temperature and composition for both air annealed (top panel) and Ar annealed (bottom panel) films. The conductivity is represented by the color intensity scale and the phases are indicated by the background colors. ................................................................. 96
Figure 5.11 X-ray diffraction spectrum showing the amorphous to crystalline transformation. The x-ray diffraction spectrum for the as deposited, 500°C and 600°C air annealed compositions from 69.9 to 79.8% In (columns 4 to 6, library 4). The insets show the raw detector images, which indicate the crystallized material is (222) textured although not normal to substrate surface but is textured toward the In$_3$O$_3$ sputtering gun......................................................... 100

Figure 5.12 Conductivity, mobility and carrier concentration for IZO films sputtered at 40W with varying oxygen contents. Inset A shows the change in film transmission normalized to the substrate with carrier concentration, N ($\times 10^{19}$/cm$^3$). Inset B shows the results of the Drude model (dotted line) applied to the transmission of IZO(Ar) on glass (normalized to air)........................................ 108

Figure 5.13 X-ray diffraction spectrum for the films deposited with Ar, Ar+6% O$_2$ and Ar+4% H$_2$. Inset A shows an electron diffraction pattern obtained from IZO(Ar) Line scans across the electron diffraction patterns of all three samples are shown in Inset B. Inset C shows a high resolution image IZO(Ar)................................................................. 109

Figure 5.14 Panel A shows the conductivity as a function of oxygen content for different IZO target powers. The inset shows the variation in carrier concentration and mobility for the films deposited with 2% O$_2$. Panel B depicts the conductivity as a function of the normalized deposition rate, %O$_2$/target power................................................................. 113

Figure 5.15 Conductivity, mobility and carrier concentration for IZO films deposited with argon plus hydrogen at 40W. The inset shows the change in transmission as a function of hydrogen content........................................................................................................ 114

Figure 5.16 Panel A shows $\alpha^2$ and $\alpha^{1/2}$ versus energy as a function of carrier concentration, N. The x-intercepts indicate the direct optical band gap ($E_{opt}$, top portion of panel A) and indirect optical band gap. Panel B illustrates the variation in the direct (top line) and indirect optical band gaps as a function of N$^{23}$. The y-intercept is taken as the direct ($E_g$). The analysis supports this being a direct band gap material................................................................. 116

Figure 5.17 RMS roughness of the three IZO films deposited with Ar, Ar+6%O$_2$ and Ar+4% H$_2$. The line with markers represents the rms roughness for indium zinc oxide films deposited by co-sputtering from two oxide targets. The insets show the AFM scan images relating to IZO(4%H$_2$) (top image) and IZO(Ar)........... 119

Figure 6.1 EPMA map of library 1. The contours indicate atomic % In for Zn. The third row was masked during deposition................................................................. 122
Figure 6.2  EPMA map of library 2. The contours indicate atomic % In for Zn. The third row was masked during deposition. .................................................. 123

Figure 6.3  EPMA map of library 3. The contours indicate atomic % In for Zn. The third row was masked during deposition. .................................................. 123

Figure 6.4  EPMA map of library 4. The contours indicate atomic % In for Zn. The third row was masked during deposition. .................................................. 124

Figure 6.5  EPMA map of library 5. The contours indicate atomic % In for Zn. The third row was masked during deposition. The optimal composition, 70% In, is now located at the center of the library.................................................. 124

Figure 6.6  Sheet resistance map of library 1. The contours indicate sheet resistance (Ω/sq). The third row was masked during deposition. ......................... 125

Figure 6.7  Sheet resistance map of library 2. The contours indicate sheet resistance (Ω/sq). The third row was masked during deposition. ......................... 126

Figure 6.8  Sheet resistance map of library 3. The contours indicate sheet resistance (Ω/sq). The third row was masked during deposition. ......................... 126

Figure 6.9  Sheet resistance map of library 4. The contours indicate sheet resistance (Ω/sq). The third row was masked during deposition. ......................... 127

Figure 6.10 Sheet resistance map of library 5. The contours indicate sheet resistance (Ω/sq). The third row was masked during deposition. ......................... 127

Figure 6.11 Transmission spectra for IZO(4.1%In), normalized to the substrate, as a function of air annealing. An increase in transmission and decrease in conductivity occurs with increased annealing................................................. 129

Figure 6.12 Reflection spectra for IZO(4.1%In), normalized to the substrate, as a function of air annealing. A decrease in reflection and decrease in conductivity occurs with increased annealing................................................. 129

Figure 6.13 Reflection image maps of library 1 for the as-deposited, 200°, 400° and 600°C air and Ar annealed conditions. All compositions for library 1 were crystalline (ZnO-type structure). .................................................. 131

Figure 6.14 Reflection image maps of library 2 for the as-deposited, 200°, 400° and 600°C air and Ar annealed conditions. All compositions for library 2 were crystalline (ZnO-type structure). .................................................. 132
Figure 6.15 Reflection image maps of library 3 for the as-deposited, 200°, 400° and 600°C air and Ar annealed conditions. All compositions for library 3 were amorphous up to 500°C. The abrupt transition in reflection occurring at 71 and 72% In following the 600°C anneal corresponds to an amorphous to crystalline (In$_2$O$_3$-type structure) transition. .......................................................... 133

Figure 6.16 Reflection image maps of library 4 for the as-deposited, 200°, 400° and 600°C air and Ar annealed conditions. The abrupt step in reflection shown in the air and argon annealed libraries corresponds to the transition from amorphous to crystalline (In$_2$O$_3$-type structure) material. The arrows indicate the amorphous region. .......................................................... 134

Figure 6.17 XRD spectrum for the amorphous glass substrate. The inset shows the XRD raw detector image. .......................................................... 135

Figure 6.18 XRD spectrum for library 1, column 10 following the 600°C air anneal. The top spectrum is the raw XRD data and the bottom spectrum shows the XRD data with the substrate (Figure 6.17) subtracted. .......................................................... 136

Figure 6.19 XRD raw detector images for library 1, columns 0, 3, 6 and 10. .......... 137

Figure 6.20 XRD raw detector images for library 2, columns 0 and 2. .............. 138

Figure 6.21 XRD spectra for library 4, 92% In (column 10) for the as-deposited, 200°, 400° and 600°C Ar annealed conditions. .......................................................... 139

Figure 6.22 XRD raw detector images for library 4, 92% In (column 10) in the as-deposited, 200°, 400° and 600°C Ar annealed conditions. .......................................................... 139

Figure 6.23 Annealing profiles for the air annealed IZO libraries. ................. 140

Figure 6.24 XRD spectra for library 4, 74% In (column 4) following the 500° and 600°C air anneals. The ZnO and In$_2$O$_3$ pdf’s are overlaid in the top and bottom panels, respectively. Peaks not assigned to either pdf are indicated with asterisks. .......................................................... 142

Figure 6.25 XRD raw detector images for library 4, 74% In (column 4) following the 500° and 600°C air anneals. .......................................................... 142

Figure 6.26 X-ray diffraction spectrum for library 4, columns 3 – 6, following the 600°C air anneal. The arrows indicate unidentified peaks that may be due to a ZnO phase. .......................................................... 143

Figure 6.27 XRD spectrum for the In$_{0.70}$Zn$_{0.30}$O$_3$ target. The inset shows the raw detector image. .......................................................... 145
Figure 6.28 Average In content for the three different samples as measured by EPMA, AES and TEM. The calculated and measured target composition is also shown. ..................................................................................................................... 148

Figure 6.29 Nernst voltage versus temperature for the amorphous IZO method of 4 coefficients measurement showing a large degree of uncertainty. The data are horizontally offset for clarity. The inset shows the Seebeck voltage versus temperature along with the linear fit. The Nernst voltage is on the order of nanovolts while the Seebeck voltage is on the order of microvolts. ...................... 151

Figure 6.30 Differentiated intensity versus energy for IZO(Ar) and IZO(6%O₂). ... 152

Figure 6.31 Differentiated intensity versus energy for IZO(Ar) and IZO(4%H₂). ... 153

Figure 6.32 Transmission and reflection data for a “thin” amorphous IZO(70%In) film. The model was only applied to the transmission data. The arrow relates the “bump” in the reflection data to the reflection of the substrate. ......................... 155

Figure 6.33 Transmission and reflection data for a “thick” amorphous IZO(70%In) film. The model was only applied to the transmission data. The reflection of the substrate is shown as the thin line. ................................................................. 156

Figure 6.34 Results of modeling both the transmission and reflection data simultaneously. The effective mass was fixed at 0.23 for this fit and all other parameters were allowed to vary. .......................................................... 156

Figure 6.35 The optical model applied to a film with N=4x10⁻⁶/cm³ from 250 to 100,000nm (0.250 to 100µm). The parameters t, εₓ, mₓ and µ were fixed while N was varied from 4x10⁻⁶ to 4x10⁻⁸/cm³ ................................................. 158

Figure 6.36 Transmission of an amorphous IZO film on glass normalized to the transmission of the glass and the transmission of air .......................................................... 159

Figure 6.37 Sheet resistance map (Ω/sq) of an undoped ZnO film. Row 3 was masked during this deposition ........................................................................................................... 160

Figure 6.38 Conductivity and thickness profiles across row 1 of the undoped ZnO film .............................................................. 160

Figure 6.39 Sheet resistance (Ω/sq) map for an undoped In₂O₃ film ............................................................... 161

Figure 6.40 Conductivity and thickness profiles across row 1 of the undoped In₂O₃ film .............................................................. 162

Figure 6.41 Conductivity as a function of deposition rate for undoped In₂O₃ and ZnO. The data points corresponding to columns 0 and 10 (C0 and C10, respectively) are also indicated ..................................................... 163

xvi
Figure 6.42  Thickness of library 2 compared to the sum of the individual In$_2$O$_3$ and ZnO depositions. The deposition conditions for library 2 were identical to those of the individual ZnO and In$_2$O$_3$ depositions........................................ 164

Figure 6.43 XRD spectra for the undoped ZnO (top panel) and In$_2$O$_3$ (bottom panel) films showing columns 0, 5 and 10. The insets show the raw detector images for columns 0 and 10.................................................................................. 166

Figure 6.44 XRD spectra for undoped In$_2$O$_3$, as-deposited IZO(92%In) and 200°C Ar annealed IZO(92%In). ........................................................................................................... 167

Figure 6.45 XRD spectrum for IZO(92%In) with the pdf for pure, unstrained In$_2$O$_3$
(a=10.117Å) and strained In$_2$O$_3$ (a=10.347Å). .......................................................... 168

Figure 6.46 Transmission, reflection and absorption spectra for amorphous
IZO(70%In) showing the combinatorial determined plasma wavelength ($\lambda_{p,combi}$) and the true plasma wavelength ($\lambda_p$).................................................................................. 170

Figure A1  Percent In measured at 10kV versus the %In measured at 20kV......... 186
Figure A2  Percent In measured at 10kV versus the %In measured at 20kV......... 186
Figure A3  The difference in %In measured at 10kV and 20kV versus the %In measured at 20kV for the thin (circles) and thick (squares) libraries......................... 187
Figure A4  %In measured at 10kV for the four thin and thick libraries.................. 188
Figure A5  %In measured at 20kV for the four thin and thick libraries.................. 188
Figure A6  Electron penetration depth ($D_e$) as a function of electron energy ($E_e$).... 190
**LIST OF TABLES**

Table 2.1 Defect equilibria notation .............................................................. 14

Table 3.1 Deposition conditions, substrate temperature, phases present and maximum conductivity for various IZO films. The composition and phase (H-homologous compound, A-amorphous, I-In2O3) corresponding to the maximum observed conductivity was found is listed next to $\sigma_{\text{max}}$ ................................................................. 39

Table 3.2 The deposition conditions and conductivities of various amorphous TCOs. .......................................................................................................................... 48

Table 4.1 Physical properties of Corning 1737 glass from Abrisa, a supplier of glass products ......................................................................................................................... 54

Table 4.2 The deposition conditions of the compositional libraries. .................. 55

Table 4.3 Atomic % In as measured by EPMA corresponding to the contour map shown in Figure 4.5. The atomic % Zn at each point is equal to 100-%In........... 57

Table 4.4 Sheet resistance data points (Ω/sq) correlating to the mapping scheme illustrated in Figure 4.1. The corresponding contour map is shown in Figure 4.7. ........................................................................................................ 60

Table 5.1 Output parameters of the Drude model applied to amorphous IZO plus/minus one standard deviation ................................................................................... 111

Table 6.1 Three different amorphous IZO samples, the sputter gas environment and the resulting functional properties ................................................................. 144

Table 6.2 Chemical analysis of three amorphous IZO films. The EPMA and AES results were obtained from the same samples while the TEM results were obtained from the thin films deposited directly on the TEM grids. .................. 147

Table 6.3 Output parameters of the method of 4 coefficients measurement on amorphous IZO(Ar) ........................................................................................................... 151
Table 6.4 Output parameters when fitting the transmission and reflection data individually and simultaneously for a "thick" amorphous IZO film. The effective mass was fixed to 0.23 for all fits.

Table 6.5 The measured deposition rate and calculated molecular impingement flux for column 5 of undoped ZnO, In$_2$O$_3$ and library 2. The density, molecular weight and calculated molar volume are also listed.
ACKNOWLEDGEMENTS

I want to express my gratitude toward the staff at NREL for supporting and encouraging me during this work. It was an outstanding environment in which to work and the people there made this experience truly enjoyable. In particular, I want to thank my NREL advisor, Dr. David Ginley, for his unwavering enthusiasm during the course of my research and the opportunity he provided me to present this work at the Third Japan-U.S. Workshop on Combinatorial Materials Science in Okinawa, Japan.

I also want to thank my advisor at the Colorado School of Mines (CSM), Professor Dennis Readey. It was a privilege to have his guidance and insight as I progressed with this work. His experience as both a scientist and teacher added depth and significance to my thesis.

Dr. John Perkins also mentored me during this work and he assisted in all aspects of my thesis. His door was always open and he was eager to discuss the results and help me with any question.

I also want to thank Dr. Maikel van Hest and Dr. Charles Teplin for their assistance with the deposition and optical systems. Maikel helped develop the deposition chamber in which the compositionally-graded libraries were deposited and Chaz was crucial in developing the automated optical analysis system which was used extensively in this work. Both Maikel and Chaz also assisted me in data preparation and analysis.

Dr. Hans-Joachim Kleebe at CSM deserves a sincere acknowledgement for teaching me the basics of TEM operation and analysis and for helping me produce
high-quality results. He took a personal interest in my work and I thoroughly enjoyed working with him.

There were many other people that I would like to acknowledge, which include Jeff Alleman, Matthew Dabney, Dr. Brian Keyes, Lynn Gedvilas, Bobby To and Dr. Phil Parilla. Jeff and Matt both took time to work with me in the lab and helped me understand and maintain the deposition systems. Brian and Lynn were critical in automating and gathering the infrared transmission and reflection data using the FTIR and Bobby To was responsible for obtaining the chemical data by EPMA. I also want to thank Phil for the time he took to discuss x-ray diffraction and analysis.

This work was supported by the US Department of Energy under contract no. DE-AC36-99-G010337 through the National Center for Photovoltaics and by the US Air Force, Wright Patterson.
CHAPTER 1
INTRODUCTION

1.1 Introduction to TCOs

Transparent conducting oxides (TCOs) are a group of materials with a unique combination of electrical and optical properties. These materials are characterized with having high conductivity (typically $>1000 \, \Omega \cdot cm^{-1}$) and high optical transmission in the visible portion of the spectrum (typically $>85\%$). TCOs are ubiquitous in advanced optoelectronic devices and typically, their role is that of a transparent electrode that is capable of transmitting light and conducting electrons. TCOs have had tremendous success in commercial devices such as liquid crystal displays (LCDs) and solar cells and this is due to two important factors. The first is that there are few alternatives when optically transparent, electrically conducting materials are required and the second is that they exhibit exceptional performance over those alternatives. Most commercial TCOs consist of ZnO, SnO$_2$ and In$_2$O$_3$ which are wide bandgap (3- 4 eV) semiconductors. By introducing point defects through dopants or vacancies, a large concentration of free carriers can be obtained, resulting in a very conducting medium.

TCOs occupy a niche among oxides and other semiconductors. For example, CdO is transparent at long wavelengths and is somewhat conducting but the small bandgap (2.2 eV) prevents it from being applicable where transmission across the visible wavelengths is required.$^{[1]}$ Alumina, Al$_2$O$_3$, is a large band gap oxide ($\sim$10 eV) but is an insulator at room temperature.$^{[2]}$ Thin films (<100nm) of silver and gold exhibit properties similar to those of TCOs and find use in niche applications. However, TCOs exhibit greater stability, durability, substrate compatibility and
typically, greater optical transmission.\textsuperscript{[3,4]} As a result, TCOs are found in the vast majority of applications where films of high optical transmission and electrical conductivity are required.

When applying TCOs in optoelectronic devices there is a compromise between the conductivity and transparency of the film. The electrical and optical properties are intimately related and many times enhancing one will degrade the other. Therefore, the scientist must fully understand the device requirements when designing and applying these materials. The most prevalent TCOs utilized today are Al:ZnO, In:SnO\textsubscript{2} and Sn:In\textsubscript{2}O\textsubscript{3}. Active research continues in developing new TCOs, both n- and p-type with increased electrical conductivity and high optical transparency. Advances in materials and the development of new applications ensure that transparent conducting oxides will be technologically significant materials for years to come.

1.2 Historical Development

The first transparent conducting oxide was discovered in 1907 by Badeker who found that thin films of cadmium, when oxidized in air became somewhat transparent and retained some electrical conductivity.\textsuperscript{[5]} The first known applications occurred during WWII when thin coatings of tin oxide were applied to the windows of high altitude bombers.\textsuperscript{[6]} This permitted the window to be electrically heated to prevent frost formation while still allowing the pilot good visibility. Tin oxide was commercially deposited by spray pyrolysis in 1947 and new applications were developed such as front contact electrodes on electroluminescent panels, resistive elements for deicing the windows of optical instruments, rectifier photocells and antistatic coatings.\textsuperscript{[5-7]} By 1956, SnO\textsubscript{2}-Sb\textsubscript{2}O\textsubscript{3} films attained conductivities as high as
$1 \times 10^3 \ (\Omega \cdot \text{cm})^{-1}$ with optical transmissions of 85-90\%.[5] Thin films of Au and Ag were of great interest as well and were competitive with TCOs. The conductivity ($>10^6 (\Omega \cdot \text{cm})^{-1}$) of such metal films was much greater than that of tin oxide but the optical transmission reached a maximum of only 80\%. The practical advantages of TCOs, however, were also in their greater hardness, stability and durability. In a materials comparison in 1956, Holland rated the hardness of indium tin oxide (ITO) and tin oxide as “exceptionally good” and that they could not be removed by “scratching with a steel pin”. This would clearly not be the case for a soft metal such as gold or silver. The TCO films also showed compatibility with a greater number of substrates. The exceptional properties of light transmission, mechanical and chemical stability and substrate compatibility proved TCOs to be of greater advantage in many situations.

Scientific interest and the potential of new applications fueled research on the fundamental mechanisms of conductivity in these materials through the 1960s. But greater national interest and funding of TCOs exploded in the 1970s as a result of the Arab oil embargo and the energy crunch.[8] The need for energy efficiency and renewable energy devices emerged rapidly as oil prices skyrocketed. The opportunities for TCOs emerged in two ways. The first was in the field of photovoltaics and although this was not a new field, the energy crunch resulted in increased government spending and awareness of such devices and subsequently, on the research and development of TCOs. Since the 1970s consumer demand for solar energy has also increased which has in turn helped fuel research on TCO coatings. Figure 1.1[9] illustrates the increase in photovoltaic device sales from 1988 to 2001 for the world market.

The second opportunity for TCOs that emerged in the 1970s was in the field of energy efficient windows. Prior to 1973 approximately 5\% of the national energy consumption was related to the heating, cooling and lighting of buildings.[8] This massive use of energy directly resulted from inefficient windows that allowed
excessive thermal energy to enter and leave the building. To combat, this the federal government initiated a program to develop energy efficient windows that would selectively transmit and reflect infrared radiation, thereby reducing these energy costs. The development of these windows was one in which TCOs and thin metal films proved to be complementary. Similar to metals, TCOs reflect long wavelength radiation and change from reflecting to transmitting at the plasma frequency. However, this occurs at a shorter frequency or longer wavelength for TCOs than metal films. Therefore, the use of both materials would allow selected wavelengths to be reflected or transmitted through the window.

![Graph](image)

Figure 1.1 Sales in megawatts of photovoltaic devices.\[^9\]

The significance of these energy efficient or low-e windows cannot be understated. By 1995 the cumulative energy savings attributed to low e- windows for the United States approached $2.1 billion while their market share grew to 35% by
2000. It is estimated that U.S. businesses and consumers will experience a net savings of $17 billion by 2015. An extended benefit of this energy savings is in the reduction of greenhouse gas emissions. By 1996 the annual production of TCO coated glass utilized primarily for windows was greater than 73 km². Today, fluorine doped tin oxide is commonly used as the coating for low-e windows. Tin oxide has an emissivity of about 0.16 and as such is very efficient in preventing radiative heat loss through windows. The commercial success of low-e windows has helped drive funding and research of TCO coatings for over 20 years.

The national focus on energy conservation and pollution control during the 1970s also prompted the development and use of TCOs as gas sensors. Extensive work was conducted on tin oxide and zinc oxide as detectors of CO, CO₂, H₂, H₂S, alcohols and hydrocarbons. These devices were designed to monitor hazardous gases and optimize combustion reactions. Tin oxide was also pursued as a sensor for smoke detectors. By 1983 TCOs were employed in a multitude of devices such as electrochromic displays, light-emitting diodes and liquid crystal displays. TCO coatings continued to be applied as heat mirrors and found use as antifogging and deicing elements on the windows of cars, airplanes and ships. These films also provided use as electrostatic discharge paths on device surfaces. Two other applications developed during the early 1980s included touch-sensitive switches and microwave shielding. In 1983 a status review of the field by Chopra, et al. concluded that the goal of future research would include obtaining metallic conductivity while maintaining optical transparency and the continued tailoring of infrared reflectivity for heat mirror applications.

Transparent conducting oxides remained technologically relevant materials throughout the 1980's and 1990's and new applications continued to develop. The exploding field of liquid crystal displays (LCDs) relied on TCOs as the transparent electrode. The extensive number of LCD applications for consumers, industry and
government, continued to drive interest and research of these materials. Figure 1.2 illustrates the impact of flat panel display sales from 1996 to 2005.

![Figure 1.2 Sales trend for flat panel displays.][10]

Today, most commercial TCOs are n-type and as recently as 1995 Hartnagel, et al. stated that all TCOs are n-type. However, there was growing interest in the mid-1990s of utilizing TCOs for their semiconducting as well as optical properties. To realize this required the discovery of transparent, semiconducting p-type materials. CuAlO₂ was first reported as a p-type TCO by Kawazoe, et al. in 1997. This discovery opened up a new field where these materials could be exploited as transparent semiconductors. The potential for “invisible” circuitry was perceived to be enormous for both the government and consumers. Potential applications for transparent semiconducting oxides (TSOs) range from transparent diodes, transistors, switches and amplifiers to invisible security system devices, contacts in flat-panel displays, UV emitting diodes and heterojunction partners for photovoltaics. The successful application of a transparent semiconducting oxide was realized in 2000.
when n-type ZnO and p-type SrCu₂O₂ were combined to create a UV-emitting diode. Future research in this field will focus on discovering a broader range of p-type TCOs and improving the conductivity and optical transparency.

Indium tin oxide currently has the lowest resistivity of any commercial TCO and Figure 1.3 illustrates how it has changed over the past 30 years. This figure also shows that the resistivity of ITO has stabilized around 10⁴ Ω·cm. While many researcher are interested in decreasing the resistivity further, there is also a need for TCOs with specific optical and electrical properties or other attributes, such as work function, surface properties or processibility. One challenge in developing new TCOs lies in effectively investigating the large number of potential compounds. A likely region to find such compounds is the composition space of known TCOs, such as ZnO, In₂O₃, SnO₂, CdO and Ga₂O₃, shown in Figure 1.4.

Since tin oxide was first introduced as a window defogger in WWII, the number of applications for transparent conducting oxides has exploded. Cell phone and watch displays, computer monitors and energy efficient windows all rely on TCOs for their unique combination of properties. After 50 years of research, the conductivity of these materials has increased from 10³ to 10⁵ (Ω·cm)⁻¹ and the potential for even higher conductivity does exist. Meanwhile, consumer demand for larger, higher resolution displays with greater writing speeds and faster graphics, solar cells, smart displays and low e- and electrochromic windows is stimulating government and industrial funding of TCO research.
Figure 1.3 Change in resistivity for In$_2$O$_3$, SnO$_2$ and ZnO from 1970 to 2000.$^{[20]}$

Figure 1.4 TCO composition space in which novel materials may be found.$^{[1]}$
1.3 Motivation for Research

The development of polymer substrates with the need for low temperature deposition is driving the development of “low temperature” TCOs. Presently, tin-doped indium oxide (ITO) is one of the most prevalent TCOs utilized for display applications.[10,6] Although ITO offers some of the best properties available in a TCO with a conductivity, $\sigma$, on the order of 6,000 ($\Omega\cdot$cm)$^{-1}$ and optical transmission greater than 85%, the high deposition temperature necessary (typically $\sim$350°C), increases production costs and prevents the use of temperature sensitive substrates, i.e. polymers. Therefore, it is essential that new TCOs be developed which meet these processing demands. There are also niche applications which may require TCOs with additional specific attributes such as surface smoothness, etchability and work function.[16,17] The need for next generation TCOs is the motivating force for this thesis.

The indium zinc oxide system is also interesting due to the many stoichiometric compounds such as In$_2$Zn$_2$O$_5$ that exist and the potential variation in properties with composition. For example, the Zn-rich compounds may be characterized as having an n-type dopant, In, whereas the In-rich compounds have a p-type dopant, Zn. The endpoints of this composition region, ZnO and In$_2$O$_3$, are well established TCOs and the potential of this system is of interest to the scientific and commercial community.

1.4 Research Objectives

The objective of this thesis is to thoroughly explore the ZnO-In$_2$O$_3$ (IZO) composition system. Compositionally graded samples of IZO will be deposited by dc magnetron sputtering on Corning 1737 glass substrates at 100°C. Due to the In:Zn
composition gradient present, each sample can be thought of consisting of a large number of single composition films all compiled on one substrate. Therefore, the term "library" is used to describe these samples because each library contains a large number of samples, each with a different composition. The functional and structural properties of the as-deposited libraries are characterized as a function of composition. The properties of these films will then be analyzed when they are annealed in air or argon environments. This allows for identification of the "optimal" IZO composition, which is defined as having the highest conductivity and optical transmission in the as-deposited condition and functional stability upon annealing. This composition is then optimized through depositions from a single composition target. This work contributes new information and understanding of TCOs to the field.

1.5 Thesis Organization

The basic physics and properties of TCOs are outlined in Chapter 2 and Chapter 3 presents previous experimental work on the IZO system. Chapter 4 describes the film deposition and characterization techniques. The primary results are presented in Chapter 5 in the form of one published paper and two others that have been prepared for publication. Additional results pertaining to those presented in Chapter 5 are contained in Chapter 6. Chapter 7 includes a summary and recommendations for future work. References are contained in Chapter 8. Appendix A discusses the use of electron probe microanalysis as a quantitative tool for chemical analysis and Appendix B contains the material safety data sheets for ZnO and In$_2$O$_3$. 
CHAPTER 2
THEORETICAL BACKGROUND

2.1 Introduction

An introduction to transparent conducting oxides and the history of their development was described in chapter 1. In addition, the motivation for examining the ZnO-In₂O₃ system was also established. This chapter outlines the theories of electrical conduction and optical transmission, reflection and absorption process in TCOs. These theories and equations will subsequently be used to model and characterize the optical properties of the films and extract the electrical parameters as well.

