Optoelectronic and Mechanical Properties of Sol-Gel Derived Multi-Layer ITO Thin Films Improved by Elemental Doping, Carbon Nanotubes and Nanoparticles

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Thesis submitted in a partial fulfillment of the requirements for the degree of Doctor of Philosophy in the School of Engineering & Information Technology at Murdoch University

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DECLARATION

I hereby declare that the work presented in this dissertation is my own version of research and contains as its main content work which has not been previously submitted elsewhere for the award of a degree at any tertiary education institute.

Hatem Taha
Dedication

This noble study has been dedicated to my parents, brothers, wife and children the most loving people in this planet for your love, understanding, encouragement, patience and prayers.
ABSTRACT

Transparent conductors (TCs) are an essential ingredient in numerous new applications which are emerging in the 21st century including high efficiency solar cells, rigid and tactile displays, light emitting diodes, photonics for communications and computing, energy efficient and smart windows and gas sensors, since they allow efficient light transmission while electric signals are applied or collected. So far, indium tin oxide (ITO) reflects the best trade-off between low electrical resistivity and high optical transparency, making it the first candidate as transparent conductor for most optoelectronics technologies despite its drawbacks such as expensiveness and poor mechanical characteristics. However, due to the intricacy of ITO, the coating characteristics strongly depend on the deposition conditions. Despite many developments in ITO-based transparent conductive coatings; these coating are yet to be commercialized for optoelectronic applications. Many challenges still exist in terms of the fabrication of high quality ITO-based transparent conductive coatings, in order to meet the criteria of better, cost-effectiveness and environmentally-friendly characteristics, especially in the context of transparent conductive electrodes.

In this study, the deposition conditions along with incorporating thin ITO films with transition metals (Ti and Ag), carbon nanotubes (e.g., SWCNTs) and metals nanoparticles (Ag and Au nanoparticles) were optimized to synthesize high quality ITO based TCs via a facile, environmentally friendly and cost-effective sol-gel spin-coating method. ITO thin films were fabricated with different Ti and Ag doping concentration, different annealing temperature and different geometry such as single layer, bi-layer and multi-layer. The structural, surface morphology and composition, electrical, optical and mechanical properties were characterized using a wide range of complementary techniques, namely, X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), electron dispersive X-ray (EDX), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), four point probes and Hall Effect, UV-Vis, nanoindentation and FEM modeling.

All the fabricated ITO-based TCs showed a nano-sized grain-like morphology forming a homogenous surface structure. XRD results demonstrated a relatively good crystallinity of ITO-based thin film coatings after applying a suitable heat treatment. XPS and EDX analysis corroborated the existence of the main elements for each case of thin ITO coating. In the case of
pure ITO and (Ti- and Ag-) doped ITO thin films with a thickness of 350 ±5 nm and 500 °C annealing temperature, the highest optical transparency was determined to be 92% for pure ITO, 4 at.% Ti-doped ITO and 2 at.% Ag-doped ITO thin films, while the lowest electrical resistivity of 1.6×10⁻⁴ Ω·cm was achieved for the ITO film prepared with 4 at.% Ti content. However, these thin films exhibit mechanical characteristics namely hardness and Young’s modulus in the range of (5.3 – 6.8) GPa and (128 – 148) GPa, respectively.

In order to enhance their mechanical characteristics while maintaining their optoelectronic properties, SWCNTs were incorporated with ITO with different films thicknesses (i.e. 150, 210, 250 and 320) ± 5 nm, and the characterizations were carried out with respect to the film thickness. The hardness and Young’s modulus for SWCNTs/ITO thin films were in the range of (22 – 28) GPa and (254 – 306) GPa, respectively. The lowest electrical resistivity of 4.6×10⁻⁴ (Ω·cm) was achieved for the thicker film, while the highest transmittance of 91.5 % was obtained from the thinner film. Obtained results show a significant improvement in the mechanical properties of SWCNT/ITO thin films compared with their counterparts of pure and doped ITO thin films, along with distinctly good optoelectronic properties.

To minimize the consumption of indium, ITO thin films were combined with (very thin metal-, metal nanoparticles- and metal oxide-) layers in bi-layered and tri-layered geometries of (AuI), ((Au)nI), ((Ag)nI) and ((AgO)I), and (IAuI), (I(Au)nI), (I(Ag)nI) and (I(AgO)I), respectively, with films thicknesses (~ 130 ± 5 nm). For these coating systems, the lowest electrical resistivity 1.2×10⁻⁴ Ω·cm was for ITO/Au/ITO thin film, while the highest optical transparency ~ 91.5% was for ITO/AgO/ITO thin film. Two thin films with the configurations of ITO\AgO\ITO and AgO\ITO for tri-layer and bi-layer coatings, respectively with the best optoelectronic performance were nominated as transparent conductive electrodes in designing inverted organic solar cells, and compared with pure ITO thin films. Power conversion efficiencies of 4.9%, 4.2% and 3.8% were found for ITO/AgO/ITO, AgO/ITO and ITO thin film coatings, respectively.

To conclude, sol-gel spin-coating derived ITO based transparent conductive coatings present high quality crystal structure, distinctively good optoelectronic properties as well as reasonably mechanical characteristics, and comparable with those achieved from other sophisticated
fabrication techniques such as sputtering, pulsed laser deposition, electron beam evaporation etc. All these attributes render the ITO-based coatings promising as transparent conductors in many industrial and technological applications.
Table of Contents

Title ................................................................................................................................. I
DECLARATION .............................................................................................................. II
Copyright ....................................................................................................................... III
Dedication ...................................................................................................................... IV
ABSTRACT .................................................................................................................... V
Table of Contents .......................................................................................................... VIII
List of Figures ............................................................................................................... XIV
List of Tables ............................................................................................................... XVII
Glossary of Abbreviations and Technical Symbols .................................................... XVIII
Acknowledgments ....................................................................................................... XXII
List of publications ..................................................................................................... XXIV
Conference papers ..................................................................................................... XXVI

1. CHAPTER 1 General Introduction and Review of the Early Works ..................... 1
   1.1. Transparent Conductive Materials ................................................................. 1
   1.2. Literature Review of Transparent Conductive Materials .............................. 3
   1.3. Recent Advances in Metal Oxide Based Transparent Conductive Coatings ...... 4
   1.4. Strategies to Obtain High Carrier Concentration in TCO Materials ............. 6
   1.5. Strategies to Obtain High Carrier Mobility in TCO Materials .................... 7
   1.6. P-Type Transparent Conductors ..................................................................... 10
   1.7. Introduction to ITO Thin Films ...................................................................... 11
       1.7.1. Indium Oxide and Indium Tin Oxide Structure ......................................... 11
           1.7.1.1. Indium Oxide and Indium Tin Oxide Band Structures ....................... 14
           1.7.1.2. Recent Advances in ITO Based TCOs ............................................... 15
           1.7.1.3. Survey of the progress of sol-gel derived ITO based TCO coatings .... 20
           1.7.2. Recent Advances of Some Characterization Techniques for ITO Based TCOs Coatings 21
           1.7.2.1. XRD Analysis of ITO Based TCOs ...................................................... 21
           1.7.2.2. Synchrotron X-ray Scattering Analysis of ITO Based TCOs ............... 21
           1.7.2.3. XPS Analysis of ITO-Based TCOs ...................................................... 22
2.4.7.2. Hall Effects Measurements ................................................................. 71
2.4.8. Mechanical Characterization: Nanoindentation Measurements and Finite Element
Modeling (FEM) of Thin Film Coatings .......................................................... 72
  2.4.8.1. Experimental Technique of Nanoindentation Measurement .................. 74
  2.4.8.2. Finite Element Modeling (FEM) ......................................................... 75
3.  CHAPTER 3 Improving the Optoelectronic Properties of Titanium Doped Indium Tin Oxide
Thin Films ........................................................................................................ 76
  3.1. Abstract ..................................................................................................... 77
  3.2. Introduction ............................................................................................... 78
  3.3. Experimental Techniques .......................................................................... 79
    3.3.1. Thin Films Deposition ......................................................................... 79
    3.3.2. Sol-Gel and Thin Films Preparation ..................................................... 79
    3.3.3. Analysis Techniques ........................................................................... 80
  3.4. Results and Discussions ............................................................................ 80
    3.4.1. Structural Properties ........................................................................... 80
    3.4.2. Surface Morphology Properties ........................................................... 86
    3.4.3. Electrical Properties ............................................................................ 88
    3.4.4. Optical Properties ............................................................................... 91
  3.5. Conclusions ............................................................................................... 95
4.  CHAPTER 4: Probing the Effects of Thermal Treatment on the Electronic Structure and
Mechanical Properties of Ti-Doped ITO Thin Films ........................................... 96
  4.1. Abstract ..................................................................................................... 97
  4.2. Introduction ............................................................................................... 98
  4.3. Experimental Details .................................................................................. 99
    4.3.1. Thin Films Deposition ......................................................................... 99
    4.3.2. Characterization Techniques ............................................................... 100
  4.4. Results and Discussions .......................................................................... 101
    4.4.1. Raman Analysis .................................................................................... 101
    4.4.2. Atomic Compositions and Surface Chemical Bonding States ............. 103
    4.4.3. Mechanical Properties (Hardness, Young’s modulus and Wear resistance) .... 115
  4.5. Conclusions .............................................................................................. 120
5. **CHAPTER 5: Improved Mechanical Properties of Sol-Gel Derived ITO Thin Films via Ag Doping** ................................................................................................................................. 121
   5.1. **Abstract** ................................................................................................................ 122
   5.2. **Introduction** .......................................................................................................... 123
   5.3. **Experimental Methods** ............................................................................................ 124
   5.3.1. **Raw Materials** .................................................................................................. 124
   5.3.2. **Sol-Gel and Thin Films Preparation** .................................................................. 124
   5.3.3. **Analysis Techniques** ........................................................................................ 125
   5.4. **Results and Discussions** ........................................................................................ 126
   5.4.1. **Crystallographic Structure Properties** ................................................................. 126
   5.4.2. **Morphological and EDX Analysis** .................................................................. 130
   5.4.3. **Electrical Properties** ........................................................................................ 132
   5.4.4. **Optical Properties** ............................................................................................ 136
   5.4.5. **Determination of Optical Constants** ................................................................ 141
   5.4.6. **Mechanical Characteristics** .............................................................................. 144
   5.5. **Conclusions** .......................................................................................................... 154

6. **CHAPTER 6: Novel Approach for Fabricating Transparent and Conducting SWCNTs/ITO Thin Films for Optoelectronic Applications** .................................................................................................................. 156
   6.1. **Abstract** ................................................................................................................ 157
   6.2. **Introduction** .......................................................................................................... 158
   6.3. **Experimental Section** ............................................................................................ 159
   6.3.1. **Raw Materials** .................................................................................................. 159
   6.3.2. **SWCNTs/ITO Sol Preparation and Samples Deposition** .................................... 160
   6.3.3. **Analysis Techniques** ........................................................................................ 161
   6.4. **Results and Discussions** ........................................................................................ 162
   6.4.1. **Structural Properties** ........................................................................................ 162
   6.4.2. **Elemental Compositions and Surface Chemical Bonding States** ...................... 164
   6.4.3. **Raman Studies** .................................................................................................. 167
   6.4.4. **Surface Morphology and Topography** ............................................................... 168
   6.4.5. **Electrical Properties** ........................................................................................ 172
   6.4.6. **Optical Properties** ............................................................................................ 176
List of Figures

Figure 1.1 Bixbyte crystal structure of $\text{In}_2\text{O}_3$ .......................................................... 12
Figure 1.2 $\text{In}_2\text{O}_3$ structure with two non-equivalent cationic b and d sites ......................... 13
Figure 1.3 Schematic diagram of the energy band model for ITO adopted (a) low doping level and
(b) high doping level .................................................................................................................. 15
Figure 2.1 Band gap structures of conductor, semiconductor and insulator materials .................. 34
Figure 2.2 Fermi-Dirac distribution function plot ....................................................................... 37
Figure 2.3 Location of Fermi level for intrinsic semiconductor and n-type and p-type extrinsic
semiconductors .......................................................................................................................... 38
Figure 2.4 Dependence of the free carrier density $N_e$ on the Sn concentration $c$. Dots represent
 experimental points; drawn curves represent (a) $N_{\text{In}c}$, (b) $N_{\text{In}c}(1-c)^8$ ........................................ 42
Figure 2.5 Typical spectral dependence of transparent conductive oxides .................................. 46
Figure 2.6 Complex refractive index (left) and dielectric constant (right) of ITO thin films ......... 48
Figure 2.7 The main steps of spin coating .................................................................................... 53
Figure 2.8 Flow diagram of sol-gel spin-coating process ............................................................... 57
Figure 2.9 Incident and scattered X-rays in XRD analysis ............................................................ 59
Figure 2.10 Schematic diagram of SEM technique with the CRT screen ...................................... 64
Figure 2.11 Typical Tauc plot for estimating the band gap energy of a thin film ......................... 69
Figure 2.12 A geometry defining the sheet resistance calculation ............................................... 69
Figure 2.13 Configuration of four point probes measurements .................................................... 71
Figure 2.14 A schematic diagram of Hall Effect measurements .................................................. 72
Figure 2.15 Typical loading and unloading curves of the nanoindentation .................................. 74
Figure 3.1 The XRD patterns of as deposited and post annealed ITO thin films ......................... 82
Figure 3.2 The XRD patterns of Ti-doped ITO films prepared at 2 at% and 4 at% Ti concentrations
and post annealed at different temperatures............................................................................. 83
Figure 3.3 The annealing temperature dependent grain size ....................................................... 85
Figure 3.4 Peaks shift of (222) for the ITO and Ti-doped ITO thin films annealed at 500 °C ...... 85
Figure 3.5 FESEM images of prepared and post annealed ITO thin films .................................. 87
Figure 3.6 FESEM images of Ti-doped ITO thin films, (a1-a4) for 2 at% and (b1-b4) for 4 at% Ti
concentrations and post annealed at different temperatures ..................................................... 87
Figure 3.7 Electrical resistivity of pure ITO and Ti-doped ITO thin films for 2 at% and 4 at% Ti
centrations and post annealed at different temperatures ......................................................... 89
Figure 3.8 Variations of carrier concentration and Hall mobility of ITO and Ti-doped ITO thin films
for 2 at% and 4 at% Ti concentrations with annealing temperature ......................................... 90
Figure 3.9 Optical transmittance of pure ITO and Ti-doped ITO thin films annealed at different
temperatures .......................................................................................................................... 92
Figure 3.10 Estimated optical band gaps of pure ITO and Ti-doped ITO thin films for 2 at% and 4
at% Ti concentrations post annealed at different ................................................................. 94
Figure 4.1 Raman shift of Ti-doped ITO films (a): 2 at % and (b): 4 at % of Ti, annealed at different
temperatures ......................................................................................................................... 103
Figure 4.2 XPS survey scans of Ti-doped ITO films (a): 2 at % and (b): 4 at % of Ti, annealed at different temperatures ...................................................................................................................... 104
Figure 4.3 In 3d XPS spectra of Ti doped ITO films (a): 2 at % and (b): 4 at % Ti, annealed at different temperatures ...................................................................................................................... 106
Figure 4.4 Sn 3d XPS spectra of Ti doped ITO films (a): 2 at % and (b): 4 at % Ti, annealed at different temperatures ...................................................................................................................... 108
Figure 4.5 Ti 2p XPS spectra of Ti doped ITO films (a): 2 at % and (b): 4 at % Ti, annealed at different temperatures ...................................................................................................................... 109
Figure 4.6 O 1s XPS spectra of Ti doped ITO films (a): 2 at % and (b): 4 at % Ti, annealed at different temperatures ...................................................................................................................... 111
Figure 4.7 Cl 2p XPS spectra of Ti-doped ITO films (a): 2 at % and (b): 4 at % Ti, annealed at different temperatures ...................................................................................................................... 112
Figure 4.8 Load-displacement curves of Ti-doped ITO films (a): 2 at % and (b): 4 at % Ti, annealed at different temperatures ...................................................................................................................... 116
Figure 4.9 Hardness and Young’s modulus of Ti doped ITO films (a): 2 at % and (b): 4 at % Ti, annealed at different temperatures ...................................................................................................................... 119
Figure 5.1 The XRD patterns of as deposited and annealed ITO thin films ................................................. 127
Figure 5.2 The XRD patterns of as deposited and annealed Ag-doped ITO films prepared at different Ag concentrations ............................................................................................................................................. 128
Figure 5.3 Variations the crystallite size of as deposited and annealed ITO and Ag-doped ITO thin films with Ag concentration ............................................................................................................................................. 130
Figure 5.4 FESEM images of annealed ITO and Ag-doped ITO thin films at different Ag concentrations ............................................................................................................................................. 131
Figure 5.5 EDX analyses of annealed (a): ITO and (b): Ag-doped ITO thin films .................................131
Figure 5.6 Electrical resistivity and conductivity of ITO and Ag-doped ITO thin films with different Ag concentration, (a): as deposited and (b): annealed ................................................................................................. 134
Figure 5.7 Mobility and carrier concentration of ITO and Ag-doped ITO thin films with different Ag concentration, (a): as deposited and (b): annealed ................................................................................................. 135
Figure 5.8 Transmittance spectra of ITO and Ag-doped ITO thin films with different Ag concentration, (a): as deposited and (b): annealed ................................................................................................. 137
Figure 5.9 Optical band gap of ITO and Ag-doped ITO thin films with different Ag concentration, (a): as deposited and (b): annealed ................................................................................................. 139
Figure 5.10 Variation the absorption coefficient of ITO and Ag-doped ITO thin films with different Ag concentration, (a): as deposited and (b): annealed ................................................................................................. 141
Figure 5.11 Variation the refractive index of ITO and Ag-doped ITO thin films with different Ag concentration, (a): as deposited and (b): annealed ................................................................................................. 143
Figure 5.12 Variation the extinction coefficient of ITO and Ag-doped ITO thin films with different Ag concentration, (a): as deposited and (b): annealed ................................................................................................. 144
Figure 5.13 Typical load-displacement curves of ITO and Ag-doped ITO thin films with different Ag concentration, (a): as deposited and (b): annealed ................................................................................................. 146
Figure 5.14 Variation the hardness and Young’s modulus of ITO and Ag-doped ITO thin films with different Ag concentration, (a): as deposited and (b): annealed ................................................................................................. 148
Figure 5.15 Variation of hardness with grain size ($D^{1/2}$) of ITO and Ag-doped ITO thin films with different Ag concentration, (a): as deposited and (b): annealed ........................................ 150
Figure 5.16 (a): FEM modelling result of von Mises stress distribution of as-deposited ITO film and (b): a comparison of displacement in two different films under study, top: ITO with 6% Ag film and bottom: pure ITO film ........................................................................................................ 153
Figure 6.1 XRD pattern of SWCNT/ITO thin films prepared at various thicknesses and annealed at 350 °C ........................................................................................................ 153
Figure 6.2 Effect of film thickness on the grain crystallite size of SWCNTs/ITO thin films ........ 163
Figure 6.3 XPS wide scans of SWCNTs/ITO thin films prepared at various thicknesses and annealed at 350 °C ........................................................................................................ 163
Figure 6.4 High resolution scans of (a)- In3d, (b)- Sn3d, (c)- O1s and (d)-C1s of SWCNTs/ITO thin films ........................................................................................................ 165
Figure 6.5 Raman spectra of SWCNTs/ITO thin film ........................................................................................................ 167
Figure 6.6 FESEM images of SWCNTs/ITO thin films prepared at various thicknesses and annealed at 350 °C ........................................................................................................ 168
Figure 6.7 Elemental distributions of SWCNTs/ITO thin films (annealed at 350 °C) by EDX ....... 169
Figure 6.8 AFM images of SWCNTs/ITO thin films annealed at 350 °C................................. 170
Figure 6.9 Variations of (a) electrical resistivity and conductivity, (b) mobility and carrier concentration of SWCNTs/ITO thin films with film thickness ........................................ 171
Figure 6.10 Schematic diagram of free carrier injection from ITO network to SWCNTs and carrier transfer in SWCNTs/ITO thin film ........................................................................................................ 175
Figure 6.11 Optical transmittance spectra of SWCNT/ITO thin films annealed at 350 °C......... 176
Figure 6.12 Absorption coefficients of SWCNT/ITO thin films annealed at 350 °C.............. 177
Figure 6.13 Tauc plot of SWCNT/ITO thin films annealed at 350 °C................................. 177
Figure 6.14 Hardness and Young’s modulus of SWCNTs/ITO thin films annealed at 350 °C...... 179
Figure 6.15 XRD patterns of Ag-NPs and Au-NPs colloidal solutions........................................ 181
Figure 7.2 XRD patterns of (a) bi-layer and (b) tri-layer thin films annealed at 500 °C............ 193
Figure 7.3 Top-view images of bi-layer (a1 – a4) and tri-layer (b1 – b4) thin films. Cross-sectional images for (c1) - IAu1 and (c2) - I(Au)$_n$I thin films ................................................................. 195
Figure 7.4 Schematic diagram shows the differences in the formation of the mid-layer thin film coatings ........................................................................................................ 196
Figure 7.5 High resolution scans of (a)- In 3d, (b)- Sn 3d and (c)- O 1s of IAu1 thin film ............... 198
Figure 7.6 Transmittance spectra of (a)- bi-layer and (b)- tri-layer thin films .......................... 202
Figure 7.7 Absorption coefficient of (a)- bi-layer and (b)- tri-layer thin films .......................... 202
Figure 7.8 Variations of the band gap energy of (a)- bi-layer and (b)- tri-layer thin films ........ 203
Figure 7.9 Refractive index spectra of (a)- bi-layer and (b)- tri-layer thin films .......................... 205
Figure 7.10 Extinction index spectra of (a)- bi-layer and (b)- tri-layer thin films .......................... 207
7.11 (a)- Device architecture and (b)- $J-V$ characteristic curves of the fabricated and compared OSCs in this investigation ............................... 210
List of Tables