2.2 Electrical Properties

Transparent conducting oxides are characterized by having metal-like conductivity, which results from a large free carrier concentration. The conductivity in units of (Ω·cm)⁻¹ is defined as

\[ \sigma = Ne\mu \]

Equation 2.1

where \( N \) is the carrier concentration (#/cm³), \( e \) is the electron charge (C) and \( \mu \) is the mobility (cm²/V·s). Typically the carrier concentration is on the order of \( 10^{19}-10^{20}/\text{cm}^3 \) for TCOs compared to \( 10^{22}/\text{cm}^3 \) for metals such as copper and gold. The mobility is defined as
\[ \mu = \frac{e\tau}{m_e} \]

Equation 2.2

where \( m_e^* \) is the electron effective mass and \( \tau \) is the scattering time. The effective mass describes how easily the electrons move through the material under an applied electric field whereas \( \tau \) indicates the amount of time between scattering events. The mobility of typical TCOs is on the order 10-50cm\(^2\)/Vs which is similar to that of Cu (32cm\(^2\)/Vs) and Au (57cm\(^2\)/Vs).\(^{[21]} \) For comparison, the mobility of Si, Ge and GaAs are 1,350, 3,900 and 8,500cm\(^2\)/Vs, respectively.\(^{[22]} \) The scattering time is a function of the different scattering mechanisms in the material, which include lattice or phonon scattering, ionized impurity scattering, neutral impurity scattering and electron-electron scattering.\(^{[3]} \) Per Matthiessen’s rule,\(^{[21]} \) the electron mobility is the sum of the individual components and is given as

\[ \frac{1}{\mu_e} = \frac{1}{\mu_{ii}} + \frac{1}{\mu_L} + \frac{1}{\mu_N} + \frac{1}{\mu_{ee}} \]

Equation 2.3

where \( \mu_e \) is the electron mobility, \( \mu_{ii}, \mu_L, \mu_N, \) and \( \mu_{ee} \) are the mobility components due to ionized impurity, lattice, neutral impurity and electron scattering, respectively. As the influence of these different scattering mechanisms increases, the overall mobility decreases. Typically, ionized impurity scattering has the greatest influence on electron mobility in a doped semiconductor whereas the effects of electron-electron interactions limiting the mobility can be neglected.\(^{[3,21]} \) The parameters affecting these different mobility terms are given as

\[ \mu_{ii} \propto T^{3/2}N_{ii}^{-2/3} \]
\[ \mu_L \propto T^{-3/2} \]
\[ \mu_N \propto N_N^{-1} \]

Equation 2.4
where $N_i$ is the ionized impurity concentration and $N_N$ is the neutral impurity concentration. The temperature term in $\mu_n$ accounts for the dependence on impurity ionization with temperature. Grain boundary scattering is another mechanism that can reduce the mobility of electrons in TCO films. However, this effect is not significant and in many cases, the mean free path of the electron is much smaller than the grain size which reduces the effect even further.\textsuperscript{[23]}

Free electrons in metal oxides are generated from several different sources, which include an excess of the metal, a deficiency of oxygen or through doping. In pure, defect-free ZnO, for example, the oxidation state of Zn is +2, O is −2 and all of the lattice sites are occupied. However, free electrons can be generated if defects, either interstitial atoms, substitutional atoms or vacancies, exist. This is illustrated in the following equilibrium reactions\textsuperscript{[24]}

$$Zn(g) \Leftrightarrow Zn_i^{**} + 2e'$$ \hspace{1cm} \textit{Equation 2.5}

$$O_o^{+} \Leftrightarrow \frac{1}{2} O_2(g) + V_o^{**} + 2e'$$ \hspace{1cm} \textit{Equation 2.6}

$$In_2O_3(s) \Leftrightarrow 2In^{+}_{zo} + 2O_o^{+} + \frac{1}{2} O_2(g) + 2e'$$ \hspace{1cm} \textit{Equation 2.7}

The notation for these reactions is listed in Table 2.1.
Table 2.1 Defect equilibria notation.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn(g)</td>
<td>Zinc gas</td>
</tr>
<tr>
<td>Zn$_i^{**}$</td>
<td>Zn atom in an interstitial position, the two solid circle superscripts indicate a +2 charge on this ion</td>
</tr>
<tr>
<td>O$_o^{**}$</td>
<td>Oxygen atom on an oxygen lattice site, the superscript denotes that there is no change in oxidation state</td>
</tr>
<tr>
<td>V$_o^{**}$</td>
<td>A vacancy on an oxygen lattice site with a net charge +2</td>
</tr>
<tr>
<td>$e'$</td>
<td>A free electron generated to maintain charge neutrality, the superscript indicates a negative charge</td>
</tr>
<tr>
<td>O$_s$(g)</td>
<td>Removal of oxygen from the solid in the form of gas</td>
</tr>
<tr>
<td>In$_2$O$_3$(s)</td>
<td>Crystalline In$_2$O$_3$</td>
</tr>
<tr>
<td>In$_{Zn}^{**}$</td>
<td>In atom on a Zn lattice site with a net increase in charge of +1 from a Zn$^{2+}$</td>
</tr>
</tbody>
</table>

Equation 2.5 describes the case of two free electrons being generated due to a Zn$^{2+}$ interstitial in the ZnO crystal structure whereas equation 2.6 shows free electron generation due to the formation of oxygen vacancies. The case of indium doped ZnO is shown in equation 2.7 where In$^{3+}$ substitutes for Zn$^{2+}$ on the Zn lattice site, oxygen is on the oxygen lattice site and 2 free electrons are generated to maintain charge neutrality.

All of these equilibrium reactions result in an increase in conductivity through the generation of free electrons. To characterize this, an equilibrium constant, K, can be introduced which relates the equilibrium concentration of free electrons and donor species (dopant or vacancy). For the case of free carrier generation due to oxygen vacancies (equation 2.6) the equilibrium constant is written as

$$K = \left[ V_o^{**} \right] \left[ e' \right]^2 \left( \frac{1}{p_o^{**}} \right)$$

Equation 2.8
where the brackets represent the concentration (site fraction) of oxygen vacancies and free electrons and $p_{v_o}$ represents the partial pressure of oxygen. If two free electrons are generated with each vacancy, then

$$2[V_o^{**}] \propto [e]$$

*Equation 2.9*

and the free electron site fraction is given as

$$[e] \propto (2K)^{3/4} p_v^{-1/2}$$

*Equation 2.10*

This results in the conductivity being inversely proportional to oxygen partial pressure

$$\sigma \propto p_v^{-1/2}$$

*Equation 2.11*

To a first order, equation 2.11 indicates that the conductivity will be optimized when $p_{v_o}$ is as small as possible.

Similar equations can be written for the defect equilibria of In$_2$O$_3$ however, for Zn-doped In$_2$O$_3$, the difference in valence state (Zn$^{2+}$, In$^{3+}$) results in the generation of holes instead of electrons. The equilibrium reaction in this case can be written as

$$\frac{1}{2}O_2 + 2ZnO \Leftrightarrow 2Zn^{2+} + 3O^{+} + 2h^+,$$

*Equation 2.12*

where Zn replaces an In ion on the In lattice site, resulting in a net charge of $-1$ for each substitution and two positive holes are generated to maintain charge neutrality. Free electrons can be generated in In$_2$O$_3$ as illustrated in equation 2.6 and as shown in the following reaction

$$In(g) \Leftrightarrow In^{+++} + 3e^-.$$

*Equation 2.13*
As a result of the high free electron concentration the Fermi energy, $E_F$, lies within the conduction band and the material is referred to as a “degenerate” semiconductor. This occurs because the electron concentration is greater than the density of states.$^{[22]}$ The energy of these electrons is given as

$$E_F = \frac{\hbar^2 k_F^2}{8\pi^2 m_e},$$  

*Equation 2.14*

where $k_F$ is the Fermi wave vector, defined as

$$k_F^3 = 3\pi^2 N$$  

*Equation 2.15*

and $\hbar$ is Planck’s constant.$^{[23]}$ The transition from non-degenerate to degenerate occurs at the Mott critical density, $N_c$.$^{[25,26]}$ This is given as

$$N_c \approx 0.2/a_H,$$  

*Equation 2.16*

where $a_H$ is the Bohr radius which is defined as

$$a_H = \frac{4\pi\varepsilon\varepsilon_0 \hbar^2}{m_e e^2}$$  

*Equation 2.17*

and $\varepsilon$ is the static dielectric constant.$^{[25,26]}$ The Mott critical density for In$_x$O$_{1-x}$, assuming a dielectric constant of $\sim 8.9$ and an effective mass of $\sim 0.3$ is calculated to be $\sim 3 \times 10^{18}/\text{cm}^3$, which is two orders of magnitude less than what is typically found in TCOs such as optimized ITO.$^{[13,27]}$

The Drude theory is commonly applied to describe the behavior of the free electrons in a degenerate TCO. This theory applies the kinetic theory of gases to a free electron “gas” in the film. There are four basic assumptions of this model which include that (1) the interaction of electrons between collisions is zero (2) electron-ion collisions are instantaneous events which change the electron velocity immediately,
(3) the probability of an electron undergoing a collision per unit time is $1/\tau$ and (4) electrons attain thermal equilibrium with the surroundings only through collisions.\textsuperscript{[23]} As will be shown in section 2.3 on the optical properties of TCOs, the Drude theory also relates the electrical and optical parameters.

2.3 Optical Properties

The transmission, reflection and absorption characteristics of a TCO film are shown in Figure 2.1. The transmission (T) and reflection (R) were experimentally determined and the absorption (A) was calculated as $A = 100 - T - R$. The salient features include high transmission in the visible portion of the spectrum (450-750nm), an abrupt decrease in transmission at short wavelengths (~350nm) due to the band gap, a decrease in transmission and increase in reflection around 1500nm with low transmission and high reflection at long wavelengths (~1500nm). The long wavelength point at which the transmission decreases, reflection increases and the absorption shows a maximum occurs at the plasma wavelength which is given as

$$\lambda_p = \left( \frac{4\pi^2 c^2 m^* \varepsilon_\infty \varepsilon_0}{N e^2} \right)^{1/2},$$

Equation 2.18

where $c$ is the speed of light, $\varepsilon_\infty$ is the permittivity of free space, $\varepsilon_0$ is the high frequency permittivity. At this wavelength, the frequency of the light is the same as the natural resonant frequency of the collective electron oscillations and the free electrons oscillate in phase with the electric field vector of the incident wave, absorbing the maximum amount of energy.\textsuperscript{[1]} This point is indicated in Figure 2.1 by the arrow. The term plasma frequency is also often used to describe this point and is defined as
\[
\omega_p = \frac{2\pi c}{\lambda_p} = \left( \frac{Ne^2}{\varepsilon_{\infty} m_e} \right)^{1/2} = \left( \frac{\sigma}{\varepsilon_{\infty} \tau} \right)^{1/2}.
\]

Equation 2.19

A strong correlation between the electrical properties and optical properties exists in TCO films as indicated by equation 2.18 where \( \lambda_p \propto \frac{1}{N^{1/2}} \). Because of this inverse relationship, a balance between \( N \) and \( \lambda_p \) must be achieved in order to optimize the conductivity without the absorption moving to the optical wavelengths.

Figure 2.1 The transmission, reflection and absorption characteristics of a typical TCO.
The optical properties of TCO films can be explained on the basis of Drude's theory of free electrons. A plane-polarized electromagnetic plane wave of angular frequency $\omega$ moving in the $z$-direction and vibrating in the $x$-direction as a function of time, $t$, can be written as

$$c^2 \frac{\partial^2 E_x}{\partial z^2} = \varepsilon \frac{\partial^2 E_x}{\partial t^2} + \frac{\sigma}{\varepsilon_0} \frac{\partial E_x}{\partial t},$$

*Equation 2.20*

where $c$ is the speed of light, $\varepsilon$ is the relative permittivity and $\sigma$ is the conductivity. A solution to this equation is of the form,

$$E_x = E_0 \exp[i\omega(t - \frac{zn}{c})],$$

*Equation 2.21*

where $n$ is the index of refraction. Differentiating equation 2.20 once with respect to $t$ and twice with respect to $t$ and $z$ results in a complex index of refraction

$$(n^*)^2 = \varepsilon - \frac{\sigma}{\varepsilon_0 \omega} i = \varepsilon - \frac{Ne^2\tau}{\varepsilon_0 \omega m_e} i,$$

*Equation 2.22*

which can be written in the form

$$(n^*)^2 = n^2 - k^2 - 2nki,$$

*Equation 2.23*

where $k$, the extinction coefficient, describes the attenuation of the incident wave as it propagates through a medium.

The relative permittivity, $\varepsilon$, is due to polarization (P) of the material based on the interaction of the incident electromagnetic wave and the free electrons and is given as

$$\varepsilon = 1 + \frac{P}{\varepsilon_0 E},$$

*Equation 2.24*
where \( E \) is the field strength of the plane-polarized wave. The polarization is the sum of the dipole moments per unit volume of the free electrons and equals

\[
P = e\lambda N,
\]

\textit{Equation 2.25}

where \( e \) is the electron charge and \( \lambda \), the displacement of the electrons due to the electric field component of the electromagnetic wave, is given as

\[
\lambda = \frac{-eE}{m_e^*\omega^2}.
\]

\textit{Equation 2.26}

Combining equations 2.24 – 2.26 yields the complex permittivity

\[
\varepsilon^* = 1 - \frac{e^2N}{m_e^*\varepsilon_o\omega^2}
\]

\textit{Equation 2.27}

\[
\varepsilon^* = \varepsilon_1 - i\varepsilon_2 = n^2 - k^2 - 2nki,
\]

\textit{Equation 2.28}

where \( \varepsilon_1 \) and \( \varepsilon_2 \) are the real and imaginary components, respectively. The real component therefore equates to

\[
\varepsilon_1 = n^2 - k^2 = \varepsilon_{\infty} \left(1 - \frac{\omega_p^2}{\omega^2 + \frac{1}{\tau^2}}\right) = \varepsilon_{\infty} - \frac{\tau\sigma}{\varepsilon_o (1 + \omega^2\tau^2)}.
\]

\textit{Equation 2.29}

The imaginary component of the dielectric constant is given as

\[
\varepsilon_2 = 2nk = \frac{\omega_p^2\varepsilon_{\infty}}{\omega\tau (\omega^2 + \frac{1}{\tau^2})} = \frac{\sigma}{\omega\varepsilon_o (1 + \omega^2\tau^2)}
\]

\textit{Equation 2.30}
where \( \tau \) is the scattering time and the number of scattering events per second is given as \( \frac{1}{\tau} \).

Equations 2.22 and 2.23 illustrate the relationship between the optical parameters, \( n \) and \( k \), to \( N \) and \( \mu \), the electrical parameters. Figures 2.2-2.5 illustrate how variations in mobility and carrier concentration affect the transmission and reflection characteristics of a TCO. Figure 2.2 illustrates how the transmission of a TCO film in the long wavelength regime increases as the carrier concentration decreases. Figure 2.3 illustrates the corresponding decrease in reflection as \( N \) decreases. This results from the plasma wavelength shifting to longer wavelengths as \( N \) decreases, equation 2.18, which gives the relationship \( \lambda_p \propto \frac{1}{N^{1/2}} \).

![Graph](image)

Figure 2.2 Change in transmission spectra as the carrier concentration varies. The parameters, \( t \), \( \mu \), \( \epsilon_r \), and \( m_e^* \) were fixed (\( t \)=film thickness). The periodic variation at short wavelengths is due to constructive and destructive interference from reflections at the substrate-film and film-air interface. The index of the glass substrate was assumed to be 1.5.
Figure 2.3 Change in reflection spectra as the carrier concentration varies. The parameters, $t$, $\mu$, $\varepsilon_{\infty}$, and $m^*_e$ were fixed.

The effect of a changing mobility on the transmission of a TCO is shown in Figure 2.4, where it can be seen that as the mobility increases, the decrease in $T$ becomes more dramatic. This corresponds to a steeper increase in reflection as shown in Figure 2.5. The result is that the absorption decreases and becomes more localized as the mobility increases. Therefore, in addition to increasing the conductivity, a high mobility is desired for TCOs because of the reduced absorption at $\lambda_p$. 
Figure 2.4 Change in transmission spectra as the mobility varies. The parameters, $t$, $N$, $\varepsilon_\infty$, and $m_e^*$ were fixed.

Figure 2.5 Change in reflection spectra as the mobility varies. The parameters, $t$, $N$, $\varepsilon_\infty$, and $m_e^*$ were fixed.
The index of refraction and extinction coefficient can be determined by modeling the reflection (R) and transmission (T) of the film with the Fresnel equations, where\textsuperscript{[301]}

\[
R = \frac{(n_0 - n_i)^2 + k_i^2}{(n_0 + n_i)^2 + k_i^2}
\]

Equation 2.31

and

\[
T = \frac{4n_0n_i}{(n_0 + n_i)^2 + k_i^2}.
\]

Equation 2.32

The terms \(n_0\) and \(n_i\), refer to the indexes for the two mediums through which the wave is traveling. In the case of a single film in air, the term \(n_0\) is equal to 1.0 and \(k_i\) is the extinction coefficient of the film.

Four distinct wavelength/frequency regions can be identified from Figure 2.1.

(1) High reflectivity region, \(\omega < \omega_p\) (\(\lambda > \lambda_p\))

In the long wavelength, low frequency region where \(\omega < \omega_p\) and assuming \(\omega > \frac{1}{\tau}\), the real component of dielectric constant (equation 2.29) becomes

\[
\varepsilon_1 = \varepsilon_\infty \left[1 - \frac{\omega_p^2}{\omega^2}\right] < 0
\]

Equation 2.33

and the imaginary component (equation 2.30) reduces to

\[
\varepsilon_2 = \varepsilon_\infty \frac{\omega_p^2}{\omega^3 \tau} > 1.
\]

Equation 2.34

The index of refraction then becomes
\[ n = \frac{\omega \varepsilon_{\infty}^{1/2}}{2\omega^2 \tau} \]

*Equation 2.35*

and

\[ k = \varepsilon_{\infty}^{1/2} \frac{\omega p}{\omega} \]

*Equation 2.36*

The reflectivity, given in equation 2.31 is then close to unity and the TCO behaves like a metal by reflecting infrared radiation.

(2) Transparent region, \( \omega > \omega_p \) (\( \lambda < \lambda_p \))

In this region the frequency is greater than the plasma frequency (\( \omega > \omega_p \)) and assuming \( \omega > \frac{1}{\tau} \), the dielectric constant becomes

\[ \varepsilon_1 = \varepsilon_{\infty} \left[ 1 - \frac{\omega_p^2}{\omega^2} \right] \approx \varepsilon_{\infty} > 0 \]

*Equation 2.37*

and

\[ \varepsilon_2 = \varepsilon_{\infty} \frac{\omega_p^2}{\omega^2 \tau} \ll 1. \]

*Equation 2.38*

The real component is positive and the imaginary component is at a minimum.

The index of refraction then becomes

\[ n = \varepsilon_{\infty}^{1/2} \sqrt{1 - \left( \frac{\omega_p}{\omega} \right)^2} \approx \varepsilon_{\infty}^{1/2} \]

*Equation 2.39*

and
\[ k = \varepsilon_\infty^{1/2} \left( \frac{\omega_p^{1/2}}{2\omega^2 \tau} \right) = 0. \]

*Equation 2.40*

The material acts as a dielectric in this region and R and T reduce to

\[ R = \left| \frac{(n_0 - n_i)^2}{(n_0 + n_i)^2} \right| \]

*Equation 2.41*

and

\[ T = \frac{4n_0n_i}{(n_0 + n_i)^2}. \]

*Equation 2.42*

(3) Plasma frequency region, \( \omega \to \omega_p \) \((\lambda \to \lambda_p)\)

As the frequency approaches the plasma frequency \( \omega \to \omega_p \), the material becomes strongly absorbing as the electrons oscillate in phase with the electric field component of the incident electromagnetic wave. In this case, the dielectric constant becomes

\[ \varepsilon_1 = \varepsilon_\infty \left( 1 - \frac{\omega_p^2}{\omega^2} \right) \approx 0 \]

*Equation 2.43*

and

\[ \varepsilon_2 = \frac{\varepsilon_\infty}{\omega_p \tau}, \]

*Equation 2.44*

assuming \( \omega > \frac{1}{\tau} \). The fact that the real component is zero indicates that the index is equal to the extinction coefficient \( n = k = \left( \frac{\varepsilon_\infty}{2\omega_p \tau} \right)^{1/2} \) at the plasma frequency.
(4) Band Gap Absorption

The optical band gap, $E_{\text{opt}}$, of semiconductors can be measured through the absorption coefficient, $\alpha$, which is defined as

$$\alpha = \frac{4\pi k}{\lambda}. \quad \text{Equation 2.45}$$

This can be determined from the transmission data by

$$T = \frac{(1 - R)^2 e^{-\alpha t}}{1 - R^2 e^{-2\alpha t}}, \quad \text{Equation 2.46}$$

where $T$ is the transmission of the film, $R$ is the reflection from the air-film interfaces and $t$ is the film thickness. When the product $\alpha t$ is large, the denominator in equation 2.46 can be neglected, which returns

$$T = (1 - R)^2 e^{-\alpha t}. \quad \text{Equation 2.47}$$

The solution for $\alpha$ yields

$$\alpha = \frac{-\ln \left( \frac{T}{(1 - R)^2} \right)}{t}. \quad \text{Equation 2.48}$$

Typically, the relationship between $\alpha$ and energy ($h\nu$) is taken as $\alpha = A(h\nu - E_{\text{opt}})^{1/2}$ for TCOs and this has been applied to both crystalline and amorphous materials.\cite{1, 27, 29, 36} This approach to modeling $E_{\text{opt}}$ is based on allowed direct transitions within a parabolic band (transition at $k=0$ is possible). The optical band gap, $E_{\text{opt}}$, is determined by extrapolating the linear portion of the curve to $\alpha^2=0$. The constant, $A$, is defined as

$$A = \frac{e^2 (2m_r)^{3/2}}{nch^2 m_e^*}. \quad \text{Equation 2.49}$$
and $m_r$ is the reduced mass of the carriers.\cite{32,33,37,38} Several other empirical relationships have been observed for amorphous materials such as Ge, Si, As$_2$Se$_3$, As$_2$Te$_3$ and Se, which include $\alpha \cdot h\nu = \text{const}(h\nu - E_{opt})$, $\alpha \cdot h\nu = \text{const}(h\nu - E_{opt})^2$ and $\alpha \cdot h\nu = \text{const}(h\nu - E_{opt})^3$.\cite{26} These models are based on either a relaxation of $k$ conservation or an indirect transition.\cite{26,39}

The relationship between the optical and electrical constants allows N and $m_r^*$ to be extracted from fitting the optical data. In addition, the thickness of these films can be determined by modeling the interference fringes in the visible portion of the spectrum. The reflected and transmitted amplitudes given by a thin film on an infinitely long, non-absorbing substrate are given by the Fresnel equations

$$R = \frac{r_1 + r_2 e^{-2i\delta_1}}{1 + r_1 r_2 e^{-2i\delta_1}},$$

*Equation 2.50*

and

$$T = \frac{t_1 t_2 e^{-i\delta_1}}{1 + r_1 r_2 e^{-2i\delta_1}},$$

*Equation 2.51*

where $r_1$, $r_2$, $t_1$ and $t_2$ are the reflection and transmission coefficients at interface 1 and 2 (equations 2.31 and 2.32).\cite{28} The term $\delta_1$ is the change in phase of the wave as it traverses the medium and is given as

$$\delta_1 = \frac{2\pi}{\lambda} n_i d_i \cos \theta,$$

*Equation 2.52*

where $\theta$ is the angle of incidence ($\theta=0^\circ$ indicates normal incidence). The change in transmission of a TCO film as the thickness varies is depicted in Figure 2.6. By holding all other parameters constant and changing the thickness, it is apparent that the transmission at “long” wavelengths increases as the thickness decreases. The corresponding reflection spectra are shown in Figure 2.7.
Figure 2.6 Change in transmission as the thickness of the film varies.

Figure 2.7 Change in reflection spectra as the thickness of the film varies.
2.4 Crystal Structure

In$_2$O$_3$ has the cubic c-type rare earth oxide crystal structure known as bixbyite with a lattice parameter of 10.117 Å and a space group symmetry of Ia3$\text{d}$.\textsuperscript{[3]} The bixbyite structure contains two crystallographically non-equivalent In sites as shown schematically in Figure 2.8. This results in indium-oxygen distances of 2.13, 2.19 and 2.23 Å.\textsuperscript{[40, 41]} The In$_2$O$_3$ unit cell contains a total 80 atoms, 32 indium and 48 oxygen. The bixbyite structure can also be described in terms of a highly defective fluorite (CaF$_2$) crystal structure. CaF$_2$ consists of an fcc lattice with Ca at 0,0,0 and a basis of 1 Ca and 2 F per lattice site, where the fluorine atom occupies all eight of the tetrahedral interstices. The analogy to In$_2$O$_3$ is that the In atoms take the place of the calcium and the oxygen atoms occupy 3/4 of the fluorine sites. However, the coordination of In is 6-fold, not 8-fold as is the Ca ion in CaF$_2$ and there are two non-equivalent In sites as previously mentioned.

Crystalline zinc oxide has the hexagonal wurtzite crystal structure with lattice parameters of a=3.24 Å and c=5.19 Å. The structure consists of hexagonally close-packed O atoms with Zn atoms located in half of the tetrahedral sites.\textsuperscript{[42]} In addition, the ZnO crystal has polar symmetry due to the OZn$_{6}^{2-}$ point along the c-axis. The ZnO crystal structure is shown schematically in Figure 2.9.

The ground-state electron configuration of In, Zn and O are [Kr]4d$^{10}$5s$^{2}$5p$^{1}$, [Ar]3d$^{10}$4s$^{2}$ and [He]2s$^{2}$2p$^{4}$, respectively. The ionic radii of In$^{3+}$, Zn$^{2+}$ and O$^{2-}$ are reported to be 0.81, 0.74 and 1.40Å, respectively.\textsuperscript{[25]} There is a difference of \textasciitilde 10% between the ionic radii of In$^{3+}$ and Zn$^{2+}$.

It is well known that a series of crystalline, single-phase homologous compounds can form in the composition range Zn$_{k}$In$_{2}$O$_{k+3}$ for k=1 to k=29.\textsuperscript{[42-45]} These materials are characterized by intermittent layers of InO$_{2}^{2-}$ in a ZnO matrix where the
(002) spacing decreases and the InO$_2$ layer spacing increases as $k$ increases.\cite{42,44} This is illustrated in Figure 2.10 for the compound Zn$_3$In$_2$O$_8$, where $k=5$.

In addition to the ZnO, In$_2$O$_3$ and homologous crystal structures, amorphous compounds have also been observed for various IZO compositions.\cite{46}

![In$_2$O$_3$ crystal structure](image)

**Figure 2.8** Crystal structure of In$_2$O$_3$, showing the two non-equivalent In cation sites.

![ZnO crystal structure](image)

**Figure 2.9** Crystal structure of ZnO.
Figure 2.10 Layered Zn$_3$In$_2$O$_8$ homologous compound along the [010] from Dupont et al.\textsuperscript{[42]}
2.5 Band Structure

The calculated band structure of ZnO and assumed band structure of In$_2$O$_3$ are parabolic as shown in Figure 2.11.$^{[27,47-49]}$ The dispersion relations for the valence and conduction bands are given as

$$E_v(k) = \frac{-\hbar^2k^2}{2m_v}$$

Equation 2.53

and

$$E_c(k) = E_g + \frac{\hbar^2k^2}{2m_c}$$

Equation 2.54

respectively, for the non-degenerate semiconductors, where $m_v$ and $m_c$ are the valence band and conduction band effective masses, $k$ is the wave vector and $E_g$ is the intrinsic band gap.$^{[3]}$ The reported band gaps, $E_g$, for ZnO and In$_2$O$_3$ are 3.5 and 3.75eV, respectively.$^{[3]}$ At carrier concentrations below the Mott critical density ($\sim 10^{18}/\text{cm}^3$), the measured band gap of the material, $E_{opt}$, is equal to $E_g$. As the carrier concentration increases to $\sim 10^{18}$ to $10^{22}/\text{cm}^3$, both band gap broadening and band gap shrinkage occur resulting in a band gap of the form

$$E_{opt} = E_g + \Delta E_{BM} - \Delta W$$

Equation 2.55

where $\Delta E_{BM}$ is the increase in the band gap due to filling of the conduction band by free carriers and $\Delta W$ is shrinkage of the intrinsic band gap as a result of electron interaction and impurity scattering.$^{[27,50-55]}$ This effect is shown schematically in Figure 2.11. The increase in the optical gap, $\Delta E_{BM}$ is known as the Burstein-Moss shift and was discovered independently by both researchers in 1954.$^{[56,57]}$ The Burstein-Moss shift is written as
\[ \Delta E_{BM} = \frac{\hbar^2}{2m_{vc}^*}(3\pi^2N)^{2/3} \]

Equation 2.56

for direct gap materials. The term \( m_{vc}^* \) is the reduced effective mass and is given as

\[ \frac{1}{m_{vc}^*} = \frac{1}{m_v^*} + \frac{1}{m_c^*} \]

Equation 2.57

where \( m_v^* \) and \( m_c^* \) are the valence band and conduction band effective masses, respectively. \([3, 32, 36, 56, 59]\) The Burstein-Moss shift shows a linear increase in \( E_{opt} \) with \( N^{2/3} \). However, the decrease in \( E_g \) due to the downward shift of the conduction band and upward shift of the valence band results in a measured band gap, \( E_{opt} \), which is less than what would be expected if \( \Delta E_{BM} \) were the only band gap affecting term.

The band gap narrowing term is written as

\[ \Delta W = \hbar \Sigma_c(k_f, \omega) - \hbar \Sigma_v(k_f, \omega) \]

Equation 2.58

where \( \hbar \Sigma_c(k_f, \omega) \) and \( \hbar \Sigma_v(k_f, \omega) \) are the shifts in the conduction and valence bands due to mutual exchange and Coulomb interactions between electrons. \([27, 53, 55]\) The effect of the band gap narrowing terms has been shown to be one-half to one-third the magnitude of the Burstein-Moss shift. \([27]\)
Figure 2.11 Band structure of a crystalline semiconductor showing an unfilled conduction band (left) and a filled conduction band (right).

The band structure shown in Figure 2.11 represents that of a crystalline material where the density of states is zero within the energy gap. This is not the case for many amorphous materials where mid-gap states can exist as shown schematically in Figure 2.12. The existence of mid-gap states leads to the term mobility gap, which is the energy gap separating the localized from extended states. The band tailing shown in Figure 2.12 results from the structural disorder that disrupts the continuous bands of a crystalline material. The midgap states are thought to arise from defect centers such as dangling bonds which could act as both donors and acceptors. These mid-gap states affect the optical properties by allowing electron transitions to occur from these states to the conduction band at energies less than the band gap, $E_g$. 
Figure 2.12 Density of states versus energy for an amorphous semiconductor.\textsuperscript{[60]}

\[ g(E) \approx 10^{20} \text{ cm}^{-3} \text{ eV}^{-1} \]
CHAPTER 3
PREVIOUS EXPERIMENTAL WORK

3.1 Introduction

This section describes the previous experimental work that has been performed on various indium zinc oxide compounds and other amorphous TCOs. Comparisons between composition, deposition conditions, conductivity and phases are presented here. The results of annealing studies on various IZO compositions are also included in this section.

3.2 Phase Regions and Conductivity

The phases present when depositing IZO films have varied between different researchers depending on the deposition parameters. For example, Hara, et al. observed an amorphous phase for indium contents between 88 and 92% when using dc magnetron sputtering at 20°C on polycarbonate substrates.[63] but this is a composition region that is typically crystalline (In$_2$O$_3$ structure) when sputtering at low temperature.[46, 62, 63] The formation of the homologous compounds has also been found to be sensitive to substrate temperature. The group of Moriga, et al. observed the homologous compounds between 20 and 34%In when depositing IZO by dc magnetron sputtering at 150°C but this composition region was amorphous when deposited at 50°C.[62] Similar trends were observed by Mikawa, et al. when depositing IZO films by pulsed laser deposition (PLD).[64] They found the amorphous region extended from ~20 to 70%In at 110°C but at 250°C these compositions were
crystalline (homologous series). The work by Naghavi, et al. found the homologous compounds between ~45 and 90%In when depositing IZO by PLD at 500°C. At higher and lower In contents, the structure was that of In₂O₃ or ZnO, respectively. Indium zinc oxide films have also been deposited by atmospheric pressure chemical vapor deposition (APCVD) at 350°C and under these conditions, the amorphous region extended from 20 to 80% In. This contrasts to films sputtered at 350°C in this composition range that were crystalline and indexed to the homologous compound, Zn₂In₂O₅. Table 3.1 lists the deposition conditions, substrate temperature and phases present for IZO films deposited by various researchers. The maximum conductivity observed along with composition and type of phase at which it occurred are also listed. The data are also presented in Figure 3.1 to illustrate the overlap in composition for the different phases. It is apparent that the composition range over which amorphous IZO appears varies significantly and has been shown to extend from ~16 to 92%In when depositing by low pressure metal organic chemical vapor deposition (LPMOCVD) and sputtering, respectively. The maximum conductivity reported is ~5,000 (Ω·cm)⁻¹ for crystalline IZO sputtered at room temperature using ion beam assisted deposition (IBAD). The most conducting amorphous film reported is ~4,350 (Ω·cm)⁻¹ at 80%In by sputtering.
Table 3.1 Deposition conditions, substrate temperature, phases present and maximum conductivity for various IZO films. The composition and phase (H-homologous compound, A-amorphous, I-In$_2$O$_3$) corresponding to the maximum observed conductivity is listed next to $\sigma_{\text{max}}$.

<table>
<thead>
<tr>
<th>Deposition (%)In</th>
<th>T (°C)</th>
<th>Phases Present (Composition Range:%In)</th>
<th>$\sigma_{\text{max}}$ (%In(phase) (Ω·cm)$^{-1}$)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLD</td>
<td>500</td>
<td>0-10 10-67 67-100</td>
<td>1,500:50% (H) [65, 66]</td>
<td></td>
</tr>
<tr>
<td>APCVD</td>
<td>350</td>
<td>0-20 20-80 80-100</td>
<td>2,500:25% (A) [73]</td>
<td></td>
</tr>
<tr>
<td>Sputtering</td>
<td>RT</td>
<td>84</td>
<td>1,700:84% (A) [74]</td>
<td></td>
</tr>
<tr>
<td>Sputtering</td>
<td>RT</td>
<td>92</td>
<td>2,300:92% (A) [18]</td>
<td></td>
</tr>
<tr>
<td>Sputtering</td>
<td>RT 150</td>
<td>84</td>
<td>1,960:84% (A) [75]</td>
<td></td>
</tr>
<tr>
<td>Sputtering</td>
<td>RT 200</td>
<td>84</td>
<td>2,645:84% (A) [75]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>RT 250</td>
<td>84</td>
<td>2,754:84% (A) [75]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>RT 300</td>
<td>84</td>
<td>2,770:84% (A) [75]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>RT 350</td>
<td>84</td>
<td>2,481:84% (A) [75]</td>
<td></td>
</tr>
<tr>
<td>Sputtering</td>
<td>50</td>
<td>0-20 20-34 20-89 89-100 80-100</td>
<td>4,350:80% (I) [46, 62]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>0-20 20-34 34-80 89-100 80-100</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>0-20 20-50 34-80 89-100 80-100</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>0 20-43 34-80 89-100 80-100</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>350</td>
<td>0 20-43 34-80 89-100 80-100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spray Pyrolysis</td>
<td>402</td>
<td></td>
<td>909:3% [76]</td>
<td></td>
</tr>
<tr>
<td>LPMOCVD</td>
<td>450</td>
<td>0-10 16-40 50-100</td>
<td>1,000:75% (I) [71]</td>
<td></td>
</tr>
<tr>
<td>Sputtering + IBAD</td>
<td>RT</td>
<td>84</td>
<td>4,950:84% (H) [72]</td>
<td></td>
</tr>
<tr>
<td>Sputtering</td>
<td>RT 250</td>
<td>70</td>
<td>2,560:70% (A) [69]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>70</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>350</td>
<td>70</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sputtering</td>
<td>RT</td>
<td>88-92</td>
<td>3,450:88% (A) [70]</td>
<td></td>
</tr>
<tr>
<td>Sputtering</td>
<td>RT</td>
<td>70</td>
<td>2,650:70% (A) [68]</td>
<td></td>
</tr>
<tr>
<td>Sputtering</td>
<td>100</td>
<td>0-45 45-80 80-100</td>
<td>3,000:75% (A) [63]</td>
<td></td>
</tr>
</tbody>
</table>
Figure 3.1 Phase regions as a function of composition for IZO films deposited by various techniques at different temperatures.
### 3.3 IZO Annealing Studies

Various annealing studies have been performed on IZO compositions. The group of Jung, et al. focused on room temperature deposition of 84%In, IZO(84%In), and they annealed those amorphous films in vacuum up to 600°C.\[^{75}\] The XRD spectra for this is shown in Figure 3.2. The annealing was performed for 60 minutes at each target temperature and crystalline material was observed only after the 600°C anneal. This phase was also observed when they increased the substrate temperature to 350°C during deposition. Crystallization of amorphous IZO(84%In) was also observed between 500° and 600°C by differential thermal analysis (DTA).\[^{75}\]

![Figure 3.2 XRD spectra for IZO (84%In) annealed in vacuum for 1 hour at each target temperature. The (222) peak evident at 600°C corresponds to the In₂O₃ phase.\[^{75}\]](image)

Figure 3.3 illustrates the change in mobility, carrier concentration and resistivity for IZO(84%In) samples deposited at room temperature and then annealed at 300°C for 1 hour under different atmospheres.\[^{75}\] Despite the amorphous nature of
these films, the increase in mobility with annealing was attributed to an "improvement in crystallinity". A slight decrease in resistivity was observed for the vacuum annealed film ($\sigma \sim 2200(\Omega \cdot \text{cm})^{-1}$).\textsuperscript{[75]}

![Figure 3.3](image)

Figure 3.3 The variation in mobility, carrier concentration and resistivity for IZO(84%In) when annealed at 300°C for 1 hour under various environments.\textsuperscript{[75]}

The group of Kim, \textit{et al.} deposited "micro-crystalline" IZO(67%In) at room temperature (RT) with varying amounts of oxygen. Figure 3.4, panel a illustrates the change in resistance for those films as they were heated to 650°C in vacuum.\textsuperscript{[77]} The heating rate was 7°/min and the resistance measurement was carried out during the anneal. The time to reach 600° was approximately 89 minutes. The resistance of the samples at room temperature varied dramatically with oxygen content. The resistance of all the films converged to $\sim 50\Omega$ by 400°C and remained steady up to 650°C. The decrease in resistance with increasing annealing temperature for the samples deposited with oxygen was attributed to desorption of oxygen from those films. The resistance at room temperature, 650°C and at room temperature following the anneal are shown in Figure 3.4, panel b.
Films of this composition (67% In) were also annealed in air using the same approach as the vacuum annealed ones (Figure 3.4) and the results are presented in Figure 3.5. All of the films show a significant variation in resistance as the temperature is increased and the resistance is between ~10³ and 10⁴ Ω for all of them at 650°C. Panel b of Figure 3.5 shows the variation in resistance for the films that were initially
annealed in vacuum (Figure 3.4) as they were reannealed in air up to 650°C. All of the films are stable up to ~400°C and then show a similar increase in resistance with temperature. The variations in resistance at RT and the increases in resistance with air annealing are attributed to the adsorption of oxygen on the grain boundaries.\textsuperscript{[77]}

Figure 3.5 Change in resistance of IZO(67%In) during annealing from RT to 650°C in air for films deposited at RT with varying amounts of O\textsubscript{2} (panel a). Panel b shows the resistance of the vacuum annealed films (Figure 3.4) when they were reannealed in air up to 650°C.\textsuperscript{[77]}
The group of Minami, *et al.* also examined the stability of IZO sputtered from a target containing 70% In and compared this to ZnO and In$_2$O$_3$.[69] The change in resistance of those films as a function of temperature is shown in Figure 3.6. The stability of IZO(70%In) appears much greater than either ZnO or In$_2$O$_3$ as the resistance does not increase significantly until ~400°C.

![Figure 3.6](image)

**Figure 3.6** Variation in resistance for ZnO (a), In$_2$O$_3$ (b) and IZO(70%In) (c) films which were annealed at 500° for 1 hour in air. [69]

The thermal stability of Zn-rich IZO, IZO(3%In), deposited by spray pyrolysis at 675K (402°C) compared to ZnO is shown in Figure 3.7.[70] The resistivity of IZO(3%In) was ~$10^{-5}$ Ω·m in the as-deposited condition and did not change upon annealing up to 650K (377°C). The resistivity of this film decreased slightly when annealed in oxygen for 30 minutes at 650K with a final resistivity of ~$3\times10^{-5}$ Ω·m at RT. The undoped ZnO film showed a significant decrease in resistivity when
annealed in vacuum and a significant increase in resistivity when annealed in oxygen. IZO(3%In) showed much greater thermal stability than pure ZnO when annealed up to 650K for 30 minutes. However, the resistivity of IZO(3%In) increased by several orders of magnitude when annealed up to 800K (527°C).\textsuperscript{[76]}

![Diagram showing change in resistivity with temperature in vacuum (●) and oxygen (○) environments for pure ZnO (---) and IZO(3%In) (---).\textsuperscript{[76]}](image)
These IZO annealing studies have shown that the compositions examined are much more electrically stable than ZnO or In$_2$O$_3$ and that annealing in oxygen is detrimental to the conductivity of these films. However, the conductivity can be slightly improved by annealing in vacuum. The increase and decrease in conductivity has been primarily attributed to the desorption and adsorption of oxygen in the film.\textsuperscript{[69, 75-77]}

### 3.4 Other Amorphous TCOs

In addition to amorphous IZO, several other amorphous TCOs have been reported, which include In$_2$O$_3$, ITO, CdO:Ge, CdO:Pb, AgSbO$_3$, In$_2$Zn$_2$O$_4$ and Zn$_2$SnO$_4$.\textsuperscript{[36, 78-88]} Table 3.2 outlines the deposition conditions and conductivities of these films, which are as-deposited unless otherwise noted. Amorphous In$_{0.70}$Zn$_{0.30}$O$_y$ with a conductivity of $\sim$3,000 (Ω-cm)$^{-1}$\textsuperscript{[63]} is among the best of any amorphous TCO available.
Table 3.2 The deposition conditions and conductivities of various amorphous TCOs.

<table>
<thead>
<tr>
<th>Material</th>
<th>Deposition Technique</th>
<th>Deposition Temperature</th>
<th>Conductivity</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>In$_2$O$_3$</td>
<td>Ar beam sputtering</td>
<td>RT</td>
<td>2,000</td>
<td>[36, 39]</td>
</tr>
<tr>
<td>In$_2$O$_3$</td>
<td>PLD</td>
<td>RT</td>
<td>4,000</td>
<td>[78]</td>
</tr>
<tr>
<td>In$_2$O$_3$:5wt%SnO$_2$</td>
<td>PLD</td>
<td>RT</td>
<td>2,100</td>
<td></td>
</tr>
<tr>
<td>In$_2$O$_3$:10wt%SnO$_2$</td>
<td></td>
<td>RT</td>
<td>1,800</td>
<td></td>
</tr>
<tr>
<td>In$_2$O$_3$:9.9wt%SnO$_2$</td>
<td>Electron beam</td>
<td>125°-165°C</td>
<td>50-66</td>
<td>[82]</td>
</tr>
<tr>
<td>In$_2$O$_3$:12mol%SnO$_2$</td>
<td>Evaporation</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AgSbO$_3$</td>
<td>RF sputtering</td>
<td>RT</td>
<td>0.00001</td>
<td>[84]</td>
</tr>
<tr>
<td>2CdO•GeO$_2$</td>
<td>RF sputtering plus</td>
<td>RT</td>
<td>50-100</td>
<td>[80, 89]</td>
</tr>
<tr>
<td></td>
<td>H$^+$ implantation</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AbSbO$_3$</td>
<td>Heating to 500°C</td>
<td></td>
<td>0.3</td>
<td>[90]</td>
</tr>
<tr>
<td>AbSbO$_3$</td>
<td>Heating to 650°C</td>
<td></td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>Cd$_2$GeO$_4$</td>
<td>Li$^+$ implantation</td>
<td></td>
<td>13</td>
<td></td>
</tr>
<tr>
<td>Cd$_2$GeO$_4$</td>
<td>H$^+$ implantation</td>
<td></td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>Cd$_2$PbO$_4$</td>
<td>Heating to 250°C</td>
<td></td>
<td>390</td>
<td></td>
</tr>
<tr>
<td>InGaZnO$_4$</td>
<td>PLD</td>
<td>RT</td>
<td>200</td>
<td>[91]</td>
</tr>
<tr>
<td>Zn$_2$SnO$_4$</td>
<td>RF sputtering</td>
<td>RT</td>
<td>20</td>
<td>[88]</td>
</tr>
<tr>
<td>In$<em>{0.70}$Zn$</em>{0.30}$O$_y$</td>
<td>DC sputtering</td>
<td>RT</td>
<td>2,650</td>
<td>[69]</td>
</tr>
<tr>
<td>In$<em>{0.70}$Zn$</em>{0.30}$O$_y$</td>
<td>DC sputtering</td>
<td>100°C</td>
<td>3,000</td>
<td>[63]</td>
</tr>
</tbody>
</table>
CHAPTER 4

FILM DEPOSITION AND CHARACTERIZATION

4.1 Introduction

The film growth and characterization techniques are described in this chapter. All films were grown by sputter deposition from ZnO, In₂O₃ and a mixed ZnO-In₂O₃ oxide target. The various deposition parameters examined included sputter gas composition, target power and film growth time. Characterization techniques included chemical, electrical, optical and structural analysis. The combinatorial analysis involved mapping the properties of the film as a function of composition. A routine was established such that the compositionally-graded IZO libraries were mapped in a 4 row by 11 column format, designated Rows 0-3 and Columns 0-10. The relationship of the row and column scheme for the 5cm x 5cm samples with regard to the sputtering targets is shown in Figure 4.1. The distance between the rows and columns was 12.5 and 4mm, respectively.

4.2 Film Deposition: DC Magnetron Sputtering

The sputtering process is a standard thin film deposition technique. This technique involves bombarding a target with energetic gas ions that eject small atom and ion clusters, which subsequently deposit on a substrate. Some benefits of the sputtering process include: all materials can sputtered, compounds are sputtered
stoichiometrically and the deposition rate can be very uniform. In direct current (dc) sputtering, a glow discharge is achieved by introducing an inert gas (typically Ar) into an evacuated chamber and applying a high potential between two electrodes (the target and substrate). Ionization of the Ar gas can occur with the formation of a radical and a free electron by the following reaction

$$Ar \rightarrow Ar^+ + e$$

*Equation 4.1*

The positive ion is then accelerated toward the cathode (target) while the electron is accelerated away from it. The free electron gains energy as it is repelled from the cathode and can generate additional argon ions through the reaction

$$e + Ar \rightarrow Ar^+ + 2e$$

*Equation 4.2*
This reaction assists in sustaining the plasma. The argon radical can undergo several different processes when striking the target. If the momentum of \( \text{Ar}^+ \) is small, the probability of it ejecting a target atom will also be correspondingly small and it can be reflected and retain its energy. However, if the \( \text{Ar}^+ \) strikes the target with a large amount of energy, a target atom can be ejected from the surface (sputtered) and the \( \text{Ar}^+ \) is recoiled with a significant loss of energy. The \( \text{Ar}^+ \) can also generate secondary electrons from the target, which may react with \( \text{Ar} \) neutrals via equation 4.2.

Magnets are often used to enhance the sputtering process and are placed behind the target to confine the free electrons around the target surface. This technique is termed “magnetron sputtering”. The benefit of the magnetron is that the magnetic field traps electrons in the region above the target, thereby increasing the time in which they interact with \( \text{Ar} \) atoms. The result is that the magnetron helps create a higher plasma density in front of the target by the reaction expressed in equation 4.2, which allows for a lower sputter gas pressure. The benefit of maintaining a lower gas pressure is that the sputtered particles retain a higher kinetic energy upon reaching the substrate, the deposition rate is increased and lower target voltages may be used. A problem, however, is that the target sputters in a non-uniform manner, resulting in an erosion trench or “racetrack”. The racetrack occurs because, as the electrons are accelerated away from the cathode due to the electric field, \( E \), they experience a force parallel to the surface of the target due to the magnetic field, \( B \). This is the Lorentz force and is given as

\[
\vec{F} = \vec{F}_E + \vec{F}_B = q_e \, \vec{E} + q_e \, v \times \vec{B}
\]

*Equation 4.3*

where \( \vec{F}_E \) and \( \vec{F}_B \) are the forces on the electron due to the electric field and magnetic field, respectively, \( q_e \) is the electron charge and \( v \) is the velocity of the electron. The plasma density is therefore greatest in this circular region around the target and therefore, the sputter rate is highest there. A magnetron is shown in Figure 4.2.
Figure 4.2 Illustration of a magnetron showing the magnetic field and path of the electrons.
The compositionally-graded IZO libraries were deposited by dc magnetron sputtering from two-inch diameter In$_2$O$_3$ (99.99%) and ZnO (99.999%) sintered ceramic targets (SCI Engineered Materials) for 6 minutes in Ar gas at a pressure of 4.5 mTorr. Corning 1737 glass (2”x2”) was used for substrates and the substrate heater temperature was 100°C for all depositions. The physical properties of the substrate are listed in Table 4.1. A schematic of the sputtering geometry showing the orientation of the targets to the substrate is shown in Figure 4.3. A roughing pump was used to achieve a pressure of <100mTorr before opening a gate valve which connected a cryopump to the chamber. A base pressure of $10^{-7}$ to $10^{-6}$ Torr was achieved prior to deposition. Various target powers, listed in Table 4.2, were chosen to achieve a composition range of 4 to 95 atomic % In for Zn. As a result of the co-sputter geometry, thickness gradients were also observed in the compositionally graded libraries. Single composition films were deposited from a 2” diameter In$_{0.70}$Zn$_{0.30}$O$_y$ target in Ar, Ar+O$_2$ and Ar+H$_2$. Films were deposited at 27, 40 and 60W at times of 20 to 60 minutes. Additional information concerning the deposition of IZO films can be found in chapter 5.
Table 4.1 Physical properties of Corning 1737 glass from Abrisa, a supplier of glass products.

<table>
<thead>
<tr>
<th>Mechanical Properties</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (20°C)</td>
<td>2.54g/cm³</td>
</tr>
<tr>
<td>Young's Modulus</td>
<td>7.14x10⁴ kg/mm²</td>
</tr>
<tr>
<td>Poisson's Ratio</td>
<td>0.22</td>
</tr>
<tr>
<td>Shear Modulus</td>
<td>2.88x10³ kg/mm²</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Viscosity</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Working Point (10⁴ poises)</td>
<td>1312°C</td>
</tr>
<tr>
<td>Softening Point (10¹⁰ poises)</td>
<td>975°C</td>
</tr>
<tr>
<td>Annealing Point (10¹² poises)</td>
<td>721°C</td>
</tr>
<tr>
<td>Strain Point (10¹⁴.5 poises)</td>
<td>666°C</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Thermal Expansion</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Expansion (0-300°C)</td>
<td>37.6x10⁻⁶/°C</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Optical Properties</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength (nm)</td>
<td>435.8 480.0 486.1 546.1 589.3 643.8 656.3</td>
</tr>
<tr>
<td>Index of Refraction</td>
<td>1.5290 1.5250 1.5244 1.5207 1.5186 1.5166 1.5160</td>
</tr>
</tbody>
</table>

Figure 4.3 Plan view of the sputtering chamber showing the orientation of the targets and the substrate.
Table 4.2 The deposition conditions of the compositional libraries.

<table>
<thead>
<tr>
<th>Library</th>
<th>In$_2$O$_3$ Power (watts)</th>
<th>ZnO Power (watts)</th>
<th>Atomic % In for Zn</th>
<th>Film Thickness Range (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L1</td>
<td>15</td>
<td>75</td>
<td>4-15</td>
<td>245-157</td>
</tr>
<tr>
<td>L2</td>
<td>60</td>
<td>75</td>
<td>15-50</td>
<td>312-264</td>
</tr>
<tr>
<td>L3</td>
<td>60</td>
<td>25</td>
<td>35-70</td>
<td>105-190</td>
</tr>
<tr>
<td>L4</td>
<td>75</td>
<td>7</td>
<td>70-95</td>
<td>82-199</td>
</tr>
<tr>
<td>L5</td>
<td>75</td>
<td>15</td>
<td>46-87</td>
<td>119-217</td>
</tr>
</tbody>
</table>

4.3 Chemical Analysis

Electron probe micro analysis (EPMA) mapping was utilized to measure the relative atomic ratio of indium to zinc (20kV, 2.5x10$^{-8}$A, probe diameter~20µm). The EPMA results were referenced to bulk InP and Zn metal standards and no quantitative corrections were applied to account for the thickness of these films. EPMA involves bombarding a sample with electrons (typically 10-20 keV) and analyzing the emitted x-ray spectra. X-rays of specific energies called characteristic x-rays are used to “fingerprint” the elements in the sample. The generation of characteristic x-rays is illustrated in Figure 4.4. In this process the incoming electron ejects an inner shell electron, an electron from an outer shell reduces its energy by “dropping” into the empty orbital and the difference in energy is emitted as the characteristic x-ray. One criterion for utilizing EPMA is that the specimen must be electrically conducting. Otherwise, it must be coated with a conducting film such as carbon or silver, prior to analysis. The compositionally-graded IZO libraries were mapped in the 4 row, 11 column format illustrated in Figure 4.1. A typical EPMA contour map showing the In to Zn concentration gradient across the library is shown in Figure 4.5 with the corresponding measured data points listed in Table 4.3.
Figure 4.4 Generation of characteristic x-rays, adapted from Williams, et al.[93]

Figure 4.5 Typical EPMA map of a 5cm x 5cm compositional library, where the contours indicate the atomic % In to Zn. The mapping was performed in a 4 row by 11 column format as illustrated in Figure 4.1. The contours were created by interpolating between the 44 measured data points, which are listed in Table 4.3.
Table 4.3 Atomic % In as measured by EPMA corresponding to the contour map shown in Figure 4.5. The atomic % Zn at each point is equal to 100-%In.

<table>
<thead>
<tr>
<th>Row</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.9</td>
<td>4.3</td>
<td>5.0</td>
<td>5.9</td>
<td>6.9</td>
<td>7.9</td>
<td>9.8</td>
<td>11.4</td>
<td>12.5</td>
<td>15.1</td>
<td>16.6</td>
</tr>
<tr>
<td>1</td>
<td>3.9</td>
<td>4.2</td>
<td>4.9</td>
<td>5.3</td>
<td>6.2</td>
<td>7.7</td>
<td>9.0</td>
<td>10.6</td>
<td>12.9</td>
<td>14.3</td>
<td>16.2</td>
</tr>
<tr>
<td>2</td>
<td>3.7</td>
<td>4.1</td>
<td>4.9</td>
<td>5.5</td>
<td>6.2</td>
<td>7.1</td>
<td>8.1</td>
<td>9.9</td>
<td>11.6</td>
<td>13.4</td>
<td>15.1</td>
</tr>
<tr>
<td>3</td>
<td>3.7</td>
<td>4.2</td>
<td>4.7</td>
<td>5.4</td>
<td>5.9</td>
<td>6.9</td>
<td>8.4</td>
<td>9.5</td>
<td>11.3</td>
<td>12.9</td>
<td>15.3</td>
</tr>
</tbody>
</table>

### 4.4 Electrical Measurements

The sheet resistance ($R_s$) of the IZO films was characterized with automated 4-point probe mapping. The sheet resistance is defined as

$$Rs = \frac{1}{\sigma t}$$

*Equation 4.4*

where $t$ is the film thickness and the units of $R_s$ are $\Omega$/square. The resistance, $R$, of a material is defined as

$$R = \frac{l}{obt}$$

*Equation 4.5*

where $l$ is the length and $b$ is the width. For a sample where $b=l$, $R$ reduces to

$$R = \frac{1}{\sigma t} = R_s$$

*Equation 4.6*
The 4-point probe measurement is a standard technique for measuring sheet resistance and in this measurement, a constant current is passed through the outer two probes and the voltage drop is measured between the inner two probes as shown schematically in Figure 4.6. The conductivity of the film is then given as\textsuperscript{[3]}

\[
\sigma = \left( \frac{V}{I \left( \frac{2\pi}{1/d_1 + 1/d_2 - 1/(d_1 + d_2) - 1/(d_2 + d_3)} \right)} \right)^{-1}
\]

*Equation 4.7*

where \(d\) is the probe spacing. For probes of equal spacing, \(d_1 = d_2 = d_3 = d_4\) the conductivity becomes

\[
\sigma = \left( \frac{V}{I \cdot 2\pi d} \right)^{-1}
\]

*Equation 4.8*

When the material is infinite compared to the probe spacing, the conductivity reduces to\textsuperscript{[3]}

\[
\sigma = \left( \frac{V}{I \cdot \pi} \right)^{-1}
\]

*Equation 4.9*

and finally

\[
\frac{1}{\sigma} = 4.53 \frac{V}{I} = R_s.
\]

*Equation 4.10*

For the measurements on the compositionally graded libraries, the four co-linear probes were oriented so that the measurement axis was perpendicular to the concentration and thickness gradients. The composition gradient along the length of the 4 point probe averaged \(\pm 0.9\%\) and the average thickness gradient across the probe was \(\pm 1.6\%\). A typical sheet resistance map is shown in Figure 4.7 with the corresponding measured data points, which were used to create the map, listed in Table 4.4.
The conductivity of the films can then be determined from the relationship

\[ \sigma = \frac{1}{t \cdot R_s} \]

*Equation 4.11*

Figure 4.6 Schematic illustration of the 4-point probe technique. A constant current (I) is forced through the outer two probes and the voltage drop across the inner two probes is measured.

Figure 4.7 Typical sheet resistance map of a 5cm x 5cm compositional library where the contours indicate the sheet resistance (Ω/sq). The sheet resistance mapping was performed in a four row by 11 column format as shown in Figure 4.1. The measured data points corresponding to this map are listed in Table 4.4.
Table 4.4 Sheet resistance data points (Ω/sq) correlating to the mapping scheme illustrated in Figure 4.1. The corresponding contour map is shown in Figure 4.7.

<table>
<thead>
<tr>
<th>Row</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>61.9</td>
<td>58.1</td>
<td>56.8</td>
<td>59.0</td>
<td>65.1</td>
<td>76.8</td>
<td>95.0</td>
<td>115.0</td>
<td>130.8</td>
<td>144.1</td>
<td>158.1</td>
</tr>
<tr>
<td>1</td>
<td>66.1</td>
<td>57.9</td>
<td>51.4</td>
<td>50.5</td>
<td>54.6</td>
<td>63.6</td>
<td>77.4</td>
<td>95.9</td>
<td>118.7</td>
<td>141.0</td>
<td>155.9</td>
</tr>
<tr>
<td>2</td>
<td>79.4</td>
<td>74.4</td>
<td>65.6</td>
<td>57.4</td>
<td>58.2</td>
<td>66.5</td>
<td>78.8</td>
<td>96.4</td>
<td>119.5</td>
<td>145.6</td>
<td>164.2</td>
</tr>
<tr>
<td>3</td>
<td>83.8</td>
<td>75.4</td>
<td>64.2</td>
<td>57.2</td>
<td>59.2</td>
<td>66.3</td>
<td>77.8</td>
<td>93.8</td>
<td>114.6</td>
<td>137.5</td>
<td>156.3</td>
</tr>
</tbody>
</table>

Hall measurements were also performed on select IZO films using the Van der Pauw method. The Hall effect describes the induced voltage across a film when a magnetic field (B) is applied perpendicular to that of an applied electric field (E), as shown in Figure 4.8. The potential drop in the material as a result of the Hall effect is termed the Hall voltage, $V_H$, and is given as

$$V_H = EW$$

*Equation 4.12*

where $W$ is the distance between the probes. The Hall coefficient ($R_H$) and sheet Hall coefficient ($R_{hs}$) are defined as

$$R_H = \frac{V_H t}{IB} = \frac{1}{Nq}$$

*Equation 4.13*

and

$$R_{hs} = \frac{R_H}{t}$$

*Equation 4.14*
respectively, where $I$ is the current, $N$ is carrier concentration and $q$ is the charge of the current carrying particle. The carrier concentration and mobility can then be derived as

$$N = \frac{1}{qR_H}$$  \hspace{2cm} \textit{Equation 4.15}$$

and

$$\mu = \frac{R_{HS}}{R_s},$$ \hspace{2cm} \textit{Equation 4.16}$$

respectively. It is of interest to note that the mobility can be derived without knowledge of the sample thickness.

![Figure 4.8 Hall effect in a thin film, where the electrons are deflected to one side of the film due to the magnetic field, $B_z$.](image)
Hall measurements were performed on 0.5cm x 1.0cm pieces cut from the as-deposited libraries. This geometry was chosen to minimize the inherent composition and thickness gradients and the contacts were placed at the edges of the sample. For the single composition samples, 1cm x 1cm pieces were cut from row 0 of the 5cm x 5cm film and the contacts were placed at the corners.

4.5 Optical Measurements

The optical properties were determined using a combination of spectrometers. A multi-channel fiber-optically-coupled CCD-array-based spectrometer (Ocean Optics) and a Fourier Transform Infra-Red (FTIR) spectrometer (Nicolet) were used to determine the UV/VIS/NIR (0.25 - 1.7 μm) and infrared (1.7 – 25 μm) transmission and reflection characteristics, respectively. The spot size for the UV/VIS/NIR analysis was ~1mm while that of the IR analysis was ~5 mm. The Ocean Optics setup utilized a deuterium lamp and tungsten filament along with an InGaAs detector. The Ocean Optic transmission and reflection measurements were made normal to the film and the reflection data were normalized to an Al mirror calibrated by the National Institute for Standards and Technology (NIST). The FTIR transmission measurements were also performed normal to the substrate but the reflection measurements were made at 30° off normal incidence with a gold mirror as a reference and a deuterated triglycine sulfate detector. The transmission and reflection characteristics of the Corning 1737 glass substrate are shown in Figure 4.9.
4.6 Structural Analysis

The phases present were determined with x-ray diffraction (XRD) and transmission electron microscopy (TEM). XRD measurements were performed using a Scintag DMS 2000 diffractometer with Cu Kα radiation at 45kV and 36mA. Diffraction occurs when the atoms scatter the incident wave coherently and the wave interferes constructively. This happens when Bragg’s law is satisfied,

\[ n\lambda = 2d \sin \theta \]

Equation 4.17

where n is an integer, \( \lambda \) is the incident x-ray wavelength (\( \lambda = 0.154 \text{nm} \)), d is the plane spacing and \( \theta \) is the Bragg angle, the angle of incidence. The diffraction of x-rays is shown schematically in Figure 4.10.
Figure 4.10 Illustration of the Bragg condition.