Table 1.1 Typical TCO materials and their related dopants and compounds .......................................... 9
Table 2.1 Examples of semiconductor materials .......................................................................................... 35
Table 2.2 Comparison of some important binary TCOs and their corresponding preparation methods and optoelectronic properties ...................................................................................... 48
Table 3.1 Structural parameters for the ITO and Ti-doped ITO thin films at 2 at.% and 4 at.% Ti concentration and post annealed at different temperatures .................................................................................. 86
Table 3.2 The optical and electrical parameters of as prepared and post annealed ITO and Ti-doped ITO thin films for 2 at.% and 4 at.% Ti concentrations ........................................................................... 93
Table 4.1 Elemental compositions of Ti doped ITO thin films at 2 at.% and 4 at.% Ti concentrations after being annealed at different temperatures ................................................................. 105
Table 4.2 Fitting results of the XPS data of Ti doped ITO films for the core level binding energies .................................................................................................................................................. 113
Table 4.3 Mechanical properties of Ti doped ITO films after being annealed at different temperatures ............................................................................................................................................. 119
Table 5.1 Structural parameters for as deposited and annealed ITO and Ag-doped ITO thin films .................. 128
Table 5.2 Electrical and optical properties for as deposited and annealed ITO and Ag-doped ITO thin films ............................................................................................................................................. 133
Table 5.3 Mechanical properties for as deposited and annealed ITO and Ag-doped ITO thin films ............................................................................................................................................. 147
Table 6.1 Elemental compositions of SWCNTs/ITO thin films annealed at 350 °C .................. 165
Table 6.2 Electrical properties of SWCNTs/ITO, pure ITO and Ti-doped ITO thin films ........... 173
Table 6.3 Structural, and optical properties of SWCNTs/ITO, pure ITO and Ti-doped ITO thin films ............................................................................................................................................. 178
Table 6.4 Mechanical properties of SWCNTs/ITO thin films annealed at 350 °C and Ti-doped ITO thin film annealed at 400°C ............................................................................................................................................. 181
Table 7.1 Structural parameters of the fabricated bi-layer and tri-layer thin films ..................... 194
Table 7.2 Variation of the atomic percentage of the main elements for bi-layer and tri-layer thin films ............................................................................................................................................. 196
Table 7.3 3 Electric properties of fabricated bi-layer and tri-layer thin films ............................. 200
Table 7.4 Optical, sheet resistance and FOM values of synthesized thin films .......................... 204
Table 7.5 Photovoltaic performance parameters of fabricated OSCs ........................................... 210
Table 8.1 A comparison of the best achieved results of ITO-based TCOs thin films fabricated in this study ......................................................................................................................................................... 215
# Glossary of Abbreviations and Technical Symbols

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Definition</th>
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<tbody>
<tr>
<td>LEDs</td>
<td>Light Emitting Diodes</td>
</tr>
<tr>
<td>TCMs</td>
<td>Transparent Conductive Materials</td>
</tr>
<tr>
<td>T</td>
<td>Optical Transparency</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Electrical Resistivity</td>
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<tr>
<td>TCOs</td>
<td>Transparent Conductive Oxides</td>
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<tr>
<td>HDTV</td>
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<td>Carbon Nanotubes</td>
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<td>PVA</td>
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<tr>
<td>HOMO</td>
<td>Highest Occupied Molecular Orbital</td>
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<td>LUMO</td>
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<td>PEDOT:PSS</td>
<td>poly (3, 4- ethylenedioxythiophene): poly (styrenesulfonate)</td>
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<td>Density of Impurity Scattering Centers</td>
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<td>Low Frequency Relative Permittivity of Low-Loss Dielectrics</td>
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<tr>
<td>$g(x)$</td>
<td>Screening Function</td>
</tr>
<tr>
<td>$m^*$</td>
<td>Electron Effective Mass</td>
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<tr>
<td>$V$</td>
<td>Volt</td>
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<tr>
<td>$s$</td>
<td>Second</td>
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<tr>
<td>$\lambda_{\text{gap}}$</td>
<td>Band Gap Absorption</td>
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<tr>
<td>$\lambda_p$</td>
<td>Plasma Edge or Plasma Wavelength</td>
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<tr>
<td>UV</td>
<td>Ultraviolet</td>
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<td>IR</td>
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<td>$\omega_p$</td>
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<td>$\omega_{\text{gap}}$</td>
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<td>$&lt;n&gt;$</td>
<td>Complex Refractive Index</td>
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<tr>
<td>$n$</td>
<td>Refractive Index of Low-Loss Dielectrics</td>
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<tr>
<td>$n_o$</td>
<td>Refractive Index of Air</td>
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<tr>
<td>$n_1$</td>
<td>Refractive Index of the Substrate</td>
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<td>$c$</td>
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<td>$\nu$</td>
<td>Speed of Light in A Medium</td>
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$k$  Extinction Coefficient  
$\varepsilon$  Complex Dielectric Constant  
$t$  Thin Film Thickness  
$\varepsilon_1$  Real Part of Dielectric Constant  
$\varepsilon_2$  Imaginary Part of Dielectric Constant  
$\alpha$  Absorption Coefficient  
$C_0$  Initial Solvent Concentration  
$\omega$  Spinning Speed  
RF  Radio Frequency  
DC  Direct Current  
2D, 3D  Two Dimensions, Three Dimensions  
PLD  Pulsed Laser Deposition  
FDTD  Finite-Difference Time-Domain  
LCD  Liquid Crystal Display  
R2R  Roll-to-Roll  
OSCs  Organic Solar Cells  
XRD  X-ray Diffraction  
XPS  X-ray Photoelectron Spectroscopy  
HRTEM  High Resolution Transmission Electron Microscopy  
TD-DFT  Time Dependent Density Function Theory  
HF  Hartree Fock  
FEM  Finite Element Modeling  
PVP  Polyvinylpyrrolidone  
HTL  Hole Transport Layer  
ETL  Electron Transport Layer  
PCE  Power Conversion Efficiency  
$V_{oc}$  Open Circuit Voltage  
FF  Fill Factor  
PET  Polyethylene terephthalate  
DI  Deionized  
rpm  Revolution per Minute
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<tr>
<td>GO</td>
<td>Graphene Oxide</td>
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<td>D</td>
<td>Crystal Size</td>
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<td>$B, \text{ (FWHM)}$</td>
<td>Full Width at Half Maximum</td>
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<tr>
<td>$a$</td>
<td>Lattice Constant</td>
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<tr>
<td>$V_H$</td>
<td>Hall Voltage</td>
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<td>$B$</td>
<td>Magnetic flux Density</td>
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<td>$H$</td>
<td>Hardness</td>
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<td>$E$</td>
<td>Elastic (Young’s) Modulus</td>
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_Hatem Taha_

Murdoch University

March 2018
List of publications


Conference papers


4. Ehsan Mohammadpour, Zhong-Tao Jiang, Mohammednoor Altaraweh, Bogdan Z. Dlugogorski, Mohammad Rahman, Hantarto Widjaja, **Hatem Taha**, "Study the structural changes in CrAlN coatings by in-situ synchrotron radiation X-ray diffraction". Australian Institute of Physics (AIP) Postgrad Student Conference, October 2015, University of Western Australia, WA, Australia.


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CHAPTER 1 General Introduction and Review of the Early Works

1.1. Transparent Conductive Materials

In many daily optoelectronic devices, such as touch screens, solar cells, displays, smart widows, sensors and light emitting diodes (LEDs), light needs to be efficiently transmitted while applying or collecting electrical signals. This function is recognized by specific groups of materials named as transparent conductive materials (TCMs) whose characteristics impact the performance of the optoelectronic devices and accordingly their specifications differ based on their requirements. For instance, the optical scattering (haze) can decrease the clearness in displays but increases the efficiency in solar cells. On the other hand, the surface roughness and work function are very crucial for LEDs, yet they are less important in touch screens. Mechanical flexibility is indispensable for flexible applications but not important for devices fabricated on rigid substrates. However, both optical transparency (T) and electrical resistivity (ρ) are essential factors for all the aforementioned optoelectronic devices. Each TCM has a trade-off between optical transparency and electrical resistivity, since the higher the TCM film thickness the lower both T and ρ will be.

Materials like metals are usually electrically conductive but do not transmit light, whereas, materials like glass are highly transparent but electrical insulating. The challenge of fabricating TCMs is to decouple these two characteristics in such a way that one can tune the optical transparency without impacting the electrical properties and vice versa. To attain this, most efforts have been in developing dielectric transparent materials into conductive ones without significantly affecting their optical transparency. E.g. transparent conductive oxides (TCOs) [1]. So far, the most important applications of TCMs are as electrodes for photovoltaic cells, displays and LEDs [2]. The key technical drivers of commercial products are cost effectiveness, low power consumption, large-sized devices, minimum reflection, simplified value chain, thinness and robustness, flexibility and ease of patterning.

Over the past few decades, the majority of TCO materials were based on three main n-type TCOs, In2O3, ZnO and SnO2 thin films. These mainly experimental studies were accomplished
with the aims of improving the performance of these TCOs to meet ever-increasing industrial demands with various specific requirements.

Within these aforementioned TCOs, In$_2$O$_3$ and/or tin-doped In$_2$O$_3$ (named as indium tin oxide or ITO) are the most widely used. ITO has reached the industrial level, especially with the use of the sputtering deposition process. However, thin ITO films can also be fabricated by other physical and/or chemical methods. For optoelectronic applications and devices, countless research has been carried out on improving either the electrical conductivity or the transparency of thin ITO films. The optical transparency can be optimized by introducing a proper level of oxygen gas into the sputtering chamber or heating up the substrates during or after the fabrication process [3, 4]. Alternatively, the electrical conductivity can be improved by increasing the film thickness, thermal treatment (pre-heating the substrates or post annealing process) and introducing foreign atoms as dopants to the host structure. However, there is a trade-off between the electrical conductivity and the transmittance of thin ITO film. For example, the electrical resistivity of ITO might be increased when an excess amount of oxygen is present or it severely annealed \( (i.e., > 500 \, ^\circ C) \), despite the enhancement of its optical transparency. In general, the physical properties of semiconductors are characteristic of both the properties of the host structure and the presence of impurities and defects. Dopant impurities which mainly substitute the host atoms provide electronic states in the band-gap close to the conduction and valence band edges and hence control the conductivity and the type of the material. These electronic states (so-called shallow level impurities) facilitate a wide range of semiconductor characteristics. On the other hand, other impurities along with crystal structure defects introduce deeper electronic states (named as deep level defects) in the band-gap that can also tune the properties of the semiconductor but may make a semiconductor inappropriate for its proposed applications. It is therefore important to control carefully the deposition process to fine-tune the desired characteristics of ITO based TCO thin films.

It is believed that the performance of ITO thin films in an optoelectronic device is linked to its structural, morphological, electrical and optical characteristics. High quality ITO films are mainly deposited within high vacuum systems \( via \) physical processes including chemical vapor deposition or sputtering techniques. Both methods are energy intensive due to their high vacuum
system requirement, their high squandered energy through sample fabrication and their high cost of maintenance [5].

Recent development in the synthesis of TCOs highlight the need for materials with good optoelectronic properties along with a cost-effective and environmentally-friendly fabrication process. In this context, the sol-gel process is potentially a very promising technique and can meet these criteria [6, 7]. The sol-gel process is a well-known simple, low-cost and environmentally friendly fabrication technique resulting in a thin film with uniform chemical composition. Also, it is a wet chemistry process where the precursors are commonly in the form of colloidal solutions that transform into extensive networks of discrete or continuously-connected molecules. The sol-gel method facilitates fine-tuning of coating parameters including, homogeneity, thickness, particle size distribution, absorber particle size and chemical composition of the synthesized thin film. All these eventually make the sol-gel technique a good prospect for scaling up to an industrial level [8-10]. Dutta et al. [11] carried out a comparative study of sol-gel versus sputtering ITO thin films, and they proposed that a simple and low-cost sol-gel method can effectively replace the expensive sputtering technique in fabricating high quality ITO thin films. The most important benefit of the sol-gel process over conventional coating techniques is its capability to tailor the microstructure of the fabricated coatings at low temperatures [12].

1.2. Literature Review of Transparent Conductive Materials

The past few decades have witnessed an extraordinary increase in both volume and variety of optoelectronic applications in to the consumer-electronic markets. Along with this growth, there has also been a switch to devices that provide eye-catching features including energy efficiency, transparency, tactility, stretchability and flexibility [13]. Most optoelectronic devices with these properties necessitate transparent electrodes that facilitate these functionalities. Sustainable production of transparent electrodes with easily available raw materials is also an important benchmark for successful commercialization. The well-known TCMs include metal oxide thin films so-called transparent conductive oxides (TCOs), graphene, carbon nanotubes, metal nano (-particles, --wires and rods) and conductive polymers. This section includes comprehensive
literature reviews, fundamental theories and principles, and recently published studies on the importance, characteristics and applications of metal oxides based transparent conductive coatings for their optoelectronic and mechanical properties.

1.3. Recent Advances in Metal Oxide Based Transparent Conductive Coatings

Electrically conductive and optically transparent TCOs thin films are an extraordinary class of material that achieves high value of electrical conductivity while maintaining a high optical transparency in the visible region of the light spectrum. Since the first realization of such type of material, vast amount of research and development have been gone into marketable these thin films. The combination of optical transparency and electrical conductivity of TCOs is usually not observed in stoichiometric materials, but can be successfully achieved by fabricating these materials with a non-stoichiometric composition or by incorporating appropriate dopants to the host lattice.

The most common commercial TCM products so far are based on TCOs materials. In 1907 Baedeker discovered that he could produce a transparent thin cadmium film while sustaining electrical conductivity by thermally oxidizing cadmium to produce a cadmium oxide (CdO) thin film. In 1937, a tin oxide thin film was fabricated by post-oxidation of an evaporated metal film. With the development of the chemical deposition process (pyrolysis) in 1940s, tin oxide (SnO$_2$) from SnCl$_4$ and indium oxide from InCl$_3$ were synthesized and the indium oxide thin film had electrical conductivity of 10 S/cm. The early uses of TCOs were as transparent electrodes and anti-static coatings in electroluminescent panels and as transparent electrical heaters for airplane windshield de-frosting in World War 2 [14]. With the development of vacuum deposition systems in the late 1950s and 1960s, ITO thin films were successfully fabricated via vacuum evaporation of In/Sn metals and via direct current (DC) and radio frequency (RF) sputtering of metal In/Sn alloy targets. Thin film deposition of metal oxide compounds using vacuum evaporation was found to be a more controllable process starting with fully oxidized (stoichiometric) or partially oxidized (sub-oxide) materials, than starting with metal targets and supplying the required amount of oxygen for reaction. Studies on preparing and sintering powders of metal oxides as sputtering targets to fabricate TCO thin films started, in order to attain an easy and scalable process. Vossen in 1970s [15] used oxidized targets and an RF sputtering system to fabricate ITO and SnO$_2$ films. Investigation of doped binary compounds
such as indium oxide and tin oxide were continued in the 1980s along with huge developments in vacuum deposition hardware and equipment.

Most TCOs are binary or ternary compounds, containing one or two metallic elements. Their resistivity can be as low as $10^{-4}$ $\Omega\cdot$cm, and their wide optical band gap ($E_g$) can be greater than 3 eV. Although, this combination of conductivity and transparency is usually impossible in intrinsic stoichiometric oxides, it can be achieved by producing a non-stoichiometric material or by doping.

The usefulness of transparent conductive oxide thin films depends on both their electrical and optical properties. Therefore, both these parameters have to be considered together with other parameters such as stability, electron work function, corrosion resistance, mechanical flexibility and compatibility with substrate as appropriate for the applications [16, 17]. Other considerations are the readily available raw materials and their recyclability along with economical and sustainable fabrication method which are important criteria in choosing the appropriate TCO materials for successful commercialization [18].

The demand for TCOs has risen recently due to their role as key components of electrodes in touch screen technology, liquid crystal displays and photovoltaic solar cells [19-21]. Other applications include waveguides in plasmonic devices, bio-analytical devices, antireflective coatings and organic light emitting devices [22-25]. So far, the highest dollar-value market for TCOs is as transparent electrodes in flat panel displays, valued at $US 97 billion in 2014 and expected to reach $US 135 billion in 2020 [26].

During the last three to four decades, countless TCOs were developed from this interesting field. While some of the TCOs had long been known as intrinsic $n$-type semiconductors, their potential as transparent conductive materials came to be realized later by numerous research groups [27]. Efforts speedily moved on from intrinsically (un-doped) TCOs in which the conductivity is related to oxygen vacancies, defects and lattice interstitial, to extrinsically (doped) TCOs such as ITO and indium doped tin oxide [28, 29]. The most common TCOs have been so far tin oxide (SnO$_2$), indium oxide (In$_2$O$_3$), indium tin oxide (In$_2$O$_3$;Sn or ITO), zinc oxide (ZnO) and aluminium doped zinc oxide (AZO), which have found application in electronic and
optoelectronic devices[30-33]. Of these TCOs, ITO is the most important TCO used in the last few decades.

1.4. Strategies to Obtain High Carrier Concentration in TCO Materials

Works have been carried out to improve the performance of ITO based transparent conductive coatings via enhancing the electrical and optical characteristics. Most of the efforts were focused on improving the electrical properties while maintaining the optical transparency [34]. This can be achieved throughout different processes, systems and mechanisms including doping, thermal treatment, or incorporating with other materials, etc. The most effective way was found to be by using a suitable dopant atom which results in increasing the carrier concentration in the film material [35]. Both carrier concentration and carrier mobility were reported to be crucial factors for improving electrical conductivity [36-38].

The number of electrons in TCO materials can be increased by doping them with elements that have higher valence electron count than that of the host. For instance, tin atoms with a valence of four acts as a cationic dopant in the indium oxide lattice when replacing indium. Since indium has a valence of three, the Sn can donate an electron to the conduction band results in n-doping of the lattice. Furthermore, there are studies on the use of tellurium (Te) [39], erbium (Er) [40, 41], germanium (Ge) [42, 43], silicon (Si) [44], fluorine (F) [45-47], sulphur (S) [48] and zinc (Zn) [49-51] as dopants for indium. Nevertheless, most studies have been carried out on tin-doped indium oxide [52-54]. All the aforementioned studies aimed to maximize the carrier concentration, thereby improving the electrical conductivity of the film coatings without altering their carrier mobility. The relatively low impurity concentration in the host matrix (~ 1 - 5 at %) is a trade-off between carrier concentration and increasing scattering centres at the dopant sites. When the carrier concentration in a TCO is very low compared to a metal element, the mobility of these carriers becomes a very important factor in determining the electrical conductivity of the TCO [55]. Other macroscopic parameters to optimise the doping level have also been postulated. For example, a high dopant level leads to distortion of the crystal structure, therefore neither the generation of oxygen vacancies nor the generation of Sn$^{4+}$ ions on substitutional sites will be effective [56]. Also, excessive distortion in the form of an inter-granular amorphous phase is observed [57, 58]. On the other hand, it has been reported that excessive tin oxide inversely affected the characteristics of ITO coatings through the formation of a continuous SnO$_2$
precipitate at the grain boundaries [59]. Since doping is the most effective mechanism to improve the optoelectronic characteristics of ITO, different types of elements were employed recently for this purpose. While some of these elements have different ionic radii relative to the host ions, others were nominated based on their physical or chemical nature, stability, robustness, high work function, etc. These elements include silver (Ag) [60], copper (Cu) [61], titanium (Ti) [62], molybdenum (Mo) [63] and chromium (Cr) [64], to name a few. Introduction of an impurity atom with smaller ionic radius than that of the host ensures that the original crystalline structure will not change, however, this dopant could enhance the crystalline quality of the host [65].

The effect of thermal treatment onto the electrical properties has also been extensively studied. Heat treatment can be performed either through the deposition process (pre-heating the substrate) or after deposition process (post annealing). Currently, the majority of the fabrication techniques include a relatively high substrate temperature ($\geq300$ °C). It has been reported that the sputtered ITO film exhibits a structure changing from amorphous to polycrystalline after annealing [66]. Also, thermal annealing can oxidize the non-stoichiometric compositions of both indium oxide and tin oxide and results in a re-arrangement of the atoms in the form of stable polycrystalline thin films [67]. Beside the traditional heat treatment process, post annealing in vacuum and in oil bath was also reported. An ITO thin film annealed at 350 °C in silicon oil was reported to show a better crystalline structure with grain size of 51 nm compared to the same thin film annealed at same temperature under vacuum [68].

1.5. Strategies to Obtain High Carrier Mobility in TCO Materials

Conventionally, the carrier mobility has been increased by enhancing the crystalline quality by means of appropriate thermal treatment, choice of suitable deposition technique and choice of substrate. It has been widely reported that TCO thin films fabricated without pre heating the substrate or post annealing process show low carrier mobility due to scattering by point defects and/or grain boundaries [69, 70]. However, a post deposition calcination process even at ambient conditions decreases point and dislocation defects in amorphous or poorly crystallised TCO thin films, by enlarging their crystallite size and improving the overall crystallite quality [71]. Another very important factor that controls the properties of TCO thin films is selecting a suitable deposition method and its corresponding conditions. For example, TCO thin films
prepared with highly energetic particles may have large crystallite size, however, an extreme transfer of momentum could deteriorate the film structure and therefore the carrier mobility [72]. For instance, the discharge voltage at the surface of the target (during sputtering deposition process) repels both neutral argon atoms and negative oxygen ions that reach the substrate with kinetic energy (~100eV) and distorts the crystal lattice of the TCO thin film [73]. Therefore, RF sputtering with low discharge voltage is preferred for obtaining TCO films with high values of carrier mobility [74]. A typical system of pulsed laser deposition with kinetic energy of particles varied from (1eV – 100eV) was reported to be easier to control than sputtering, and resulted in better TCO thin film structures and higher carrier mobility [75]. Control of crystal structure of the TCO thin film by using a highly oriented substrate can also increase the carrier mobility by improving the film crystallinity. ITO thin films are often grown on yttria-stabilised zirconia (YSZ) substrate because the lattice constant matching between ITO or indium oxide (10.18Å) and YSZ (10.20Å) is excellent. Kamie et al. have used an electron beam deposition technique to grow epitaxial ITO layers onto (111) YSZ substrate [76]. Their results indicated that the ITO layers have excellent crystallinity as confirmed by reflective high energy electron diffraction, low energy electron diffraction and X-ray photoelectron diffraction. These ITO layers also demonstrated carrier mobility in the range of (30 - 40) cm² V⁻¹ s⁻¹ at room temperature.

So far, the manufacturing of TCOs has been limited to three metal oxides, In₂O₃, SnO₂ and ZnO along with mixtures of these such as ITO and zinc-doped In₂O₃ (IZO) [77] or with other dopants such as fluorine (F), antimony (Sb), gallium (Ga), aluminium (Al), boron (B) etc. that yield F-doped SnO₂ [78, 79], Sb-doped SnO₂ [55, 80], F-doped ZnO [81, 82], Ga-doped ZnO [83, 84], Al-doped ZnO [85, 86], B-doped ZnO [87, 88] etc. As for other conventional TCOs, these materials are formed with metal atoms that have electronic configuration of (n-1)d¹⁰ns² [89, 90]. The excellent interaction of oxygen p states and metal s states leads to metal-oxide orbital overlap in these structures and gives rise to low effective electron masses, thereby, the formation of a wide band gap energy (Eg > 3 eV), permitting the transmittance of light in the visible region and below. All these materials are very important host lattices for optoelectronic applications [91, 92]. Recently, other materials with TCO characteristics were reported including titanium oxide (TiO₂) and calcium aluminate (12CaO.7Al₂O₃) [93, 94]. Binary and ternary compounds and solid solutions with suitable optical, electrical and mechanical characteristics have also been developed for numerous applications [95-97]. Since early in the 1990s, multi-cation TCOs which
consist of metal ions beyond the conventional In, Sn, Zn and Cd have been developed. These materials which include Ga$_2$O$_3$, GaInO$_3$ and MgIn$_2$O$_4$ have attracted wide attention [98]. Multication oxides of InGaZnO$_4$, InGaMgO$_4$, InAlMgO$_4$ and InAlCdO$_4$ fabricated in the form of layered structures which have identified the hybrid nature of the conduction band due to the strong hybridization between the states of each cation and its neighbouring oxygen atoms in the matrix [99-101]. An interesting approach for improving the TCOs performance was based on employing correlated metals such as SrVO$_3$ and CaVO$_3$, where strong electron-electron interaction leads to a significant increase in the density of effective electron mass in the TCO matrix and hence decrease the plasma frequency at fixed electrical resistivity [102]. Table 1.1 summarizes some important TCO materials and their related dopants and compounds.

Table 1.1 Typical TCO materials and their related dopants and compounds

<table>
<thead>
<tr>
<th>Materials</th>
<th>Dopants or compounds</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>In$_2$O$_3$</td>
<td>Sn, Ti, Mo, Zr, Ge, Ta, Hf, W, Te, F, Nb</td>
<td>[30, 103-105]</td>
</tr>
<tr>
<td>SnO$_2$</td>
<td>As, Nb, F, Ta</td>
<td>[106, 107]</td>
</tr>
<tr>
<td>ZnO</td>
<td>Al, Ga, In, B, F, Ti, Zr, Y, S, Hf, V, Sc, Ge</td>
<td>[108-110]</td>
</tr>
<tr>
<td>Ga$_2$O$_3$</td>
<td>Sn</td>
<td>[111, 112]</td>
</tr>
<tr>
<td>CdO</td>
<td>In, Sn, Sm</td>
<td>[113, 114]</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>Nb, V, Ta</td>
<td>[115-118]</td>
</tr>
<tr>
<td>In$_2$O$_3$-ZnO</td>
<td>Zn$_2$In$_2$O$_5$, Zn$_3$In$_2$O$_6$</td>
<td>[119]</td>
</tr>
<tr>
<td>In$_2$O$_3$-SnO$_2$</td>
<td>In$_4$Sn$<em>3$O$</em>{12}$</td>
<td>[120]</td>
</tr>
<tr>
<td>ZnO-SnO$_2$</td>
<td>Zn$_2$SnO$_4$, ZnSnO$_3$</td>
<td>[121, 122]</td>
</tr>
<tr>
<td>GaInO$_3$, (Ga, In)$_2$O$_3$</td>
<td>Sn, Ge</td>
<td>[123]</td>
</tr>
<tr>
<td>Zn-In$_2$O$_3$-SnO$_2$</td>
<td>Zn$_3$In$_2$O$_5$-In$_4$Sn$<em>3$O$</em>{12}$</td>
<td>[77]</td>
</tr>
<tr>
<td>CdO-In$_2$O$_3$-SnO$_2$</td>
<td>CdIn$_2$O$_4$-Cd$_2$SnO$_4$</td>
<td>[124]</td>
</tr>
<tr>
<td>CdSb$_2$O$_6$</td>
<td>Y</td>
<td>[125]</td>
</tr>
</tbody>
</table>
1.6. P-Type Transparent Conductors

All high performance TCOs used in industrial applications are n-type binary systems with polycrystalline features and doped with halides, group XIII or XV elements. Equivalent p-type transparent conductive materials have yet to be industrialized. Recently, there have been some reports on p-type transparent conductors in the literature; however, their electrical conductivities and figures of merit are still orders of magnitudes less than those of n-type transparent conductors. Transparent p-type conductors could be useful in numerous applications including, interconnection layers (recombination junctions) in tandem photovoltaic, electrodes provide carrier selectivity and carrier collection in photovoltaic devices and electrodes for fully transparent devices [126]. Fabricating an optimal un-doped or doped p-type TCO seems to be more difficult than n-type TCOs. This difficulty stems from the ionicity of the metallic atoms and the electronic structure of the wide band gap metal oxide with strong localization of holes (large effective mass) at oxygen 2p states [127]. These localized holes require high energy to overcome a high ionization potential in order to move through the crystal lattice, resulting in low hole-mobility [128]. To cope with this result and improve the hole-mobility, most p-type TCOs similar to their n-type counterparts, require high thermal treatment to enhance their crystal quality. The highest p-type conductivity of 220 Scm$^{-1}$ was reported for Mg-doped CuCrO$_2$ thin film [129]. High p-type conductivity has also been investigated practically in perovskites-structured TCOs such as SrIn$_x$Ti$_{1-x}$O$_3$ and Sr$_x$La$_{1-x}$CrO$_3$ [130, 131], spinel-structured TCOs such as NiCo$_2$O$_4$ [132] and composite or amorphous oxides such as In-doped MoO$_3$ and ZnO-Rh$_2$O$_3$ [133, 134].

An alternative strategy is to look beyond oxides to materials such as CuI [135, 136]. Non-oxide wide band gap materials with N, S or P anions have also attracted much attention for p-type materials due to their more delocalized valence bands resulting in lower hole effective masses [128]. This new strategy has been established experimentally via Cu-based transparent chalcogenides and oxychalcogenides include BaCu$_2$S$_2$, CuAlS$_2$, BaCu$_2$(S, Se)F and Cu-Zn-S which resolve the issues of localised O 2p orbital, achieving electrical conductivity higher than 10 Scm$^{-1}$ [137-139].

The majority of the p-type transparent conducting materials discussed previously have carrier concentrations of the order of (10$^{17}$ - 10$^{19}$ cm$^{-3}$) and usually conduct by hopping mechanism or an
activated transport mechanism. For instance, the chalcogenide-based systems are degenerately doped semiconductors with a conductivity found to be independent of temperature, limited by ionized impurity scattering and have smaller band gap energy compared to oxides. Compensation by deep donors could decrease the hole density and the mobility through increasing ionized impurity scattering. This trade-off was discovered theoretically for some oxide based materials investigations [140]; however, a more general process directing non-oxides would be valuable. To avoid this trade-off, Varley et al. proposed a system of boron phosphide with wide band gap larger than 3.1 eV and low hole mass [141]. To conclude, while $n$-type TCOs can achieve high conductivity even in their amorphous state, $p$-type TCOs show lower conductivity at quite high temperature.

1.7. Introduction to ITO Thin Films

Indium Oxide and Indium Tin Oxide (ITO) are very interesting transparent conducting oxides (TCOs). Although band theory predicts them to have wide direct band gaps ($> 3.5$ eV), they are electrically conductive $n$-type semiconductors. The direct wide band gap makes the transmission window between wavelengths 300 - 1500 nm, depending on the processing conditions. In the ultraviolet region - high energy (short wavelengths) electronic transitions from the valence band to the empty states in the conduction band limit the transmission up to the band gap. In the infrared region - low energy (long wavelengths) light is reflected due to the quasi-free electron plasma. Therefore, the wavelength cut-off in the infrared region depends on the charge carrier density. Weiher and Ley [142] have calculated the indirect band gap for ITO which is about 2.62eV, but it is still not widely reported in the literature. The combination of high transmittance in the visible range and high electrical conductivity, make ITO thin films suitable for optoelectronic and electroluminescence applications. Typical ITO films have transmittance close to 90% in the range of 400 - 700 nm and electrical resistivity below $2 \times 10^{-4}$ $\Omega \cdot$cm. ITO films also have high luminous transmittance, high infrared reflectance, excellent substrate adherence, quite good hardness ($\sim 5 – 6$ GPa), and chemical inertness.

1.7.1. Indium Oxide and Indium Tin Oxide Structure

The structure of Indium tin oxide (ITO) and indium oxide (In$_2$O$_3$) are closely related. During the synthesis of In$_2$O$_3$, which is classified as an ionically bound semiconductor oxide, some defects
are formed and these defects involve interstitial indium atoms and oxygen vacancies. Since these defects are electrically charged, ionized impurity scattering is unavoidable in In$_2$O$_3$ and ITO. In$_2$O$_3$ crystallizes in a cubic bixbyite structure (C-type rare-earth sesquioxide structure) with a space group $Ia3$ and a standard lattice parameter of 10.118 Å (JCBDS card no. 06-0416). The In$_2$O$_3$ unit cell consists of 80 atoms, which show a fluorite-related superstructure Figure 1.1.

![Figure 1.1 Bixbyite crystal structure of In$_2$O$_3$ [143]](image)

One quarter of the oxygen anions residing along the four $<111>$ axes are missing, 32 sites are occupied by cations located in two non-equivalent six-fold coordinated sites, 8 In$^{3+}$ ions are located on trigonally compressed octahedral sites named as (b site) and the rest of the In$^{3+}$ ions are located at highly distorted octahedral sites (d site). Both b and d sites can be described as a cube with eight corners and the indium atoms exist in the centre of this distorted cube. Six corners occupied by oxygen atoms and the remaining two corners are empty. In the b sites, the oxygen vacancies are located along the body diagonal while, they are located along the face
diagonal for the d sites. Figure 1.2 shows the schematic representation of cubic \( \text{In}_2\text{O}_3 \) structure with two non-equivalent cataionic b and d sites.

Based on his in-situ electrical property measurements, De Wit [144] reported that \( \text{In}_2\text{O}_3 \) is an anion-deficient \( n \)-type semiconductor where the intrinsic oxygen vacancies population (~ 1%) limits the electron concentration. This electron concentration deficiency continues at high temperature even under equilibrium deposition conditions.

![Figure 1.2 In\(_2\)O\(_3\) structure with two non-equivalent cataionic b and d sites [145]](image)

Indium Tin Oxide (ITO) is produced by doping \( \text{In}_2\text{O}_3 \) with tin (Sn) atoms which replace the \( \text{In}^{3+} \) atoms from the cubic bixbyite structure of indium oxide. ITO films have a lattice parameter in the range of (10.12 - 10.31 Å) close to that of \( \text{In}_2\text{O}_3 \) (10.118 Å). The Sn atoms create an interstitial bond with oxygen and form \( \text{SnO} \) or \( \text{SnO}_2 \). Thus, they have a valency of +2 or +4, respectively, which has a direct effect on the conductivity of ITO. The \( \text{SnO}_2 \) (\( \text{Sn}^{4+} \)) acts as an \( n \)-type donor releasing electrons to the conduction band. On the other hand, the lower valence state occurs due to the reduction in carrier concentration which results because a hole is created and acts as a trap and reduces conductivity. However, in ITO, not only the tin atoms but also oxygen vacancies contribute to the carrier density and hence to the high conductivity, where in the ideal case, each doubly charged oxygen vacancy contributes two free electrons. It has been observed that the Sn dopant concentration can play an important role in controlling defects that are
Theoretical electronic structure calculations by Odaka et al. [146] used a primitive unit cell having 40 atoms (similar to that of In$_2$O$_3$ crystal). With one In atom either at b-site or d-site substituted by an Sn atom, resulting in a system of 2.5 at.% Sn concentration along with approximately $1 \times 10^{21}$ cm$^{-3}$ free electron concentration, if each substituted Sn atom donated one electron. The latter theoretical calculation is in good agreement with the experimental results reported by Shigesato et al. [36] on ITO thin films having the same free electron concentration along with very low electrical resistivity. This implies that the super-cell model appears to be a useful approximation of real ITO thin film coatings.

1.7.1.1. **Indium Oxide and Indium Tin Oxide Band Structures**

Despite the observed high sensitivity of their characteristics to growth conditions [147], it is generally accepted that the electronic band structure is a key factor for understanding the unique interplay between electrical and optical properties of TCOs. However, the band structure of In$_2$O$_3$ and ITO is very complicated to model due to the complexity of both the lattice structure and electronic interaction in these materials. Therefore, the characteristics of In$_2$O$_3$ and ITO are commonly described and discussed on the basis of an assumed band structure comprising of an isotropic parabolic conduction band [146].

Based on Electron Spectroscopy for Chemical Analysis (ESCA)/XPS measurements, Fan and Goodenough [148] were the first to report a typical schematic energy band model for In$_2$O$_3$ and ITO as presented in Figure 1.3. Although this band model is generally simplified, it is still widely used and the only one offering a qualitative explanation of the observed concurrent high electrical conductivity and optical transparency in ITO thin films. This band model shows band gap energy of (3.5eV) along with high optical transparency in the visible region. The conduction
band was assumed to be principally from indium 5s electrons while the valence band from oxygen 2p electrons and the Fermi level is very close to the conduction band.

![Energy band diagram for ITO](image)

Figure 1.3 Schematic diagram of the energy band model for ITO adopted (a) low doping level and (b) high doping level [148]

At low doping level, the density of states for donor atoms is low and is formed below the conduction band while the Fermi level lies between the donor level and the bottom band edge of the conduction band (Figure 1.3a). On the other hand, at high doping level, the donor density increases and the donor states overlap the conduction band (Figure 1.3b).

1.7.1.2. Recent Advances in ITO Based TCOs

As stated earlier, ITO remains the key component in most optoelectronic devices that require transparent conductive electrodes owing to its two key characteristics, electrical conductivity and
optical transparency in the visible range. ITO has been fabricated in different forms, shapes and structures including thin films, nanoparticles, nanowires, nanorods, 2D and 3D structures. Of these, ITO thin films have been widely fabricated and studied as a function of deposition technique and conditions, dopant types, dopant concentration, substrate types, film thickness, etc. As for other TCOs, all these parameters were found to play significant roles in improving the performance of TCO thin films through enhancing both electrical conductivity and optical transparency which also strongly depend on the crystalline structure of the ITO thin film. It has been extensively observed that heat treatment led to enhanced crystalline quality of ITO thin films along with their grain size, thereby, improving the optoelectronic performance [149]. The properties of ITO thin films are strongly dependent on different parameters including thin film nature, geometry (thickness), which are also associated with deposition techniques and their corresponding conditions and post deposition processes. Recently, Amalathas and Alkaisi have reported that the electrical and optical properties of sputtered ITO thin films are strongly dependent on the film thickness. They found that when the film thickness increased from 75 nm to 225 nm, the minimum sheet resistance assigned to be 27.5 Ω/sq along with carrier concentration of $1.12 \times 10^{21}$ cm$^{-3}$ were achieved [150]. Further investigations on the effect of ITO film thickness on the optoelectronic characteristics have also been carried out by many groups of researchers [52, 151, 152]. Additionally, efforts on employing an appropriate dopant to improve the carrier mobility of ITO thin films were made. Other dopants including Mo, W, Ti and Nb have also shown promise. A Mo-doped ITO thin film with a molar ratio (In:Sn:Mo = 9.6:2:2) was prepared via aerosol-assisted chemical vapor deposition (AACVD) and exhibited a mobility of the order of 119 cm$^{2}$ V$^{-1}$ s$^{-1}$ compared with the same thin film without Mo which showed a mobility of 25 cm$^{2}$ V$^{-1}$ s$^{-1}$. With further increase of the Mo (mol%) up to 5(mol%), the mobility dropped to 109 cm$^{2}$ V$^{-1}$ s$^{-1}$ while the carrier concentration increased to $7 \times 10^{20}$ cm$^{-3}$ yielding the lowest resistivity of $8.3 \times 10^{-5}$ Ω cm [153]. This implies that higher conductivity is best achieved through combining high mobility with relatively low carrier concentration rather than low mobility with higher carrier concentration.

Since the deposition technique also exerts a significant impact on the performance of an ITO thin film, different techniques have been employed to fabricate high quality ITO coatings and the competition between these techniques continues up to the present. DC sputtering and RF
sputtering [154, 155] are the most widely used techniques for fabricating ITO based TCO coatings for industrial development, due to high deposition rate, possibility of using available sputtering system and good reproducibility [5]. Other techniques such as chemical vapor deposition (CVD), Pulsed laser deposition (PLD), thermal evaporation, electron beam evaporation, spray pyrolysis, sol-gel process, to name a few, have also been employed for this purpose [6, 156-160]. Usually, magnetron sputtering depositions are implemented at high substrate temperatures which achieve the best results in terms of thin film conductivity and transparency. However, numerous applications such as flexible devices require a quite low deposition temperature. For this reason, the RF sputtering technique was mostly employed by researchers to investigate this challenging task.

The increasing demands for advanced devices requires new electrodes with a resistivity lower than that achieved before and with optical properties higher than those of the present generation of materials. Minimizing the consumption of indium while maintaining the optoelectronic properties may be achieved by combining ITO films with other thin metal films that have a resistivity in the range of $10^{-6}$ $\Omega$cm. Bi-layer and multi-layer systems have been reported to be an efficient strategy for obtaining high quality ITO based TCO thin films. Of these systems, combining a metal layer with ITO thin films (i.e., ITO/metal or metal/ITO), insertion of a metal layer between two ITO thin films (ITO/metal/ITO) or even encapsulating ITO thin film by two metal layers (metal/ITO/metal) have been proposed as new strategies for TCM production. Although (metal/ITO/metal) and metal/ITO structure offer very low electrical resistivity, they suffer from a great reduction in optical transparency due to the single or double opaque metal layer. Recently, bi-layer ITO/metal thin films were reported by Ng et al. [161]. The authors investigated the effect of different types of metal layers such as (Ag, AuSn, In, Ni, Sn and SiO$_2$) on the optical and electrical properties of ITO thin films. Their results showed a decrease in the electrical resistivity from $16.2 \times 10^{-4}$ to $7.58 \times 10^{-4}$ $\Omega$ cm by inserting a thin metal layer underneath the ITO film. TCO/metal/TCO multilayer structures have also been proposed to be interesting TCOs due to their higher electrical and optical properties relative to those of a single-layered TCO thin film. This multi-layer structure gives excellent optoelectronic properties despite its quite low thickness. Most of these structures were fabricated to be 100 nm thick or less from similar or even different TCOs thin films encapsulating a thin metal layer. This metal layer is the key aspect to determine the lowest available resistivity. Silver is the most widely
used metal in these systems due to its very low electrical resistance compared to other elements [162].

Optimization of the electrical and optical characteristics of sputtered indium gallium zinc oxide/Ag/indium gallium zinc oxide (IGZO/Ag/IGZO) multilayer thin films with respect to IGZO film thickness has been investigated by Kim and his research group [163]. In their study, the authors reported that the transmission edge slightly broadened and red shifted toward lower energies and the free carrier density decreased while the mobility was almost stable along with increasing IGZO thickness. Also, for further understanding the optical properties, the authors recalculated the transmittance spectra in the wavelength range (300 – 800 nm) using Finite-Difference Time-Domain (FDTD) modeling. Theoretical results for transmittance spectra were fairly similar to the experimental ones. Nickel doped indium zinc oxide (NIZO) multilayer thin films with Ag layer were deposited via RF magnetron sputtering technique and studied as effective transparent conductive electrodes for liquid crystal display (LCD) devices. Despite the loss of optical transparency, the Ag layer brought improvement in the electrical resistivity and figure of merit values [164]. Besides Ag, other conductive elements including gold (Au), copper (Cu), chromium (Cr), platinum (Pt) etc., to name a few, have also been employed in such thin film systems [165-168]. The majority of recent thin film solar cells and flat panel displays are based on glass substrates which offer a rigid support and can withstand high temperatures required for consecutive fabricating processes [169-172]. However, it is important to replace the rigid substrates by flexible plastics which provide easier handling than panes of glass. Polymer foils and/or flexible substrates are light, bendable and have a price advantage relative to rigid glass, thereby, allowing cost-effective mass production by a roll-to-roll (R2R) manufacturing processes [20]. However, they cannot withstand the high temperature required for industrial mass production processes. On the other hand, it is very difficult to fabricate high quality transparent electrodes on these substrates due to the quite high temperature required for obtaining high electrical conductivity. Compared to a single-layered traditional ITO thin film, the tri-layer systems have exhibited high conductivity, low absorption in the visible range and room temperature deposition process. The latter has encouraged researchers around the world to develop low temperature thin film coatings [173-175]. The most recent investigation in this sense was made by Kim et al. on sputtered ITO/Ag/ITO thin film at room temperature as electrodes for organic solar cells [176]. The authors have reported superior results of this coating system
compared with those of a high-temperature-fabricated single-layered ITO thin film. Silver oxide has also been reported as a substitute for the metal layer in tri-layer thin film coatings for flexible electronic applications. The observed optoelectronic results of ITO/AgOx/ITO are comparable with those of common ITO/Ag/ITO; however, an improvement in the power-conversion efficiency was achieved for highly flexible organic solar cells (OSCs) [177]. All the aforementioned multilayer thin films were fabricated using Dc or RF sputtering system. However, other techniques such as thermal evaporation and direct laser patterning have also been used for depositing such coatings [178-180].