A second diffractometer (Bruker) was also utilized for measurement of the IZO libraries. This system is equipped with a 2D large area detector, an automated sample-positioning stage and utilized Cu Kα radiation. The compositionally-graded libraries were positioned such that the incident x-ray beam would strike along contours of constant composition i.e. perpendicular to the composition gradient. The 2D large area detector permitted short data acquisition times and provided information on the degree of texturing. In addition, the sample could be positioned at different values of θ, which allowed for detection of additionally diffracted x-rays in these textured films as shown schematically in Figure 4.11.
A Philips 200kV scanning transmission electron microscope (STEM) equipped with a LaB₆ single crystal filament was also utilized to examine the structure of amorphous IZO. Thin samples (~35nm) were sputtered directly onto standard holey carbon TEM grids. The TEM functions by bombarding the sample with high energy (200keV) electrons. A number of interactions occur as shown schematically in Figure 4.12, but the elastically scattered electrons are important for imaging and diffraction. Similar to XRD, the electrons which satisfy Bragg’s law diffract and are focused to a single point using magnetic lenses. Both diffraction patterns and high resolution images were obtained with this technique. Diffraction of the electrons in the TEM occurs because of the wave-like nature of the particles. The accelerating potential was 200kV resulting in an electron wavelength of 0.0251Å and velocity of 2.086×10⁸m/s. The plane spacing crystals (dₜₚ) can be determined from electron diffraction patterns by the equation...
\[ d_{hkl} = \frac{\lambda L}{R} \]

*Equation 4.18*

where \( \lambda \) is the electron wavelength, \( L \) is the camera length and \( R \) is the distance from the forward scattered central beam to a diffraction point. The product \( \lambda L \) is termed the camera constant and is equal to 24 mm \( \cdot \) Å for this work. For amorphous materials, the diffraction pattern consists of broad, circular rings which are indicative of diffuse elastic scattering. Despite a lack of crystal structure, the nearest neighbor spacing can be calculated from equation 4.18. To obtain the diffraction patterns for the amorphous material, the magnification was set to 36,000X using a spot size of 3, condensor aperture #2 and the selected area aperture was not used. The exposure time was 2 seconds for the diffraction patterns.

**Figure 4.12** Multiple scattering events occur as an electron beam impinges on a thin sample, which includes transmission of electrons.\[^{93} \]
4.7 Morphology

Atomic force microscopy (AFM) was used to determine the surface roughness of the IZO films. The instrument was operated in direct contact mode with silicon cantilever tips and the 5μm scan stage. The operation of the AFM consists of scanning the Si tip across the sample while a laser, focused on the cantilever, monitors the deflection of the tip. This is illustrated in Figure 4.13.

![Illustration of the operation of an atomic force microscope](image)

Figure 4.13 Illustration of the operation of an atomic force microscope.[95]

4.8 Method of 4 Coefficients

The method of 4 coefficients was utilized to obtain the density of states effective mass, $m_e^*$. By measuring the resistivity, Hall coefficient, Nernst coefficient and Seebeck coefficient, the $m_e^*$, Fermi energy and an independent scattering parameter are extracted. A schematic illustration showing the Hall, Seebeck and Nernst effects is given in Figure 4.14. The sample geometry required for this measurement is shown in Figure 4.15 and was obtained by photolithography and
etching the amorphous IZO film in concentrated HCl for ~30 seconds. Measurement of the Hall coefficient, $R_h$, and resistivity ($\rho = \sigma^{-1}$) are described in section 4.4. The Seebeck coefficient is a measurement of the thermoelectric effect in which a temperature gradient is applied to the sample and a voltage is produced between the hot and cold ends due to diffusion of the more energetic ("hot") and less energetic ("cold") electrons. The Seebeck coefficient is given as

$$\alpha = \frac{\Delta V_{2,4}}{\Delta T_{2,4}}$$

*Equation 4.19*

where $\Delta V_{2,4}$ and $\Delta T_{2,4}$ are the voltage and temperature differences between contacts 2 and 4, Figure 4.15. To measure the Nernst coefficient, a magnetic field is applied perpendicular to the film as a temperature gradient is applied. This results in the Nernst voltage, $V_{Nernst}$, which arises because of the difference in kinetic energy of the "hot" and "cold" electrons. The electrons with different energies are deflected to different ends of the sample. The Nernst coefficient, $Q$, is measured by the following equation,

$$Q = \frac{E_y}{\frac{\partial T}{\partial x} B_z}$$

*Equation 4.20*

where $E_y$ is the induced electric field, $B_z$ is the applied electric field and $\frac{\partial T}{\partial x}$ is the temperature gradient across the film. Finally, the density of states effective mass is determined from the previous measurements by the equation

$$m_e^* = \left(\frac{3N}{\pi}\right)^{2/3} \frac{g_h^2}{k_B T} \left(\alpha - \frac{Q}{|R_h| \sigma}\right)$$

*Equation 4.21*
Figure 4.14 Illustration of the Hall, Seebeck and Nernst effects in an n-type parabolic band material. The magnetic field, $B_z$, is directed out of the page and $V_{\text{drift}}$ and $V_{\text{diffusion}}$ are the electron drift and diffusion velocities, respectively.\textsuperscript{[1]}

Figure 4.15 Film configuration necessary for the method of 4 coefficients measurement.\textsuperscript{[96]}
4.9 Auger Electron Spectroscopy

Auger electron spectroscopy (AES) was utilized to examine differences in the chemical states of different IZO films. This technique is similar to EPMA in that the sample is bombarded with energetic electrons, which cause inner shell electrons to be ejected, resulting in the emission of a photon as shown in Figure 4.4. This photon can interact with another inner shell electron, causing it to be ejected from the sample. This electron, the Auger electron, is part of the secondary electron spectrum and has a characteristic energy, which is measured to identify the element present. The Auger transition involves three atomic energy levels and for zinc this occurs most readily between the L and M orbitals. The Auger transition in zinc is therefore written as Zn_{LM}. Changes in the chemical states of elements can be observed as the nature of its chemical bond shifts. For example, as the oxidation state of a metal increases, the binding energy of the core electrons will shift as well, resulting in Auger electrons of different energies. AES is considered a surface technique and chemical information is obtained from the first 2 to 10 atomic layers. However, sputtering is commonly used to obtain information about the interior of the sample and to depth profile.\textsuperscript{[95]}
CHAPTER 5

PRIMARY RESULTS

5.1 Introduction

The primary results of this thesis are presented in the form of one published journal article and two others, which have been submitted for publication. The articles include, “The Electrical, Optical and Structural Properties of In$_x$Zn$_{1-x}$O$_y$ (0≤x≤1) Thin Films by Combinatorial Techniques” by Taylor, et al., “Functional and Structural Stability of Next Generation Indium Zinc Oxide TCOs”, by Taylor, et al., and “Amorphous In$_{0.70}$Zn$_{0.30}$O$_y$ Thin Films Sputtered at Room Temperature”, by Taylor, et al.


Indium-zinc-oxide (IZO) compositional libraries were deposited with DC magnetron sputtering onto glass substrates at 100°C and analyzed with high throughput, combinatorial techniques. The composition range from 4 to 95 atomic % In for Zn was explored. A peak in conductivity with $\sigma$ > 3000(Ω·cm)$^{-1}$ was observed at an indium content of ~70%. The mobility exceeded 30cm$^2$/V·s and the carrier
concentrations were greater than 8x10^{20}/cm^3. Crystalline phases were observed for In concentrations less than 45% and greater than 80% with an intermediate amorphous region. The low indium content films have a zinc oxide type structure with a ZnO (002) spacing ranging from ~2.61 to 2.85 Å for 4% In and 45% In, respectively. For indium contents between 82% and 95%, the In_2O_3 (222) spacing varied from 2.98 to 2.99 Å. Regardless of the composition or the degree of crystallinity, all films showed high optical transparency with the transmission >80% across the visible spectrum.

5.2.1 Introduction

Transparent conducting oxides (TCOs) combine high optical transparency in the visible spectrum (typically >85%) with high electrical conductivity (typically >1000 Ω^{-1}·cm^{-1}). This unique combination of properties allows these materials to be utilized as transparent electrodes in many opto-electronic devices such as LCD displays and solar cells.\textsuperscript{[10,12]} Presently, ZnO:Al, In_2O_3:Sn and SnO_2:F are the primary TCOs being utilized for such applications.\textsuperscript{[6,10]} However, there are also applications requiring TCOs with specific optical and electrical properties or other attributes, such as work function, surface properties or processibility.\textsuperscript{[16-18]} One challenge in developing new TCOs lies in effectively investigating the large number of potential compounds. A likely region to find such compounds is the composition space formed by mixing known TCOs, such as ZnO, In_2O_3, SnO_2, CdO and Ga_2O_3.\textsuperscript{[19]} To facilitate exploration of this composition space, a series of combinatorial high throughput tools was developed to characterize the compositional libraries that are sections of this composition space.\textsuperscript{[97]} The focus of this work is the ZnO-In_2O_3 system. In_{x}Zn_{1-x}O (IZO) is a promising family of materials for display applications due to the potential for high performance with a low temperature deposition (<100°C) and the ease of patterning in dilute HCl.\textsuperscript{[73,98]}
Compositionally graded libraries of indium-zinc-oxide were deposited onto 2"x2" glass substrates at 100°C by co-sputtering from two targets. Following deposition, a series of automated tools was utilized to characterize the electrical, optical and structural properties as a function of composition. The complete ZnO-In$_2$O$_3$ system was examined through the deposition of only four 2"x2" libraries with one additional library deposited in a transition region of interest. The maximum conductivity for any composition was found at ~70 atomic % In for Zn. In addition, this film was discovered to be amorphous.

5.2.2 Experimental Approach

Two-inch diameter In$_2$O$_3$ (99.99%) and ZnO (99.999%) sintered ceramic targets (SCI Engineered Materials) were DC magnetron sputtered for 6 minutes at various powers with an Ar gas pressure of 4.5 mTorr. Corning 1737 glass (2"x2") was used for substrates and the substrate heater temperature was 100°C for all depositions. A schematic of the sputtering geometry showing the orientation of the targets to the substrate is shown in Figures 4.1 and 4.3. A base pressure of $10^{-7}$ to $10^{-6}$ Torr was achieved in the chamber prior to deposition. Various target powers were chosen to achieve a composition range from 4 to 95 atomic % In for Zn. Table 3.2 lists the ZnO and In$_2$O$_3$ target powers for the five different libraries discussed here, the resulting composition range and the film thickness across each library. Film thicknesses were determined from optical fringes and confirmed by Dektak measurements.

The combinatorial materials analysis focused on measuring a fixed set of 44 locations on each 2"x2" library in a 4 row by 11 column format. The electrical, optical and structural analysis all focused on the same 44 points on each library, allowing for simple cross-correlation of the results. The rows were located 12.5 mm apart and the columns were 4 mm apart.
Electron probe micro analysis (EPMA) mapping was utilized to measure the relative atomic ratio of indium to zinc (20kV, 2.5x10^{-8} A, probe diameter~20μm). The EPMA results were referenced to bulk standards and no quantitative corrections were applied to account for the thickness of these films. Sheet resistance values were characterized with automated 4-point probe mapping. During these measurements, the four co-linear probes were oriented so that the measurement axis was perpendicular to the concentration and thickness gradients. The composition gradient along the length of the 4 point probe averaged ±0.9% and the average thickness gradient across the probe was ±1.6%. A multi-channel fiber-optically-coupled CCD-array-based spectrometer (Ocean Optics) and a Fourier Transform Infra-Red (FTIR) spectrometer (Nicolet) were used to determine the UV/VIS/NIR (.25 - 1.7 μm) and infrared (1.7 – 25 μm) optical transmission and reflection characteristics. The spot size for the UV/VIS/NIR analysis was ~1mm while that of the IR analysis was ~5 mm. Therefore, some overlap between adjacent columns did occur for the IR analysis and the results obtained represent the average reflection and transmission for those columns.

Structural analysis was performed with an x-ray diffractometer equipped with a 2D large area detector and an automated sample-positioning stage (Bruker). During this analysis, the samples were positioned such that the incident x-ray beam would strike the sample along contours of constant composition i.e. perpendicular to the composition gradient. A non-combinatorial Hall measurement system (Bio-Rad) was utilized to measure mobility and carrier concentration values on 0.5cm² (1cm x 0.5cm) samples cut from the full 2”x2” libraries. These pieces show both thickness and concentration gradients but, due to the small sample size, these effects were minimized. The average variation in indium content of the 0.5cm² samples was ±4.3% and the average thickness gradient was ±2.6%. Therefore, although the conductivity, mobility and carrier concentration values obtained through these measurements represent the average values for those pieces, the uncertainty in In
content (±4.3%) is small compared to the overall composition range (4 to 95 atomic % In for Zn) covered in the experiment.

5.2.3 Results and Discussion

Figure 5.1 shows the conductivity ($\sigma$) as a function of In content for the five libraries. The data consists of one row of 11 data points from each of the libraries collected 19 mm below the top edge of the 2"x2" sample. Since the composition gradient is very small vertically, the electrical properties from multiple rows of a single library are nearly identical. Therefore, for clarity, only one row of data from each library is shown. The conductivity data were derived from the optical thickness ($t_{opt}$) and sheet resistance (Rs) from the relation $\sigma = (t_{opt} \times Rs)^{-1}$. From left (0% In) to right (100% In), an initial peak in conductivity of ~750 (Ω·cm)$^{-1}$ occurs at an indium content of approximately 5%. The conductivity then decreases to a minimum of ~300 (Ω·cm)$^{-1}$ in the 15% indium region before increasing to a maximum of $\sigma \approx 3000$ (Ω·cm)$^{-1}$ at an indium content of ~75%. The conductivity then drops to 100 (Ω·cm)$^{-1}$ at 95% In. While the overlap between L1 and L2 at 15% In and L3 and L4 at 70% indium is not perfect, the overall trend across the In$_2$O$_3$-ZnO system is clear. The data from the additional transition region library, L5, is shown with open circles and confirms that a peak in conductivity occurs around 70%. A similar maximum in conductivity has also been observed by others at ~75 atomic % In.$^{[62, 69, 73]}$
Figure 5.1 Conductivity as a function of indium content for the five IZO libraries.

The UV, visible and infrared transmittance and reflectance for a composition of 64% In (column 5 of library 5) are shown in the top panel of Figure 5.2. The black line depicts the transmission (T) normalized to the glass substrate which is opaque beyond 5μm. It is important to note that this film shows good transparency (~80-95%) in the visible (0.4-0.7μm) region. The onset of UV absorption due to the fundamental bandgap of the material is also evident as the transmission drops dramatically in the short wavelength region. The reflection (R) spectrum shows oscillations due to constructive and destructive interference in the visible region followed by a local minimum at 1.5μm before an increase in the infrared to a maximum of 80%. This broad increase in IR reflectivity is characteristic of TCOs and is due to the collective plasma oscillations of the conduction electrons.\(^3\) A reflectance image plot of library 5 is shown in the bottom panel of Figure 5.2. These films show the expected change from transparency to reflectivity in the IR at the plasma wavelength. As suggested by the Drude model\(^3\), the minimum in R just before the reflectivity rise in the IR is taken to be the plasma wavelength, \(\lambda_p\), the optical wavelength corresponding to the collective electron plasma oscillation frequency. The plasma wavelength is overlaid
in both panels of Figure 5.2 as the black dots. The carrier concentration, N, can be determined from $\lambda_p$ and is calculated as, $N = (4\pi^2 c^2 m^* e_0 \varepsilon_\infty) / (\lambda_p^2 e^2)$, where c is the speed of light, $m^*$ is the electron effective mass ($m^* = 0.3 m_e$), $\varepsilon_0$ is the permittivity of free space, $\varepsilon_\infty$ is the high frequency permittivity ($\varepsilon_\infty = 4$) and e is the electron charge. Library 5 shows a range in $\lambda_p$ from 1.4μm to 3.64μm at 74% and 87% In, respectively. This correlates to a change in carrier concentration from $1.01 \times 10^{20}$/cm$^3$ ($\lambda_p = 3.64$μm) to $6.83 \times 10^{20}$/cm$^3$ ($\lambda_p = 1.4$μm).

Figure 5.2 Transmission and reflection characteristics of a typical film (top panel). Reflectance image plot with the estimated plasma wavelength overlaid for library 5 (bottom panel).
Figure 5.3 shows the x-ray diffraction spectra obtained from libraries 1 through 4. The range in atomic % In for each library is noted on the right axis. The spectrum for library 1 (L1) shows a strong peak at $2\theta \approx 34^\circ$ for 4% indium, which then decreases as the indium content increases to 16%. Library 2 (L2) shows a similar trend with a strong peak beginning at 14% In and then decreasing with increasing indium content. The x-ray diffraction spectrum for library 3 (L3) consists primarily of one broad, weak peak, indicative of amorphous material, at $2\theta \approx 32^\circ$. Library 4 (L4) also shows an amorphous region for the first four locations and then it becomes increasingly crystalline. The transition from amorphous to crystalline occurs at $\approx 75\%$ In. The strongest peaks for L1 and L2 are attributed to the (002) of ZnO ($2\theta = 34.4^\circ$) while the strongest peaks observed in L4 are attributed to the (222) of In$_2$O$_3$ ($2\theta = 30.58^\circ$). A discontinuity is observed in x-ray intensity between L1 and L2 despite the overlap in indium content. The overlap in the amorphous regions between L3 and L4 is in good agreement and the global trends are clear. Similar trends in the crystallinity of IZO films has been reported by others.$^{[62],[100]}$

The arrows A and B point to individual spectra from L1 and L2, respectively. Both locations contain 15% In but the two spectra are significantly different. To further examine this difference the raw detector images for A and B are shown as insets to Figure 5.3 with $\chi$ on the vertical axis and $2\theta$ on the horizontal axis. Portions of the Debye rings occur in these images along arcs of constant $2\theta$ and the dashed line shows the detector location for diffraction from planes normal to the substrate. Inset A shows a broad distribution in $\chi$ of diffracted x-rays along a $2\theta$ arc of $\approx 32.8^\circ$, indicating a low degree of texturing within the material. Inset B shows a more highly oriented material as the diffracted beam has greater intensity and greater localization in $\chi$. The primary diffraction peak of B is centered at $2\theta$ of $\approx 33.5^\circ$. The uniform dispersion in $\chi$ shown in A indicates the [002] direction is not normal to the substrate but is randomly oriented. However, in Inset B, the localization of the diffracted beam
below the dashed line in B indicates the [002] direction is oriented toward the ZnO sputtering gun. The differences between the two spectra can be explained by variations in the local growth environment at each location. Column 10 of library 1 (A) was located closer to the low power 15 watt In$_2$O$_3$ target, while column 2 of library 2 (B) was located closer to the high power 75 watt ZnO target. As a result, the deposition rates varied significantly with A being 27nm/sec and B being 57nm/sec. Despite the differences for these two locations, the combinatorial analysis provides a clear view of the overall crystalline-amorphous-crystalline transition, occurring in the In$_2$O$_3$-ZnO system for samples deposited at 100°C.

Figure 5.3  X-ray diffraction spectrum for the four libraries. The composite spectrum represents 11 data points from a single row of libraries 1 through 4. The inset shows the raw detector images for library 1, column 10 (A) and library 2, column 1 (B).
Figure 5.4 illustrates the change in the full-width-half-maximum (FWHM) (panel a) and plane spacing (panel b) as a function of indium content. A significant increase in the FWHM ($\Delta$2$\theta$) is observed between 46 and 80% indium. The FWHM in this region ($\sim$2.2$^\circ$) yields an average crystallite size of $\sim$37Å per Scherrer’s formula, which estimates the crystallite size as a function of the x-ray wavelength, FWHM and $\theta$.$^{101,102}$ Based on the spacing of (002) ZnO and (222) In$_2$O$_3$, this is on the order of $\sim$13 atoms. The location of these weak peaks at 2$\theta$ of $\sim$32$^\circ$ falls directly between the diffraction angles of 34.4$^\circ$ for (002) oriented ZnO and 30.5$^\circ$ for (222) oriented In$_2$O$_3$. The peak location for the amorphous 1737 glass substrate occurs at a 2$\theta$ of $\sim$29$^\circ$. The combination of peak location ($\sim$32$^\circ$), FWHM (2.2$^\circ$) and estimated crystallite thickness ($\sim$37Å) validates the term “amorphous” for these films. The (002) (d=2.6Å) and (222) (d=2.92Å) spacing of ZnO and In$_2$O$_3$ are shown as dashed lines in panel b. For the IZO samples measured the separation is approximately 2.61 Å at 4% In and increases to 2.85Å at 45% In, corresponding to the observed 2$\theta$ values of 34.24$^\circ$ and 31.26$^\circ$, respectively. This increase in lattice constant with indium content is not surprising as the ionic radii of In$^{3+}$ is 0.81 Å while Zn$^{2+}$ is 0.74 Å.$^{23}$ These values for interplanar spacing also agree with those extrapolated and proposed for the Zn$_k$In$_{2-k}$O$_{k+3}$ homologous series for k=1 to k=29, which are shown as a dotted line in panel b.$^{42}$ The planar spacing for the indium-rich compounds shows an increase from 2.98Å at 82% In to a maximum of 2.99Å at 92% In, corresponding to the observed peak 2$\theta$ values of 29.92$^\circ$ and 29.80$^\circ$.
Figure 5.4 FWHM (panel a) and the change in the (002) and (222) spacing (panel b) for libraries 1 through 4. The dotted line shows the c-axis interatomic spacing of the Zn$_k$In$_2$O$_{k+3}$ homologous compounds.\[42\]

Figure 5.5 compares the electrical properties of IZO determined with automated combinatorial mapping tools (solid symbols) with those determined by conventional Hall measurements (open symbols). The samples used for the discrete Hall measurements were cut from libraries 1 through 4. The amorphous region is also indicated in grey in this Figure. The highest conductivity, as determined from the Hall measurements, occurs at an indium content of \(~68\%\), correlating closely with the data from Figure 5.1, shown again here as the solid symbols. The conductivity ($\sigma$) is $\sigma=\text{N} \mu \text{e}$ where e is the electron charge, N is the carrier concentration and $\mu$ is the
mobility. The carrier concentration (panel b) increases from $4.33 \times 10^{20}$ to $8.69 \times 10^{20}/\text{cm}^3$ as the Hall mobility (panel c) decreases from 33.2 to 23.5 cm$^2$/V·s in the amorphous region. The combinatorial carrier concentration, $N_{\text{combi}}$, was calculated from $\lambda_p$, as shown in Figure 5.2. The Hall carrier concentrations correlate well with $N_{\text{combi}}$ and show that the simple approach of calculating N from the estimated plasma wavelength is reasonable for combinatorial analysis. Mobility values >20 cm$^2$/V·s are good for TCOs and comparable to those of crystalline ITO grown at 250° by RF magnetron sputtering.$^{[103]}$

![Figure 5.5 Conductivity (panel a), carrier concentration (panel b) and mobility (panel c) as measured by combinatorial tools (closed symbols) and discrete Hall measurements (open symbols).]
The results obtained on the IZO system correlate very well with the structural, electrical and optical results previously published.\textsuperscript{[62,69,73,100]} Similar properties have been observed in IZO films deposited by techniques such as chemical vapor deposition,\textsuperscript{[67]} suggesting they are characteristic of the material system and not just sputtered IZO films. The combinatorial approach employed here permitted characterization and property measurement of the entire ZnO-In\textsubscript{2}O\textsubscript{3} system with the deposition of only five libraries. Further investigation of the affects of dopants and deposition temperature on the properties of IZO will be conducted with combinatorial techniques.

\textbf{5.2.4 Summary}

This work focused on the electrical, optical and structural properties of the ZnO-In\textsubscript{2}O\textsubscript{3} system. By co-sputtering and controlling the power to each target, compositionally graded libraries ranging from 4 to 95 atomic \% In for Zn were created in only five depositions. High throughput, combinatorial techniques were utilized to characterize the composition, structure, electrical and optical properties of these thin films. Indium contents < \~45\% yielded a crystalline phase with a lattice constant close to that of ZnO (002). An amorphous region was observed for indium contents from \~45\% to \~80\%. As the indium content increased above \~82\%, a crystalline phase was seen with a diffraction pattern corresponding to In\textsubscript{2}O\textsubscript{3}. The highest mobility (>30cm\textsuperscript{2}/V·s) and carrier concentration (>8x10\textsuperscript{20}/cm\textsuperscript{3}) were found in the amorphous region. The peak conductivity of \~3000(Ω·cm)\textsuperscript{-1} was observed at \~67\% In from the Hall measurement and at \~75\% In from the combinatorial analysis. All films showed high optical transmission (>80\%) in the visible spectrum.

Transparent conducting oxides (TCOs) are becoming an increasingly critical components in photovoltaic cells, low-e windows, flat panel displays, electrochromic devices and flexible electronics. For each of these applications there is an associated set of application specific criteria. To date tin-doped indium oxide, zinc oxide and fluorine-doped tin oxide have been the mainstays of the TCO industry, however, none of them are optimum for all applications, resulting in considerable compromises in terms of properties. Most of these materials are in fact single composition crystalline materials that tend to center on a specific set of properties. In this paper, we report on a family of amorphous TCOs formed from In$_2$O$_3$ and ZnO that can be compositionally tuned over a wide range and have demonstrated some significantly improved properties over conventional materials. We have employed combinatorial/hiuthroughput sputter deposition to explore the entire compositional space and coupled it to a set of high-throughput analysis tools tailored to TCOs. Particularly interesting is the compositional range between 50 and 75% In. In this range the TCO is amorphous, extremely smooth (<4Å rms ), has very good conductivity (~3000 (Ω·cm)$^{-1}$), transparency (>90% in the visible) and demonstrates remarkable functional and structural stability with heating up to 600°C. That this amorphous material demonstrates such a set of properties is remarkable and clearly raises questions as to the accepted belief that crystalline materials are the best opto-electronic materials.
5.3.1 Introduction

The growth of the photovoltaics and flat panel display industries in recent years coupled with the advent of organic light emitting diodes (OLED) and organic photovoltaics (OPV) has placed new demands on the performance of the transparent conducting oxide (TCO) layer.\textsuperscript{10,12} Today, tin-doped indium oxide (ITO) is one of the most prevalent TCOs utilized for display applications.\textsuperscript{6,10} Although ITO offers some of the best properties available in a TCO with a conductivity, $\sigma$, on the order of 6000 $(\Omega\cdot\text{cm})^{-1}$ and optical transmission greater than 85%, the high deposition temperature necessary (typically $\sim$350$^\circ$C), increases production costs, prevents the use of temperature sensitive substrates (i.e. polymers). In addition, ITO is also difficult to pattern. This is also true of other doped In$_2$O$_3$ TCOs such as Ti:In$_2$O$_3$, which has high conductivity ($\sim$6000 $(\Omega\cdot\text{cm})^{-1}$) but also requires a high deposition temperature.\textsuperscript{104} There are also increasing niche applications which require TCOs with specific attributes such as surface smoothness, etchability, work function and temperature stability.\textsuperscript{16,17} The exploration of TCO phase space is complicated and has progressed rather slowly, in particular research has tended to focus on line compounds, leaving much of composition space, even in simple systems, unexplored. In principle, combinations of metal oxides such as ZnO, In$_2$O$_3$, SnO$_2$, Ga$_2$O$_3$ and Al$_2$O$_3$ may exist, which could be deposited at low temperatures with specific properties sufficient for next generation devices. In order to explore this "composition space", we have developed a set of combinatorial tools which allows us to deposit and characterize the properties of TCOs in a high-throughput fashion. We have employed this experimental methodology to explore the ZnO-In$_2$O$_3$ system by first depositing and characterizing the as-deposited films and then ascertaining their functional and structural stability to thermal processing by annealing them in air and argon
environments. The result has been the identification of a very stable set of amorphous compositions with excellent TCO properties in the 50-75% In composition range.

5.3.2 Results & Discussion

There is considerable interest in the chemical, electrical and optical stability of TCO materials deposited at low temperatures on a variety of inorganic and organic substrates. This is being driven by the processing demands of polymer-based electronics including displays, OLEDs, PV and flexible electronics. There is also an increasing desire to reduce process temperatures in general while maintaining the structural and functional stability of these materials. Indium-zinc-oxide (IZO) films have been deposited at 100°C and have demonstrated high conductivity (~3000 (Ω·cm)^{-1}) and optical transparency (>85%) comparable to optimized "high temperature" TCOs such as ITO.\textsuperscript{105} In addition, conductivity uniformity and surface roughness are also of critical importance when processing real devices. For instance, if an organic layer is spun or inkjet printed directly upon the TCO, depositing a smooth, homogeneous film will depend on the characteristics of the TCO beneath it. Finally, since many other solid state devices are processed at elevated temperatures in various environments, the TCO must also be resistant to degradation in these conditions.

To produce compositionally-graded "libraries" of IZO, we simultaneously sputtered ZnO and In_{2}O_{3} targets from opposite directions with each inclined at ~30° to the 5cmx5cm glass substrate. We applied a set of automated, combinatorial diagnostic tools to the libraries, including structural, optical, electrical and compositional characterization. The experimental methodology was designed such that each tool measured the same 11 spots across the composition gradient of the library. Therefore, this technique provides instant cross correlation of the material properties with
composition. Three distinct structural regions for the as-deposited material are observed across the ZnO-In$_2$O$_3$ system as shown in the x-ray diffraction (XRD) image intensity map of Figure 5.6. These regions consist of crystalline material at both low and high In contents with an intermediate amorphous region. The 2θ locations of the ZnO (002) and In$_2$O$_3$ (222) are indicated as dashed lines in the figure. Libraries 1 and 2 (L1 and L2, respectively) show a strong primary peak at 2θ ~ 34° which correlates to the (002) of ZnO. This peak shifts to lower 2θ with increasing indium content, indicating an increase in the (002) spacing. A similar shift in the (002) peak has been observed by Naghavi, et al. Library 3 (L3) shows very little scattered intensity, indicative of amorphous material and library 4 (L4) shows an amorphous region ending and becoming crystalline at 74% In (note: the % In is the cation ratio of In:Zn, In/(In+Zn)). For In contents greater than 74%, L4 shows a primary diffraction peak at 2θ ~30°, corresponding to the (222) of In$_2$O$_3$. The composition range 35 to 45% In can be deposited either crystalline (L2) or amorphous (L3). This difference in structure despite the same composition is attributed to the different absolute and relative target powers utilized and local growth conditions. The variation in structure indicates the sensitivity of the material in this composition range to the deposition conditions. In Figure 5.6, the insets show the x-ray raw detector images for 4% In, 69% In and 92% In with χ on the vertical axis and 2θ on the horizontal axis. Chi (χ) represents the angular distribution of the diffracted x-rays around a scattering cone of constant angle (2θ). For a randomly oriented, polycrystalline sample, the detector images would show discrete curved bands of nearly constant intensity along the arc. Portions of the Debye rings are visible and the localized diffracted intensity in χ for each inset indicates that the ZnO and In$_2$O$_3$ phases are not randomly oriented, but (002) and (222) textured, respectively. However, the degree of texturing for the Zn-rich compositions decreases as the In content increases. Similarly, the texturing of the
In-rich films decreases as the Zn content increases. Differences in texturing between similar compositions can be attributed to the geometry of the co-sputtering system.\textsuperscript{[63]}

Figure 5.6 Structural properties of as-deposited IZO. X-ray diffraction image intensity map for the 4 as-deposited libraries (L1-L4) shows both crystalline and amorphous regions. The insets show the raw detector images for 4%, 69% and 92%In. The texturing of 4%In is approximately normal to the substrate and that of 92%In is toward the In$_2$O$_3$ gun. The different composition ranges were obtained by varying the sputtering conditions from the two targets.

Variations in the structure of deposited IZO thin films also exist between different researchers such as Hara, \textit{et al.} who observed the amorphous to crystalline transition at \textasciitilde 96% In when using dc magnetron sputtering at 20°C on polycarbonate substrates.\textsuperscript{[61]} The group of Moriga, \textit{et al.} show the In$_2$O$_3$ structure (bixbyite), amorphous region and ZnO structure (wurtzite) when depositing IZO by dc magnetron
sputtering at 50°C and the appearance of a homologous compound at 150°C.\textsuperscript{[62]}
Despite these variations, it is clear that three distinct phase regions exist for IZO
deposited at 100°C. However, the exact composition at which the material transforms
from crystalline to amorphous varies on the deposition conditions. This is true for
both the Zn-rich and In-rich ends of the composition system.

To further characterize the structural properties of the libraries as a function of
composition, the full width at half max (FWHM) and lattice plane spacings for the
IZO films were determined from the XRD data shown in Figure 5.7. By calculating
the FWHM, the transition from crystalline to amorphous material is clearly observed,
as shown in the top panel. The FWHM for the crystalline material ranges between
$\sim 0.3$ and $0.6^\circ$ and increases to $\sim 2.2^\circ$ for the amorphous films. In addition, the
difference in crystallinity between L2 and L3 around 40% In is also emphasized by a
significant increase in the FWHM. The transition from amorphous back to crystalline
material occurs when the FWHM decreases between 72 and 80% In.
The shift of the primary peak to lower 2θ shown in Figure 5.6 for the Zn-rich films
correlates with an increase in the (002) spacing in Figure 2 since $d_{hkl}=\lambda/2\sin\theta$, where
$d_{hkl}$ is the spacing of the $(hkl)$ plane, $\lambda$ is the incident x-ray wavelength and $\theta$ is the
diffraction angle. The increase in $d_{002}$ with increasing In content is expected since the
ionic radius of In$^{3+}$ is 0.81 Å compared to 0.74 Å for Zn$^{2+}$.\textsuperscript{[25]} Although the diffraction
patterns of these Zn-rich films cannot be indexed to the series of homologous
Zn$_k$In$_2$O$_{k+3}$ compounds, the (002) spacing does correlate to that observed for the series,
reproduced in the bottom panel (blue line) for $k=1$ to $k=29$.\textsuperscript{[42]} Similar to the displaced
ZnO (002), the (222) of the as-deposited In-rich films is also found to be highly
displaced.
Figure 5.7 Analysis of the X-ray diffraction spectra. The full width at half maximum (FWHM) and calculated d-spacing for as deposited and 600°C Ar annealed libraries. The horizontal, dashed lines in the bottom panel indicate the d-spacing for ZnO (002) and In$_2$O$_3$ (222). Insets A and B show the structural transformations occurring at 4% In and 92% In, respectively. The vertical dashed lines in the insets show the 2θ positions for ZnO (002) and In$_2$O$_3$ (222). The d-spacing for the amorphous region represents the nearest neighbor spacing for those compositions. The red, hour-glass shaped symbol in the bottom panel at 70% In is the nearest neighbor spacing as determined by a TEM electron diffraction pattern and it agrees well with XRD data. The dotted line represents the d$_{002}$ of the Zn$_k$In$_2$O$_{k+3}$ homologous compounds.\textsuperscript{42}
The conductivity, film roughness and index of refraction for the four libraries are shown in Figure 5.8. The corresponding phase fields, obtained from the x-ray diffraction spectra in Figure 1, are shown as the background color. The conductivity shows a maximum of \( \sim 3000 \, (\Omega \cdot \text{cm})^{-1} \) at \( \sim 70\% \) In which is similar to that observed by others in this composition region.\(^{62, 63, 69, 73} \) However, a broad range of highly conducting material is found throughout the amorphous composition range of 45-72\% In.

The conductivity is given as \( \sigma = N \mu e \), where \( N \) is the carrier concentration, \( \mu \) is the mobility and \( e \) is the electron charge. The as deposited, amorphous IZO compositions show a Hall mobility of \( \sim 30 \text{cm}^2/\text{V} \cdot \text{s} \) and only a slight change in carrier concentration with composition.\(^{63} \) The fact that \( N \) is unaffected by composition in this range (\( \sim 45-80\% \text{In} \)) indicates that the primary doping mechanism is not a result of the In to Zn ratio, but is most likely due to oxygen deficiencies. This was observed in amorphous \( \text{In}_2\text{O}_3 \) by Bellingham, \textit{et al.} who showed that a typical TCO dopant such as tin has negligible effect on the carrier concentration and it is primarily a function of the oxygen partial pressure during deposition.\(^{36} \) In terms of manufacturability of amorphous IZO, this gives a large operating window for the sputter target composition. However, the oxygen partial pressure during deposition may be a critical factor in achieving the most conducting film.

The smoothness of the TCO layer can be a critical parameter in obtaining the highest quality devices whether they are polymer-based displays or silicon solar cells. The as-deposited, amorphous IZO films show an rms roughness of \( \sim 0.4\text{nm} \), as indicated by the red data in Figure 5.8. This is an order of magnitude less than that of the crystalline films. The roughness of these amorphous films is similar to that observed by others and is much smoother than that obtained by Kim, \textit{et al.} who deposited amorphous IZO (92\% In) on polyethylene terephthalate substrates (rms \( \sim 1.4 \))
Most importantly, the amorphous films are much smoother than commercial ITO, which has an rms roughness of ~4nm.\textsuperscript{72, 74, 75}

Figure 5.8 The conductivity, surface roughness and index of refraction for IZO deposited at 100°C. While the index of refraction varies slightly for all compositions, the conductivity shows a maximum and the roughness is at a minimum in the amorphous region, which is shown as the background color.

The index of refraction for TCOs is typically around 2.0\textsuperscript{3} and we found that it varies from ~1.9 to ~2.2 across the ZnO-In$_2$O$_3$ composition line. This was calculated by modeling the transmission data in the spectral region of 450 to 750 nm with the Fresnel equations, assuming both no absorption and a constant index in this wavelength region.\textsuperscript{28} The results of this approach show that the index in the amorphous region does not vary from the crystalline regions and it correlates closely to that obtained by others.\textsuperscript{58, 75, 106} An index of 2.6 was reported by Minami, \textit{et al.} for amorphous IZO(50% In) deposited at room temperature by dc magnetron
sputtering\textsuperscript{[73]}, which is higher than we found. The results of Jung, \textit{et al.} show that the index for IZO films sputtered from an IZO oxide target (84\% In) as a function of $O_2$ content, substrate temperature and sputtering gas decreases by only $\sim 10\%$ from 450nm to 750nm.\textsuperscript{[75]} Therefore, the assumption of a constant index when modeling the transmission data over this spectral region is reasonable for these combinatorial experiments.

Another critical characteristic of TCOs is the optical transparency. Figure 5.9 shows the optical transmission data for the four libraries as color plots for wavelengths from 0.3 to 4.6\,$\mu m$. These data represent the transmission of films on the glass normalized to the transmission of a blank substrate, which is opaque beyond $\sim 5\mu m$. The transmission and reflection spectra (black line) for L3, column 11 (71\% In) are shown at the top of the as-deposited column. This composition has the highest conductivity of any of the as deposited films with $\sigma \sim 3000$ (\O\,cm)$^{-1}$. The transmission spectrum shows the optical band gap at $\sim 0.37\mu m$ where the transmission drops dramatically between $\sim 0.4$ and 0.3\,$\mu m$. This material has high transmission in the optical portion of the spectrum (0.45 to 0.75\,$\mu m$) and the measured spectrum show interference effects due to the film thickness.

The decrease in transmission from 1.5 to 5\,$\mu m$ is associated with a corresponding increase in reflection (top panel) at the plasma wavelength, $\lambda_p$, which in the Drude (free electron) model is given by $\lambda_p = (4\pi^2 c^2 m^* \epsilon_\infty \epsilon_{\text{HF}} / \text{Ne}^2)^{1/2}$, where $c$ is the speed of light, $m^*$ is the electron effective mass ($m^* = 0.3m_e$), $\epsilon_\infty$ is the permittivity of free space, $\epsilon_{\text{HF}}$ is the high frequency permittivity ($\epsilon_{\text{HF}} = 4$), $e$ is the electron charge and N is the free carrier concentration.\textsuperscript{[83]} Hence, since the long wavelength limit of the transparency is given by the plasma wavelength, which varies as $\lambda_p \propto N^{-1/2}$, there is a fundamental tradeoff between conductivity ($\sigma \propto N$) and infrared transparency. Therefore, it is important that N is chosen to collectively optimize the conductivity and optical transparency. For this combinatorial analysis, $\lambda_p$ was determined by
Figure 5.9 Optical properties of IZO films. Transmission image maps for the four compositional libraries in the as deposited, 600°C air and 600°C argon annealed conditions. The transmission spectrum shown at the top of each column is that of the highest conducting material in that group. The corresponding reflection data (black line) is also shown. The plasma wavelength is indicated by the black circles. The optical band gap of the material is shown at the right.
assuming it to be approximately equal to the wavelength at which the reflection minimum is observed, just prior to the increase in the long wavelength region. In Figure 5.9, the plasma wavelength is overlaid on the transmission data as the solid black circles. All of the features in the transmission spectrum for 71% In (top panel) are found at the other compositions to varying degrees as shown in the image intensity maps. It can be seen that variations exist at both the short and long wavelengths. However, in the optical portion of the spectrum, the transmission is ~90% for all compositions, regardless of conductivity or crystal structure.

The optical transmission (T) is given as \[ T = \frac{(1 - R)^2 e^{-\alpha t}}{1 - R^2 e^{-2\alpha t}} \], where \( R \) is the reflection, \( t \) is the film thickness and \( \alpha \) is the absorption coefficient. The optical band gap for direct band to band transitions can be determined by plotting \( \alpha^2 \) versus energy and extrapolating the linear portion of the curve to \( \alpha^2 = 0 \). This approach has been taken by many groups studying various crystalline and amorphous TCOs.\[27,29-36\] The change in optical band gap is shown in the right-hand column of Figure 5.9 and varies from ~3.3 to 3.5eV for the as deposited films.

For device processing, it is critical that the TCO layer be capable of withstanding all subsequent processing steps, regardless of temperature or atmosphere. To investigate the stability of these films to thermal processing, two sets of libraries were annealed respectively in flowing air or argon at temperatures from 100° to 600°C for 1 hour intervals. Following each anneal, the properties of the films were characterized to determine what changes, if any, occurred. The results of these experiments are shown in Figure 5.10 with the conductivity represented on a color intensity scale from \( \log(\sigma) = 0.0 \) to \( \log(\sigma) = 3.5 \). The scale minimum of \( \log(s) = 0.0 \) was chosen in order to preserve contrast and the data points from the different libraries are offset for clarity. The structural regions and conductivity for the as deposited material, shown in Figures 5.6 and 5.8, respectively, are shown again here for reference as the bottom row, As Dep.
Figure 5.10 Electrical and structural changes of IZO upon annealing. The conductivity of the IZO films is shown as function annealing temperature and composition for both air annealed (top panel) and Ar annealed (bottom panel) films. The conductivity is represented by the color intensity scale and the phases are indicated by the background colors.
The conductivity of the Zn-rich compositions (L1 and L2) annealed in air (top panel) decreases monotonically as the libraries are annealed in sequential 1 hour anneals up to 600°C. Following the 600°C anneal, the conductivity is less than 0.10 (Ω·cm)^{-1} for all compositions of L1, indicated by the black colored symbols. L2 shows a similar trend, however, the conductivity across the library after the final anneal is not as uniform as L1 with the maximum and minimum being 25(Ω·cm)^{-1} at 13.2% In (column 1) and 0.58(Ω·cm)^{-1} at 23.0% In (column 5), respectively. There is no phase change for any composition of L1 and L2 after the final anneal however, a shift in the (002) is observed at 400°C as shown with inset A of figure 2 for 4% In. This shift to higher 2θ results in a decrease in the d_{002} and suggests a relaxation of strain in the lattice. A discrepancy in conductivity exists in the overlap between L1 and L2 around 15% In and this is attributed to the different film thicknesses and texturing which could affect the kinetics of diffusion of oxygen into the material. Diffusion of oxygen into the film and the elimination of oxygen vacancies is probably the primary mechanism reducing the carrier concentration.

The first significant change in conductivity for the air-annealed In-rich compositions (L3 and L4) is observed at 200°C between 85 and 92% In. At this point the conductivity drops from 385 (Ω·cm)^{-1} (100°C anneal) to less than 10 (Ω·cm)^{-1} for L4, column 11 (92%In), shown as the transition from orange to dark red on the color scale. This abrupt drop in conductivity corresponds with a recrystallization of the In_{2}O_{3} crystal structure as illustrated with inset B of Figure 5.7 for 92% In. The recrystallized region expands to 82% In following the 300°C anneal and ~78% In by the 500°C anneal.

Following the 600°C anneal, only two amorphous films, 69.9% and 71.7% In have crystallized as indicated by the arrow in the top panel of Figure 2. The composition 69.9% In shows only a single primary peak at 2θ ~ 30°, which correlates to the (222) of In_{2}O_{3} while the compositions 71.7 to 79.8% In show an unknown phase
in addition to the In$_2$O$_3$ phase. The phase field that contains both the In$_2$O$_3$ and unknown phase is indicated by the gold background. Jung et al. also observed the crystallization of amorphous IZO in this temperature range by differential thermal analysis.[75] The maximum conductivity for any composition after the 600°C air anneal is \( \sim 200 \text{ (} \Omega \cdot \text{cm})^{-1} \) at 66% In. The conductivity of the Zn-rich and In-rich crystalline compounds decreased between 3 and 4 orders of magnitude with the minimum being \( \sim 0.04 \text{ (} \Omega \cdot \text{cm})^{-1} \) at 4% In. The fact that the conductivity of amorphous IZO decreased by just over 1 order of magnitude when subjected to six sequential air anneals from 100° to 600° is remarkable and shows that this material is quite robust, both electrically and structurally to thermal processing in air. In addition, the In-rich compositions have undergone recrystallization.

The results of the argon annealing experiments are shown in the bottom panel of Figure 5.10 and show the dramatic effect of the gas atmosphere during annealing. The maximum conductivity following the 600°C anneal is \( \sim 1350 \text{ (} \Omega \cdot \text{cm})^{-1} \) at 64.4% In while the minimum is \( \sim 6 \text{ (} \Omega \cdot \text{cm})^{-1} \) at 82% In. The Zn-rich and In-rich films both show the peak shifts and phase transformations that were observed for the air annealed libraries. For the In-rich libraries, the onset of the unidentified phase was observed after the 500°C anneal between 72 and 78% In, 100°C lower than for the air annealing.

The amorphous to crystalline transformation is demonstrated in the x-ray diffraction spectra for the as deposited, 500°C and 600°C air anneals in Figure 5.11 for the composition range 69.9% to 79.8% In. The crystalline phase observed at 69.9% In after the annealing at 600°C can be indexed to the In$_2$O$_3$ crystal structure, however a large portion of the amorphous “bump” is still evident (indicated by the arrow), suggesting a significant volume fraction of retained amorphous phase. The insets A and B show the raw detector images for 69.9% In following the 500° and 600°C air anneals. Inset A shows no sharp peaks whereas inset B shows that the crystallized
phase is (222) textured although not centered in $\chi$ on the XRD detector. This phase is oriented in the direction of the In$_2$O$_3$ gun and suggests that some form of ordering occurred in the amorphous material that provided a template for the growth of the crystalline phase. Texturing of the film toward the sputtering target was observed previously for the Zn-rich compositions$^{[63]}$ and has been observed in titanium doped In$_2$O$_3$ (TTiO) when using a similar sputter geometry.$^{[104]}$ The middle panel, 74.0% In, shows a small peak in the as deposited film which correlates to In$_2$O$_3$ (222). This peak grows in intensity with increasing anneal time and temperature and the new phase(s) appears at 600°C. Although two of these peaks agree well with ZnO (100) and (101), several peaks exist at higher 2$\theta$ (46.5°, 49.9°, 55.5° and 67.5°), which do not correlate well with either phase. In the temperature range 1100° to 1200°C, a two-phase mixture of In$_2$O$_3$ and Zn$_x$In$_{1-x}$O$_8$ was found from ~27% to 100% In by Moriga, et al.$^{[44]}$ However, none of the peaks from the Zn$_x$In$_{1-x}$O$_8$ powder diffraction file correlate with the unidentified peaks. In addition, positive matches could not be made with any of the Zn$_x$In$_{2-x}$O$_{4x}$ (k=2-5, 7, 17, 19) homologous compounds. As the composition increases to 79.8% In, the ZnO (100) is not evident, the ZnO (101) has decrease significantly in intensity and by 81% In, the (101) has completely disappeared. The XRD spectra suggest a phase separation of In$_2$O$_3$ and a ZnO-type compound in the composition range ~72 to 80% In at temperatures between 500° and 600°C.

Next, the effects of thermal processing on the optical properties are discussed. Significant increases in transmission at the longer wavelengths are observed for all libraries following the 600°C air anneal, Figure 5.9. The plasma wavelength occurs at wavelengths beyond 5$\mu$m as a result of the reduction in free carriers and therefore cannot be overlaid on the transmission image plots. The increase in $\lambda_p$ corresponds with the decrease in conductivity shown in Figure 5.10. Following the 600°C air anneal, the maximum conductivity is found at 62% In and the transmission and reflection spectrum for this film are shown in the top panel of figure 4.
Figure 5.11 X-ray diffraction spectrum showing the amorphous to crystalline transformation. The x-ray diffraction spectrum for the as deposited, 500°C and 600°C air annealed compositions from 69.9 to 79.8% In (columns 4 to 6, library 4). The insets show the raw detector images, which indicate the crystallized material is (222) textured although not normal to substrate surface but is textured toward the In₂O₃ sputtering gun.

The decrease in transmission due to the band gap of the material is still observed, however, it occurs at a longer wavelength or lower energy. The shift in the optical band gap can be explained by the Burstein-Moss effect which is essentially a conduction band filling effect with \( \Delta E_{BM} = \left(3^{2/3} \hbar^2 N^{2/3}/(8\pi^2 m_e^*) \right) \). Here \( \hbar \) is Plank's constant, \( N \) is the carrier concentration, and \( m_e^* \) is the electron effective mass.\[^3, 56, 57\] Neglecting electron-electron and electron-impurity scattering, the optical band gap is given as \( E_{opt} = E_i + \Delta E_{BM} \), where \( E_i \) is the intrinsic band gap of the material.\[^3\] The result is that as \( N \) decreases, the optical band gap occurs at a lower energy or longer
wavelength, due to $\Delta E_{BM}$ term. Therefore, the decrease in $E_{opt}$ due to a loss of free electrons correlates with the increase in transmission at the long wavelengths and the observed decrease in conductivity. The loss of free electrons is attributed to the diffusion of oxygen into the film and the elimination of oxygen vacancies, the primary doping mechanism.

The results of the argon annealed samples are also shown in Figure 4. Libraries 1 and 4 show similar transmission spectra to the air annealed libraries. However, L2 and L3 show significantly less change in the transmission at the longer wavelengths after thermal processing, indicating a higher carrier concentration in this composition region. This was to be expected, as the conductivity of these films, particularly the amorphous ones, remained high. The transmission and reflection spectra for 64% In are shown in the top panel. This sample has a conductivity of $\sim 1350 \, (\Omega\cdot\text{cm})^{-1}$ following the final Ar anneal with its transmission spectrum falling in between that of the as-deposited and air-annealed samples. Neglecting the effects at the short and long wavelengths, it is clear that neither air nor argon annealing degrades the optical transmission of these films for most of the visible spectrum.

IZO films deposited at 100°C in the composition range 50-75 %In are amorphous with excellent TCO properties. In addition, we find compositional tolerance for cation stoichiometry, very smooth surfaces and great thermal stability. While all of the compositions along the In$_2$O$_3$-ZnO composition system are TCOs, it is clear that amorphous IZO ($\sim 70\%$ In) offers the best combination of properties for many applications. This material combines high conductivity, surface smoothness and optical transparency with a resistance to thermal degradation when annealed in either air or argon. In addition although the conductivity is $\sim 1/2$ that of optimized ITO, amorphous IZO (70% In) consumes much less In than conventional ITO ($\sim 91\%$ In), which is an increasingly important issue. Overall this work challenges the conventional viewpoint that crystalline materials are necessary for optoelectronic
applications and shows that amorphous materials deserve consideration. This also suggests the expansion of the search methodology into additional TCO composition space for the discovery of more, complex amorphous materials.

### 5.3.3 Methods

Two-inch diameter In$_2$O$_3$ (99.99%) and ZnO (99.999%) sintered ceramic sputtering targets (SCI Engineered Materials) were used to deposit films by DC magnetron sputtering for a fixed time of 6 minutes at various powers with an Ar gas pressure of 4.5 mTorr. Corning 1737 glass (5cmx5cm) was the substrate held at 100°C for all depositions. The targets were inclined at approximately 30° to the substrate normal.\(^{63}\) The chamber pressure was $10^{-7}$ to $10^{-6}$ Torr prior to deposition. Various target powers were chosen to achieve a composition range from 4 to 95 atomic % In. Table I lists the ZnO and In$_2$O$_3$ target powers for the four different libraries discussed here, the resulting composition range and the film thickness across each library. Film thicknesses were determined from the optical fringes and confirmed by Dektak measurements.

The combinatorial materials analysis focused on measuring a fixed set of 44 locations on each substrate in a 4 row by 11 column format. The electrical, optical and structural analysis all focused on the same 44 points on each library, allowing for correlation of the results. The rows were located 12.5 mm apart and the columns were 4 mm apart.

Electron probe micro analysis (EPMA) mapping was utilized to measure the relative atomic ratio of indium to zinc (20kV, 2.5x10$^{-8}$A, probe diameter~20µm). The EPMA results were referenced to bulk standards and no quantitative corrections were applied to account for the thickness of these films. Sheet resistance values were characterized with automated 4-point probe mapping. During these measurements, the
four co-linear probes were oriented so that the measurement axis was perpendicular to the concentration and thickness gradients. A multi-channel fiber-optically-coupled CCD-array-based spectrometer (Ocean Optics) and a Fourier Transform Infra-Red (FTIR) spectrometer (Nicolet) were used to determine the UV/VIS/NIR (0.25 - 1.7 μm) and infrared (1.7 – 25 μm) optical transmission and reflection characteristics. The spot size for the UV/VIS/NIR analysis was ~1mm while that of the IR analysis was ~5 mm. Therefore, some overlap between adjacent columns did occur for the IR analysis and the results obtained represent the average reflection and transmission for those columns. Structural analysis was performed with an x-ray diffractometer equipped with a 2D large area detector and an automated sample-positioning stage (Bruker). During this analysis, the samples were positioned such that the incident x-ray beam would strike the sample along contours of constant composition i.e. perpendicular to the composition gradient. The roughness of the films was determined by atomic force microscopy (AFM) on pieces cut from the larger 5cm x 5cm libraries.

Following analysis of the as-deposited libraries, rows 1 and 2 were cut from the libraries for the annealing experiments. Row 1 of the 4 libraries was sequentially annealed in flowing air for 1 hour from 100 to 600°C at 100° intervals. Following the 1 hour anneal at the desired temperature, the samples were cooled to 100°C and removed to ambient conditions. The electrical, optical and structural properties were then characterized. This entire annealing procedure was repeated for row 2 of the 4 libraries but in an atmosphere of Ar. The ultra high purity argon (99.999%) passed through an oxygen filter and moisture trap (Advanced Specialty Gas) prior to entering the annealing chamber.
5.4 "Amorphous In$_{0.70}$Zn$_{0.30}$O$_y$ Thin Films Sputtered at Room Temperature", in publication (Journal of Applied Physics), Matthew P. Taylor, Hans-Joachim Kleebe, Dennis W. Ready, Maikel F.A.M. van Hest, Charles W. Teplin, Jeff L. Alleman, Matthew S. Dabney, Lynn M. Gedvilas, Brian M. Keyes, Bobby To, John D. Perkins, David S. Ginley.

Amorphous indium zinc oxide (IZO) films were deposited by dc magnetron sputtering at room temperature onto Corning 1737 glass substrates from a mixed In$_2$O$_3$-ZnO target (In$_{0.70}$Zn$_{0.30}$O$_y$) using Ar, Ar+O$_2$ and Ar+H$_2$. A transparent film (T>85% in the visible) with a maximum conductivity of ~2,000(Ω·cm)$^{-1}$ was achieved with a carrier concentration (N) of 33x10$^{19}$/cm$^3$ and a mobility (μ) of 33.0cm$^2$/V·s when depositing in Ar. This film was extremely smooth with an rms roughness of 0.13nm. As oxygen was increased up to 6%, N decreased to 4x10$^{16}$/cm$^3$. The mobility, however, remained largely unaffected by the O$_2$ content and varied from a maximum of 37.1 to minimum of 18.8cm$^2$/V·s. The decrease in carrier concentration due to the incorporation of oxygen during deposition was found to be strongly dependent on the target power. The introduction of H$_2$ did little to increase the carrier concentration, but at 4% H$_2$, the optical properties were significantly degraded to a transmission of only ~55% in the visible. XRD, TEM and EPMA did not reveal any significant difference between this film and the other amorphous films deposited from this target. However, the surface rms roughness of the film deposited with 4% H$_2$ (1.81nm) was much greater than that of the film deposited with just argon (0.13nm). The direct band gap of In$_{0.70}$Zn$_{0.30}$O$_y$ was 3.23eV and was found to vary linearly with N$^{2/3}$. 


5.4.1 Introduction

Transparent conducting oxides (TCOs) are widely used in photovoltaics cells, low e- windows, flat panel displays and electrochromic devices. The growth of organic-based opto-electronic devices (OLED and OPV) in recent years has placed additional processing demands on the TCO layer.\textsuperscript{[10,12]} Tin doped indium oxide (ITO) is one of the most prevalent TCOs used for display applications and offers high conductivity ($\sim$6,000 (\(\Omega\cdot\text{cm}\))\textsuperscript{-1}) and optical transparency (>85\%). However, the high deposition temperature (typically $\sim$350°C) makes this incompatible with organic-based substrates. Previously, work was performed on the In$_2$O$_3$-ZnO (IZO) composition system by combinatorial techniques at 100°C in order explore its potential as a “low temperature” TCO.\textsuperscript{[63]} A wide range of compositions ($\sim$45-75\% In) were found to be both amorphous and highly conducting, however, the composition of 70 atomic\% In and 30 atomic\% Zn (IZO(70/30)) had the highest conductivity ($\sim$3000 \(\Omega\cdot\text{cm}\))\textsuperscript{-1} in the as-deposited state.\textsuperscript{[63]} In addition, the amorphous IZO films showed extremely smooth surfaces with an rms roughness <0.4nm.

To expand on the results of the combinatorial analysis of the IZO system, optimization of IZO(70/30) was performed by depositing thin films by dc magnetron sputtering at various target powers and sputtering gas compositions. The transmission data were modeled with the Drude model and the results were correlated with Hall measurements and the method of 4 coefficients.\textsuperscript{[107]}

5.4.2 Experimental Procedure

The target was prepared from ZnO (99.999\%, lot#B9717014, Puratrem) and In$_2$O$_3$ (99.999\%, lot#B7204022, Puratrem) powders and mixed such that the cation
ratio was 30% Zn:70% In. The calculated target composition is written as \text{In}_{0.70}\text{Zn}_{0.30}\text{O}_x. The powders were mixed and ground together with a ceramic mortar and pestle and pressed in a 5cm die to 175MPa for ~ 3 minutes. The target was then placed on a platinum foil-covered alumina “boat” and sintered in air at 800°C for approximately 24 hours. Following the anneal, the target was furnace-cooled, reground, pressed and sintered again. X-ray diffraction revealed the target to be a two-phase mixture of ZnO and In$_2$O$_3$. The IZO thin films were deposited by dc magnetron sputtering from the 5cm target at 27, 40 and 60W. The deposition time at 27W was ~60 minutes while it was ~20 minutes at 60W. The time was varied in order to obtain films of approximately constant thickness. The target to substrate distance was ~20cm and a base pressure of $10^{-7}$ to $10^{-6}$ torr was achieved prior to deposition. Film thicknesses were determined from the optical interference fringes.