Recently, ITO has been investigated in different forms such as nanoparticles, nanowires, nanorod, 2D and 3D structure. The XRD analysis carried out by Pramod et al. on indium oxide nanoparticles confirms the formation of polycrystalline features similar to that of layered ITO thin films [181]. Also, the authors discussed and calculated the optical properties in terms of transparency, direct and indirect optical band gap. Further investigations on the gas sensing properties of the prepared thin films have also been reported by the authors. Surface modification of ITO nanoparticles have been reported by Lee and co-authors [182]. In their study, the authors demonstrated that effective surfactant removal can improve the electronic performance of ITO nanoparticles, which were uniformly assembled onto glass and silicon substrates via a spin-coating process. ITO nanorods were employed as an anode in polymer light emitting diodes (LEDs). The optical characteristics of these nanorods were investigated via dark-field optical microscopy and transmission spectroscopy, and the results revealed that the optical transparency and the light scattering properties of ITO nanorods were better than those of ITO thin films [183]. Additionally, multifunctional single crystalline ITO nanowires with controlled Sn doping were fabricated through a vapor transport process by Gao et al. [184]. The authors have reported these ITO nanowires as promising TCOs where a thin film of these nanowires exhibits a sheet resistance as low as 6.4 Ω/sq and measurements on single nanowire show a resistivity of the order of $2.4 \times 10^{-4}$ Ω cm along with free carrier density up to $2.6 \times 10^{20}$ cm$^{-3}$. ITO thin films are also fabricated and characterized as a three dimensionally structured electrode for current collection applications in lithium ion (Li-ion) batteries [185]. Further investigations on the electrochemical stability of this 3D structure of ITO with WO$_3$ as a negative electrode demonstrates the 3D ITO structure can successfully perform as a suitable current collector.
1.7.1.3. Survey of the progress of sol-gel derived ITO based TCO coatings

So far, the sol-gel process has been developed and extensively used as alternative technique for producing different kinds of transparent conductive thin films. This section presents a survey of using the sol-gel process for fabricating ITO based TCO thin films.

Kesim and Durucan [186] have been reported the effect of incorporating oxalic acid dihydrate in ITO solution on to the optoelectronic properties of ITO thin films. The oxalic acid concentration in the ITO solution was varied (0.05, 0.1, 0.3, 0.5 or 1.0) M. Their results show that the film formation efficiency, homogeneity and surface coverage were improved with the addition of oxalic acid. Also, a sheet resistance of 3.8 kΩ/sq and optical transparency of 93% were achieved for 45 nm ITO film. Eco-friendly pure aqueous sol-gel process was modified by Misra [187] and co-authors to fabricate ITO thin films. DI-water was used as an alternative to organic solvents for preparing the ITO solution, and the resulted thin films were annealed at (200 – 400 °C) in step of 50 °C, and treated with argon plasma. The authors reported that the sheet resistance of 45 nm ITO thin film was considerably decreased to 443 Ω/sq after 2h of plasma treatment. In addition, the XPS results established that the number of oxygen vacancies in thin ITO film increased with increasing annealing temperature and applying the plasma treatment. Ren et al [188] have studied the effect of using benzoylacetone (BzAch) as a chemical modifier in the preparation of nanocrystalline ITO films with plasmon electrochromic properties. The BzAch was found to decrease the crystallite size of ITO thin film, and the growth of these crystals was governed by varying the BzAch concentration in the ITO film materials. Also, ITO film shows significant localized surface plasmon resonance absorption features that can be influenced via electrochemical doping. The plasmonic mechanism in ITO films revealed a significant reversible and persistent variation in their optical transparency in the near-infrared range of the electromagnetic radiation.
1.7.2. Recent Advances of Some Characterization Techniques for ITO Based TCOs Coatings

1.7.2.1. XRD Analysis of ITO Based TCOs
The crystallographic characteristics are a key factor in improving the performance of ITO. The XRD spectra of the ITO thin films fabricated on glass substrates at room temperature have been widely reported to be amorphous in nature [189]; however, XRD analysis of ITO films synthesized at different temperatures shows the formation of crystalline structure. Bragg peaks observed around 31.5°, 35.5°, 51.2°, 60.8° were identified as a body centred cubic bixbyite structure with space group of $Ia\overline{3}/cubic$ and a lattice parameter of the order of 10.20Å similar to In$_2$O$_3$ (JCPDS card 06-0416). Features for polycrystalline ITO thin films are demonstrated by the (222), (400), (411), (332), (440) and (622) reflection directions of In$_2$O$_3$. Also, at high annealing temperature, the degree of crystallinity of ITO phase was improved along the (222) plane [190-192]. Both the cubic and rhombohedral structures with broadened diffraction lines were observed by Korosi and his research group [193] for spin coated ITO thin films treated with NH$_3$ and annealed at 550 °C. These broadened peaks reflect the overlap of several reflection lines of the aforementioned crystal phases.

1.7.2.2. Synchrotron X-ray Scattering Analysis of ITO Based TCOs
The structural evolution of transparent ITO/Ag/ITO thin films has been investigated as a function of annealing temperature by means of synchrotron X-ray scattering. The results showed that the as deposited and 200 °C annealed ITO/Ag/ITO thin films have similar weak (222) and (400) reflection planes of ITO. This shows that the synthesized thin films at low temperature consisted of nanocrystalline ITO and Ag phases and there was no significant change in the crystalline structure below 200 °C. With increasing annealing temperature above 300 °C, the ITO/Ag/ITO thin films shown strong crystalline structure with peaks featured at (211), (222), (400) and (440) reflection orientations similar to ITO, indicating high crystalline quality of the top and bottom ITO layers. Also, strong Ag peaks observed at (111) and (220) planes demonstrated enhanced crystal structure of the Ag layer after annealing [194].
1.7.2.3. XPS Analysis of ITO-Based TCOs

XPS analysis has been implemented to investigate the surface electronic structure of ITO coatings. Multiple oxidation states for indium e.g., In\(^0\) and In\(^{3+}\) and tin e.g., Sn\(^{2+}, \; 4^+\) were observed, while oxygen was from lattice, surface and subsurface. Residual carbon was also observed at the film surface even after etching. Removing the impurities from the top surface of sol-gel derived ITO thin film coatings has been reported to decrease the electrical resistivity of such coatings [195]. It was noted that the increase of tin concentration in the ITO matrix promoted the reduction of In\(^{3+}\) to In\(^0\) which is similar to oxygen being etched out of the film surface through argon sputtering [196-198].

1.7.2.4. High Resolution Transmission Electron Microscopy (HRTEM) Analysis of ITO Based TCOs

HRTEM analysis was performed to study the degradation mechanism of post annealed ITO/Ag/ITO thin films. The cross-sectional HRTEM image of as deposited ITO/Ag/ITO thin film shows well-defined top ITO layer, mid Ag layer and bottom ITO layer without any observable interfacial layers, and the mid layer appears as a continuously connected layer between both bottom and top ITO layers. On the other hand, cross sectional HRTEM images of 600 °C annealed ITO/Ag/ITO thin films show that discrete Ag islands were formed between the crystalline top and bottom ITO layers. Decreased optical transparency and increased electrical resistivity of annealed thin films was attributed to the formation of these discrete Ag islands which gave rise to light and electron scattering. The high magnification images of the as deposited and annealed samples expose the transformation of continuous Ag layer for as deposited sample to discrete Ag islands due to the agglomeration of Ag atoms during the annealing process. At high annealing temperature, the top ITO layer exhibited the formation of grain boundaries that act as an oxygen diffusion path from this top layer to the Ag layer. Further investigations reveal that in some regions, both the top and bottom layers were connected with the absence of the Ag layer due to lateral diffusion of Ag atoms. All these processes eventually
result in degradation of the electrical and optical properties of ITO/Ag/ITO thin films at high annealing temperature (600 °C) [194].

1.7.2.5. **Computational Modeling Analysis of ITO Based TCOs**

Computational modelling analysis of different materials and their corresponding structures and properties can be very beneficial in interpreting experimental results and identifying different types of materials for specific applications. So far, several investigations have focused on the principles and parameters required in development of ITO based TCOs.

ITO and indium oxide are reported to have similar body centred cubic (BCC) structure. The electronic characteristics including excitation energy, dipole momentum, frontier molecular orbital energies, absorption wavelengths, along with the complete vibrational analysis and the optimized structural parameter calculations of indium oxide were obtained from Time Dependent Density Function Theory (TD-DFT) and the Hartree-Fock approximation (HF), as reported by Panneerdoss et al. [199]. The authors have confirmed that indium oxide composites have BCC framework with C2v point group symmetry, and the most stable structure has a preferred (222) reflection plane of the bixbyite structure with symmetrical In-O bonds. In and O atoms are coupled linearly, where the O atom is centred and two In atoms bonded symmetrically with equal inter-nuclear distance to form a V-shape structure. Also, the calculated highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energies confirm the inter charge transformation within the structure, resulting in enhanced band gap energy.

1.7.2.6. **Mechanical Characteristics and Finite Element Modeling (FE) for ITO Based TCOs**

ITO is likely to be susceptible to cracking and delamination due to its brittle nature and to the large misfit in hardness and Young’s modulus values between the ITO coating and the substrate. Therefore, it is believed that the mechanical properties of ITO coatings play a significant role in determining the performance of the optoelectronic device. However, there is little information on the mechanical characteristics of ITO based TCO coatings particularly in the (nano- or micro-) structure scales. Recently, an interesting combination of experimental nanoindentation measurements and theoretical finite element modelling were performed by Gupta et al. to
investigate the mechanical behaviour of thick sputter deposited ITO thin films grown on Si substrate [200]. In their investigations, the contributions of the substrate and the film coating were considered in a power law formulation based nonlinear material model. Experimental $p-h$ curves were effectively simulated by finite element modelling. Also, the FE model successfully predicted the stress-strain curves, the vertical deformation distribution throughout the film thickness and the Von-Mises stress distribution with respect to the horizontal distance from the indenter to the axis of symmetry. The FE model also predicted yield strength of 2.2 GPa and 7.75 GPa for ITO thin film and silicon substrate, respectively.

1.8. Alternatives to Metal Oxides Based TCMs

With the vast demand for TCMs in recent decades, research on new materials which are non-metal oxide based transparent conductors has increased. These materials include graphene, CNTs, metal nanowires, conductive polymers and perovskite materials. AS for the TCOs, these materials have also witnessed a gradual development since their first discovery.

Two-dimensional (2D) materials have been extensively proposed as transparent conducting electrodes in electronic and optoelectronic devices due to their atomic monolayer thickness (that allowing high optical transparency over the visible range of the electromagnetic radiation) and the probability of ballistic transport (without electrons scattering even at room temperature). Among these materials, graphene layers are arguably the most widely used as potential TCMs for their high optical transparency (~2.3% visible light absorbed per single graphene layer), their high carrier mobility ($10^3$-$10^4$ cm$^2$V$^{-1}$s$^{-1}$) and their mechanical flexibility [201-203]. High electron mobility have been achieved for graphene thin films grown by CVD on boron nitride substrates [204]. Despite this high mobility, the electrical conductivity is quite low compared with other TCMs, which is largely due to its inherently low carrier density ($< 10^{13}$ cm$^{-3}$) [203].

Many investigations were carried out aiming to increase the carrier density via a multilayer graphene thin film growth [205], impurity doping [206] and a recent method using intercalation doping [207]. Also, graphene has proven itself operable in flexible PV devices under bending of 138° compared to operable bending of 60° in a brittle ITO cell [208]. It has been reported that four layers of graphene are required to obtain good optical transparency along with a sheet
resistance as low as that for ITO of the order of 30 $\Omega$/sq [209]. CNT networks are also one of the materials recently developed as an efficient substitute to ITO and other TCO materials in the state of the art of optoelectronic devices, particularly, those for flexible electronics, due to the extraordinary mechanical and electrical (even under extreme bending conditions) characteristics these networks possess [210]. CNTs have been extensively adopted for production of composite materials for printed electronics. Nano-composite films of CNTs were electrochemically deposited on conducting ITO and Ag grid printed on PET substrate, and the results revealed that the composite films exhibit non-linear optical characteristics along with antireflective performance over a visible to long IR range, allowing their potential application as optical materials [211]. Besides that, Mo and co-workers [212] have reported a high performance TC coating made by combining an Ag grid with CNTs. These thin films exhibit tremendous overall performance with a sheet resistance of 14.8 $\Omega$/sq and 82.6% transmittance at room temperature. Their analysis also indicates that the improvement in the conductivity of the hybrid Ag grid/CNTs coatings was related to the filling spaces between the Ag grids and interconnecting the CNTs with Ag nanoparticles. Moreover, the hybrid coatings exhibit high flexibility along with excellent mechanical strength compared to an ITO coating. The electrical and optical properties of CNT thin films were evaluated by Hwang et al. [213] as a function of post (fuming- and immersion-) nitric acid treatments. The treated CNT thin films possessed lower sheet resistance and improved optical transparency over the visible range of 210 $\Omega$/sq and 90%, respectively, compared to those thin films that had not undergone acid treatment. However, the mechanism by which acid treatment improved the optoelectronic properties of CNT based thin films is still unclear. Earlier reports attributed this improvement to the effective removal of residual amorphous carbon on the surface of CNTs and the decreasing of the cross-junction resistance between CNTs [214-216]. Additionally, a random mesh structure of metallic nanowire film coatings, especially Ag-NWs has attracted considerable attention as a high performance flexible TC film. These TC films have been extensively adopted in solar cells, displays and touchscreens to achieve new-generation optoelectronic devices that can be bent, compressed, stretched, twisted and deformed into complex, non-planar shapes while maintaining high conductive performance, integration and reliability. Lee et al. [217] have demonstrated Ag-NWs based flexible transparent conductive composite thin films comprise of a spin-coated Ag-NW layer followed by a buffer layer of sputtered indium doped zinc oxide (IZO). The latter has a
significant potential in prohibiting the surface oxidation of the Ag-NWs, thereby, successfully avoiding undesirable changes in the conductivity. In their study, a significant enhancement in the sheet resistance value of pristine Ag-NWs was achieved after being buffered with IZO layers, (19.84 Ω/sq and 10.35 Ω/sq) for Ag-NWs and Ag-NWs/IZO thin films, respectively. Recently, transparent conducting films (TCFs) based on Ag-NWs were successfully fabricated as a function of spraying times, annealing time and solution concentration through a simple spraying process by Hu and co-workers [218]. Polyvinylpyrrolidone (PVP) was used to modify the interface of the substrate. A quite stable low sheet resistance of 30 Ω/sq was obtained in this study, even after 500 cycles of bend testing with bending radius of 5 mm. Conductive polymers (so-called intrinsically conducting polymers) are organic polymers that possess excellent electrical conductivity. The superior potential of these materials is their simple processability, mainly by dispersion. PEDOT:PSS is the most extensively used and commercially available conducting polymer due to its high optical transparency, suitable thermal stability, high mechanical flexibility and easy solution based processability [219-222]. Unfortunately, it has low electrical conductivity compared to other conductive polymers. However, the conductivity of pure PEDOT:PSS has been improved through solvent treatment including dimethyl sulfoxide (DMSO), sulphuric acid (H_2SO_4) and ethylene glycol (EG) [223-225]. Introduction of appropriate dopant atoms has also proven to be beneficial in improving the conductivity of PEDOT:PSS films. In this sense, copper bromide (CuBr_2) has been adopted to dope PEDOT:PSS as the HTL in polymer solar cells [226]. A significant improvement in the conductivity and the power conversion efficiency (PCE) of doped PEDOT:PSS has been observed by the authors (5.6 × 10^{-2} Scm^{-1} and 7.05%, respectively) compared to those of undoped (1.9× 10^{-4} Scm^{-1} and 5.84%, respectively). This improvement has been attributed to two mechanisms, (1) the weakening of the cumblic attractions between PEDOT and PSS components, and (2) the increase of the work function value of PEDOT:PSS with CuBr_2 doping which results in increase of both the open circuit voltage (V_{oc}) and the filling factor (FF) of the solar cell. Further investigations to improve the performance of optoelectronic devices based on hybrid TCFs are continuing.
1.9. **Industrial Applications of TCO**

TCOs have been extensively used in various industrial applications and ITO seems to be the most widespread TCOs employed due to its advantages discussed previously, despite its cost perspective. The main three commercial applications of TCOs thin films in terms of the surface area covered and their total values are solar cells, flat panel displays and coatings on architectural glass.

1.9.1. **Transparent Conductive Electrodes in Solar Cells**

TCO films that act as transparent electrodes are employed in almost solar cells. The main considerations in selecting the appropriate TCO for this purpose, besides transparency and lateral conductivity, are processing requirements, electronic compatibility with adjacent layers in the solar cell and stability under environmental conditions. Design of a conventional photovoltaic (PV) solar cell consists of deposition of different layers consequently on rigid or flexible substrates such as glass or PET. Of course, some of these layers are TCO electrodes (anode and cathode). The TCO anode is deposited on glass substrate, followed by hole transparent layer (HTL) such as poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS). The photoactive layer which is directly connected to a low-work function and reflective metallic cathode is deposited upon the HTL. In some cases, there is no need for an intermediary electron transport layers (ETL). ITO is the most widely proposed TCO anode in a PV cell.

1.9.2. **Transparent Conductive Electrodes in Information Displays**

Since the mid-1990s, transparent organic light emitting diode (TOLED) displays have been in development [227]. Evolution in the fields of TCs and active matrix organic light emitting diode (AMOLED) displays has resulted in their combining to establish a new and exciting generation of transparent AMOLED displays. Early TOLED displays consisted of a quite high work function TCO anode (typically ITO) with a low work function metal cathode such as Au, Ca or Ag-Mg, encapsulating an organic semiconductor layer along with ETL and HTL transport layers. While even a thin metallic cathode layer can hinder the optical transparency by 50% [228], prototype transparent televisions have been developed by Samsung through adoption of twin ITO electrodes [229]. However, the challenge continues to discover a cathode layer with comparable
optoelectronic properties to ITO but a lower work function for efficient electron injection. Recently, it has been observed both theoretically [230] and experimentally [231] that doping of ZnO with Ga or Al can effectively reduce its work function and increase its surface carrier concentration. Similarly, in order to enhance band alignment with HTL layer and hence overall device efficiency, most recent investigations have also intended to increase the work function of the ITO anode [232]. The usual industrial deposition of ITO via sputtering could damaging the underlying organic layers of the OLED device [233]. However, deposition of additional protective layers via thermal evaporation, prior to the sputtering process, has thus far been able to address the damage issue [229]. Additionally, it has been reported that with many TCO thin films such as F-doped SnO₂, Sb-doped SnO₂ and B-doped ZnO, the chemical vapour deposition technique can often produce films with superior optoelectronic properties to those achieved via sputtering [78, 79, 87, 88, 234]. In recent years, many results have been reported for experimental investigations and computational modelling concerning the modification of the work function of doped TCOs [92, 230, 232], and it is predicted that the ongoing correlation between experimental and theoretical approaches can provide tangible development to this quickly growing field.

1.9.3. Transparent Conductive Electrodes in Architectural Glass

TCO coatings are widely applied to architectural glass as part of multilayer stacks. In this context, the electrical conductivity is immaterial, but the high infrared reflectivity is exploited, to minimize heating costs in the winter and air conditioning costs in the summer. Almost 25% of plane glass is coated, and energy preserving coatings are required in various areas of applications. The most common technique for applying such coatings is via a very stable and low-cost, atmospheric pressure chemical vapour deposition (APCVD), along with the float glass fabrication route. However, the APCVD technique is not very adaptable due to limitations of the available options for the coating architecture. A more expensive, but also more flexible process is magnetron sputtering. Usually, many rotating targets (e.g. 20-60) are placed in a long modular vacuum chamber and multilayer stacks are deposited when the glass plates are moved underneath various cathodes.
1.10. Challenges and Significances of the Study

Both the optical and electrical properties of ITO are correlated and could be tailored to a wide range of optoelectronic applications. ITO thin films are very sensitive to microstructure and crystallinity, and show brittle surface structure. Increasing ongoing demands from industrial and technological applications for high quality optoelectronic devices showing higher performance limits involve maintaining the structure properties including (crystallinity, phases and stoichiometry) as well as the morphology properties including (texture and crystallite size), which govern the electrical, optical and mechanical properties of thin polycrystalline ITO films. The nanostructure of ITO is itself sensitive to fabrication conditions. Therefore, controlling this nanostructure is necessary to produce high quality thin films with suitable optoelectronic and mechanical characteristics for such applications.

Most of the industrial and technological applications are looking for fabricating high quality ITO thin films either from low-cost materials or by using simple, clean and efficient fabricating techniques. However, high quality ITO thin films were mostly fabricated via physical vapour deposition techniques provided with complicated high vacuum systems and control unit such as sputtering, pulsed laser deposition, electron beam evaporation, chemical vapour deposition, etc. These techniques when combined with expensive indium result in high-cost end products. Therefore, fabricating high quality ITO thin films using a low-cost technique still represent the main challenge for researchers over the globe. In this study a simple, low-cost and environmentally friendly sol-gel spin-coating method was used to fabricate high crystalline quality thin ITO films comparable to those fabricated from complicated physical vapour deposition techniques. The optoelectronic and mechanical properties of ITO thin films were improved by using suitable dopants and annealing temperatures. Also, ITO-based multi-layer thin film coatings were successfully fabricated via sol-gel spin-coating method, and used as electrodes in OSCs application with improved power conversion efficiency.