The sheet resistance was measured by the standard 4-point probe technique. A multi-channel fiber-optically-coupled CCD-array-based spectrometer (Ocean Optics) and a Fourier Transform Infra-Red (FTIR) spectrometer (Nicolet) were used to determine the UV/VIS/NIR (0.25 - 1.7 μm) and infrared (1.7 - 25 μm) optical transmission and reflection. Structural analysis was performed with an x-ray diffractometer equipped with a 2D large area detector (Bruker) and by transmission electron microscopy (Philips CM200 STEM, operating at 200keV). The TEM samples were prepared by depositing ~35nm thick IZO films directly onto holey carbon TEM grids. The film roughness was determined by atomic force microscopy (AFM). A Hall measurement system (Bio-Rad) was used to determine the free electron concentration and mobility.
5.4.3 Results and Discussion

The transport properties of ~150nm thick In$_{0.70}$Zn$_{0.30}$O thin films deposited at 40W with varying amounts of oxygen are shown in Figure 5.12. A conductivity ($\sigma$) of 1960($\Omega$-cm)$^{-1}$ is obtained for the film deposited in pure Ar and $\sigma$ continuously decreases as the O$_2$ content increases during deposition. In addition, all of these films are found to be amorphous as shown in Figure 5.13. The conductivity is given as $\sigma=Ne\mu$, where $e$ is the electron charge. The mobility and carrier concentration obtained from the Hall measurement for the film deposited with pure Ar (IZO(Ar)) are 37.1cm$^2$/V·s and 33.0 x10$^{19}$/cm$^3$, respectively. As oxygen is introduced into the sputtering chamber, a monotonic decrease in carrier concentration is observed and at 6% O$_2$ (IZO(6%O$_2$), N has decreased by four orders of magnitude from IZO(Ar) to 4x10$^{16}$/cm$^3$. The carrier concentration in amorphous IZO has been shown to vary only slightly with composition, suggesting that oxygen vacancies may be the primary doping mechanism in this material.$^{63}$ The mobility increased slightly to 48cm$^2$/V·s at 2% O$_2$ and then decreased to 15cm$^2$/V·s at 6% O$_2$. Similar mobility and carrier concentration trends have been observed by others for amorphous IZO deposited from In$_2$O$_3$ targets containing 10 wt% ZnO (84 atomic% In).$^{75,108}$ In addition, the mobilities obtained for the films in this work are comparable to that of IZO deposited by co-sputtering and to crystalline ITO.$^{63,103}$

The mobility, given as $\mu=\tau/m_e^*$, where $\tau$ is the scattering time and $m_e^*$ is the electron effective mass, shows very little dependence on the O$_2$ content. Assuming a constant effective mass, this indicates that the scattering mechanisms in the film do not change significantly with carrier concentration. Therefore, despite the addition of 6% O$_2$ to the sputtering gas, the scattering time only decreased by a factor of 2.2 from IZO(Ar). The most likely scattering mechanism in amorphous IZO and the
The predominant scattering mechanism in TCO films is ionized impurities.\cite{3} In addition, the work by Bellingham et al. reported that this is the case for amorphous In$_2$O$_3$.\cite{39}

![Graph showing conductivity, mobility, and carrier concentration for IZO films sputtered at 40W with varying oxygen contents. Inset A shows the change in film transmission normalized to the substrate with carrier concentration, N ($x10^{19}$/cm$^3$). Inset B shows the results of the Drude model (dotted line) applied to the transmission of IZO(Ar) on glass (normalized to air).]

Figure 5.12 Conductivity, mobility and carrier concentration for IZO films sputtered at 40W with varying oxygen contents. Inset A shows the change in film transmission normalized to the substrate with carrier concentration, N ($x10^{19}$/cm$^3$). Inset B shows the results of the Drude model (dotted line) applied to the transmission of IZO(Ar) on glass (normalized to air).

The conductivity and mobility of amorphous In$_{0.70}$Zn$_{0.30}$O$_y$ is similar to that of other TCOs.\cite{3} However, this is surprising given the amorphous nature of the material with structural order approximately on the order of a single interatomic distance. By contrast, the conductivity of amorphous metals is $\sim$100 times lower than that of the
corresponding crystalline material. Amorphous In$_2$O$_3$ has a conductivity similar to that of its crystalline counterpart, which Bellingham, et al. explained by its large electron mean free path and electron wavelength. Analyzing the mean free path and wavelength in amorphous IZO yields a similar result.

![Figure 5.13](image)

Figure 5.13 X-ray diffraction spectrum for the films deposited with Ar, Ar+6% O$_2$ and Ar+4% H$_2$. Inset A shows an electron diffraction pattern obtained from IZO(Ar). Line scans across the electron diffraction patterns of all three samples are shown in Inset B. Inset C shows a high resolution image IZO(Ar).

The Fermi level in degenerate semiconductors lies in the conduction band and the energy of these electrons, the Fermi energy, is given as $E_F = \frac{\hbar^2 k_F^2}{8\pi^2 m_e}$, where $k_F$ is the
Fermi wave vector, defined as \( k_F^2 = \frac{3\pi^2}{8}N \) and \( h \) is Planck's constant.\(^{[23]}\) In addition, the thermal velocity of these electrons, \( v_F \), is given as \( v_F = \left( \frac{6E_F}{5m_e} \right)^{1/2} \). Assuming \( m_e^* \sim 0.3 \) and \( N=33 \times 10^{19}/\text{cm}^3 \) results in a Fermi energy of 0.58eV and a thermal velocity of \( 4.12 \times 10^5 \text{m/s} \). The electron wavelength, \( \lambda_e \), and mean free path, \( \ell \), in amorphous ZnO are then calculated to be 5.9 and 2.6 nm, respectively (\( \lambda_e = \frac{h}{m_e^* v_F}, \ell = \frac{v_F \mu m_e^*}{e} \)). These values are approximately 10x greater than the length of any structural order in the amorphous solid. It can be concluded that the free electrons are not affected by the variable background potential and are, therefore, not scattered by the structural disorder. This conclusion has also been reached by groups studying amorphous AgSbO₃, Cd₂PbO₄ and Cd₂GeO₄ who have attributed the large mean free path to an overlap of the 5s spherical orbitals, which are relatively insensitive to structural disorder.\(^{[80, 89, 90]}\)

For the films deposited with 4% and 6% O₂ (\( N=0.019 \) and \( 0.004 \times 10^{19}/\text{cm}^3 \), respectively) where the material is non-degenerate, the thermal velocity (\( v_{th} \)) is given as \( v_{th} = \left( \frac{3k_B T}{m_e^*} \right)^{1/2} \), where \( k_B \) is Boltzmann's constant.\(^{[21]}\) Assuming a constant electron effective mass results in a mean free path of \( \sim 0.7 \text{nm} \), which is still greater than the nearest neighbor distance of \( \sim 0.3 \text{nm} \).

Inset A of Figure 5.12 shows the transmission of ZnO and glass normalized to the glass substrate, which is opaque beyond \( \sim 5 \mu \text{m} \), for films of varying \( N \). Two common features are observed in all three spectra shown in the inset, the first being the decrease in transmission at short wavelengths (\( \sim 0.35 \mu \text{m} \)) due to the band gap of the material. The second common feature is that of high transmission (\( T>90\% \)) in the optical portion of the spectrum (0.45 to 0.75μm). At the longer wavelengths, the transmission is seen to be a strong function of \( N \). The optical properties of these films
can be characterized by the Drude model of free electrons and the decrease in transmission corresponds to an increase in reflection and absorption, occurring at the plasma wavelength, $\lambda_p$.\(^3\) The plasma wavelength is given as $\lambda_p = (4\pi^2 c^2 m^* \varepsilon_0 \varepsilon_r / Ne^2)^{1/2}$, where $c$ is the speed of light, $\varepsilon_0$ is the permittivity of free space, $\varepsilon_r$ is the high frequency permittivity and at this wavelength, the free electrons oscillate in phase with the electric field vector of the incident wave.\(^1\) The plasma wavelength is found to vary from 5.65 to 2.01$\mu$m for carrier concentrations of 4.2 to 33.0x10¹⁹/cm³, respectively.

Inset B shows the results of fitting the IZO(Ar) data, normalized to air, with the Drude model from 500 to 2,660nm and the results are presented in Table 5.1. The mobility as determined from the Hall measurement was fixed at 37.1cm²/V·s. The index of refraction ($n$) in the optical wavelength region is given as $n = \varepsilon_n^{1/2}$, and was calculated to be 1.95, which is a typical value for TCOs\(^3\) and the carrier concentration is slightly lower (20x10¹⁹/cm³) than that obtained from the Hall measurement (33x10¹⁹/cm³). The Drude model returned an effective mass of 0.229, which is slightly lower than that (0.3) of ITO.\(^3\) The method of 4 coefficients\(^{11,96}\) was utilized to verify this result and the effective mass was found to be 0.23 by this technique. The effective mass is determined by measuring the Seebeck, Nernst and Hall coefficients on a single film. This independent, non-optical technique shows excellent agreement with the Drude model for characterizing degenerate, amorphous In₀.₇₀Zn₀.₃₀Oₓ.

<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>N (x10¹⁹/cm³)</th>
<th>$\varepsilon_n$</th>
<th>$m^*_e$</th>
<th>$\mu$ (cm²/V·s)</th>
<th>Chi Square</th>
</tr>
</thead>
<tbody>
<tr>
<td>173.1 ± 0.17</td>
<td>19.99 ± 0.08</td>
<td>3.82 ± 0.004</td>
<td>0.229 ± 0.0005</td>
<td>37.1</td>
<td>557</td>
</tr>
</tbody>
</table>

Table 5.1 Output parameters of the Drude model applied to amorphous IZO plus/minus one standard deviation.
The structure of these films was analyzed by both x-ray and electron diffraction as shown in Figure 5.13. The x-ray diffraction spectrum for IZO(Ar) and IZO(6%O₂) are nearly identical, showing that the O₂ content did little to affect the structure. The electron diffraction pattern for IZO(Ar) is shown as inset A. The broad, circular rings are indicative of diffuse elastic scattering from an amorphous structure and the nearest neighbor spacings were calculated to be 2.82 and 1.63Å from the inner and outer rings, respectively. The electron diffraction pattern of IZO(6%O₂) is nearly identical to that of IZO(Ar). Line scans across them are shown in inset B and are offset for clarity. It can be seen from inset B that the spacings of the inner and outer rings are nearly identical for the two deposition conditions. A high-resolution image of the amorphous IZO(Ar) film is shown in inset C along with a Fourier-filtered image (inset to panel C), which allows a reduction of background noise. The lack of ordering observed in the high-resolution image combined with the electron and x-ray diffraction patterns clearly illustrates the amorphous nature of all three films, independent of deposition parameters.

The effect of varying both the target power and oxygen content on conductivity is shown in Figure 5.14, panel A. When sputtering in pure Ar the conductivity was ~2,000(Ω-cm)⁻¹ for all target powers. The introduction of oxygen degraded all of the films, however, the effect was minimized as the target power was increased. The conductivity varies by over 1 order of magnitude at 2% O₂ and by over 3 orders of magnitude at 3% O₂ for 27 and 60 Watts. The inset shows the carrier concentration (x10¹⁹/cm³) and mobility (cm²/V·s) for the three samples deposited with 2% O₂. All three samples have a similar mobility (49.8 at 60W and 35.1 at 27W), however, N varies between 12.1 to 0.5x10¹⁹/cm³ for 60W and 27W, respectively. The deposition rates for these films were ~2.6, 5.1 and 8.4 nm/min at 27, 40 and 60W, respectively. This illustrates that the incorporation of oxygen into the film is a strong function of the film deposition rate. At 6% O₂ the conductivity only varies by a factor
of 10, indicating that at this concentration, the deposition rate is becoming less of a factor as the conductivity appears to be converging at ~0.1 (Ω·cm)^{-1}. Figure 5.14, panel B shows the conductivity as a function of the normalized deposition rate, which is defined as the percent oxygen divided by target power. This figure defines the operating conditions for obtaining the most conducting film and illustrates that small amounts of oxygen can be tolerated if the target is operated at high power and the film is therefore deposited quickly.

![Graph showing conductivity as a function of oxygen content for different IZO target powers.](image)

**Figure 5.14** Panel A shows the conductivity as a function of oxygen content for different IZO target powers. The inset shows the variation in carrier concentration and mobility for the films deposited with 2% O₂. Panel B depicts the conductivity as a function of the normalized deposition rate, %O₂/target power.

The transport properties of IZO deposited with forming gas (Ar+H₂) are shown in Figure 5.15. The target power was 40W for this series of depositions. The
conductivity varies between 1,000 and 1,600 (Ω·cm)$^{-1}$ for the three films deposited with H$_2$. The mobility decreased from 37.1 to 18.8cm$^2$/V·s as the hydrogen content increased from 0 to 4%. The carrier concentration decreased slightly at 1.1% and then increased to 46.4x10$^{19}$/cm$^3$ for the film deposited with 4% H$_2$, denoted as IZO(4%H$_2$).

![Graph](image)

**Figure 5.15** Conductivity, mobility and carrier concentration for IZO films deposited with argon plus hydrogen at 40W. The inset shows the change in transmission as a function of hydrogen content.

The transmission of these films is shown in the inset to Figure 5.15. The spectrum for 1.1% and 2.4% H$_2$ are typical of a TCO, but IZO(4%H$_2$) is notable as the transmission is ~55% in the visible region. Although this suggests that the film was partially reduced during deposition and conducting second phase particles may be reducing the transmission, no other phase is observed by XRD or TEM (Figure 5.13). This film does have the highest carrier concentration but the lower mobility (18.8cm$^2$/V·s) results in a conductivity of only 1,397(Ω·cm)$^{-1}$. Despite the lack of a
crystalline phase or discernible changes in the electron diffraction pattern, the opacity of this film suggests nano-sized conducting particles are causing scattering in the film, leading to a reduction in transmission.

The optical band gap, $E_{\text{opt}}$, of semiconductors can be determined through the relationship of the absorption coefficient, $\alpha$, and energy, $\hbar \nu$, where $\alpha=4\pi k/\lambda$ and $k$ is the extinction coefficient. Typically, the relationship between $\alpha$ and $\hbar \nu$ is taken as $\alpha=A(\hbar \nu-E_{\text{opt}})^{1/2}$ for band to band transitions in TCOs and this has been applied to both crystalline and amorphous materials. The constant, $A$, is $A=\varepsilon^2(2m_\text{v}^*)^3/(n\hbar^2 m_\text{e}^*)$ and $m_\text{v}^*$ is the reduced mass of the carriers, $n$ is the index of refraction and $c$ is the speed of light. Figure 5.16, panel A shows $\alpha^2$ versus energy and a shift in the optical band gap from 3.46 to 3.19 eV as $N$ varies from 33.0x10$^{19}$/cm$^3$ to 0.004x10$^{19}$/cm$^3$. $E_{\text{opt}}$ is determined by extrapolating the linear portion of the curve to $\alpha^2=0$. This approach to modeling $E_{\text{opt}}$ is based on allowed direct transitions within a parabolic band (transition at $k=0$ is possible). The absorption coefficient was determined from the transmission data by $T=\frac{(1-R)^2 e^{-\alpha t}}{1-R^2 e^{-2\alpha t}}$, where $T$ is the transmission, $R$ is reflection and $t$ is the film thickness. Several other relationships between $\alpha$ and $\hbar \nu$ have been observed for amorphous materials such as Ge, Si, As$_2$Se$_3$, As$_2$Te$_3$ and Se, which include $\alpha\cdot\hbar \nu=\text{const}(\hbar \nu-E_{\text{opt}})$, $\alpha\cdot\hbar \nu=\text{const}(\hbar \nu-E_{\text{opt}})^2$ and $\alpha\cdot\hbar \nu=\text{const}(\hbar \nu-E_{\text{opt}})^3$. These approaches are based on a relaxation of $k$ conservation, which signifies that the uncertainty in $k$, $(\Delta k=1/\delta)$, is approximately equal to $k_F$, which results in $\Delta k/k_F\sim1$. However, $\Delta k/k_F\sim0.1$ for amorphous IZO, which indicates that the relaxation of $k$ conservation is very weak and the approach taken in modeling the band gap (assuming direct optical transitions to a parabolic conduction band) is valid.
Figure 5.16 Panel A shows $\alpha^2$ and $\alpha^{1/2}$ versus energy as a function of carrier concentration, $N$. The x-intercepts indicate the direct optical band gap ($E_{\text{opt}}$, top portion of panel A) and indirect optical band gap. Panel B illustrates the variation in the direct (top line) and indirect optical band gaps as a function of $N^{2/3}$. The y-intercept is taken as the direct ($E_g$). The analysis supports this being a direct band gap material.
The absorption coefficient for indirect transitions is the sum of phonon absorption ($\alpha_a$) and phonon emission ($\alpha_e$) terms, $\alpha(hv) = \alpha_a(hv) + \alpha_e(hv)$. These can be written as $\alpha_a(hv) = \frac{A(hv - E_g + E_p)^2}{\exp \frac{E_p}{k_B T} - 1}$ and $\alpha_e(hv) = \frac{A(hv - E_g - E_p)^2}{1 - \exp \frac{E_p}{k_B T}}$, where $E_p$ is the phonon energy and $k_B$ is Boltzmann's constant. Typically, the relationship $\alpha \approx \text{const}(hv - E_i)^2$, where $E_i$ is the indirect transition energy gap, is used and this has been applied to many different TCOs. Analysis of an indirect band gap for amorphous IZO is shown in Figure 5.16. A straight line is not easily fit to the $\alpha^{1/2}$ versus $hv$ curves and a plot of the indirect optical gap versus $N^{2/3}$ results in substantial deviation from a linear fit, as opposed to that obtained in the direct band gap analysis. This indicates that the indirect band gap model is not appropriate for characterizing the optical transitions occurring in this material and that it is a direct gap semiconductor.

Figure 5.16, panel B shows that $E_{opt}$ varies linearly with $N^{2/3}$. The increase in $E_{opt}$ with $N$ can be described by $E_{opt} = E_g + \Delta E_{BM}$, where $E_g$ is the intrinsic band gap and $\Delta E_{BM}$ is the Burstein-Moss shift, given as $\Delta E_{BM} = \frac{3^{2/3} h^2 N^{2/3}}{8 \pi^2 c^2 m_v^*}$. The term $m_v^*$ is the reduced effective mass and is defined as $\frac{1}{m_v^*} = \frac{1}{m_v} + \frac{1}{m_c^*}$, where $m_v^*$ and $m_c^*$ are the valence band and conduction band effective masses, respectively. The y-intercept of the linear fit is taken as $E_g$ and the slope is inversely proportional to $m_v^*$. This results in a direct band gap of 3.23eV and a reduced effective mass of 0.74. The indirect band gap, $E_i$, was determined to be 2.43eV, however, the data are not well fit by a straight line, which indicates this is not an indirect gap material. The direct band gap correlates closely to that obtained for crystalline IZO sputtered from Zn+3wt%In and (ZnO)$_2$In$_2$O$_3$ targets. However, those authors determined $E_{opt}$ through the relationship of $(\alpha h\nu)^2$ to $h\nu$. The valence band electron effective mass is calculated to
be \(-0.33\). Other authors have reported a negative valence band mass and equated this to a valence band curving in the same direction as the conduction band.\cite{32,112,113}

Many researchers working on TCOs have attributed the shift in the band gap to just the Burstein-Moss shift and neglected other interactions.\cite{31,58,106} However, more recent work on ZnO, SnO\(_2\), Ti:ZnO and ITO has accounted for band gap narrowing effects, resulting in positive values for \(m_v^*\), which is expected from band structure calculations.\cite{27,53,55,114} The high concentration of free electrons in a degenerate TCO causes a downward shift in the conduction band due to Coulomb interactions and mutual exchange forces and the measured band gap can be written as

\[ E_{opt} = E_g + \Delta E_{BM} + \hbar \sum_c(k,\omega) - \hbar \sum_v(k,\omega), \]

where \(\hbar \sum_c\) and \(\hbar \sum_v\) are the self energies due to electron-electron and electron-impurity scattering.\cite{27} The Mott critical density, given as \(N_c \sim 0.2/a_B\), where \(a_B\), the Bohr radius, is defined as \(a_B = \frac{4\pi \varepsilon \varepsilon_0 \hbar^2}{m_e^2}\) and \(\varepsilon\) is the static dielectric constant, is approximately \(2 \times 10^{18}/\text{cm}^3\) for these films.\cite{25,26} This value was calculated assuming \(m_e^* = 0.23\) and \(\varepsilon = 8.7\) (\(\varepsilon_{\text{ZnO}} = 8.5\), \(\varepsilon_{\text{In}_2\text{O}_3} = 8.9\)).\cite{3} Therefore, the carrier concentration of these films lies well within the metal-insulator transition region and the presence of effects should not be surprising.

The rms roughness of IZO(Ar), IZO(6\%O\(_2\)) and IZO(4\%H\(_2\)) are 0.13, 0.29 and 1.81 nm, respectively. This is shown in Figure 5.17 where the rms roughness of the substrate is shown as the dashed line and the solid line represents the rms roughness of IZO films deposited by co-sputtering from ZnO and In\(_2\)O\(_3\) targets.\cite{115} The two insets show AFM scan images for IZO(4\%H\(_2\)) (top image) and IZO(Ar) (bottom image) and it is important to note that the gray scales for the two images are different.

Amorphous In\(_{0.70}\)Zn\(_{0.30}\)O\(_y\) shows excellent surface smoothness which is on the order of that observed by others examining amorphous IZO and is much smoother than commercial ITO (rms~4nm).\cite{72,74,75}
Figure 5.17 RMS roughness of the three IZO films deposited with Ar, Ar+6% O₂ and Ar+4% H₂. The line with markers represents the rms roughness for indium zinc oxide films deposited by co-sputtering from two oxide targets. The insets show the AFM scan images relating to IZO(4%H₂) (top image) and IZO(Ar).

5.4.4 Conclusions

The maximum conductivity for any IZO film deposited was ~2,000(Ω·cm)^-1 and was obtained when depositing in Ar. The carrier concentration decreased dramatically as oxygen was introduced into the chamber while the mobility remained largely unaffected. The decrease in carriers due to the incorporation of oxygen during deposition was found to be strongly dependent on the target power or deposition rate. The introduction of H₂ did little toward increasing the carrier concentration, but at 4% H₂ the optical transmission was severely degraded. Structural analysis did not reveal any significant difference between the films deposited in Ar, Ar+O₂ or Ar+H₂. The
band gap of amorphous $\text{In}_{0.7}\text{Zn}_{0.3}\text{O}_y$ (3.23eV) was found to be lower than either $\text{ZnO}$ (3.5eV) or $\text{In}_2\text{O}_3$ (3.75eV)[3] and was very smooth with an rms roughness of 0.13nm.
CHAPTER 6
ADDITIONAL RESULTS

6.1 Introduction

Additional functional and structural results are presented here that are not included in the three publications of chapter 5. Section 6.2 contains data concerning the compositional libraries while section 6.3 has additional results regarding the single composition IZO study. Additional results pertaining to optical modeling are presented in section 6.4 and properties of undoped ZnO and In$_2$O$_3$ are discussed in section 6.5. Analysis of the plasma wavelength characterization technique is presented in section 6.6.

6.2 Compositionally Graded IZO Libraries

Included in this section are additional data on the compositionally-graded IZO libraries, which are discussed in detail in sections 5.2 and 5.3. These additional data include chemical and sheet resistance mapping, optical properties and structural data for the as-deposited and annealed libraries.

6.2.1 Chemical Profiles

The EPMA maps for the compositional libraries used for the annealing study are shown in Figures 6.1-6.4. The third row, Row 3, was masked during deposition
for normalization of the transmission data. Therefore, only rows 0-2 were mapped. The EPMA maps reveal a systematic increase in the In:Zn distribution from left to right and almost no gradient in the vertical direction. Figure 6.5 shows the EPMA map for library 5, which was deposited such that composition $\text{In}_{0.70}\text{Zn}_{0.30}\text{O}_y$ was located in the center of the sample. This was done to verify that the peak in conductivity observed at this composition (Figure 5.1) was not dependent on the target-substrate distance or location on substrate, but was a true material property. The deposition chamber showed very good reproducibility when depositing multiple libraries.

![Figure 6.1 EPMA map of library 1. The contours indicate atomic % In for Zn. The third row was masked during deposition.](image)
Figure 6.2 EPMA map of library 2. The contours indicate atomic % In for Zn. The third row was masked during deposition.

Figure 6.3 EPMA map of library 3. The contours indicate atomic % In for Zn. The third row was masked during deposition.
Figure 6.4 EPMA map of library 4. The contours indicate atomic % In for Zn. The third row was masked during deposition.

Figure 6.5 EPMA map of library 5. The contours indicate atomic % In for Zn. The third row was masked during deposition. The optimal composition, 70%In, is now located at the center of the library.
6.2.2 Electrical Properties

The sheet resistance maps correlating to the as-deposited libraries are shown in Figures 6.6-6.9. There is very little gradient in the vertical direction, which correlates well with the composition gradients shown in Figures 6.1-6.4. As a result of this electrical and compositional uniformity, the libraries were sectioned into three different rows, where row 0 was utilized for the Hall measurements and the air and argon annealing studies were performed on rows 1 and 2, respectively.

![Sheet resistance map of library 1. The contours indicate sheet resistance (\(\Omega/\text{sq}\)). The third row was masked during deposition.](image)

Figure 6.6 Sheet resistance map of library 1. The contours indicate sheet resistance (\(\Omega/\text{sq}\)). The third row was masked during deposition.
Figure 6.7 Sheet resistance map of library 2. The contours indicate sheet resistance ($\Omega$/sq). The third row was masked during deposition.

Figure 6.8 Sheet resistance map of library 3. The contours indicate sheet resistance ($\Omega$/sq). The third row was masked during deposition.
Figure 6.9 Sheet resistance map of library 4. The contours indicate sheet resistance (Ω/sq). The third row was masked during deposition.

Figure 6.10 Sheet resistance map of library 5. The contours indicate sheet resistance (Ω/sq). The third row was masked during deposition.
6.2.3 Optical Properties

The transmission spectra of the libraries following deposition and the 600°C air and 600°C argon anneals are found in section 5.3, “Functional and Structural Stability of Next Generation Indium Zinc Oxide TCOs”, by Taylor, et al. The primary change, which occurs upon annealing, is an increase in transmission and decrease in reflection, indicating a decrease in the free electron concentration (see section 2.3). Representative transmission and reflection spectra, illustrating this point, are shown in Figures 6.11 and 6.12. Figure 6.11 illustrates an increase in transmission with increasing annealing temperature, which correlates to a significant decrease in conductivity. The corresponding reflection spectra are shown in Figure 6.12, where the reflection decreases as the conductivity decreases. The loss of free electrons for the air annealed samples can be attributed to diffusion of oxygen into the film and the subsequent reduction of oxygen deficiencies. Additional discussion of these results is contained in section 5.3, “Functional and Structural Stability of Next Generation Indium Zinc Oxide TCOs”, by Taylor, et al.

The libraries that were annealed in Ar also showed a decrease in conductivity with annealing time and temperature, although this was not as severe as for the air annealed libraries (Figure 5.10). The reduction in conductivity for these libraries is assumed to be due primarily to a loss of free electrons as indicated by changes in the optical properties. The decrease in free electrons for these samples may be attributed to the structural changes occurring within the sample upon annealing. For example, the ZnO (002) shifts from 2θ ~ 32° to 34.4°, similar to pure ZnO, during the anneal. The shift may be associated with a reduction of strain, a diffusion of oxygen, zinc and indium atoms. All of these changes could result in the reduction of dangling bonds and free electrons. Figures 6.13 – 6.16 show optical reflection image maps for the air annealed and argon annealed libraries. These figures shows wavelength (nm) versus composition (% In). It is apparent that the reflection decreases with increasing
temperature, particularly following the 600°C anneal for all compositions and for both annealing environments.

Figure 6.11 Transmission spectra for IZO(4.1%In), normalized to the substrate, as a function of air annealing. An increase in transmission and decrease in conductivity occurs with increased annealing.

Figure 6.12 Reflection spectra for IZO(4.1%In), normalized to the substrate, as a function of air annealing. A decrease in reflection and decrease in conductivity occurs with increased annealing.
Comparison of the air and Ar annealed libraries reveals that, although the reflection decreases for both series, the reflection stays higher for the Ar annealed films. This is quite apparent for the 400° and 600°C anneals. For example, the decrease in R seen in library 1 around 10% In after the 400°C air anneal is much more dramatic than that seen for the argon annealed library. The difference between the air and argon annealed libraries is quite clear when comparing the library 2 data, Figure 6.14. The reflection data for library 2 following the 400°C air anneal at ~15,000nm is ~20% whereas it is ~70% for the Ar annealed film. This difference is also seen clearly in library 3, Figure 6.15. However, a sudden decrease in reflection is observed at ~71% In for both films following the 600°C anneal. This abrupt change corresponds to the crystallization of the amorphous film as discussed in section 5.3. This change in reflection due to a change in structure is also shown in library 4 (Figure 6.16) around 74% In for both annealing conditions. Following the 400°C air anneal, the abrupt transition in R occurs between ~78 and 82% In and then shifts to between ~70 and 74% In for the 600°C air anneal. This shift to lower indium content corresponds to the change in phase observed in this region upon annealing (see section 5.3).
Figure 6.13 Reflection image maps of library 1 for the as-deposited, 200°, 400° and 600°C air and Ar annealed conditions. All compositions for library 1 were crystalline (ZnO-type structure).
Figure 6.14 Reflection image maps of library 2 for the as-deposited, 200°, 400° and 600°C air and Ar annealed conditions. All compositions for library 2 were crystalline (ZnO-type structure).
Figure 6.15 Reflection image maps of library 3 for the as-deposited, 200°, 400° and 600°C air and Ar annealed conditions. All compositions for library 3 were amorphous up to 500°C. The abrupt transition in reflection occurring at 71 and 72% In following the 600°C anneal corresponds to an amorphous to crystalline (In₂O₃-type structure) transition.
Figure 6.16  Reflection image maps of library 4 for the as-deposited, 200°, 400° and 600°C air and Ar annealed conditions. The abrupt step in reflection shown in the air and argon annealed libraries corresponds to the transition from amorphous to crystalline (In$_2$O$_3$-type structure) material. The arrows indicate the amorphous region.
6.2.4 Structural Data

The XRD data presented in chapter 5 are of the IZO on glass with the spectrum of the amorphous glass substrate subtracted. The XRD spectrum for the Corning 1737 glass substrate is shown in Figure 6.17. Figure 6.18 shows the XRD spectrum for library 1, column 10 before and after the substrate is subtracted. The value of performing this step is apparent when attempting to identify peaks of low intensity such as the one at 2θ ~ 46°, indicated by the arrow. In the raw XRD spectrum, this peak is not clearly resolved, however, after subtracting the substrate, it is much more prominent.

Figure 6.17 XRD spectrum for the amorphous glass substrate. The inset shows the XRD raw detector image.
Figure 6.18 XRD spectrum for library 1, column 10 following the 600°C air anneal. The top spectrum is the raw XRD data and the bottom spectrum shows the XRD data with the substrate (Figure 6.17) subtracted.

The combinatorial, co-sputter deposition resulted in structural changes that were not solely due to the composition gradient as discussed in the paper, “The Electrical, Optical and Structural Properties of In\textsubscript{x}Zn\textsubscript{1-x}O\textsubscript{y} (0≤x≤1) Thin Films by Combinatorial Techniques” by Taylor, et al. (section 5.2). The x-ray diffraction raw detector images are shown in Figure 6.19 for library 1, columns 0, 3, 6 and 10. The localization in χ of the diffracted x-rays decreases from 4.1 to 17.7%In (column 0 to column 10) and may appear to be due to the change in composition (see sections 5.2.3 and 5.3.2 for additional discussion of χ). The XRD raw detector images for library 2, 13.2 and 17.8% In (columns 0 and 2) are shown in Figure 6.20. The images from library 2 show much more localization of the diffracted intensity, indicating a greater degree of texturing, than the corresponding compositions of library 1. The ZnO target
power was the same for library 1 and 2, however, the In$_2$O$_3$ power was 15W for library 1 and 60W for library 2. Therefore, the 17.7\% In film in library 1 (column 10) was located further from the high power target while that composition in library 2 (column 2) was much closer to the high power ZnO target (see Figure 4.1). While the change in indium content may play a role in the texturing of the film, it is apparent that the target-substrate distance is very significant.

Figure 6.19 XRD raw detector images for library 1, columns 0, 3, 6 and 10.
As discussed in section 5.3, the In-rich compounds recrystallized upon annealing at 200°C and this is shown in Figure 6.21 for library 4, column 10. Figure 6.22 shows the XRD raw detector images corresponding to the spectra shown in Figure 6.21. This figure shows that the texturing of the recrystallized In$_2$O$_3$ is nearly identical to the as-deposited material, which is slightly toward the In$_2$O$_3$ target. This suggests that the as-deposited material provided a template for the recrystallized grains and that the growth of the new phase was constrained by the texturing of the original phase.
Figure 6.21 XRD spectra for library 4, 92% In (column 10) for the as-deposited, 200°, 400° and 600°C Ar annealed conditions.

Figure 6.22 XRD raw detector images for library 4, 92% In (column 10) in the as-deposited, 200°, 400° and 600°C Ar annealed conditions.
6.2.5 Annealing Profiles

The IZO libraries annealed in air and argon were cooled down in the furnace until the internal temperature was 100°C. The annealing profiles (temperature versus time) for the air annealed IZO libraries are show in Figure 6.23. The annealing profiles for the Ar annealed libraries were nearly identical to those shown in Figure 6.23.

Figure 6.23 Annealing profiles for the air annealed IZO libraries.
6.2.6 Unidentified Crystalline Phase

An unidentified crystalline phase was observed after annealing the air-annealed IZO libraries at 500°C. The paper, "Functional and Structural Stability of Next Generation Indium Zinc Oxide TCOs", by Taylor et al. discusses this in detail. Figure 6.24 shows the XRD spectra for library 4, 74% In (column 4), after the 500° and 600°C air anneals with X=90° and X=55° spectrum. The powder diffraction files (PDF) for ZnO and In₂O₃ are overlaid on these spectra in the top and bottom panels respectively. Several possible matches can be made for both phases which include (100) and (101) for ZnO and (222), (431) and (440) for In₂O₃, however, there are several peaks that are not clearly indexed to either phase, as indicated by the asterisks. In the temperature range 1100° to 1200°C, a two-phase mixture of In₂O₃ and Zn₃In₂O₈ was found from ~27% to 100% In by Moriga, et al.⁴¹ However, none of the peaks from the Zn₃In₂O₈ PDF correlate with what is observed in Figure 6.24. In addition, PDFs from the homologous series ZnₖIn₂O₈₋₃ (k=2-5, 7, 17, 19) were examined and a positive match could not be made with any.

Figure 6.25 shows the raw detector images for 74% In following the 500° and 600°C air anneals. The localization of the diffracted intensity in χ for the 500°C annealed film shows that the film is (222) textured. However, the diffracted intensity is located slightly above the middle of the detector, which indicates that the texturing is not normal to the substrate but is in the direction of the In₂O₃ sputtering gun. Following the 600°C air anneal, the intensity of the (222) peak increases and many new peaks emerge. Two of the new peaks do correlate with (100) and (101) of ZnO as shown in Figure 6.24, however, the fact that the prominent peak at 2θ~67.8° and other weaker peaks do not clearly correlate with either crystal structure prevents positive identification of the new phase(s).
Figure 6.24 XRD spectra for library 4, 74% In (column 4) following the 500° and 600°C air anneals. The ZnO and In$_2$O$_3$ pdf’s are overlaid in the top and bottom panels, respectively. Peaks not assigned to either pdf are indicated with asterisks.

Figure 6.25 XRD raw detector images for library 4, 74% In (column 4) following the 500° and 600°C air anneals.
The region in which the ZnO and unidentified diffraction peaks appear is quite limited in composition. Figure 6.26 shows the X=90° x-ray diffraction spectra for library 4 in the composition range 69.9 to 81.8%In. The peaks which may be associated with a ZnO phase only appear between ~70 and 80%In and are indicated by arrows. The two peaks at ~55.5° and 67.5° that do not correlate to either phase are denoted with a question mark. The evolution and disappearance of those unassigned peaks correlates with those of the ZnO (100) and (101), which suggests they may be related to the same phase.

Figure 6.26 X-ray diffraction spectrum for library 4, columns 3 – 6, following the 600°C air anneal. The arrows indicate unidentified peaks that may be due to a ZnO phase.
6.3 Single Composition IZO

This section contains additional results from the experiments involving single composition IZO. The primary results of this work are found in the paper, “Amorphous In$_{0.70}$Zn$_{0.30}$O$_y$ Thin Films Sputtered at Room Temperature”, by Taylor, et al. (section 5.4). The data contained in this section relate to different amorphous IZO samples that were deposited from the same target but have very different functional properties, which are listed in Table 6.1.

Table 6.1 Three different amorphous IZO samples, the sputter gas environment and the resulting functional properties.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Sputter Gas Environment</th>
<th>Conductivity ($\Omega \cdot \text{cm})^1$</th>
<th>% Transmission @ 700nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>IZO(Ar)</td>
<td>Ar</td>
<td>2000</td>
<td>93</td>
</tr>
<tr>
<td>IZO(4%H$_2$)</td>
<td>Ar+4%H$_2$</td>
<td>1400</td>
<td>60</td>
</tr>
<tr>
<td>IZO(6%O$_2$)</td>
<td>Ar+6%O$_2$</td>
<td>0.01</td>
<td>93</td>
</tr>
</tbody>
</table>

6.3.1 Target Preparation, Analysis and Composition

The single composition IZO target was prepared from ZnO (99.999%, lot#B9717014, Puratrem) and In$_2$O$_3$ (99.999%, lot#B7204022, Puratrem) powders, see Appendix B for material safety data sheets. The mass ratio was 9.035g ZnO to 35.903g In$_2$O$_3$, which yielded 0.111 moles of ZnO to 0.129 moles of In$_2$O$_3$ and a metals ratio of 30%Zn:70%In. The calculated target composition can be written as In$_{0.70}$Zn$_{0.30}$O$_y$. The powders were mixed and ground together in a ceramic crucible and
pressed in a 2” die to 25,000psi for ~ 3 minutes. The target was then carefully removed, placed on a platinum foil covered alumina “boat” and sintered in air at 800°C for approximately 24 hours. The furnace was then turned off and the target cooled down inside the closed system. The target was then reground, pressed and sintered again and this procedure was performed three times. The target was found to be a two-phase mixture of ZnO and In₂O₃ as shown in Figure 6.27. The raw detector image is shown in the inset with χ on the y-axis and 2θ on the x-axis. The uniform, circular rings are a clear indication of the polycrystalline nature of the target, which contrasts to the raw detector images for the deposited films (Figure 6.19).

Figure 6.27 XRD spectrum for the In₀.₇₀Zn₀.₃₀Oₓ target. The inset shows the raw detector image.
6.3.2 Chemical Analysis: EPMA, TEM, AES

A small piece of the target was analyzed by EPMA in five different spots, resulting in an average atomic percent of 66.0%In to 34.0%Zn. The maximum and minimum indium content was 69.8% and 64.1%, respectively. The amorphous IZO films deposited from the single composition target showed extremely different properties when sputtered in Ar, Ar+4%H₂ and Ar+6%O₂ (Table 6.1). To further examine the difference between these films, the metals ratio was examined by EPMA, AES and TEM. Ten random spots on each sample were measured by EPMA while the AES survey was performed on a single spot after 60 seconds of sputter cleaning with Ar. The EPMA and AES analyses were performed on the same samples. Energy dispersive spectroscopy was performed on the TEM samples as well. However, these were not the same samples as analyzed by EPMA and AES. The results of the analysis are presented in Table 6.2. Slight variations exist in the cation content of the three samples measured by EPMA. The maximum and minimum average In contents of 64.58% and 60.35% were observed in IZO(Ar) and IZO(6%O₂), respectively. However, this difference should have only a very small effect on the conductivity as it has been shown that a broad peak in conductivity exists for as-deposited IZO between ~45-75% In (Figure 5.1). The effect of hydrogen in the sputter gas did not result in a significant difference in In content with the average being 61.53% as determined by EPMA. The AES results vary significantly from the EPMA. The In content varied from 71.3 to 75.2% for the same three samples, a difference of approximately +10 from the EPMA results. Analysis of the three TEM samples shows an indium content ranging from 55.74 to 60.77%, slightly lower than the EPMA results. The TEM analysis reveals a large chi squared value for the Zn measurement compared to the In measurement. This indicates a much larger degree of uncertainty in the Zn measurement. However the correlation with the EPMA results indicates this may not be significant.
Table 6.2 Chemical analysis of three amorphous IZO films. The EPMA and AES results were obtained from the same samples while the TEM results were obtained from the thin films deposited directly on the TEM grids.

<table>
<thead>
<tr>
<th>Sample</th>
<th>EPMA Results</th>
<th>AES Results</th>
<th>TEM Results</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%In</td>
<td>%Zn</td>
<td>%In</td>
</tr>
<tr>
<td>IZO(Ar)</td>
<td>Minimum 63.5490</td>
<td>33.7314</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Maximum 66.2686</td>
<td>36.4510</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Average 64.5801</td>
<td>35.4199</td>
<td>75.2</td>
</tr>
<tr>
<td></td>
<td>Sigma 0.7742</td>
<td>0.7742</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Chi Squared</td>
<td>4.27</td>
<td>329.55</td>
</tr>
<tr>
<td>IZO(4%H₂)</td>
<td>Minimum 60.8100</td>
<td>37.8147</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Maximum 62.1853</td>
<td>39.1900</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Average 61.5284</td>
<td>38.4716</td>
<td>71.3</td>
</tr>
<tr>
<td></td>
<td>Sigma 0.4553</td>
<td>0.4553</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Chi Squared</td>
<td>8.99</td>
<td>1454.16</td>
</tr>
<tr>
<td>IZO(6%O₂)</td>
<td>Minimum 58.9861</td>
<td>38.5858</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Maximum 61.4142</td>
<td>41.0139</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Average 60.3497</td>
<td>39.6503</td>
<td>72.6</td>
</tr>
<tr>
<td></td>
<td>Sigma 0.8272</td>
<td>0.8272</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Chi Squared</td>
<td>7.37</td>
<td>1746.00</td>
</tr>
</tbody>
</table>

Figure 6.28 shows the average percent indium for each sample along with the calculated and measured In content of the target. The results of this comparison reveal that significant variations can exist between different measurements. Reasons for this may include the application of bulk InP and Zn standards to quantify the metals content in these thin films and the possibility that signals from the substrate may overlap and interfere with those of In and Zn. The low In values for the samples measured in the TEM may be due to overlap between the Zn Kα (8.63keV) and Cu
$K_a$ (8.04keV) and $K_p$ (8.91keV) signals (the copper signal comes from the TEM grid), which result in an artificially high Zn count. The use of additional techniques such as inductively coupled plasma (ICP) spectroscopy and Rutherford backscattering spectroscopy (RBS) could be beneficial in correlating these measurements.

Figure 6.28 Average In content for the three different samples as measured by EPMA, AES and TEM. The calculated and measured target composition is also shown.
6.3.3 Method of 4 Coefficients

The output parameters of the method of 4 coefficients measurement on IZO(Ar) are listed in Table 6.3. The analysis returned a conduction band effective mass of 0.22, which was determined by measuring the Hall coefficient \( R_H \), Nernst coefficient \( Q \) and Seebeck coefficient \( \alpha \), as defined in section 4.8. The negative Hall coefficient indicates that electrons are the dominant charge carrier and the material is n-type. The mobility and carrier concentration were 35.9 cm\(^2\)/V·s and 30.8×10\(^{19}\)/cm\(^3\), respectively. This compares very well with the Bio-Rad Hall measurement, which returned values of 37.1 cm\(^2\)/V·s and 33×10\(^{19}\)/cm\(^3\). The negative Seebeck coefficient also confirms that the material is n-type and the value of –15.2 µV/K is close to that of crystalline cadmium stannate, molybdenum-doped In\(_2\)O\(_3\) (IMO) and ITO\([1,116]\). The Seebeck coefficient was described in section 4.8 (equation 4.19) and is also given as\([1,88,107]\)

\[
\alpha = \frac{2}{3} \frac{k_B T}{q h^2} \left( \frac{\pi}{3N} \right)^{2/3} m^* \left\{ s + \frac{3}{2} \right\},
\]

\textit{Equation 6.1}

where \( s \) is the scattering parameter, which can be determined from the four coefficients by\([1,88,107]\)

\[
s = \frac{3}{2} \left( \frac{Q}{R_H \sigma} \right) + \lambda.
\]

\textit{Equation 6.2}

The term \( \lambda \) describes the nonparabolicity of the conduction band and is given as

\[
\lambda = 3 \frac{N}{m^*_e} \frac{d m^*_e}{dN},
\]

\textit{Equation 6.3}
which can be obtained from the slope of the curve of the effective mass versus carrier concentration. This was assumed to be zero in this analysis, which resulted in a scattering parameter of 0.017. The scattering parameters for acoustic-phonon, optical-phonon, neutral impurity and ionized impurity scattering are $-1/2$, $1/2$, 0 and $3/2$, respectively. Therefore, a value of 0.017 ($\sim$0.0) may be due to neutral impurity scattering, however, a variety of scattering mechanisms could be occurring as was also observed in cadmium stannate.\textsuperscript{[96]} Figure 6.29 shows the results of the Nernst and Seebeck measurements. Multiple measurements were made at each $\Delta T$ and a large degree of uncertainty exists at each point. This uncertainty is due to the sensitivity of the voltmeter in measuring these extremely small voltages (nV) and could be a result of stray voltages which are developed in the sample wires when the magnet is on due to vibrations from the closed-cycle helium cryostat.\textsuperscript{[88]} Despite the uncertainty in the Nernst data, the effective mass is largely unaffected because $\alpha \gg \frac{Q}{R_n \sigma}$ (see equation 4.21). The scattering time and Fermi energy were calculated to be $4.6 \times 10^{-15}$ s and 0.747 eV, respectively. The Fermi energy agrees well with that (0.723 eV) calculated by the equation\textsuperscript{[21]}

$$E_F = \left( \frac{\hbar}{8m_e} \right) \left( \frac{3N}{\pi} \right)^{2/3}$$

\textit{Equation 6.4}

for a degenerate semiconductor at 0K, assuming an effective mass of 0.23.
Table 6.3 Output parameters of the method of 4 coefficients measurement on amorphous IZO(Ar).

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Parameter</th>
<th>Measured Value</th>
<th>Calculated Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_H$</td>
<td>Hall Coefficient (m^3/C)</td>
<td>-2.02x10^{-8} ± 6.2x10^{-10}</td>
<td></td>
</tr>
<tr>
<td>$\mu$</td>
<td>Mobility (cm^2/Vs)</td>
<td>35.9 ± 1.6</td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>Carrier Concentration (/cm^3)</td>
<td>30.8x10^{19} ± 0.95x10^{19}</td>
<td></td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Seebeck Coefficient (uV/K)</td>
<td>-15.2 ±0.5</td>
<td></td>
</tr>
<tr>
<td>s</td>
<td>Scattering Parameter</td>
<td>0.017 ± 0.009</td>
<td></td>
</tr>
<tr>
<td>Q</td>
<td>Nernst Coefficient (uV/KT)</td>
<td>6.0x10^{-4} ± 3.4x10^{-4}</td>
<td></td>
</tr>
<tr>
<td>$\tau$</td>
<td>Scattering Time (s)</td>
<td>4.6x10^{-15} ± 0.3x10^{-15}</td>
<td></td>
</tr>
<tr>
<td>$E_F$</td>
<td>Fermi Energy (eV)</td>
<td>0.747 ± 0.030</td>
<td></td>
</tr>
<tr>
<td>$m_e^*$</td>
<td>Effective Mass</td>
<td>0.229 ± 0.010</td>
<td></td>
</tr>
</tbody>
</table>

Figure 6.29 Nernst voltage versus temperature for the amorphous IZO method of 4 coefficients measurement showing a large degree of uncertainty. The data are horizontally offset for clarity. The inset shows the Seebeck voltage versus temperature along with the linear fit. The Nernst voltage is on the order of nanovolts while the Seebeck voltage is on the order of microvolts.
6.3.4 Auger Spectroscopy

Due to the significant variations in conductivity and optical transparency between the three amorphous IZO films, IZO(Ar), IZO(4%H₂) and IZO(6%O₂), (Table 6.1), Auger electron spectroscopy (AES) was employed to search for potential variations in the oxidation states of the In and Zn cations. Figures 6.30 and 6.31 show the differentiated AES spectra for IZO(Ar), IZO(6%O₂) and IZO(Ar), IZO(4%H₂), respectively. There is no discernible change in the oxidation states of the In, Zn or O atoms from this analysis and suggests the chemical states are the same. However, minor chemical variations may exist that were not observed due to the resolution of the instrument.

Figure 6.30 Differentiated intensity versus energy for IZO(Ar) and IZO(6%O₂).
Figure 6.31 Differentiated intensity versus energy for IZO(Ar) and IZO(4%H₂).

6.4 Optical Modeling

The equations utilized to model the optical data and obtain the electrical parameters (N, μ, m*), film thickness (t) and high frequency dielectric constant (ε∞) were discussed in section 2.3. The model is based on the reflection and transmission of light by a single film on an infinitely long, non-absorbing substrate. The model was applied to the transmission of the TCO/substrate stack normalized to the transmission of air. As shown in Figure 4.6 the transmission of the substrate decreases markedly at ~2,600nm (2.6 μm), due to absorption by the glass. Therefore, the model was only applied to the optical data between 500 and 2,600 nm, assuming no substrate absorption in this region and a constant index of refraction of 1.5. An index of 1.5 yields a reflection of 4% at the air/substrate interface (nair=1.0), therefore, the raw transmission data was multiplied by 1.04 to account for this loss. The corrected transmission data then represented that of the IZO on an infinitely long, non-absorbing
glass substrate. One drawback of this approach is the limited spectral region over which the model may be applied (≈500-2,600 nm). By modeling the reflection data, the range over which the model may be applied can be extended to 25,000 nm (25 μm). One problem encountered in doing this, however, was that for thin films (<300 nm), the measured reflection data did not correlate to what was predicted by the Drude model, which is illustrated in Figure 6.32 for amorphous IZO(70% In). In this figure the model accurately represents the transmission data in the range 450 – 2,500 nm. However, if the reflection data is modeled with those fit parameters, a large discrepancy exists between what is predicted (dashed line) and what was measured (solid line). Figure 6.33 is that of amorphous IZO(70% In) which is ≈ 2X thicker than the film in Figure 6.32 and shows that for the thicker film, the reflection data is accurately represented by the transmission data fit parameters. This discrepancy in the reflection data between the thin and thick films could be due to significant substrate reflection and absorption processes that are recorded in the reflection data of the thinner film. For example, the “bump” in the reflection data in Figure 6.32 at ≈9,000 nm clearly correlates with the peak in substrate reflection at that wavelength. In addition, the two local minimums in reflection occurring at ≈600 and 1,500 nm coincide with the maximum reflection of the substrate (≈8%). The reflection of the thicker film is also systematically higher in the visible region than anticipated by the model, however, the local minimum in R at ≈1,500 nm is much lower than the reflection of the substrate and the “bump” at 9,000 nm is not evident. This data suggest that the effect of the substrate is minimized in the reflection of the thicker film and indicates that film thickness is significant in accurately modeling the reflection data, whereas it is not so for transmission. The “good” reflection characteristics of the film in Figure 6.33 allow both the transmission and reflection to be modeled simultaneously. The results of this simultaneous fit are shown in Figure 6.34 and the results compare favorably to those when only the transmission data is fit. The fit range and output parameters for modeling the transmission and reflection spectrum
individually and then simultaneously are listed in Table 6.4, along with the standard deviation and chi square for each fit. The best fit is obtained from the transmission data and the value of chi square increases as the reflection data is modeled. The results of the Hall measurements on this sample are also shown in Table 6.4 for comparison. The Hall carrier concentration and mobility are most closely obtained from the optical model when fitting the reflection data, despite the larger chi square. The reflection fitting shows a systematically smaller thickness and larger high frequency permittivity. It should also be noted that this "thick" film shows a slightly larger carrier concentration (44.2x10^{19}/cm^3) and smaller mobility (28.8 cm^2/V·s) than that of the "thin" amorphous IZO film (N=33.0x10^{19}/cm^3, \mu=37.1 cm^2/V·s).

Figure 6.32  Transmission and reflection data for a "thin" amorphous IZO(70%In) film. The model was only applied to the transmission data. The arrow relates the "bump" in the reflection data to the reflection of the substrate.
Figure 6.33 Transmission and reflection data for a “thick” amorphous IZO(70%In) film. The model was only applied to the transmission data. The reflection of the substrate is shown as the thin line.

Figure 6.34 Results of modeling both the transmission and reflection data simultaneously. The effective mass was fixed at 0.23 for this fit and all other parameters were allowed to vary.
Table 6.4 Output parameters when fitting the transmission and reflection data individually and simultaneously for a “thick” amorphous IZO film. The effective mass was fixed to 0.23 for all fits.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>T Fit</th>
<th>R Fit</th>
<th>R Fit</th>
<th>T &amp; R Fit (simultaneous)</th>
<th>Hall Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fit range (nm)</td>
<td>550–2,666</td>
<td>550–25,050</td>
<td>550–2,666</td>
<td>550–2,6660, T</td>
<td>550–25,050, R</td>
</tr>
<tr>
<td>t (nm)</td>
<td>398 ± 0.76</td>
<td>375 ± 0.55</td>
<td>373 ± 0.48</td>
<td>383 ± 0.66</td>
<td>398</td>
</tr>
<tr>
<td>N (x10^{19}/cm^3)</td>
<td>31.7 ± 0.12</td>
<td>41.1 ± 0.11</td>
<td>42.0 ± 0.10</td>
<td>35.3 ± 0.09</td>
<td>44.2</td>
</tr>
<tr>
<td>μ (cm^2/V·s)</td>
<td>36.4 ± 0.13</td>
<td>31.2 ± 0.11</td>
<td>28.5 ± 0.11</td>
<td>40.0 ± 0.08</td>
<td>28.8</td>
</tr>
<tr>
<td>ε_∞</td>
<td>4.15 ± 0.01</td>
<td>4.92 ± 0.01</td>
<td>4.99 ± 0.01</td>
<td>4.40 ± 0.01</td>
<td></td>
</tr>
<tr>
<td>m^*</td>
<td>0.23</td>
<td>0.23</td>
<td>0.23</td>
<td>0.23</td>
<td></td>
</tr>
<tr>
<td>Chi Square</td>
<td>3,821</td>
<td>7,835</td>
<td>3,529</td>
<td>20,317</td>
<td></td>
</tr>
<tr>
<td>σ (Ω·cm)^{-1}</td>
<td>1,848</td>
<td>2,054</td>
<td>1,917</td>
<td>2,262</td>
<td>2,039</td>
</tr>
</tbody>
</table>

One limitation in applying the model over such a limited spectral range (~500 – 2,600nm) can be seen when characterizing films of low carrier concentration. In the case where N is less than ~10^{19}/cm^3, the plasma wavelength is greater than 2,600nm and the model cannot extract the electrical information from the data. This point is illustrated in Figure 6.35, where the model is applied to the transmission of a film with N=4x10^{16}/cm^3, as determined by Hall measurement. The thickness, high frequency permittivity, effective mass and mobility have been fixed but N is varied from 4x10^{16} to 4x10^{18}/cm^3. All three fits appear to work over the range 450 to 2,200nm, however, it is only at much longer wavelengths that the fits diverge from each other. Therefore, the model could return a result ranging anywhere from N=10^{16} to 10^{18}/cm^3 and it would appear correct when modeling from 450 to 2,200nm.
Figure 6.35 The optical model applied to a film with \(N=4\times10^{16}/\text{cm}^3\) from 250 to 100,000nm (0.250 to 100\(\mu\text{m}\)). The parameters \(t\), \(\varepsilon_r\), \(m^*\), and \(\mu\) were fixed while \(N\) was varied from \(4\times10^{16}\) to \(4\times10^{18}/\text{cm}^3\).

Despite the limitation of only being able to model the transmission data to \(\sim2,600\text{nm}\), quantitative comparisons between different data can be made to \(\sim5,000\text{nm}\), the transmission limit of the substrate. This is possible by normalizing the transmission of the IZO/glass stack to the transmission of the glass as shown in Figure 6.36. An optical model that could account for this normalization would be beneficial in fitting portions of the spectrum that have be previously neglected.
Figure 6.36 Transmission of an amorphous IZO film on glass normalized to the transmission of the glass and the transmission of air.

6.5 Undoped ZnO and In$_2$O$_3$

Films of undoped ZnO and In$_2$O$_3$ were deposited in the combinatorial deposition system with the sputtering geometry illustrated in Figure 4.3. A sheet resistance map for the undoped ZnO film is shown in Figure 6.37. The ZnO target power was 75W, the time was 6 minutes, the pressure was 4.5mTorr and the substrate temperature was 100°C for this deposition, which was identical to that used in the deposition of library 2. The sheet resistance varies by 3 orders of magnitude across this sample and the conductivity and thickness profiles for row 1 are shown in Figure 6.38. A maximum conductivity of 27 (Ω·cm)$^{-1}$ was obtained at column 0 and it dropped to ~0.2 (Ω·cm)$^{-1}$ for columns 6 to 10. The film thickness varied linearly across this sample from ~190 to 70nm and the calculated deposition rate was ~31.6nm/min at column 0 and 11.6nm/min at column 10, which is to be expected due
to the geometry of the deposition system. The resulting normalized deposition rate at column 0 was 0.42nm/min·Watt for the ZnO target.

![Sheet resistance map (Ω/sq) of an undoped ZnO film. Row 3 was masked during this deposition.](image)

Figure 6.37  Sheet resistance map (Ω/sq) of an undoped ZnO film. Row 3 was masked during this deposition.

![Conductivity and thickness profiles across row 1 of the undoped ZnO film.](image)

Figure 6.38  Conductivity and thickness profiles across row 1 of the undoped ZnO film.
The corresponding sheet resistance map, conductivity and thickness profiles for the undoped In$_2$O$_3$ film are shown in Figures 6.39 and 6.40, respectively. The target power was 60W, the time was 6 minutes, the pressure was 4.5mTorr and the substrate temperature was 100°C for this deposition, which was identical to that used in the deposition of library 2. The sheet resistance is much more uniform for the In$_2$O$_3$ film and the conductivity varies across row 1 from $\sim$4,600 to 260 (\(\Omega\cdot\text{cm}\))$^{-1}$ for columns 0 and 10, respectively. The thickness also varies linearly and ranges from $\sim$26 to 160nm for columns 0 and 10, respectively. The film was sufficiently thin between columns 0 and 3 that optical modeling of the thickness was not possible and it was determined by linear extrapolation. The deposition rate varied from $\sim$4.3 to 27nm/min for columns 0 and 10, respectively and the normalized deposition rate at column 10 was $\sim$0.45nm/min·Watt, which is close to the ZnO normalized deposition rate ($\sim$0.42nm/min·Watt).

![Figure 6.39 Sheet resistance (\(\Omega\)/sq) map for an undoped In$_2$O$_3$ film.](image-url)
The two samples show very different trends in conductivity with deposition rate. The conductivity of the ZnO film increases significantly with deposition rate while that of the In$_2$O$_3$ films decreases as the deposition rate increases as illustrated in Figure 6.41. In both cases, the conductivity is highest at column 0 and then decreases by varying amounts. The doping mechanisms for ZnO and In$_2$O$_3$ were discussed in section 2.2 and if oxygen deficiencies are the primary electron generating source (equation 2.6) in these undoped films, the data suggest a higher oxygen partial pressure on the In$_2$O$_3$ side of the chamber (see Figures 4.1 and 4.3). This is also the same side as the argon and oxygen gas sources and even though oxygen was not used during deposition of these films, a small leak may account for the lower conductivity on that side of the film.
Figure 6.41 Conductivity as a function of deposition rate for undoped In$_2$O$_3$ and ZnO. The data points corresponding to columns 0 and 10 (C0 and C10, respectively) are also indicated.

As stated previously, the deposition conditions for the undoped ZnO and In$_2$O$_3$ films were identical to those used for library 2 of the combinatorial samples, which suggests that the film thickness of library 2 should equal the sum of the individual components. However, the optically determined thickness of library 2 was greater than the sum of the thicknesses of the individual ZnO and In$_2$O$_3$ depositions as shown in Figure 6.42. The use of profilometry (Dektak) verified the results of the optical model, which confirms that the deposition rate did increase when both targets were operated simultaneously. The linear deposition rate, $\frac{dh}{dt}$ (cm/s), is given as$^{92}$

$$\frac{dh}{dt} = \frac{J \cdot M}{\rho \cdot N_A}$$

Equation 6.5
where \( J \) is the molecular deposition flux (molecules/cm\(^2\)-sec), \( M \) is the molecular weight (g/mol), \( \rho \) is the film density (g/cm\(^3\)) and \( N_A \) is Avagadro's number. The ratio of \( \frac{M}{\rho} \) is the molar volume (cm\(^3\)/mol) and these values are presented in Table 6.5. The molecular impingement flux for library 2, column 5 (11.28x10\(^{16}\)mc/cm\(^2\)-s) was assumed to be equal to the sum of the ZnO (8.84x10\(^{16}\)mc/cm\(^2\)-s) and In\(_2\)O\(_3\) (2.44x10\(^{16}\)mc/cm\(^2\)-s) fluxes at that point. The molar volume for library 2, column 5 was calculated to be 24.32cm\(^3\)/mol, which is between that of ZnO (14.53 cm\(^3\)/mol) and In\(_2\)O\(_3\) (38.67 cm\(^3\)/mol). Therefore, an increase in the molar volume in this composition range due to incorporation of In in the ZnO structure could result in a deposition rate \((dh/dt)\) greater than anticipated. The library 2 compositions (~15-50%In) were shown to have the ZnO-type crystal structure (see section 5.2.3, Figure 5.3) with a significant increase in the (002) spacing from pure ZnO (Figure 5.4). For library 2, column 5, \( d_{002} \) is approximately 2.79 Å whereas it is 2.60 Å for ZnO, which correlates to an increase in the unit cell volume. The incorporation of indium \((M=114.82\ \text{g/mol})\) into the unit cell could simultaneously increase the molecular
weight of the IZO compounds in this composition range, resulting in a increase in the molar volume and an increase in the deposition rate, $\frac{dh}{dt}$.