1.11. Research Questions Addressed in this Study

- Can a simple, cost effective and environmentally friendly method be used to produce high quality thin ITO films with properties comparable to those prepared from
complicated and costly physical vapour deposition techniques such as sputtering, pulsed laser deposition, electron beam evaporation, etc.?

- Is it possible to control the fabrication conditions of the sol-gel spin-coating process to fabricate high crystalline quality thin film coatings?
- Can suitable annealing temperatures be identified that will not significantly change the structural properties of ITO but improve the network?
- Can the carrier concentration of sol-gel derived ITO-based thin films be increased by doping with metals that have higher valency and work function values compared to indium? This increment could be made either by substituting the host atoms by dopant atoms with high valency that contribute extra free charge carriers in the ITO network, or by enhancing the injection of the free carriers from metals that have high work function values.
- Can the carrier mobility of sol-gel derived ITO-based thin films be enhanced through improvement of the crystalline quality of these films by doping and/or heat treatment, and by combining the ITO with conducting material such as CNTs that may provide highly conducting pathways to the free electrons within the ITO structure?
- Can the sol-gel process be beneficial in fabricating the ITO thin films with different materials in bi-layer and tri-layer coatings with low films thicknesses that offer optoelectronic properties comparable to thick single ITO film?
- Can the mechanical properties of brittle ITO thin films be improved via doping, applying heat treatments and incorporating a robust material such as CNTs in the ITO matrix?

1.12. Methodology

The methodology developed in this experimental work was designed to address each of the research questions posed in the previous section.

The sol-gel process was used as low-cost alternative to physical vapour deposition techniques to prepare ITO thin films. This was then combined with a spin-coating approach to prepare uniform thin films on suitable substrates such as soda-lime glass slides. In addition to the low-cost and ease of operation, the sol-gel spin-coating approach has the potential to be scaled-up for large surface thin film coatings.
A number of experimental variables were manipulated in the sol-gel spin-coating process to achieve high crystalline quality thin films including, solution concentration, solution viscosity, spin-coater dispensing rate, spin-coater rotation speed, calcining process, film thickness. The spin-coating deposition parameters consist of three main steps with different spinning speed and spinning time. These steps include: (1) dispensing the sol onto the rotated substrates, (2) spreading the sol uniformly and (3) drying the thin films. These steps were followed by a calcined process at specific temperature which depends on the solution concentration, and the deposition process was repeated until the desired film thickness was achieved. The thin films thicknesses were varied in the range of (150 – 350 ± 5 nm).

Annealing was carried out in the range of (350 – 600 °C) throughout the present study to improve the crystalline quality and enhance the homogeneity of the prepared thin films.

Doping the ITO thin films was achieved by incorporating selected 3d transition metal salts in the sol-gel process including titanium (IV) isopropoxide (Ti(OCH(CH₃)₂)₄), silver nitrate (AgNO₃) and CNTs. The level of Ti and Ag dopants was varied in the range of (2 – 10 at.%), while CNTs were incorporated at a level of 0.25 wt.% Combining of the dopant level and annealing temperatures were explored to achieve high carrier concentration and mobility as well as good mechanical properties in the fabricated ITO thin films.

ITO thin films were combined with metal-, metal nanoparticles- and metal oxide- layers in the geometries of bi-layered and tri-layered thin film coatings with thicknesses of ~ 130 ± 10 nm. These combined layers could facilitate obtaining optoelectronic properties comparable to thick single ITO film (≥ 350 nm).

Structural, surface morphology and roughness, surface composition/electronic structure, electrical, optical and mechanical properties were investigated using a variety of complementary techniques, such as X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Raman analysis, scanning electron microscopy (SEM) and field emission scanning electron microscopy (FESEM), energy dispersive X-ray spectroscopy (EDS), atomic force measurements (AFM), 4-point probes, Hall effect measurements, UV-Vis spectrophotometry, and nanoindentation and FEM measurements.
1.13. Outline of the Dissertation

This dissertation consists of eight chapters. **Chapter 1** provides general introduction together with a review of relevant literature, challenges, significance, research questions, and methodology used in the current study. **Chapter 2** includes the background aspects of ITO and its correlated optoelectronic characteristics along with the theory of sol-gel spin coating method and the equipment and characterization techniques used in this work. **Chapters 3 to 7** comprise the main findings obtained from the characterization of the synthesized thin film coatings with further discussions and commentaries. In particular, **Chapter 3** includes the results obtained from Ti doping including the effects of Ti concentration and annealing temperature on the structural, morphological, electrical and optical properties of Ti-doped ITO thin films. The contents of this chapter have been published in Semiconductor Science and Technology (Journal article 1). **Chapter 4** describes the surface chemical bonding states and mechanical properties of Ti-doped ITO thin films. The major results of this chapter have been published in Journal of Alloys and compounds (Journal article 2). The results presented in **Chapter 5** cover the effects of Ag additive on the mechanical, structural and optoelectronic properties of ITO thin film coatings. The results of this chapter have been published in Materials Today Communications (Journal article 3). The major results of incorporating SWCNTs with ITO thin films have been extensively described in **Chapter 6** in terms of the structural, morphological, optoelectronic and mechanical characteristics. The findings of this chapter have been published in The Journal of Physical Chemistry C (Journal article 4). **Chapter 7** presents the optoelectronic properties of bi-layered and tri-layered ITO-based thin films. A summary of the present work, the need for further developments and scope of further investigations are presented in **Chapter 8** as Conclusions and future works. Since this is a thesis by publications, the reader may find some repeated information, especially in the introductions of some chapters and/or in the discussion of the results.
CHAPTER 2 Background Theory of Transparent Conductive Materials, Sol-Gel Process and Characterization Techniques

2.1. Transparent Conductive Materials

Transparent and conductive materials (TCMs) are a class of materials, which are characterized by very low electrical sheet resistance and simultaneously high optical transparency. These materials have attracted much attention so far on account of their extraordinary and tremendously useful characteristics. [92, 235].

2.1.1. Material Types

Solid state materials can be categorized with respect to their electrical conductance into three main categories: conductors, semiconductors and insulators, and the electrical characteristics of given materials depend on the electronic populations of the different allowed bands. While conductors have abundance of free electrons for electric conduction, insulators have no free electrons under atmospheric conditions for electrical conduction. Semiconductors have electrical characteristics that lie in between those of conductors and insulators [236]. The band gap structures of conductors, semiconductors and insulators are shown in Figure 2.1. Among the aforementioned materials, semiconductors are the one of great interest. Therefore, the semiconductor materials will be discussed in more details in the next section.

2.1.2. Semiconductors

In this type of material, the free electrons can be easily excited from the almost filled valence band to the almost empty conduction band because they generally have small band gap energy (~ 1 - 3eV). Semiconductors behave like insulators at zero Kelvin where there are no free electrons in the conduction band. However, with increasing temperature, some of the free electrons are excited into the conduction band and the electrical conductivity of semiconductor materials increases. In addition, the excited electrons leave behind positive holes in the valence band. The resultant semiconductor current is determined by summing both electron and hole currents that flowing in opposite directions.
Figure 2.1 Band gap structures of conductor, semiconductor and insulator materials

Semiconductor materials can be categorized into three main categories including: elemental semiconductor, composite semiconductor (III-V composites and II-VI composites) and alloy semiconductor. Since early nineteenth century when the research on semiconductor materials started, many semiconductors have been discovered and investigated. The most well-known elemental semiconductor materials are silicon (Si) and germanium (Ge) which both belong to group 14 of the periodic table of elements. In the mid of last century, germanium was the most employed semiconductor in photodiodes and rectifiers. However, it was not suitable for applications at high temperature or of weak current consumption. Later, silicon replaced germanium semiconductors owing to its low cost and low power consumption. Composite semiconductors were built with two or more different elements such as gallium Ga (III) and arsenide (As) to form semiconductor gallium arsenide GaAs (III-V) and aluminum Al (III), Ga and As in the form of Al$_x$Ga$_{1-x}$As. These composite and alloy semiconductors were demonstrated to have optical and electrical characteristics that were not achievable with elemental semiconductors. Table 2.1 shows examples of each type of semiconductor material.
Table 2.1 Examples of semiconductor materials

<table>
<thead>
<tr>
<th>General classification</th>
<th>Specific examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>1- Elemental semiconductors</td>
<td>Si, Ge</td>
</tr>
<tr>
<td>2a- III-V composite semiconductors</td>
<td>GaAs, GaSb, AlP, GaN, AlAs, GaP, InP, InSb, InAs, SiC</td>
</tr>
<tr>
<td>2b- II-IV composite semiconductors</td>
<td>CdS, CdTe, CdSe, HgS, ZnO, ZnS, ZnTe, ZnSe</td>
</tr>
<tr>
<td>3- Alloys</td>
<td>Al_{x}Ga_{1-x}As, GaAs_{1-x}P, GaIn_{1-x}As_{1-y}P_{y}, Hg_{1-x}Cd_{x}Te</td>
</tr>
</tbody>
</table>

Semiconductor materials can also be classified as intrinsic or extrinsic based on stoichiometry. Intrinsic semiconductors or undoped semiconductors are pure semiconductors i.e., there is no foreign atom in their crystalline structures. The number of free carriers is therefore determined by the characteristics of the semiconductor itself. In such type of materials, the number of excited electrons and the number of holes are equal \((n = p)\). In general, the population of thermally excited free carriers in most intrinsic semiconductor materials at room temperature is very low. Therefore, intrinsic semiconductor materials have high electrical resistivity and hence low electrical conductivity [237]. Extrinsic semiconductors can be defined as modified intrinsic semiconductors through adding impurity atoms which improve their number of free carriers and therefore electrical conductivity. Depending on the desired carrier type, a selected impurity atom (so-called dopant atom) can be added into the intrinsic semiconductor. Dopant atoms are atoms of a different element which have either more or less valence electrons than the intrinsic semiconductor. These dopant atoms can act as acceptors or donors to pure semiconductors. Acceptor dopant atoms have less valence electrons than the replaced atoms in the host lattice. Thus, they provide excess holes to the host resulting in increased hole carrier concentration, thereby forming a \(p\)-type semiconductor. On the other hand, donor dopant atoms have more valence electron than the replaced atoms in the intrinsic semiconductor lattice. These donor atoms donate free electrons to the conduction band of the host material, lead to excess free electrons to the intrinsic semiconductor and hence creating an \(n\)-type semiconductor [238].
2.1.3. Fermi-Dirac Statistics and Fermi Level

Fermi-Dirac statistics or Fermi-Dirac distribution function can be applied to determine the distribution of electrons over energy states in any solid state material. In the case of semiconductor materials at thermal equilibrium, the electron energy distribution is described by the law of Fermi-Dirac distribution function and therefore provides carrier concentration at a certain temperature without external excitations such as electric field, pressure or light. At certain temperatures, continuous thermal agitation leads to the excitation of electrons from the valence band to the conduction band [239]. The density of electrons (the number of electrons per unit volume) in an intrinsic semiconductor is determined by the electron density $n(E)$ in an incremental energy range $dE$ [240, 241]. The electron density is also given by multiplying the density of states $N(E)$ which represent the density of allowed energy states per unit volume per energy range by the probability of occupying that energy range $F(E)$ as in the following relations:

$$n = \int_0^{E_{top}} n(E) \, dE = \int_0^{E_{top}} N(E)F(E) \, dE \quad (2.1)$$

The integration limit is taken from the bottom of the conduction band ($E_c$) (which is taken to be $E = 0$ for simplicity) to the top of the conduction band ($E_{top}$).

The probability of an electron to occupying an electronic state of energy $E$ is given by the Fermi-Dirac distribution function.

$$F(E) = \frac{1}{1 + e^{(E-E_F)/KT}} \quad (2.2)$$

where $K$ is the Boltzmann constant, $T$ the absolute temperature in Kelvin and $E_F$ is called the Fermi energy or the Fermi level which is defined as the energy state where the probability of being occupied by an electron is equal to one-half.

In the high energy region (i.e., $E - E_F >> KT$), the probability of a state being occupied decreases exponentially with increasing $E$ and equation (2.2) can be approximated as:

$$F(E) = e^{-(E-E_F)/KT} \quad (2.3)$$

Equation (2.3) is known as the Boltzmann approximation.
In the low energy region \((i.e., E - E_F \ll KT)\), the occupation probability of a state approaches 1. Therefore, the low energy states tend to be fully occupied and equation (2.2) can also be approximated with:

\[
F(E) = 1 - e^{-(E_F - E)/kT}
\]  

(2.4)

Also, in the low energy region, the probability of a state being occupied by holes is:

\[
1 - F(E) = e^{-(E_F - E)/kT}
\]  

(2.5)

Figure 2.2 shows the Fermi-Dirac distribution function [241].

![Fermi-Dirac distribution function plot](image)

Figure 2.2 Fermi-Dirac distribution function plot [241]

It is very important to understand that there is only one Fermi level in a system at thermal equilibrium. The \(F(E)\) is symmetrical around the Fermi level. When the number of energy states in the conduction band is equal to the number of energy states in the valence band, and the number of electrons in the conduction band is the same as the number of holes in the valence band, the Fermi level will lie in the middle of the band gap. For an \(n\)-type semiconductor material where the number of electrons in the conduction band is more than the number of holes
in the valence band, the Fermi level will be closer to the bottom of the conduction band. Similarly, for p-type semiconductor materials where the number of holes in the valence band is more than the number of electrons in the conduction band, the Fermi level will be closer to the top of the valence band. Figure 2.3 illustrates the location of the Fermi level for an intrinsic semiconductor and n-type and p-type extrinsic semiconductors [241].

![Diagram](image)

**Figure 2.3 Location of Fermi level for intrinsic semiconductor and n-type and p-type extrinsic semiconductors [241]**

### 2.1.4. Semiconductors and Transparent Conducting Oxides

A subset of semiconductor materials, transparent conducting oxides have become of great interest so far, due to their combining of high optical transparency and electrical conductivity. Among TCOs, ITO is still the most extensively used material in daily optoelectronic applications. The physical properties of semiconductors in general and TCOs in particular are determined by the properties of the host crystal, the impurities and crystalline defects. Dopant atoms which substitute for host crystal atoms introduce electronic states in the band gap energy close to the conduction and valence band edges and hence determine the conductivity type of the material as discussed previously. These so-called shallow level defects facilitate a wide range of TCOs properties and their corresponding applications. However, foreign impurities along with crystalline defects of the host which generate electronic states deeper in the band gap energy
(known as deep level defects), can also modify the properties of the TCOs and therefore make these materials unsuitable for their intended purposes. It is then important to control carefully the doping level to fine-tune the required characteristics.

2.1.5. Electrical Properties of ITO Films

2.1.5.1. Carrier Concentration

Generally, the transport process in a polycrystalline structure is more complex than in a single crystal structure. Thin films of ITO may consist of crystalline or amorphous phases or a mix of them. In general, polycrystalline thin films have better optoelectronic properties than amorphous ones [242]. This especially occurs when thin films are deposited on preheated substrates or after annealing the amorphous thin films [243, 244]. In ITO thin films, introducing the Sn atoms leads to reduce electrical resistivity if these atoms are thermally activated (i.e., diffusion of Sn atoms from interstitials and/or grain boundaries to In sites), which increases the number of the free electrons in the conduction band [245, 246]. However, for as deposited ITO films, this process is not efficient enough at room temperature (RT). As a result, the resistivity at low substrate temperatures is generally higher compared to In$_2$O$_3$ thin films because the Sn atoms can act as scattering centres [247].

The electrical conductivity ($\sigma$) basically depends on both the concentration ($N_e$) and mobility ($\mu$) of the free carriers as follows:

$$\sigma = N_e \times \mu \times e$$  \hspace{1cm} (2.6)

where $e$ is the electron charge.

Therefore, high carrier concentration and carrier mobility should be simultaneously considered to obtain high conductivity ITO thin films. In$_2$O$_3$ acts as an insulator in its stochiometric form. However, indium oxide can achieve high $n$-type doping levels (~ $10^{19}$ cm$^{-3}$) due to its intrinsic defects (so-called oxygen vacancies (Vo)) if fabricated in its oxygen decient form. The generation of oxygen vacancies contributes two free electrons to the In$_2$O$_3$ matrix as follows:
\[ O_2^\infty \rightarrow \frac{1}{2} O_2(g) + V_0 + 2e^- \]. Consequently, different electrical properties can be achieved depending on the stoichiometry of In\(_2\)O\(_3\) (i.e., without doping) [4].

Most research efforts have been directed to increase the electrical conductivity of In\(_2\)O\(_3\) thin films by increasing the number of free carriers via tin doping. Despite some success, this process is self-limiting, especially when the dopant atoms occupy random sites in the host matrix (e.g. at the grain boundaries) which impair the carrier mobility while increasing the carrier concentration. Therefore, achieving the lowest electrical resistivity is a trade-off between carrier concentration and carrier mobility. Johnson and Lark-Horovitz [248] deduced a relation for a completely degenerate semiconductor as follows:

\[
\mu = (4e/h)(\pi/3)^{1/3} N^{-2/3} = 9.816 \times 10^{14} N_e^{-2/3}
\]

This relation shows that the carrier concentration and mobility are no longer independent. Moreover, at high doping levels, the observed carrier concentration of ITO thin films is lower than expected. This implies that some of the tin atoms remain electrically inactive.

### 2.1.5.1.1. Defect Models

As mentioned before, the free carriers for ITO films are due to two different defects; oxygen vacancies and substitutional tetravalent tin atoms which govern and control the free carrier density in the bixbyite structure. Frank and Köstlin [249] performed numerous experiments and analyses on ITO films with different tin contents, synthesized via chemical vapor deposition (spray pyrolysis) and treated in reducing and oxidizing atmospheres. Accordingly, they proposed the formation of the following lattice defects.

**A. Neutral defect (Sn\(_2^\bullet O_1^\bullet\))**

This neutral defect is formed when two Sn\(^{4+}\) ions which are not on nearest neighbor positions, are loosely bound to an interstitial oxygen anion. This interstitial defect dissociates on annealing under reducing conditions and O\(_1^\bullet\) may drift away:

\[
Sn_2^\bullet O_1^\bullet \leftrightarrow 2Sn^\bullet + 2e^- + \frac{1}{2} O_2^{(g)}
\]
\[ O_i^{x} + 2e^- \leftrightarrow O_i^+ \]  \hspace{1cm} (2.9)

B. Neutral defect \((\text{Sn}_2\text{O}_4)^x\)

This neutral defect is formed at high doping level when two nearest neighbor \(\text{Sn}^{4+}\) ions are bound to three nearest neighbors on regular anion sites and an interstitial oxygen ion on a nearest quasianion site. Here, the Sn-O bond is quite strong; hence, it is a detrimental effect since it may not be reduced by heat treatment.

C. Defect \((\text{Sn}_2\text{O}_4)(\text{Sn}_2\text{O}_4)^x\)

It is composed of both of the above defects including loosely and strongly bound extra oxygen and it is a common phenomenon in very highly doped systems.

\[
(\text{Sn}_2^+\text{O}_4^-) + (\text{Sn}_2\text{O}_4)^x \leftrightarrow \left( (\text{Sn}_2^+\text{O}_4^-)(\text{Sn}_2\text{O}_4)^x \right)
\]  \hspace{1cm} (2.10)

D. Impurity ion-substitutional tin \((\text{Sn}^*)\)

Tin atom can act as a cationic dopant and substitutes the indium in the \(\text{In}_2\text{O}_3\) lattice. Since indium has a valence of three, the tin doping is providing an electron to the conduction band, resulting in \(n\)-type doping of the lattice. Therefore, the overall charge neutrality is preserved.

\[
\text{Sn}_{\text{In}} \rightarrow \text{Sn}^* + 1e^- \]  \hspace{1cm} (2.11)

E. Oxygen vacancy \(\text{VO}^{**}\)

The oxygen vacancies behave as doubly ionized donors and contribute two electrons to the electrical conductivity as shown in the following relation:

\[
O^x \rightarrow \text{VO}^{**} + 2e^- + \frac{1}{2} O_2^{(g)} \]  \hspace{1cm} (2.12)
Fabrication of ITO films in an oxygen-rich environment will lead to a film which is saturated with oxygen. Increasing heat treatment will shift both equations (2.9) and (2.10) to the left, resulting in free electrons, dissolving interstitial oxygen and substitutional Sn. Interstitial oxygen \((O_i)\) can effectively diffuse within the ITO matrix and reach the grain boundaries. At the grain boundaries, absorbed oxygen \((O_2(a))\) can be formed and desorbed. Depending on the ambient conditions, the reactions can also be reversed.

### 2.1.5.1.2. Limitation of Free Carrier Density

The plot of free carrier density versus the doping concentration of Sn is shown in Figure 2.4. Theoretically, maximum carrier density \(N_e\) due to only Sn doping in typical ITO thin film is \(N_e = N_{ln} \times c\), where \(N_{ln} = 3.0 \times 10^{22}\) cm\(^{-3}\) is the concentration of indium atoms and \(c\) is the concentration of tin atoms. As seen in Figure 2.4 (curve a), at very low tin concentration \((c < 4\ \text{at.}\%\) the free carrier density tracks a straight line, indicating that each substitutional Sn atom acts as a donor, which donates one free electron to the ITO matrix. On the other hand, at higher Sn concentration, the free carrier density rises up to a maximum at about 10 at.% tin, and then drops with further increasing \(c\) following the relation \(N_e = N_{ln} \times c \ (1 - c)^8\) (curve b). This surmises that a portion of the tin atoms are inactive at high doping level. This is because the higher the tin concentration, the more possible the tin ions occupy the nearest-neighbouring anion sites, resulting in the formation of a neutral defect \((\text{Sn}_2\text{O}_4)\) as discussed previously.

![Figure 2.4](image_url)

Figure 2.4 Dependence of the free carrier density \(N_e\) on the Sn concentration \(c\). Dots represent experimental points; drawn curves represent (a) \(N_{ln}c\), (b) \(N_{ln}c(1-c)^8\) [250]
2.1.5.2. Free Carrier Mobility of ITO Films

2.1.5.2.1. Scattering Mechanism

For ITO thin films used as transparent conductive electrodes, it is essential to make a compromise between optical transparency and electrical conductivity. Reduction of the electrical resistivity consists of either an increase in the free carrier concentration or in the free carrier mobility. However, increasing the first can also result in an increase in the visible absorption. Therefore, increasing the mobility is very important for ITO thin films for high electrical and optical characteristics.

The free carrier mobility $\mu$ can be defined as:

$$\mu = \frac{e \tau}{m_e}$$  \hspace{1cm} (2.13)

where $m_e$ is the effective electron mass in the conduction band and $\tau$ is the average collision time of electrons.

Weiher [251] and Groth [245, 252] were the first to report high Hall mobilities (160 and 170 cm$^2$/V s) for single crystal In$_2$O$_3$ and zirconium doped In$_2$O$_3$, respectively. ITO thin films mobility is strongly dependent on the disorder of the In$_2$O$_3$ structure and on the modification of the network due to the tin doping process. Therefore, a strong scattering process on the free carrier could occur at high doping concentrations. There are many sources of electron scattering which may influence the mobility, such as ionized impurity scattering, neutral impurity scattering, grain boundary and external surface scattering, acoustical phonon scattering, defect lattice scattering, etc. In the case of ITO films, which have good crystallinity, the electron scattering due to the structural disorder and dislocations is predicted to be less important and can be neglected. The scattering by acoustical phonons seemingly is also of a little importance in ITO films where there is no significant temperature dependence detected between 100 and 500$^\circ$C. Furthermore, the free carrier mobility is not affected by surface scattering unless the mean free path is comparable to the film thickness. However, for ITO films having small crystallite size, grain boundary scattering is supposed to be an important factor which contributes to decreasing the carrier mobility. It is well-known that grain boundaries act as sites for the impurities and these sites act as scattering centers for free carriers. However, for a heavily
degenerate semiconductor, the mean free path of electrons is much smaller than the crystallite size. Hence, grain boundary scattering is perhaps insignificant at high carrier densities. Weijtens [253] has reported that the mobility is mainly determined by grain boundary scattering when the carrier density is below $7 \times 10^{20}$ cm$^{-3}$. Kulkarni and Knickerbocker [254] also proposed that, for polycrystalline materials, the grain boundary scattering may predominate at very high carrier concentration ($>1 \times 10^{20}$ cm$^{-3}$) due to enhancement of the grain boundary potential.

### 2.1.5.2.2. Limitation of Carrier Mobility

Generally, the conductivity of practical transparent conductive oxides with relatively high free carrier concentrations is intrinsically limited since the free carrier concentration and the mobility cannot be independently increased. One important scattering mechanism that cannot be ignored is scattering against ionized donor impurities. These ions are important for preserving charge neutrality in highly doped thin films. However, the Coulomb interactions between the free carriers and these impurities provide a source of scattering, which is intrinsic to the doped semiconductors leading to reduced carrier mobility. This drastically affects the conductivity and the optical transmission near the infrared edge. The contribution by ionized impurities to the electrical resistivity is based on the Coulomb interaction and the relation below has been used by many researchers to define the effect of these impurity scattering centers on the mobility

$$
\mu_i = \frac{24\pi^3(\varepsilon_0\varepsilon_r)^2h^3N}{[e^3m^*g(x)Z^2n_i]}
$$

Where $N$ is the carrier concentration, $n_i$ is the density of impurities scattering centers, $m^*$ is the electron effective mass, $\varepsilon_0$ and $\varepsilon_r$ are permittivity of free space and low frequency relative permittivity respectively, $Z$ is the charge of the ionized centers, $g(x)$ is the screening function and $h$ is Planck’s constant.

For metal oxides with high free carrier density, some absorption of incident radiation takes place by interaction with the electron gas, which increases with increasing carrier concentration. Therefore, at carrier densities greater than $2\times10^{21}$ cm$^{-3}$, the TCO exhibits plasma frequencies which shift to visible light from absorbing infrared wavelengths, and reduce the transparency in the visible region. Recently, developed TCO materials, including undoped and doped binary, ternary, and quaternary compounds suffer from the above limitations. A few exceptional samples have a resistivity of $\leq 1 \times 10^{-4}$ $\Omega\cdot$cm. However, it is difficult to approach a resistivity of $4 \times 10^{-5}$
Ω.cm because additional scattering processes result from grain boundaries, neutral impurities, and other forms of structural disorder, which depend on the materials and the preparation techniques [255].

2.1.6. Optical Properties of ITO Films

The optical properties of ITO films are governed and modified by the band structure and defects. The spectral range of interest for the optical properties of ITO films lies between 200-3000 nm, and it is controlled by three different kinds of electronic excitation in different spectral regions. The electronic excitations include inter-band transitions from the valence band into the conduction band, intra-band transitions for the free carriers within the conduction band and band gap transitions. Consequently, there are three different regions that can be recognized for the transmittance curve as follow:

**Ultraviolet (UV) region:** In this region, ITO films exhibit high UV absorption related to interband transitions. This absorption is due to the fundamental direct band gap around 3.5 eV. The band gap absorption ($\lambda_{\text{gap}}$), named the absorption edge, strongly depends on the preparation technique [256], and it lies in the range of (3.5 - 4.1) eV. Manifacier *et al.* [257] observed that the higher the free electron density, the shorter the wavelength of the absorption edge. When the free electron density is very high the conduction band is partially filled up, thus the first noticeable transition happens for higher photon energy. Therefore, the free electron density is a crucial factor in defining the optical properties in this region.

**Infrared (IR) region:** In this region, the ITO films enter a reflecting area with a plasma edge or plasma wavelength $\lambda_p$ that is defined by reflectance = transmittance, with metallic properties where the metal-like infrared reflectance equals the dielectric-like transmittance [250]. Classical Drude theory can be used to explain the optical phenomenon in this region [258]. The absorption process for the free carriers in this region is important for reflectance and transmittance of the ITO films. Therefore, as in the UV region, the free electron density is a crucial factor in defining the optical properties in this region as well.
**Visible region:** In between the UV and IR regions ($\lambda_{\text{gap}}$ and $\lambda_p$), there is a very high transmittance region for around 90% of the visible wavelengths that depends on the preparation conditions. Figure 2.5 shows the typical spectral dependence of transparent conductive oxides. $\omega_p$ and $\omega_{\text{gap}}$ are the frequencies at which the plasma absorption and the band gap absorption takes place, respectively. The wide optical band gap >3.5eV prohibits inter-band transitions thereby making it transparent in this region. The transmittance window is defined by the absorption edge toward the shorter wavelengths and by the plasma edge toward the longer wavelengths.

![Figure 2.5 Typical spectral dependence of transparent conductive oxides](image)

### 2.1.6.1. Optical Constants

The optical properties of the materials are defined by the complex refractive index $<n>$ and the complex dielectric constant ($\varepsilon$). The complex refractive index describes the velocity of light in the medium ($v$) following the relation: $n = c/v$ where $c$ is the speed of light in vacuum (Eq. 2.15). The complex dielectric constant is given by equation (2.16).

\[
<n> = n + ik \tag{2.15}
\]

\[
\varepsilon = \varepsilon_1 + i\varepsilon_2 \tag{2.16}
\]
The relation between refractive index and dielectric constant is:

\[ < n > = \sqrt{\varepsilon} \]  

(2.17)

Where,

\[ \varepsilon_1 = n^2 + k^2, \quad \varepsilon_2 = 2nk \]  

(2.18)

and \( k \) is the extinction coefficient which describes the attenuation of light wave as it goes through a material. \( k \) is directly correlated to the absorption coefficient (\( \alpha \)) of a medium and is shown as:

\[ \alpha = \frac{4\pi k}{\lambda} \]  

(2.19)

where \( \lambda \) is the wavelength of light in vacuum.

The transmittance (\( T \)) is then given by:

\[ T = A \times \exp\left(-\frac{4\pi kt}{\lambda}\right)\sim\exp(-\alpha t) \]  

(2.20)

and

\[ A = \frac{16n_0n_1(n^2 + k^2)}{((n^2+n)^2 + k^2) + ((n_1+n^2 + k^2))} \]  

(2.21)

\( n_0, n \) and \( n_1 \) are the refractive indices of air, film and substrate, respectively and \( t \) is the film thickness.

As for the optical spectra, the dielectric constant also consists of three regions. In the UV region, the imaginary part of the dielectric constant increases sharply. In the visible region, the imaginary part approaches zero and in the IR region, \( \varepsilon_2 \) increases while, \( \varepsilon_1 \) decreases until it crosses zero at the plasma frequency and strongly reaches its negative value. Figure 2.6 shows the complex refractive index and dielectric constant of an ITO film.
Figure 2.6 Complex refractive index (left) and dielectric constant (right) of ITO thin films [145]

Table 2.2 Comparison of some important binary TCOs and their fabrication techniques and relevant optoelectronic properties

<table>
<thead>
<tr>
<th>Species</th>
<th>Deposition method</th>
<th>$\rho \times 10^{-4}$ (Ω.cm)</th>
<th>T%</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITO</td>
<td>PLD</td>
<td>0.77</td>
<td>85</td>
<td>[259]</td>
</tr>
<tr>
<td>ITO</td>
<td>DC sputtering</td>
<td>1.5</td>
<td>92</td>
<td>[260]</td>
</tr>
<tr>
<td>ITO</td>
<td>RF sputtering</td>
<td>1.29</td>
<td>85</td>
<td>[189]</td>
</tr>
<tr>
<td>ITO</td>
<td>Sol-gel</td>
<td>3</td>
<td>80</td>
<td>[261]</td>
</tr>
<tr>
<td>SnO$_2$:F</td>
<td>CVD</td>
<td>5.2</td>
<td>80</td>
<td>[78]</td>
</tr>
<tr>
<td>SnO$_2$:Sb</td>
<td>RF sputtering</td>
<td>20</td>
<td>85</td>
<td>[234]</td>
</tr>
<tr>
<td>SnO$_2$:N</td>
<td>RF sputtering</td>
<td>9.1</td>
<td>80</td>
<td>[262]</td>
</tr>
<tr>
<td>ZnO:Al</td>
<td>PLD</td>
<td>0.85</td>
<td>88</td>
<td>[85]</td>
</tr>
<tr>
<td>ZnO:Al</td>
<td>RF sputtering</td>
<td>2</td>
<td>80</td>
<td>[86]</td>
</tr>
<tr>
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<td>85</td>
<td>[84]</td>
</tr>
<tr>
<td>ZnO:Ga</td>
<td>RF sputtering</td>
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<td>85</td>
<td>[83]</td>
</tr>
<tr>
<td>TiO$_2$:F</td>
<td>PLD</td>
<td>16</td>
<td>95</td>
<td>[263]</td>
</tr>
</tbody>
</table>
2.2. Sol-Gel Spin Coating Process, Fundamental, Theory and Advantages

2.2.1. General Overview

Many techniques have been proposed for fabricating high quality thin film coatings. But, these generally fall into two main categories, depending on whether the process is physical or chemical [264]. Physical vapor deposition produces a thin film coating by means of thermodynamic, mechanical or electromechanical processes. Common physical deposition systems require a low pressure environment along with a complicated controlling system to functionalize thin film coatings properly. Examples of physical vapor deposition techniques include, thermal evaporation, sputtering, electron beam evaporation, pulsed laser deposition and molecular beam epitaxy [265]. Chemical deposition processes can involve gas-phase or solution-phase precursors. Gas-phase precursor-based processes include chemical vapor deposition (often involving a hydride or halide elements) and plasma enhanced chemical vapor deposition (using ionized vapor as precursor). The solution-phase precursor-based process is also known as wet chemical deposition, and the prepared thin films tend to be conformal. Examples of wet chemical deposition processes include, electroplating, spray pyrolysis and sol-gel methods [242]. Among these wet chemical processes, sol-gel is of great interest and widely used because of its low temperature and ease of handling. In the next sections, the fundamental, theory and advantages of the sol-gel process are discussed.

2.2.2. Sol-Gel Process

Fabricating thin film coatings via a sol-gel process represents the oldest application of this technique. The first patent on sol-gel thin film formation was granted to Schott and Gen in 1939 for their dip coated silicate thin film. Sol-gel derived thin film coatings of: mirror coatings have been in production since 1953, antireflection coatings since 1964 and design coatings since 1969 [266]. Over the past few decades, sol-gel thin film coatings have been widely considered for a variety of additional applications including, optical coatings [267, 268], high and low dielectric constant thin films [269], sensors [270], electro-chromic coatings [271], semiconducting anti-static coatings [272], strengthening and protective layers [273, 274], superconducting films [275], planarization and passivation layers [276] and ferroelectric coatings [277, 278]. The sol-
gel process is mainly used for the production of uniform metal oxides thin film coatings using metal alkoxides precursors. Samples fabricated via this process normally do not require annealing temperature as high as those fabricated via conventional techniques such as sputtering, thermal evaporation, chemical vapor deposition, to name a few. This makes the sol-gel process suitable for fabricating samples that are unstable at high temperatures. Compared to other conventional thin film fabricating techniques, this process requires considerably less equipment, is generally very simple, cost effective and free of difficult technical challenges that may result from using specialized equipment. This process also offers many other advantages [279]:

- Low processing temperature that allows the use of volatile components.
- The intimate mixing of the starting precursors, results in a high degree of coating homogeneity.
- Dopants can be easily introduced and controlled even at a trace level.
- The viscosity and thereby the film thickness can be adjusted by adequate choice of concentration, solvent, chelating agent, etc.
- Large area sample coating along with desired thickness and composition are obtainable.

The sol-gel method can be classified based on the solvent type into two different routes, aqueous and non-aqueous processes [280]. In aqueous sol-gel process, oxygen which supplied by water is essential for the formation of metal oxide. The key aspects such as hydrolysis, condensation and drying which are take place concurrently leading to some difficulties including, controlling the particle morphology and reproducibility of the final protocol during the sol-gel process. In non-aqueous sol-gel process, oxygen required for the formation of metal oxide is supplied from the organic solvents such as ketones, alcohols, aldehydes and/or by the metal precursors. These organic solvents not only supply the oxygen but also provide a versatile tool for controlling many other parameters such as surface properties and morphology, crystallite size and composition of the resultant metal oxide [281].

Non-aqueous process can also be divided into solvent- and surfactant- controlled approaches [282]. Surfactant-controlled processes include the transformation of the precursor species into the oxidic compound in the presence of stabilizing ligands in a specific temperature range of 250 to 350 °C. An alternative to surfactants is the use of organic solvents that act as reactant as well
as control agent for particle growth, enabling the synthesis of high purity nanomaterials in surfactant-free medium. In comparison to the synthesis of metal oxides using the surfactants, the solvent-controlled approaches are simpler because the initial reaction mixture only contains the metal oxide precursors and a common organic solvent. The synthesis temperature is in the range of 50 to 200 °C, which is also lower than in the surfactant-controlled routes. Despite solvent-controlled approaches result in some agglomeration, the dispersibility properties of the nanoparticles can be improved by post-synthetic steps [283].

Preliminary syntheses are often carried out under ambient conditions, usually without any special environment. Initial precursors are mixed together in a solution and interact easily to form a homogeneous mix [284]. This process comprises the conversion of a colloidal solution of molecular precursors via chemical reactions to a sol or gel through drying followed by post annealing at high temperature. This assists the transformation of formed sol/gel into a polycrystalline structure thin film [285]. Typical sol-gel processes for thin film coatings fabrication consist of three main steps: (a) preparation of the precursor solution, (b) depositing of the prepared solution onto the substrate and (c) annealing the xerogel film. The xerogel is defined as the dried gel at ambient conditions, while the aerogel is the dried gel in supercritical conditions [286].

2.2.3. Sol-Gel Chemistry

The sol-gel process comprises the use of metal-organic or solid inorganic precursors in a solvent which forming a colloidal dispersion. The precursors are hydrolyzed and condensed in the organic solvent resulting in inorganic polymers that consist of oxo (M-O-M) bonds. For many inorganic precursors, the hydrolysis proceeds via a proton removal from an aquo ion [M(ОН₂)]²⁺ resulting in the formation of an oxo (M=O) or hydroxo (M-OH) ligand (M=metal) [287]:

\[ \text{[MO}_n\text{H}_{2n}]^{z+} + p\text{H}_2\text{O} \leftrightarrow \text{[MO}_n\text{H}_{2n-p}]^{(z-p)+} + p\text{H}_3\text{O}^+ \]  (2.22)

Condensation reactions of hydroxo ligands give rise to the formation of inorganic polymers in which metals are bridged by oxo (M-O-M) or hydroxyl (M-μ(OH)-M) bonds [12]. The most often used metal organic precursors are metal alkoxides M(OR)₂, where R is an alkyl group CₓH₂ₓ₊₁. Usually the alkoxide is dissolved in alcohol and hydrolyzed by adding water under
acidic, neutral or basic conditions. Hydrolysis leads to the substitution of an alkoxide ligand by a hydroxyl ligand [12]:

\[
M(OR)_2 + H_2O \rightleftharpoons M(OR)_{2-1}(OH) + ROH
\]  \hspace{1cm} (2.23)

Condensation then follows a similar pattern to that of hydrolyzed inorganic precursors. Basically, the preparation of a sol-gel solution consists of the use of metal organic or inorganic precursor, aqueous, organic and/or alcoholic solvent, along with the addition of an acid/base as a catalyst [288]. The structure of the growing polymers for both metal-organic and inorganic precursors depends on the functionality of the metal and the degree of hydrolysis [289].

2.2.4. Film Formation

Several deposition options for sol-gel technique include dip-, spin-, spray-, roll- and flow-coating used to manufacture various materials in different forms: powders, fibers, monoliths and/or thin films [290]. Dip-coating and/or spin coating are the major processes adopted for manufacturing coatings via the sol-gel technique. Additionally, the sol-gel process facilitates the fabricating of multi-component film coatings with a complex structure [291].

2.2.4.1. Dip-Coating Process

After preparing the desired precursor solution, the substrate is dipped vertically into the solution for a certain time (dwell time). Then the coated sample is withdrawn slowly and steadily. Both the dipping rate and withdrawal rate are to be considered and maintained in the film fabrication. The withdrawn sample is dried for a short period of time on a hot plate or in a conventional oven, and then the coating procedure repeated until the desired thickness is achieved. Finally, thermal treatment is applied on the coated sample. Therefore, the sol-gel dip-coating process can be summarized in the following main stages: substrate preparation, sol preparation, dipping, withdrawing the coated sample and annealing.
2.2.4.2. Spin Coating Process

Spin coating is the predominant process employed for fabricating homogeneous and uniform thin film coatings with thicknesses of the order of nanometers or micrometers. The first attempts of the spin coating process were performed by Emslie and co-others [292] who considered the spreading of an axisymmetric thin film coating of Newtonian sol onto a flat substrate spinning with a constant angular velocity. Usually, the coating material is applied onto the substrate in the form of a sol from which the solvent vaporizes [293]. In this process, centrifugal force spreads the solution radially outward while the surface tension and viscous force result in a thin film to be retained on the planar substrate. The spin coating process can be classified into four major steps including, deposition of the sol, spin up, spin off and film drying [294]. The deposition of the sol, spin up and spin off occur consecutively, while the drying step occurs throughout the process. Figure 2.7 shows the main steps of spin coating process.

![Image]

Figure 2.7 The main steps of spin coating [295]
2.2.4.3. **Deposition of the Solution via Spin Coating**

Different techniques have been used to apply the solution onto the substrate and depend on the type of spin coating machine. Some machines have specific electronic injectors where the amount (volume) of solution can be controlled and maintained while the others are use syringes or droppers for this purpose. In the deposition step, the solution can be applied in different ways [296]:

1. As a bolus on the center of the substrate with the solution flowing over the rest of it.
2. In the form of heavy rain that floods the substrate.
3. As a continuous stream at the center of the substrate with the solution spreading outward over the substrate.
4. As a continuous stream from a raised distribution port that moves radially over the substrate.

The different ways for applying the solution onto the substrate depend on the concentration and viscosity of the sol, which can be achieved either by pouring the sol onto the substrate for a period of time before spinning or introduce the sol while the substrate is rotating at a constant angular velocity. In both cases the amount of solution deposited is such that the substrate top surface receives a high enough excess of the solution to be completely covered [297].

2.2.4.3.1. **Spin Up**

This stage starts when the substrate accelerates up to the final desired rotation velocity resulting in an aggressive sol rejection from the substrate. Spiral whirlpools may exist during this step due to the initial depth of the sol on the surface of the substrate. These spiral whirlpools form because of the twisting motion caused by the inertia that the top of the sol layer yields while the substrate below rotates very fast. Eventually, the resultant film thickness is thin enough and completely uniform and homogenous to be co-spinning with the substrate at the desired speed, where the viscosity balances the spinning accelerations. The final film thickness is found to be independent of the way of sol dispensing, the amount of sol applied to the substrate and the acceleration level of the substrate to the final rotating velocity [298, 299]. The resultant film thickness might
depend on the aforementioned conditions if the amount of sol is insufficient to fully cover the substrate surface or if the substrate accelerates slowly [300]. Due to the importance and complexity of the spin coating process, a huge effort has been focused on establishing experimental relationships that describe the dependence of spin coating technique on process factors. The main result of these studies was that the final film thickness \( t \) was found to be proportional to a function of the initial solvent concentration and the power of the spinning speed [301, 302] as seen in the following relation:

\[
t \sim f(C_0)\omega^b
\]  
(2.24)

where \( C_0 \) is the initial solvent concentration, \( \omega \) is the spinning speed and \( b \) was found to be -1/2 and it depends on the viscosity level and evaporation conditions.