Table 6.5 The measured deposition rate and calculated molecular impingement flux for column 5 of undoped ZnO, In$_2$O$_3$ and library 2. The density, molecular weight and calculated molar volume are also listed.

<table>
<thead>
<tr>
<th>Sample</th>
<th>ZnO</th>
<th>Library 2</th>
<th>In$_2$O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{dh}{dt}$ (cm/min)</td>
<td>2.13x10$^{-6}$</td>
<td>4.63x10$^{-6}$</td>
<td>1.56x10$^{-6}$</td>
</tr>
<tr>
<td>$J_r$ (mc/cm$^2$·min)</td>
<td>8.84x10$^{16}$</td>
<td>11.28x10$^{16}$</td>
<td>2.44x10$^{16}$</td>
</tr>
<tr>
<td>$M$ (g/mol)</td>
<td>81.37</td>
<td>277.64</td>
<td></td>
</tr>
<tr>
<td>$\rho$ (g/cm$^3$)</td>
<td>5.60</td>
<td>7.18</td>
<td></td>
</tr>
<tr>
<td>$\frac{M}{\rho}$ (cm$^3$/mol)</td>
<td>14.53</td>
<td>24.71</td>
<td>38.67</td>
</tr>
</tbody>
</table>

Figure 6.43 depicts the x-ray diffraction spectra of the ZnO and In$_2$O$_3$ films. The ZnO film (top panel) shows a shift in the (002) to lower 2θ and a decrease in intensity from column 0 to 10. The inset shows the raw detector images for columns 0 and 10 and indicates that although the intensity decreases significantly, it still appears to be somewhat (002) textured. The corresponding XRD spectra for the In$_2$O$_3$ sample are shown in the bottom panel of Figure 6.43. The In$_2$O$_3$ film appears to be somewhat (222) textured and the intensity decreases dramatically at column 0 where the film is only ~25nm thick.
Figure 6.43 XRD spectra for the undoped ZnO (top panel) and In$_2$O$_3$ (bottom panel) films showing columns 0, 5 and 10. The insets show the raw detector images for columns 0 and 10.
The XRD spectrum for column 10 shows an unexpected peak at 2θ ~29.8°. This corresponds to the primary peak observed in the as-deposited In-rich libraries as shown in Figure 6.44, which also includes the XRD spectrum for IZO(92%In) following the 200° argon anneal.

![XRD spectra](image)

**Figure 6.44** XRD spectra for undoped In$_2$O$_3$, as-deposited IZO(92%In) and 200°C Ar annealed IZO(92%In).

The displacement of the (222) peak to lower 2θ in IZO(92%In) was thought to be a result of lattice strain due to the Zn content, however, it is apparent that this phase also occurs in undoped In$_2$O$_3$. It also appears that the XRD spectrum for the undoped In$_2$O$_3$ can be resolved into the two peaks shown in the spectrum for IZO(92%In) following the 200°C anneal. Figure 6.45 shows the XRD spectra for IZO(92%In), X=55° with the In$_2$O$_3$ pdf overlaid for the unstrained cubic material where the lattice parameter (a) equals 10.117 Å and for a=10.347Å. The case of a=10.347Å represents a uniformly strained cubic lattice and results in the (222) and (211) aligning well with the
diffraction peaks at 29.8° and 21.0°, respectively. However, the (400), (440) and (622) clearly do not align with the experimental results. This indicates that this is not uniformly strained, cubic indium oxide, but is another crystal structure. Reports of indium oxide in structures other than the cubic bixbyite and the high pressure rhombohedral phase have not been found in the literature and presently, the crystal structure of this indium oxide phase is unidentified.

Figure 6.45 XRD spectrum for IZO(92%In) with the pdf for pure, unstrained In$_2$O$_3$ (a=10.117Å) and strained In$_2$O$_3$ (a=10.347Å).
6.6 Plasma Wavelength Characterization

The technique utilized to determine the plasma wavelength for the combinatorial libraries ($\lambda_{p,\text{combi}}$) relied on identifying the minimum in reflection just prior to the increase at long wavelengths. Although this technique is useful in identifying major trends across composition space (see Figure 5.5), it underestimates the true plasma wavelength ($\lambda_p$), which is defined as that wavelength where the real component of the dielectric constant equals zero (see section 2.3, equation 2.43) and the free electron absorption is at a maximum. Figure 6.46 shows typical reflection, transmission and absorption spectra for an amorphous IZO film (70%In) with $\lambda_{p,\text{combi}}$ and $\lambda_p$ overlaid as the solid circles. The different analyses define the plasma wavelength at 1.424 and 1.710nm for $\lambda_{p,\text{combi}}$ and $\lambda_p$, respectively. This results in carrier concentrations (equation 2.18, assuming $m^*_e=0.23$ and $\varepsilon_\infty=4$) of $5.06 \times 10^{20}$/cm$^3$ and $3.51 \times 10^{20}$/cm$^3$ for $\lambda_{p,\text{combi}}$ and $\lambda_p$, respectively. The carrier concentration determined by Hall measurement was $4.42 \times 10^{20}$/cm$^3$ (Table 6.4) for this sample. The Hall carrier concentration ($4.42 \times 10^{20}$/cm$^3$) and $\lambda_p$ carrier concentration ($3.51 \times 10^{20}$/cm$^3$) can be correlated, assuming $\varepsilon_\infty=5.03$ instead of 4 and then $N_{\text{Hall}}=N_{\lambda_p}$. Recalculating $N$ from $\lambda_{p,\text{combi}}$, using this assumption, returns a carrier concentration of $6.37 \times 10^{20}$/cm$^3$, an increase of 44% from $N_{\lambda_p}$. Future work will evaluate how variations in mobility and carrier concentration affect the correlation of $N$ when calculated by the two techniques.
Figure 6.46 Transmission, reflection and absorption spectra for amorphous IZO(70%In) showing the plasma wavelength determined by the combinatorial technique ($\lambda_{p, \text{combi}}$) and by the peak in the absorption ($\lambda_p$) as the open circles.
CHAPTER 7
CONCLUSIONS
AND RECOMMENDATIONS

7.1 Introduction

This chapter summarizes the work of this thesis. The chapter is divided into three sections, which summarize the individual components of this thesis: the combinatorial study, annealing study and single composition study. The chapter closes with recommendations for future work.

7.2 Combinatorial Study

This work focused on the electrical, optical and structural properties of the ZnO-In$_2$O$_3$ system. By co-sputtering and controlling the power to each target, compositionally-graded libraries ranging from 4 to 95 atomic % In for Zn were created in only four depositions. High throughput, combinatorial techniques were utilized to characterize the composition, structure, electrical and optical properties of these thin films. Indium contents < ~45% yielded a crystalline phase with a lattice constant close to that of ZnO (002). An amorphous region was observed for indium contents from ~45% to ~80%. As the indium content increased above ~82%, a crystalline phase was seen with a diffraction pattern corresponding to In$_2$O$_3$. The highest mobility (>30cm$^2$/V·s) and carrier concentration (>8x10$^{20}$/cm$^3$) were found in the amorphous region. The peak conductivity of ~3,000(Ω·cm)$^{-1}$ was observed at ~67% In from the Hall measurement and at ~75% In from the combinatorial analysis. All films showed high optical transmission (>80%) in the visible spectrum.
7.3 Annealing Study

The compositionally-graded libraries were annealed in both flowing air and argon at 1 hour intervals from 100° to 600°C. Following each anneal, the electrical, optical and structural properties of the libraries were analyzed with the high-throughput, combinatorial tools. The conductivity of all libraries decreased monotonically with annealing time and temperature regardless of the environment. However, the air annealed libraries showed a much more dramatic decrease in conductivity than the Ar annealed ones. Following the 600°C anneal, the maximum conductivity was \(~200(\Omega \cdot \text{cm})^{-1}\) at 66% In and \(~1,350(\Omega \cdot \text{cm})^{-1}\) at 64.4% In for the air and argon annealed libraries, respectively. Both series of libraries showed similar structural changes upon annealing. A shift in the ZnO (002) back to the unstrained position of 34.4° occurred at 400°C, while the In-rich films began to recrystallize in the In$_2$O$_3$ structure at 200°C. An unidentified crystalline phase was observed in the composition range 70-80% In between 500° and 600°C. While some peaks could be attributed to (222) of In$_2$O$_3$ and (100) and (101) of ZnO, there were several others that could not. Amorphous IZO was very resistant to crystallization and this only occurred following the 600°C anneals in a limited composition range of \(~69-71\% \) In. Amorphous In$_{0.70}$Zn$_{0.30}$O$_2$ was also the smoothest of any film deposited with an rms roughness of \(~0.4\)nm, which was an order of magnitude lower than the crystalline compositions. The index of refraction was also quite uniform and was found to vary from \(~1.9\) to 2.2 for the as-deposited films. All of the films showed high optical transmission and it was found to increase at long wavelengths as the films were annealed. This correlated with the decrease in conductivity and confirmed that the number of free carriers decreased with annealing.

7.4 Single Composition IZO

The combinatorial work allowed the “best” IZO composition to be identified, 70%In:30%Zn (In$_{0.70}$Zn$_{0.30}$O$_2$). A sputtering target of this composition was produced
and IZO films were deposited by dc magnetron sputtering in Ar, Ar+O\textsubscript{2} and Ar+H\textsubscript{2}. The maximum conductivity for any gas mixture or target power was \(\sim 2000 (\Omega \cdot \text{cm})^{-1}\) and was obtained when depositing in Ar. The carrier concentration decreased dramatically as oxygen was introduced into the chamber. The mobility, however, remained largely unaffected by this. The decrease in carriers due to the incorporation of oxygen during deposition was found to be strongly dependent on the target power or deposition rate. The introduction of H\textsubscript{2} did little toward increasing the carrier concentration, but 4\% H\textsubscript{2} did significantly degrade the optical transmission. Structural analysis did not reveal any significant difference between IZO(4\%H\textsubscript{2}) and IZO(Ar) or IZO(6\%O\textsubscript{2}). The band gap was found to be lower than either ZnO (3.5eV) or In\textsubscript{2}O\textsubscript{3} (3.75eV) and the films were very smooth.

### 7.5 Recommendations for Future Work

There are several areas in which additional work would be beneficial. The design of a co-sputtering chamber in which the targets were nearly normal to the substrate would be helpful in reducing the impact of target-substrate distance and location on texturing and the electrical properties. To accommodate this, 1” diameter targets could be used instead of the 2” ones used in this work, which would allow the targets to be closer together, reducing the angle of incidence. Alternative deposition techniques could also be used such as ion beam assisted deposition (IBAD) and PLD. For example, Lee, et al. reported a conductivity of almost 5,000(\Omega \cdot \text{cm})^{-1} when sputtering IZO(84\%) with IBAD at room temperature.\[^{72}\]

The addition of another metal oxide during deposition could probe TCO composition space even further (Figure 1.4). For example, a material such as SnO\textsubscript{2}, Ga\textsubscript{2}O\textsubscript{3} or Al could easily be deposited along with the single composition In\textsubscript{0.70}Zn\textsubscript{0.30}O\textsubscript{y} target. The third component could also be placed such that this gradient would be in the vertical direction. The chemical and electrical properties were found to be quite
uniform in the vertical direction when sputtering from two targets. Therefore, this would be the ideal dimension in which to add an additional component. The reasons for adding these elements is that they share a similar valence (+3 for Al and Ga, +4 for Sn) to In and the ionic radii (0.62Å and 0.71Å for Ga and Sn, respectively)\textsuperscript{251} are close to that of In (0.81Å). Therefore, these elements may readily replace indium in the amorphous structure without detrimentally affecting the conductivity. This could have a significant impact on reducing the cost of high quality, amorphous TCO films.

In addition to other materials, the temperature parameter could be examined by introducing a temperature gradient across the film. This would allow composition space and temperature space to be explored in a single deposition. As shown in section 3.2, the presence of certain phases shows a strong dependence on temperature.

X-ray photoelectron spectroscopy (XPS) could also be employed to examine the chemical states of three amorphous IZO films, IZO(Ar), IZO(6%O\textsubscript{2}) and IZO(4%H\textsubscript{2}). This technique differs slightly from AES and it is possible that if chemical differences do exist between the three samples, they could be detected by this technique. This could help explain the differences in conductivity and transmission that were observed between the three samples.
CHAPTER 8
REFERENCES


APPENDIX A

Appendix A contains additional results pertaining to the use of electron probe micro-analysis (EPMA) for quantitative chemical analysis of thin films. The indium content (atomic %In for Zn) for all libraries and single composition films studied in this thesis was determined using an accelerating potential of 20kV (section 4.3) and a wavelength dispersive spectrometer. However, a significant disparity in the measured In content exists when a potential of 10kV is used. This difference is illustrated in Figure A1, which shows the %In measured at 10kV versus %In measured at 20kV. The positive deviation from the 1:1 relationship indicates that a higher indium content is measured at 10kV than at 20kV. These data correspond to the series of libraries that were annealed in argon. These libraries are considered “thin” as the film thickness varies from ~90-300nm as indicated by the color scale. The %In reported from the 10kV measurement is approximately +15.3% at 63.7% (20kV), which is a very significant difference. Figure A2 shows the relationship between 10kV and 20kV measurements for “thick” IZO libraries, which vary from ~250-1,070nm. The deposition conditions for the thick libraries were identical to the thin ones, except for an increase in deposition time from 6 minutes (thin libraries) to 12-18 minutes. Figure A2 shows that the agreement between the 10kV and 20kV data is much better for the thick libraries.
Figure A1  Percent In measured at 10kV versus the %In measured at 20kV for “thin” IZO libraries.

Figure A2  Percent In measured at 10kV versus the %In measured at 20kV for “thick” IZO libraries.
Figure A3 shows the difference in the measured %In between 10 and 20kV versus the %In measured at 20kV, where the thin and thick libraries are indicated by circles and squares, respectively. The thickness dependence on Δ%In is clearly seen in Figure A3 where the greatest difference in the measured indium content occurs for film thicknesses below ~350nm. However, a compositional dependence is also observed, as the Δ%In is not uniform for identical thicknesses. The Δ%In for the thin libraries at ~5%In is much less than at 40%In, where the film thicknesses are approximately the same (~250-300nm).

![Graph showing difference in %In measured at 10kV and 20kV versus %In measured at 20kV for thin and thick libraries.]

Figure A3  The difference in %In measured at 10kV and 20kV versus the %In measured at 20kV for the thin (circles) and thick (squares) libraries.

The measured composition of the thin and thick libraries at 10 and 20kV is shown in Figures A4 and A5, respectively. The ZnO and In₂O₃ target powers were identical for the corresponding libraries and it is assumed that the compositions are the
same. However, the measured composition between the two series of libraries varies and better agreement is observed for the 10kV measurement.

Figure A4 %In measured at 10kV for the four thin and thick libraries.

Figure A5 %In measured at 20kV for the four thin and thick libraries.
The difference in these measurements may be explained by examining the penetration depth of the electrons in the films. The penetration depth of electrons \( D_e \) in a solid can be described as \( D_e = K \frac{E_o^{\gamma}}{\rho} \), where \( K \) is a material independent constant, \( E_o \) is the electron energy in keV, \( \gamma \) varies from 1.2 to 1.7 and \( \rho \) is the target density (g/cm\(^3\)), assuming an elemental target.\(^{[117,118]}\) The penetration depth and distribution of elastically scattered electrons are also related to \( Z^2 \) (atomic number) and \( \cos(\theta) \), the angle of incidence. The calculated penetration depth of electrons in ZZO is shown in Figure A6 assuming \( K=0.064 \), \( \gamma=1.68 \), a density of 6.39g/cm\(^3\) \((\rho_{ZnO}=5.60g/cm^3, \rho_{In_2O_3}=7.18g/cm^3)\) and normal incidence. The penetration depth for 20keV electrons is \(~1.54\mu m\) whereas it is only \(~0.48\mu m\) for 10keV electrons. In the case of 20keV electrons, \( D_e \) is much greater than the film thickness \( (t) \) of the thin libraries, whereas it is much closer to \( t \) for 10keV electrons. This results in the vast majority of the interaction volume at 20keV being located in the substrate whereas at 10keV, a much greater portion of it is located within the film. Therefore, the difference in the 10 and 20kV measurements may be due to the data analysis (background subtraction and x-ray peak integration). For the thick libraries, \( D_e \) is approximately equal to \( t \) for most of the films at 20keV and is less than \( t \) for most of the films at 10keV. Except for a few films (~75-85%In, Figure A2) the interaction volume is almost entirely contained within the film at both electron energies and a strong correlation between the two measurements is observed.
Future work will involve measuring the In:Zn ratio of both the thin and thick libraries using an accelerating potential of ~5kV. This may reduce the interaction volume to a point where it is entirely contained within the film (see Figure A6) and the substrate effects may be eliminated. Finally, it may be concluded that caution must be exercised when applying EPMA, a bulk analysis tool, to thin films. The use of additional quantitative chemical analysis tools such as Rutherford backscattering and inductively coupled plasma spectroscopy may also be required to verify the results produced by EPMA.
APPENDIX B

MATERIAL SAFETY DATA SHEET

Manufacturer: Strem Chemicals, Inc.
7 Mulliken Way
Newburyport, MA 01950-4098

STREM CUSTOMER SERVICE: (978) 442-3191
CHEMTREC (EMERGENCY ONLY): (800) 424-6300
POISON CENTER: (800) 502-8236

SECTION 1  Product Identification

CHEMICAL NAME: Zinc oxide (99.999%-Zn) PURATREM
PRODUCT NUMBER: 93-3016
CAS REGISTRY NUMBER: 1314-13-2
FORMULA: ZnO
EINECS NUMBER: 215-222-5
CHEMICAL FAMILY: metal oxide
SYNONYM: zinc monoxide

SECTION 2  Composition and Information on Ingredients

<table>
<thead>
<tr>
<th>INGREDIENT</th>
<th>CAS#</th>
<th>%</th>
<th>ACGIH (TWA)</th>
<th>OSHA (PEL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Title Compound</td>
<td>1314-13-2</td>
<td>100</td>
<td>10mg/m³ (as dust)</td>
<td>15mg/m³ (as total dust)</td>
</tr>
</tbody>
</table>

SECTION 3  Hazards Identification

EMERGENCY OVERVIEW: Irritating to skin, eyes and respiratory tract. Inhalation of high levels may produce symptoms known as metal fume fever or zinc shakes.

PRIMARY ROUTES OF EXPOSURE: Ingestion, Inhalation of dust.

EYE CONTACT: Causes slight to mild irritation of the eyes.

SKIN CONTACT: Causes slight to mild irritation of the skin.

INHALATION: Irritating to the nose, mucous membranes and respiratory tract. Inhalation may produce symptoms known as metal fume fever and zinc shakes.

INGESTION: Zinc salts have a harsh metallic taste.

ACUTE HEALTH EFFECTS: Irritating to skin, eyes and respiratory tract. Inhalation of dust may cause chills, muscle aches, nausea, fever, dry throat, cough, headache, blurred vision, vomiting and decreased pulmonary function.

CHRONIC HEALTH EFFECTS: Prolonged or repeated exposure may cause breathing difficulty and decreased pulmonary function.

NTP: No  IARC: No  OSHA: No

SECTION 4  First Aid Measures

EYE EXPOSURE: Immediately flush the eyes with copious amounts of water for at least 10-15 minutes. A victim may need assistance in keeping their eyes open. Get immediate medical attention.

SKIN EXPOSURE: Wash the affected area with water. Remove contaminated clothes if necessary. Seek medical assistance if irritation persists.

INHALATION: Remove the victim to fresh air. Closely monitor the victim for signs of respiratory problems, such as difficulty in breathing, coughing, wheezing, or pain. In such cases seek immediate medical assistance.

INGESTION: Seek medical attention immediately. Keep the victim calm. Give the victim water (only if conscious). Induce vomiting only if directed by medical personnel.
SECTION 5 Fire Fighting Measures

FLASH POINT: not applicable
AUTOIGNITION TEMPERATURE: none
EXPLOSION LIMITS: none
EXTINGUISHING MEDIUM: None. Material is non-flammable.
SPECIAL FIRE FIGHTING PROCEDURES: If involved in a fire, fire fighters should be equipped with a NIOSH approved positive pressure self-contained breathing apparatus and full protective clothing.
HAZARDOUS COMBUSTION AND DECOMPOSITION PRODUCTS: No hazardous combustion or decomposition products.
UNUSUAL FIRE OR EXPLOSION HAZARDS: No unusual fire or explosion hazards.

SECTION 6 Accidental Release Measures

SPILL AND LEAK PROCEDURES: Small spills can be mixed with vermiculite or sodium carbonate and swept up.

SECTION 7 Handling and Storage

HANDLING AND STORAGE: Store in a tightly sealed container.

SECTION 8 Exposure Controls and Personal Protection

EYE PROTECTION: Always wear approved safety glasses when handling a chemical substance in the laboratory.
SKIN PROTECTION: Wear appropriate chemical resistant gloves and protective clothing.
VENTILATION: Material may form a fine dust. If possible, handle the material in an efficient fume hood.
RESPIRATOR: If ventilation is not available a respirator should be worn. The use of respirators requires a Respirator Protection Program to be in compliance with 29 CFR 1910.134.
ADDITIONAL PROTECTION: No additional protection required.

SECTION 9 Physical and Chemical Properties

COLOR AND FORM: white pwdr.
MOLECULAR WEIGHT: 81.37
MELTING POINT (°C): none
BOILING POINT (°C): no data
VAPOR PRESSURE: not applicable
SPECIFIC GRAVITY: 5.606
ODOR: none
SOLUBILITY IN WATER: insoluble

SECTION 10 Stability and Reactivity

STABILITY: air and moisture stable solid
HAZARDOUS POLYMERIZATION: no hazardous polymerization
CONDITIONS TO AVOID: none
INCOMPATIBILITY: Strong mineral acids and bases.
DECOMPOSITION PRODUCTS: none
SECTION 11  Toxicological Information

RTECS DATA: Administration onto the skin (rabbit); Standard Draize test: 500 mg/24H. Oral (human) LDLo: 500 mg/kg. Inhalation (human); TCLo: 600 mg/m3. Oral (rat); LD: >8437 mg/kg. Intraperitoneal (rat); LD50: 240 mg/kg. Oral (mouse); LD50: 7950 mg/kg. Inhalation (mouse); LC50: 2500 mg/m3. Oral (rat); TDL0: 17431 mg/kg/90D-C. Inhalation (guinea pig); TCLo: 5900 ug/m3/3H/3D-I. Inhalation (guinea pig); TCLo: 4600 ug/m3/3H/BD-I. Oral (chicken); TDL0: 32203 mg/kg/WC-C. Oral (mammal-domestic); TDL0: 3584 mg/kg/4W-I. Oral (rat); TDL0: 6846 mg/kg. Inhalation (rat); Cytogenetic analysis: 100 ug/ml. Hamster embryo: Morphological Transformation: 1 mg/L.

CARCINOGENIC EFFECTS: No data available
MUTAGENIC EFFECTS: Inconclusive data
TETRATOCENIC EFFECTS: Insufficient data

SECTION 12  Ecological Information

ECOLOGICAL INFORMATION: Very toxic to aquatic organisms.

SECTION 13  Disposal Considerations

DISPOSAL: Dispose of according to local, state and federal regulations.

SECTION 14  Transportation Information

SHIPPING NAME (CFR): Non-hazardous
HAZARD CLASS (CFR): NA
ADDITIONAL HAZARD CLASS (CFR): NA
PACKING GROUP (CFR): NA
UN ID NUMBER (CFR): NA
SHIPPING NAME (IATA): Non-hazardous
HAZARD CLASS (IATA): NA
ADDITIONAL HAZARD CLASS (IATA): NA
PACKING GROUP (IATA): NA
UN ID NUMBER (IATA): NA

SECTION 15  Regulatory Information

TSCA: Listed in the TSCA inventory
SARA (TITLE 313): Title compound: See Category Code N982 for reporting.
SECOND INGREDIENT: none
THIRD INGREDIENT: none

SECTION 16  Other Information

DISCLAIMER: The information herein is believed to be accurate and reliable as of the date compiled. However, Strem Chemicals, Inc. makes no representation, warranty, or guarantee of any kind with respect to the information contained in this document or any use of the product based on this information.
PREPARATION DATE: 03/20/01
REVISION DATE: 02/10/05
MATERIAL SAFETY DATA SHEET

Manufacturer: Strem Chemicals, Inc.
7 Mulliken Way
Newburyport, MA 01950-4098

STREM CUSTOMER SERVICE: (978) 462-3191
CHEMTREC (EMERGENCY ONLY): (800) 424-9300
POISON CENTER: (800) 562-8236

SECTION 1 Product Identification

CHEMICAL NAME: Indium (III) oxide (99.999%-In) PURATREM
PRODUCT NUMBER: 93-4906
CAS REGISTRY NUMBER: 1312-43-2
FORMULA: In_{2}O_{3}
EINECS NUMBER: 215-193-9
CHEMICAL FAMILY: metal oxide
SYNONYM: Diindium trioxide, Inox, Indium sesquioxide, Indium trioxide

SECTION 2 Composition and Information on Ingredients

<table>
<thead>
<tr>
<th>INGREDIENT</th>
<th>CAS#</th>
<th>%</th>
<th>ACGIH (TWA)</th>
<th>OSHA (PEL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Title compound</td>
<td>1312-43-2</td>
<td>100</td>
<td>0.1mg/m³ (as In)</td>
<td>no data</td>
</tr>
</tbody>
</table>

SECTION 3 Hazards Identification

EMERGENCY OVERVIEW: May be irritating to skin and eyes and respiratory tract.
PRIMARY ROUTES OF EXPOSURE: Ingestion, inhalation
EYE CONTACT: May be a mild to severe irritant to the eyes.
SKIN CONTACT: May cause slight to mild irritation of the skin.
INHALATION: Do not breathe dust. Inhalation of powder may lead to irritation of the respiratory tract.
INGESTION: Ingestion may lead to vomiting and diarrhea.
ACUTE HEALTH EFFECTS: May be irritating to skin, eyes, mucus membranes and respiratory tract. Do not breathe dust.
CHRONIC HEALTH EFFECTS: No information available on long-term chronic effects.
NTP: No
IARC: No
OSHA: No

SECTION 4 First Aid Measures

EYE EXPOSURE: Immediately flush the eyes with copious amounts of water for at least 10-15 minutes. A victim may need assistance in keeping their eye lids open. Get immediate medical attention.
SKIN EXPOSURE: Wash the affected area with water. Remove contaminated clothes if necessary. Seek medical assistance if irritation persists.
INHALATION: Remove the victim to fresh air. Closely monitor the victim for signs of respiratory problems, such as difficulty in breathing, coughing, wheezing, or pain. In such cases seek immediate medical assistance.
INGESTION: Seek medical attention immediately. Keep the victim calm. Give the victim water (only if conscious). Induce vomiting only if directed by medical personnel.

SECTION 5 Fire Fighting Measures

FLASH POINT: none
AUTOIGNITION TEMPERATURE: none
EXPLOSION LIMITS: none
EXTINGUISHING MEDIUM: not applicable
SPECIAL FIRE FIGHTING PROCEDURES: If this product is involved in a fire, fire fighters should be equipped with a NIOSH approved positive pressure self-contained breathing apparatus and full protective clothing.

HAZARDOUS COMBUSTION AND DECOMPOSITION PRODUCTS: If involved in a fire this material may emit irritating fumes.

UNUSUAL FIRE OR EXPLOSION HAZARDS: No unusual fire or explosion hazards.

SECTION 6  Accidental Release Measures

SPILL AND LEAK PROCEDURES: Small spills can be mixed with vermiculite or sodium carbonate and swept up.

SECTION 7  Handling and Storage

HANDLING AND STORAGE: Store in a tightly sealed container. Handle the material in a ventilated area. May form a fine airborne dust.

SECTION 8  Exposure Controls and Personal Protection

EYE PROTECTION: Always wear approved safety glasses when handling a chemical substance in the laboratory.

SKIN PROTECTION: Wear protective clothing and gloves.

VENTILATION: Material may form a fine dust. If possible, handle the material in an efficient fume hood.

RESPIRATOR: If ventilation is not available a respirator should be worn. The use of respirators requires a Respirator Protection Program to be in compliance with 29 CFR 1910.134.

ADDITIONAL PROTECTION: No additional protection required.

SECTION 9  Physical and Chemical Properties

COLOR AND FORM: yellow powder
MOLECULAR WEIGHT: 277.64
MELTING POINT (°C): none
BOILING POINT (°C): no data
VAPOR PRESSURE: no data
SPECIFIC GRAVITY: 7.179
ODOR: none
SOLUBILITY IN WATER: insoluble

SECTION 10  Stability and Reactivity

STABILITY: air and moisture-stable solid
HAZARDOUS POLYMERIZATION: none
CONDITIONS TO AVOID: none
INCOMPATIBILITY: strong reducing metals
DECOMPOSITION PRODUCTS: no hazardous decomposition products.

SECTION 11  Toxicological Information

RTECS DATA: Oral (rat); lethal dose: >10 gm/kg. LDLo: 10 gms/kg. Intraperitoneal (mouse): LDLo: 5 gm/kg. Inhalation (rat); TCLI: 39500 ug/m3/4H/17W-L.
CARCINOGENIC EFFECTS: No data available
MUTAGENIC EFFECTS: No data available
TETRATOGENIC EFFECTS: No data available
SECTION 12   Ecological Information

ECOLOGICAL INFORMATION:  No information available

SECTION 13   Disposal Considerations

DISPOSAL: Dispose of according to local, state and federal regulations.

SECTION 14   Transportation Information

SHIPPING NAME (CFR):  Non-hazardous
HAZARD CLASS (CFR):  NA
ADDITIONAL HAZARD CLASS (CFR):  NA
PACKING GROUP (CFR):  NA
UN ID NUMBER (CFR):  NA
SHIPPING NAME (IATA):  Non-hazardous
HAZARD CLASS (IATA):  NA
ADDITIONAL HAZARD CLASS (IATA):  NA
PACKING GROUP (IATA):  NA
UN ID NUMBER (IATA):  NA

SECTION 15   Regulatory Information

TSCA: listed on the TSCA inventory
SARA (TITLE 313): Title Compound: not listed
SECOND INGREDIENT: none
THIRD INGREDIENT: none

SECTION 16   Other Information

DISCLAIMER: The information herein is believed to be accurate and reliable as of the date compiled. However, Strem Chemicals, Inc. makes no representation, warranty, or guarantee of any kind with respect to the information contained in this document or any use of the product based on this information.

PREPARATION DATE:  09/14/99
REVISION DATE:  09/16/04