2.2.4.3.2. Spin Off

This step starts when the substrate is rotating at a constant speed and the viscous force dominates the sol thinning behavior. The centrifugal force works to drive the sol outward off the edge of the substrate obstructed only by the viscous force. The radial drift rapidly decreases because the sol becomes very thin and solvent evaporation increases the viscosity by several orders of magnitude. Therefore, it is convenient to describe the spin coating process by two discrete mechanisms with an abrupt conversion from pure centrifugal sol-drift sol flow to pure solvent evaporation [293, 303-306]. The idea behind this separation is that the film thickness is controlled first by the centrifugal force and second by the solvent evaporation [295, 307] due to the strong concentration dependence of the viscosity, the solvent evaporation may play an important role through the flow dominated system. It was reported by Jenekhe [308] that the main effect of solvent evaporation is through altering rheological characteristics of the regime.

2.2.4.3.3. Drying of the Film

This step starts when the spin off step ends. Through this step, the centrifugal solution out flow halts and further shrinkage of the film arises due to solvent loss alone. As mentioned before, the solvent concentration profile depended on solution convection flow, the cross term in the solvent conservation equation (see Eq. 2.23). Nevertheless, the solvent conservation could be considered
independently when the spinning speed reaches zero and the solvent concentration profile dependence becomes unimportant. At this stage, the solvent evaporation rules the film thinning behaviour. Through the drying step, the dissolved or suspended materials become concentrated at the surface of the sol so as to produce a low diffusivity, high viscosity or solid skin. This leads to the formation of a thin film onto the substrate.

2.3. ITO Thin Films Synthesis

Thin ITO films preparation consists of four main steps: (1) preparation of the glass substrates, (2) sol-gel solution preparation, (3) thin film deposition and (4) thermal treatment at different temperatures of the deposited thin films. Soda-lime glass substrates were used in this study, which were cleaned carefully by using ethanol and DI-water and then sonicated in an ultra-sound bath. The concentration of ITO solution was maintained at (In:Sn = 90:10 at.%) in preparing all pure, doped and incorporated ITO thin films. Details of thin film deposition process (spinning speed and spinning time) using a Polos spin-coater was varied based on the type of dopant and/or incorporated materials used with ITO. In general, the deposition steps consist of: dispensing the prepared solution onto rotated substrate, spreading the solution and drying the thin film, followed by the calcination of the thin films on a hot plate at a suitable temperature. These steps were repeated until the desired film thickness was achieved. Annealing was performed on the resultant thin films. Details of the specific experimental conditions for fabricating ITO based transparent thin film coatings are provided in subsequent chapters. Figure 2.8 shows the flow diagram of the sol-gel spin-coating procedure.
In(NO$_3$)$_3$.5H$_2$O

[Equation]

Refluxed separately

SnCl$_2$.2H$_2$O

Doping or incorporating material

Mixed and refluxed

Ageing for 24 hours

Film deposition by spin-coater

Drying

Post annealing

Resulted thin films

Figure 2.8 Flow diagram of sol-gel spin-coating process
2.4. Instrumentations and Characterizations Techniques

Since nanoscale materials are quite different from their bulk counterparts, high precision devices and instruments are needed to study, quantify and characterize these kinds of materials. The crystalline structure and film coating surface were confirmed by XRD, XPS and EDX, whereas, the surface morphology and topography were imaged by SEM, FESEM and AFM. The electrical properties were investigated by using 4-point probe method and Hall-effect measurements, while the optical properties were characterised by UV-VIS spectroscopy. The mechanical properties were determined by a nanoindentation technique. The instruments and the characterisation techniques used in this study will be briefly discussed in the following sections.

2.4.1. XRD Measurements

XRD is one of the oldest and most effective analysis techniques for investigating the crystallographic and atomic arrangements in a crystal structure [309]. X-ray wavelengths are found to be of the same order of magnitude as the lattice constants of the crystals [310]. XRD is a non-destructive tool which works basically on the interaction between the periodical crystal lattices and the incident monochromatic X-ray radiation. This interaction happens when the X-ray beam with a certain specific incident angle ($\theta$) and wavelength ($\lambda$) hits the surface of a crystalline specimen yielding a reflected radiation pattern. Therefore, intense peaks (which are known as Bragg peaks) are produced from the reflected radiation. Bragg expressed this result by suggesting that each crystal generally consist of discrete parallel planes separated by constant distance named as inter-planar d-spacing. It was assumed that, Bragg peaks occurred if the reflected X-ray radiation from different crystal planes interfered constructively according to Bragg’s law [311].

$$n\lambda = 2d \sin \theta$$

(2.25)

where $n$ is an integer determined by the reflection order, $\lambda$ is the wavelength of the incident X-ray radiation, $d$ is the inter-planar distance (d-spacing) and $\theta$ is the angle between the incident radiation and the surface of the specimen which is also called (Bragg’s angle). Figure 2.9 shows the incident and the scattered X-ray radiation.
It is believed that most materials are not single crystals but consist of billions of small crystallites randomly orientated and are referred to as polycrystalline structures or powder form. Therefore, when these materials are examined by X-ray radiation, many inter-atomic planes from different crystallites will be realized. However, the diffraction from each plane will take place at specific diffraction angles (θ).

2.4.1.1. Analysis of XRD Data

The value of 2θ is estimated for each diffraction peak after the XRD pattern appears and the d-spacing (\(d_{hkl}\)) values calculated from 2θ values via Bragg’s law. These values are used to derive crystallographic parameters of thin films such as, identification of phases, calculation of the crystallite size, lattice parameter determination, etc.

2.4.1.2. Identifications of Phases

The XRD technique has proven itself a powerful tool to identify the phases of elements, compounds and materials, as well as, provide important information on the dimensions of the unit cell. In a crystalline structure, electrons cause a scattering to the incident X-ray radiation resulting in XRD pattern with maxima and minima peaks following Bragg’s law. From the XRD pattern, the position and the intensity of the peaks, the characteristics of crystal structure and atomic composition of material can be determined. By comparing the positions of Bragg’s peaks with standard crystalline XRD cards, the phase identification and existence of multiple phases in
a compound can be established and quantified. Furthermore, the XRD approach can also afford precise results for lattice parameters, unit cell volume, constituents of the coatings and crystal symmetry with atom positions.

2.4.1.3. Determination of Crystallite Size from XRD Data

The Debye-Scherrer equation is derived from Bragg’s law and can be used to calculate the crystallite size as follow:

\[ D = \frac{K\lambda}{\beta \cos \theta} \]  \hspace{1cm} (2.26)

where, \( K \) is Scherrer constant (constant of proportionality) which is depends on the shape of the crystal, \( \beta \) full width at half maximum (FWHM) of Bragg peak and \( \lambda \) wavelength of X-ray beam.

2.4.1.4. Determination of Lattice Parameter

The lattice parameters of a crystal structure can be easily calculated by using Bragg’s law to determine \( d_{hkl} \) value, the standard Bravias lattice relation for a cubic system and Miller indices \((hkl)\) related to the reflection orientation as follow:

\[ \frac{1}{d^2} = \frac{h^2+k^2+l^2}{a^2} \]  \hspace{1cm} (2.27)

where \( \lambda = 0.154 \pm 10^{-5} \) nm for \( Cu – K_\alpha \) radiation source, \( d \) inter-planar spacing and \( a \) lattice constant

2.4.1.5. X-ray Diffraction Measurements Technique

The X-ray diffraction data can be obtained by either reflection or transmission geometry. In this study, the XRD data was collected using a GBC EMMA X-ray Diffractometer supplied with LynxEye detector which collects the data in reflection mode. The XRD analysis was conducted at room temperature using a Cu-K\( \alpha \) radiation with a primary beam power of 35 kV and 28 mA. Cu-K\( \alpha \) primary beam radiation has a wavelength of 1.5406 Å. The fundamental diffraction peaks of the samples were measured over a 2\( \theta \) range from 20° and 70° with a step size of 0.02° and a
scanning rate of 2°/min. Both receiving and divergence slits were used to control the output intensity and the irradiated beam area from the sample. In order to get parallel X-ray beams, two solar slits were used; one after the tube and the other in front of the detector. QualX program was used for the XRD analysis in this study by inquiring the PDF-2 and PDF-4 databases and the new freely POW-COD database which has been developed by the authors of QualX program. The POW-COD database was generated based on the structure information contained in the Crystallography Open Database.

### 2.4.2. X-ray Photoelectron Spectroscopy (XPS)

XPS is well known as a powerful surface analysis tool that yields information over 5 – 10 nm probing depth, making it an accurate surface analysis technique. For instance, XPS analysis offers detection limits of 0.2-0.4 at.% for nitrogen, oxygen and carbon, 0.03 at.% for lighter transition metals and 0.001-0.005 at.% for heavy metals [313]. XPS is based on the photoelectric effect to investigate the electronic structure and the chemical composition of sample materials. It was first developed by K. Siegbahn and his research group in mid the 1960s. The fundamental idea of XPS phenomenon is the discharge of electrons from a surface which has been bombarded by energetic photons. Due to the short range of photoelectrons released out of bombarding surface, XPS is considered a highly sensitive surface analysis technique. XPS analysis is also defined in some literature as electron spectroscopy for chemical analysis (ESCA). XPS is the most common surface analysis technique to determine the chemical and electronic bonding states and the elemental composition of surfaces. XPS surface analysis is made by using soft X-rays (i.e., monochromatic photons of energy (~200 - 2000 eV) to investigate the inner shell (core level) electrons. The most widely used X-ray sources are Al Kα radiation (hv = 1486.6 eV) and Mg Kα radiation (hv = 1253.6 eV). By illuminating the atoms of a surface, placed in an ultrahigh vacuum system, by a monochromatic soft X-ray photons, a photoelectron in an inner shell is ejected with a kinetic energy (E_k) expressed by the following relation [314]:

\[ E_k = hν - E_b - φ \]  \hspace{1cm} (2.28)
where $hv$ is the kinetic energy of X-ray photon, $E_b$ is the binding energy of the orbital from which the electron is ejected and $\varphi$ is the work function of the sample. The emitted photoelectrons are moved through a hemispherical photoelectron energy analyser with energy governed by electrostatic fields prior to hitting the detector.

A typical XPS spectrum is obtained by plotting the electron count rate (y-axis) versus binding energy (x-axis). The specific binding energy indicates the element while the intensity of the peak is related to the concentration of the element in the specimen. Each element has a specific binding energy that relates to each core atomic orbital, resulting in a series of separate peaks in the photoelectron spectrum [315]. The composition of the sample can be obtained by utilising the peak height and the peak area, while the variations in the oxidation states and/or the structural configuration of the elements can be recognized by noting the shifts in the binding energies of a particular core level. Therefore, the elemental identity, elemental composition, chemical states and electronic states of the studied surface area of the sample can be analysed by the XPS technique.

2.4.2.1. Applications of XPS Technique

XPS analysis technique is mostly used in different types of material characterizations including:

- Identification of the stoichiometry of the coatings,

- Changes in surface composition of materials due to absorption, heating and radiation,

- Detection of surface contamination,

- Identification of the interface properties of nanomaterials,

- Studying multilayer film structure,

- Identification of material corrosion and degradation,

- Identification of interface reactions and diffusions, and

- Determination of the problems of protective coating caused by segregation of materials.
2.4.2.2. Experimental Procedure of X-ray Photoelectron Spectroscopy (XPS) analysis

XPS measurements were carried out via a kratos axis ultra-X-ray photoelectron spectrometer installed at Curtin University. The samples were mounted horizontally on steel sample holders using double-sided sticky copper tape and the probed surfaces were normal to the electrostatic lens. A charge neutralizer was used to balance the electron shortage on the sample surface during the measurements. The analyser entrance and electrostatic lens mode of the XPS machine were set to slot mode and hybrid ($I_{rs} = 0.6$ and aperture = 49), respectively. The background pressure of the analyser chamber was less than $10^{-9}$ Torr, which was maintained during data collection. The voltage and current of X-ray beam radiation were 12 kV and 12 mA, respectively. Primary survey scans were probed with pass energy of 80 eV, while high resolution scans were carried out with pass energy of 10 eV and step size of 0.1 eV.

The peak positions in XPS spectra are affected by both the sample surface and the spectrometer conditions. Therefore, calibration of the binding energy before XPS peak identification is important to overcome the charging effects. This is commonly done by using the C 1s peak of saturated carbon (C-H or C-C) at a binding energy of 284.6 eV. The conducted XPS data was analysed via CASA XPS software (version 2.3.15) with Shirley background subtraction.

2.4.3. Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS) and Field Emission Scanning Electron Microscopy (FESEM)

Scanning electron microscopy (SEM) analysis is one of the most powerful electron microscope techniques. SEM images materials having microscopic structure by scanning the surface of the specimen with much greater depth and much higher resolution than confocal microscopes. This technique is used to image the morphology and the surface microstructure by scanning the surface of the sample with a well-focused high energy electron beam. Based on the interactions between the primary electron beam, which is generated from an electron gun or filament and the sample, a number of signals such as secondary electrons, back scattering electrons and X-rays will be produced [316]. Both secondary electrons and back scattering electrons are of great interest because they provide information about the microstructure and the morphology of the scanned area. A photomultiplier detector is used to detect and record these signals to regenerate
an image for the surface of interest which is displayed on a screen. Figure 2.10 shows a schematic diagram of SEM technique.

![Schematic diagram of SEM technique with the CRT screen](image)

Figure 2.10 Schematic diagram of SEM technique with the CRT screen [316]

Both elemental compositions and thickness of a thin film deposited on a substrate can be accurately determined by measuring different X-ray intensities at various accelerating voltages. When the accelerated electron beam interacts with atoms in a sample, the energy generated by X-rays is dependent on the atomic structure. In other words, each atom shows a characteristic X-ray emission spectrum. Therefore, these X-rays are characteristic of the elements present in the sample. Also, these rays can be separated in the energy spectrum to identify the elemental composition of the sample. This phenomenon is known as Energy Dispersive X-ray spectroscopy (EDX). This technique provides quick analysis of the elemental composition of the sample because a spectrum in the range of 0.1 to 20 KeV can be recorded in a short time (10 ~ 100 s).

2.4.3.1. Experimental Technique of SEM

SEM has been widely used in elemental and morphological analysis of materials. It also provides very clear images of samples that are outside the capabilities of commonplace microscopes. An
SEM image is generated by a focused electron beam which hits and probes over the surface of a sample. The most important advantage of SEM is its ability to form three-dimensional images due to its great depth of field which can reach the order of micrometres at $10^4 \times$ magnification. Also, the SEM technique is relatively simply operated and maintained, compared with transmission electron microscopy (TEM). In the present study, a JCM-6000 scanning electron microscope supplied with an EDX analysis column was used to determine thin film thicknesses and the elemental compositions of the samples.

FESEM is similar to a SEM instrument, except that the FESEM is supplied with an extra field emission cathode in the electron gun. The electrons ejected from the cathode are accelerated by high electric field then focused and deflected by specific electronic lenses in a high vacuum column yielding a narrow beam that hits the specimen surface. Accordingly, secondary electrons are released from the specimen with velocities and angles related to the surface structure of the specimen. The FESEM technique provides better images compared with SEM due to the sharper probing beam at high and low electron energy, yielding both enhanced resolution of the image and minimising the damage and charging of the sample [317]. In this work, surface morphologies of synthesized thin films were examined via a PHILIPS XL 20 SEM equipped with a Zeiss Neon 40EsB FESEM with a maximum extra high tension (EHT) voltage field emission gun of 30 kV. SE2 detectors and InLens were used to obtain FESEM images at different magnifications. For FESEM analysis, samples were mounted on a sample holder using double-sided carbon tape and coated with platinum (3 nm thick) to minimise the charging effect prior to imaging.

2.4.4. Atomic Force Microscopy (AFM)

Atomic force microscopy is a common and powerful tool to image and analyse the roughness and topography of coating surfaces. In comparison with the optical and electron microscopes that image the coating’s surface, AFM involves measuring the deflection of a sharp force-sensing tip in contact with the surface. This sharp tip is usually made from Si or SiN. The changes in the coating’s surface contours result in moving the cantilever vertically (i.e., $z$-axis) for each $(x, y)$ point. A four segment-photodiode detector is used to monitor the changes in the deflection of the
cantilever and these changes are recorded and processed by computer to create a topographic image for the coating’s surface [318].

In this study, the AFM images of the fabricated thin films were obtained via a Bruker Dimension (Santa Barbara, CA) fast scan atomic force microscope. The thin films were mounted on adhesive tape prior to AFM scans, and the images were performed in tapping mode using a standard tapping mode probe (type NCHV with resonant frequency of 300 kHz and spring constant of 40N/m).

### 2.4.5. Raman Analysis

Raman spectroscopy is a common vibrational spectroscopy technique that is used for material characterization. It provides specific structural information at the atomic scale on organic and inorganic compounds [319]. Raman Effect, discovered by C. V. Raman in 1928, is based on the phenomenon of electromagnetic radiation scattering (Raman scattering) by molecules of the material [320]. When a photon of light of single wavelength interacts with a molecule in a sample, the photon may be absorbed and/or scattered. The absorption process occurs when the resonance condition is satisfied (i.e., the energy of the incident photon and the energy difference between two states of the molecule are equal), and transitions between these states are accompanied by a change in the dipole moment of the molecule. Photons which are not absorbed will be scattered elastically and/or in-elastically. Elastic scattering occurs if the scattered photon has the same energy (frequency) and therefore, wavelength as that of the incident radiation. This phenomenon is commonly known as Rayleigh scattering [321]. Inelastic scattering, referred to as Raman scattering, occurs when the energy of scattered and incident radiations are no longer equal. In Raman scattering, the molecule may either lose energy, or gain energy from the photon of light. When the scattered photon has energy lower than the incident photon, this phenomenon is known as Stokes Raman scattering. Conversely, when the scattered photon has energy higher than the incident photon, this phenomenon is known as anti-stokes Raman scattering. When a molecular vibration encourages a change in the polarizability of molecule’s electric field, vibrational Raman scattering takes place [322]. The selection rules for Raman active vibrational modes are related to molecular symmetry and enable detection of vibration modes which alter
the polarizability of the molecule. A Raman spectrum can be obtained by plotting the intensity of Raman scattered photon versus its frequency difference from the incident photon (Stokes-shifted frequencies). This difference in frequency is referred to as Raman shift, which is independent of the frequency of incident photon. Frequency shifts between the Raman scattered photons and the incident photon relate to the vibrational energy levels of the crystal and/or molecule. Several parameters such as symmetry of the crystal, molecular geometry, structural disorder, crystal strain, atomic mass, bond order, local environment and atomic environment may affect the vibrational energy. Therefore, Raman spectroscopy can help to investigate the crystal lattice vibrations, intra-molecular vibrations and other types of motions of extended solids [322].

2.4.5.1. Experimental Technique of Raman Analysis

In this study, Raman analysis was conducted using a Nicolet 6700 Fourier transform infrared (FT-IR) spectrophotometer equipped with NXR FT-Raman module. Raman spectra were collected using a Helium-Neon (He-Ne) monochromatic laser with 1064 nm excitation wavelength and 0.204 W operation power, CaF₂ beam splitter, InGaAs detector with 90° detection angle, optical velocity of 0.3165, gain of 1, aperture of 150, and 16 scans with resolution of 8 cm⁻¹ in the range of 0 - 4000 cm⁻¹.

2.4.6. Optical Properties of Thin Films

The optical characteristics of TCO thin film coatings are very important in optoelectronic applications. Thin film coatings are classified as transparent if they show a typical transparency greater than 80% in the entire visible range of the electromagnetic spectrum. Transmission or transparency is defined as the ratio of transmitted light to the incident light. The optical properties of a solid can be categorized into three phenomena named as transmission, reflection and absorption [323]. These interactions depend on the nature of the solid matter and the wavelength of the incident light. The amount of light transmitted mainly depends on the reflectivity from the front and back surface as well as the way the light is absorbed within the medium [324]. The optical properties of ITO thin films prepared in this study were characterized by means of optical transmittance measurements. The main optical properties included optical band gap energy and optical constants such as refractive index, extinction coefficient and dielectric constant that cannot be directly obtained from the measurements.
2.4.6.1. Measurements of Optical Transmittance via UV-Vis Spectroscopy

In this study, a Perkin Elmer lambda 650 UV-Vis spectrophotometer was used to collect the transmittance data of the prepared thin films. This instrument consists of a double beam light source, double monochromators with a diffraction grating, ratio recording optical system and detector (photodiode). A halogen lamp is often used as the radiation sources to cover the working wavelength range (190 - 900 nm). All reflecting optical components of this instrument are coated with silica (SiO$_2$) for durability. Prior to each optical measurement, light intensity calibration was performed and comprised in taking a baseline spectrum without sample in the measurement chamber (air blank) then uncoated substrate was also measured as a reference. This calibration process facilitates the suppression of residual noise. The transmittance spectrum of the film coatings at a desired wavelength was then conducted and compared with the reference one (uncoated substrate). For a transmission measurement, the coated side of the sample was irradiated by incident monochromatic light perpendicular to the sample surface. The optical transmittance data presented in this study consists of the transmittance of both the thin film coating and the substrate.

2.4.6.2. Band Gap Calculations

Transmission data can be used to determine thin film optical band gap energy. Jan Tauc reported that the transmittance data of a thin film coating can be used to calculate the absorption coefficient ($\alpha$) of a coating along the entire wavelength. Plotting $(\alpha h\nu)^{1/n}$ versus photon energy results in a Tauc plot, which shows the linear drop of the absorption edge. The value of $n$ depends on the type of electron transition whether it is direct ($n = 1/2$) or indirect ($n = 2$). By extrapolating the linear part of Tauc plot toward X-axis, the optical band gap energy is obtained [37]. Figure 2.11 shows a typical Tauc plot for estimating the band gap energy.
2.4.7. Electrical Properties of Thin Film Coatings

The electrical performance of the thin film coating is evaluated by means of electrical resistivity (given in Ω.cm) or sheet resistance (given in Ω/sq.) of the film. Figure 2.12 shows the geometry defining the sheet resistance of a thin film with thickness $t$. The sheet resistance is then given by the following relation [325]:

$$R_s = \frac{\rho b}{A} = \frac{\rho}{t} \quad (2.29)$$

where $t$ is the film thickness and $A$ is the effective cross-sectional area ($A=b \times h$).
Electrical conductivity is the inverse of resistivity \((\sigma = 1/\rho)\) and is expressed in Siemens per meter (S/m). In this study, the electrical properties including resistivity, conductivity, carrier concentration and Hall mobility of the synthesized thin films were investigated by means of four-point probes and Hall effects measurements. Since the electrical properties of the material are temperature dependent, all the electrical measurements adopted in this work were carried out at room temperature.

2.4.7.1. Four-Point Probes Measurements

The 4-point probe system is a powerful tool commonly used to measure the electrical resistivity and sheet resistance of semiconductor materials. Compared to traditional 2-point probe, 4-point probe gives more accurate results of material resistivity because it eliminates the contact and probe resistance. This device generally comprises of four uniformly spaced probes organized in linear configuration (see Figure 2.13). The spaces between each two neighbouring probes are 1mm. An electric current is passed through the two outer probes, while the voltage recorded from the two inner probes, which allows the measurement of the film resistivity, provided the thickness is known. The electrical resistivity is given by the following relation:

\[
\rho = \frac{\pi}{\ln(2)} t \left( \frac{V}{I} \right)
\]  

(2.30)

where \(t\) is the film thickness, \(V\) is the voltage across the inner two probes and \(I\) is the current passed through the outer two probes. For accurate resistivity measurements, the four probes must perfectly attached the film surface and the contact diameter should be smaller than the spaces between the probes [325].
2.4.7.2. Hall Effects Measurements

Hall effect is one of the most commonly used methods for characterizing electrical properties of thin film coating and materials including charge carrier concentration, carrier mobility and type of conductivity (n- or p-type). The Hall Effect is the product of a transverse voltage difference (Hall voltage $V_H$) resulting from the deflection of the charge carrier by Lorentz force, when an electric current flows through a conductor placed in a magnetic field [327]. The current and magnetic field are perpendicular to each other and the resultant Hall voltage is perpendicular to both of them. Figure (2.14) shows the scheme of Hall Effect. The sign of the Hall voltage, whether it is positive or negative, reflect the induced Lorentz force direction as well as the carrier type. The Hall voltage is expressed by the following relation:

$$V_H = -\frac{B\ell}{net}$$  \hspace{1cm} (2.31)

where $I$ and $B$ are respectively the electrical current and the magnetic field, $n$ is the carrier concentration (density), $e$ is the electron charge and $t$ is the film thickness.
Therefore, by calculating $V_H$ from identified values of $B$, $I$, $q$ and $t$, the carrier concentration can be determined. The Hall mobility is given by the following relation:

$$\mu_H = \frac{v_H}{R_s IB}$$  \hspace{1cm} (2.32)

where $R_s$ is the sheet resistance, which is determined via four-point probe.

Thus, a combination of Hall measurements and resistivity is needed to obtain both the carrier concentration and hall mobility. This is known as the Van Der Pauw method [241].

2.4.8. Mechanical Characterization: Nanoindentation Measurements and Finite Element Modeling (FEM) of Thin Film Coatings

Determination of the mechanical characteristics of different types of thin film coatings are very important for many electronic and optoelectronic systems. Mechanical characteristics including hardness ($H$) and Young’s modulus ($E$) can identify strengthening and deformation mechanisms.
on a small scale [328]. In addition, the hardness and Young’s modulus are important aspects to estimate the wear resistance of thin film based transparent conductive materials. The stability and the performance of thin film coatings could be maintained by monitoring the wear resistance behaviours of the film coatings [329]. Nanoindentation is a well-established technique performed to investigate the mechanical properties of thin film coatings at a nanometre scale. A load \( P \) is applied through a diamond head, initially in contact with the film surface. Both load and penetration depth or displacement \( h \) are controlled during the loading and un-loading measurement processes, and the penetration depth of the diamond head into the film coating is recorded, along with the applied load. Different parameters such as hardness, Young’s modulus, residual stress and fracture toughness can be investigated from the load-penetration depth curve \( P-h \) curve) [330]. The most important part in the nanoindentation system is the indenter which has to have well-known geometry and high precision. Most nanoindentation systems use a diamond indenter with specific geometry such as flat-ended cylindrical, spherical or sharp. Of these, the sharp indenter (including Vickers, cube corner and Berkovich) is preferred, especially for nano and micro-scale measurements of thin films.

Oliver and Pharr proposed that the hardness and Young’s modulus could be determined directly from a set of indentation load and penetration depth \( (p-h) \) measurements, recorded in both loading and unloading modes without the need to image the hardness impression [331]. Three important quantities can be estimated from the \( p-h \) plot: maximum load \( (P_{\text{max}}) \), the maximum displacement \( (h_{\text{max}}) \) and elastic unloading stiffness \( (S) \) (also known as the contact stiffness), which is represented by the slope of the higher part of the unloading curve within the early stage of unloading (See Figure 2.15). The hardness which is defined as a measure of how resistant a solid is to deform permanently under an applied compressive force can be calculated by the following relation:

\[
H = \frac{P_{\text{max}}}{A} \tag{2.33}
\]

where \( P_{\text{max}} \) is the maximum load and \( A \) is the area of the hardness impression (contact area).

Young’s modulus is known as the ratio of stress to strain within the elastic (Hooke) limit which can be determined from the values of contact stiffness \( S \) and contact area \( A \) via the following relation:
\[ S = \beta \frac{2}{\sqrt{\pi}} E_{\text{eff}} \sqrt{A} \]  

where \( \beta \) is a dimensionless constant taken as unity and \( E_{\text{eff}} \) can be expressed as:

\[ \frac{1}{E_{\text{eff}}} = \left( \frac{1-\sigma^2}{E} + \frac{1-\sigma_i^2}{E_i} \right) \]  

where \( \sigma \) and \( E \) are the Poisson’s ratio and Young’s modulus of the thin film, respectively. \( \sigma_i \) and \( E_i \) are the Poisson’s ratio and Young’s modulus of the indenter, respectively.

\[ \text{Figure 2.15 Typical loading and unloading curves of the nanoindentation [331]} \]

2.4.8.1. Experimental Technique ofNanoindentation Measurement

The mechanical characteristics of the thin film coatings can be determined either in lateral or depth geometry without removing the thin film from the substrate. The nanoindentation system measures the depth of penetration by a capacitance or inductance displacement sensor. The main part of this system is the indenter. In this work, the mechanical properties of the thin film coatings were investigated \textit{via} a nanoindentation workstation (Ultra-Micro Indentation System
2000, CSIRO, Sydney, Australia) supplied with a sharp Berkovich-type indenter of 5 μm radius according to Oliver and Pharr model [332]. Prior to the nanoindentation measurements, the area of the indenter head was calibrated with a standard fused silica substrate. The nanoindentation results were performed under a load control method with a maximum load of 200 nN. The low peak loading is based on the consideration that the maximum displacement during indentation should be no more than 10% of the coating thickness, and that high loading may result in micro-cracks in the coating, which is thought to be relatively brittle, compared with metal coatings. To obtain better resolution, the number of measuring points were increased to 15 during loading, and 20 during unloading, respectively.

2.4.8.2. Finite Element Modeling (FEM)

FEM was performed to study the stress distribution throughout the thin films and the substrates underneath the indentation tip and to evaluate the mechanical response of the coatings to external loading. Experimental results of the mechanical properties obtained from the nanoindentation measurements were used as input parameters in FEM modelling. COMSOL multiphysics version 3.5a software was used in the simulation, and a two dimensional (2D) axisymmetric model was built with the loading direction along the z-axis. Details of this model set-up are briefly outlined here. A spherical indenter with a radius of 5 μm loaded onto a film of 2 μm thickness placed on top of glass substrate, with a maximum indentation depth of 0.2 - 0.6 μm, was modelled. Note that this film thickness, which is different from those of our experimental thin films, was used here for a general assessment and comparison, and is designed to match the loading conditions. The consideration here is that, under real application environments, loadings with a dimension in the order of μm are more accurate than smaller and sharper ones.
CHAPTER 3 Improving the Optoelectronic Properties of Titanium Doped Indium Tin Oxide Thin Films

Paper I

3.1. Abstract

The focus of this study is on a sol–gel method combined with spin-coating to prepare high quality transparent conducting oxide (TCO) films. Structural, morphological, optical, and electrical properties of sol-gel derived pure and Ti-doped indium tin oxide (ITO) thin films were studied as a function of Ti concentration (i.e., 0, 2 and 4 at.%) and annealing temperatures (150 – 600 °C). FESEM measurements indicate that all the films are ~ 350 nm thick. XRD analysis confirmed the cubic bixbyite structure of the polycrystalline indium oxide phase for all of the thin films. Increase of the Ti ratio, as well as the annealing temperature, improved the crystallinity of the films. The highly crystallite structures were obtained at 500 °C, with average grain sizes of about 50, 65 and 80 nm for Ti doping of 0 at.%, 2 at.% and 4 at.%, respectively. Electrical and optical properties improved as the annealing temperature increased, with an enlarged electronic energy band gap and the optical absorption edge below 280 nm. In particular, the optical transmittance and electrical resistivity of samples with 4 at.% Ti content improved from 87% and 7.10×10⁻⁴ Ω·cm to 92% and 1.6×10⁻⁴ Ω·cm, respectively. The conductivity, especially for the annealing temperature at 150 °C, is acceptable for many applications such as flexible electronics. These results demonstrate that, unlike the more expensive and complex vacuum sputtering process, high quality Ti-doped ITO films can be achieved by a fast processing, simple wet-chemistry, and easy doping level control with the possibility of producing films with high scalability.
3.2. Introduction

Research on transparent conductive oxide (TCO) materials has received significant attention in order to develop a good combination of unique optoelectronic properties including high visible light transmittance and low electrical resistivity. A large number of metal oxides such as indium oxide ($\text{In}_2\text{O}_3$), tin oxide ($\text{SnO}_2$), zinc oxide ($\text{ZnO}$), titanium dioxide ($\text{TiO}_2$), cadmium oxide ($\text{CdO}$), aluminium doped zinc oxide (AZO) and indium tin oxide (ITO) are widely utilized as transparent conductive materials [126, 333, 334]. Amongst this family of materials ITO has a large number of favourable properties such as low electrical resistivity, high transparency in the visible light region, great film-substrate adhesion and good chemical stability. Therefore, ITO films are of great interest and represent the prime candidate for numerous applications in optoelectronic devices such as flat panel displays, solar cells, organic light-emitting diodes, sensors, functional glass and electro-chromic devices [153, 335-341]. Numerous techniques are employed for synthesizing ITO films such as, DC and RF magnetron sputtering, thermal evaporation, pulsed laser deposition, electron beam evaporation, screen printing and sol-gel processes [342-346]. Among the existing methods, some of them require sophisticated equipment including high vacuum systems coupled with physical vapour deposition (PVD) processes that consume a large amount of bulk material and are detrimental to the environment, which results in very expensive end products. Therefore, finding an alternative to the PVD process to synthesize high quality transparent conductive films becomes an important objective for materials scientists around the world. The sol–gel method combined with spin-coating and/or dip-coating offers certain advantages such as lower processing time, cost effectiveness, no vacuum requirements, easy control of the doping level, and producing films with high scalability, along with the flexibility of achieving desired shapes and surface areas [196, 347, 348].

The electrical conductivity of TCO films can be improved by increasing either its carrier concentration or carrier mobility. Doping $\text{In}_2\text{O}_3$ or ITO with some transition-metal elements, e.g., Mo, Ti, Nb and W, can improve their optoelectronic properties significantly as a result of (1) the smaller ionic radii and the higher mobility of these elements [349], and (2) facilitating the production of transparent conductive films with low resistivity, high electron mobility and superior near-infrared transmittance [350].
In this study, simple and low cost spin-coating derived Ti-doped ITO thin films were fabricated with two different Ti concentrations and various post annealing temperatures (400 - 600 °C). The films were then compared with pure ITO prepared under the same conditions. The roles of Ti additives and annealing temperature were examined for the effects on structural, morphological, electrical and optical characteristics, as these are effects which have not been previously looked at in detail especially that annealed at high temperature of 600 °C.

3.3. Experimental Techniques

3.3.1. Thin Films Deposition

ITO and Ti-doped ITO solutions were prepared using hydrated indium nitrate (In(NO₃)₃.5H₂O, purity 99.9%, Alfa Aesar), tin chloride dihydrate (SnCl₂.2H₂O, purity 98%, Chem-supply) and titanium(IV) isopropoxide (Ti[OCH(CH₃)₂]₄, purity 99.9%, Sigma Aldrich). All these chemicals were used as received. Absolute ethanol was used as a solvent and the ITO films were deposited onto soda-lime glass slides.

3.3.2. Sol-Gel and Thin Films Preparation

In order to prepare an ITO solution with concentration of 0.1M, the required amounts of hydrated indium nitrate In(NO₃)₃.5H₂O and tin chloride dihydrate (SnCl₂.2H₂O) were dissolved in absolute ethanol and stirred for 1 hour. The resultant solutions were then mixed and refluxed at 85 °C for 1 hour. The percentages of In was kept constant (~ 90 at.%) in all initial solutions.

Two different varieties of the Ti-doped ITO solutions were prepared with 2 at.% and 4 at.% Ti contents with respect to 0.1M of ITO solutions. In separate beakers, hydrated indium nitrate, tin chloride dihydrate and titanium (IV) isopropoxide (Ti[OCH(CH₃)₂]₄ were first dissolved in absolute ethanol and stirred for 1 hour. The resultant solutions were then mixed together and refluxed at 85 °C for 1 hour. The final solutions were aged for 24 hours at room temperature. In order to obtain uniform and homogenous thin films, glass substrates were first cleaned with detergent and rinsed in deionized water (DI water). Then, the substrates were sonicated in ethanol at 60 °C for 10 minutes, and DI water cleaning was repeated. The final step was the sonicaton of substrates in DI water at 60 °C for 10 minutes. All the glass substrates (soda–lime–
silicate with 25×25 mm dimensions) were dried in a conventional vacuum drying oven at 100 °C for 20 minutes prior to the coating process. Spin coating experimental procedures were (1) dispensing the solution on to the substrate at 300 rpm for 15 seconds, (2) spreading the solution at 2500 rpm for 20 seconds, (3) drying the solution at 4000 rpm for 20 seconds, and (4) heat treatment on a hot plate at 150 °C for 10 minutes. These steps were repeated until the desired thickness was achieved. Fabricated samples were then annealed at the temperatures of 400, 500 or 600 °C for 2 hours in air atmosphere.

3.3.3. Analysis Techniques

The structural properties of the sol–gel derived thin films were investigated via X-ray diffraction (XRD) analysis using a GBC EMMA diffractometer with CuKα radiation (λ=0.154nm). The diffraction angle (2θ) of measurement was within the range of 20° - 70° with a scanning rate of 2°/min and 2θ step size of 0.01°. The surface morphology was examined by using Zeiss Neon 40EsB field emission scanning electron microscopy (FESEM). For FESEM, the samples were mounted onto the substrate holder using double-sided carbon sticky tape and then coated with platinum (3nm thick) to reduce the charging effects prior to FESEM imaging. The electrical properties of prepared films were measured by a 4-point probe method (Dasol Eng. FPP-HS8) and the Hall-effect measurements were performed on specimens of (10×10 mm). Au contacts were thermally evaporated on the coated samples in a system of four probes. The measurements were carried out using ECOPIA HMS-2000 system with Polytec Bipolar Operation Power supplies (BPO) at 0.9 Tesla of magnetic field. The optical properties were obtained by using UV-VIS Perkin Elmer spectrometer in a wavelength range of 250 - 800 nm.

3.4. Results and Discussions

3.4.1. Structural Properties

Figures 3.1 and 3.2 show the XRD spectra for the ITO and Ti-doped ITO coatings as deposited (150 °C heat treatment only) and annealed at different temperatures, respectively. The XRD data indicate that all the films are polycrystalline with a body centred cubic bixbyite structure similar to In2O3 with space group of Ia3/cubic (JCPDS card 06-0416) as expected and there are no impure phases related to tin or titanium compounds, indicating that the prepared solutions were homogeneous. The main peaks from as deposited and post annealed thin films at temperatures of
400, 500 or 600 °C are assigned to be (222), (400), (411), (332), (440) and (622) reflection planes of In$_2$O$_3$. These results confirm the observation that the polycrystalline feature of In$_2$O$_3$ may act as a network with a body centred cubic bixpyite structure with lattice parameter of 10.118 Å [351, 352]. Both as deposited ITO and Ti-doped ITO thin films show poor crystallinity because of the crystallization temperature of ITO in the range of 150-160 °C [68, 353]. This is also consistent with Yang et al. who reported the same crystalline properties for as deposited Ti-doped ITO films [354]. As the ionic radii of Titanium (Ti$^{4+}$), tin (Sn$^{4+}$) and indium (In$^{3+}$) are 0.06, 0.07 and 0.09 nm, respectively [65], the small ionic radii of Sn$^{4+}$ and Ti$^{4+}$ imply that the crystalline structure may not change if these elements are used as dopant into In$_2$O$_3$ and/or ITO frameworks. As such, we postulate that enhancing the preferred orientation and enhancing the crystal growth of the 3-d metal-doped ITO thin films could be attributed to introduction of Ti as a dopant for these thin films [244, 355]. Figures 3.1 and 3.2 also show that for both ITO and Ti-doped ITO films the (222) and (400) peaks around 30.5° and 35.2°, respectively, are featured prominently. This indicates the coexistence of <100> and <111> textures. The films have further observable characteristics as the annealing temperature was increased, indicating enhanced crystalline quality. When the annealing temperature was increased from 150 °C to 600 °C, the ITO thin film exhibits the same (222) orientation, while the (400) diffraction peak becomes very strong for both Ti concentrations, indicating a preferred orientation in <111> direction. It has been observed by Suzuki et al. and Latz et al. that ITO films prepared by sputtering exhibit a change in the orientation direction from (222) to (400) when the substrate temperature was increased during the sputtering process [243, 356]. Kumar and Mansingh also reported that the structure and the orientation direction for ITO samples was governed by the energy of the sputtered particles reaching the substrate and they assumed that the higher energy sputtered particles orientate in the (400) direction while the thermalized sputtered particles prefer the (222) orientation [357]. However, the pure ITO thin films did not show the tendency of changing the orientation direction from (222) to (400) reported by the aforementioned studies of Suzuki et al. and Latz, et al. [243, 356] which may be attributed to the nature of sol-gel spin coating process. Regarding the Ti-doped ITO thin films adopted in this work, the change of the major orientation direction from (222) to (400) with the increase of annealing temperature is in good agreement with Pu et al. results for vacuum synthesised Ti-doped ITO films at different substrate
temperatures. They reported that the high substrate temperatures provided the ad-atoms with sufficient energy to migrate along the (400) direction [244].

Figure 3.1 The XRD patterns of as deposited and post annealed ITO thin films
Figure 3.2 The XRD patterns of Ti-doped ITO films prepared at 2at.% and 4 at.% Ti concentrations and post annealed at different temperatures.
The Scherrer equation (Eq. 2.26) was used to calculate the grain size from the line broadening or the full width at half maximum (FWHM) of the main peak (222). While, Bragg's law (Eq. 2.25) was used to estimate the inter-planar spacing (d spacing) and the standard Bravais lattice for a cubic system (Eq. 2.27) was used to obtain the lattice constant.

From Table 3.1 and Figure 3.3, it is clearly shown that the grain sizes of the thin films are enlarged with the increase in Ti-contents. This is because the additional Ti atoms act as nucleation centres that help the early coalescence of the particles, resulting in formation of larger crystals [358]. It is also found that with gradual increase in annealing temperature the grain sizes of the films are enlarged as well, reaching a maximum at 500 °C and then decreasing (see data at 600 °C). Both Ti doping level and annealing temperature enhanced the peak intensities and hence the crystalline structure for ITO and Ti-doped ITO coatings, through substitution of In atoms by both Sn and Ti atoms. Also, the vibration of the doping atoms could also result in an annealing effect that supports nucleation and growth of the film along the preferred orientations.

For the as deposited and post annealed thin films, the average calculated lattice constants of both ITO and 2 at.% and 4 at.% Ti-doped ITO films were estimated to be 10.13 Å, 10.14 Å and 10.17 Å respectively, which are slightly greater than the reported value for un-doped indium oxide of 10.118 Å. This increment in the lattice constant for both ITO and Ti-doped ITO thin films is related to the small ionic radius of both Sn and Ti relative to the substituted In atoms in the In₂O₃ matrix. Also, it appears that the extent of Sn and Ti incorporation is intensely temperature dependent, resulting in an increase in the lattice constants for ITO and Ti-doped ITO thin films compared with un-doped In₂O₃. This in turn, has a noticeable impact on the film structure leading to improved electron mobility in optimally doped films. Bourlange and co-authors attributed the increase of the lattice constant to the occupation of conduction band states which are In-O anti-bonding [359]. Also, the alteration in the lattice parameters could be associated with the growth induced stress near the film surface during doping and annealing [360], which may be raised from the oxygen deficiency and thermal expansion coefficient mismatch between the film and the substrate [361, 362]. Figure 3.4 shows the shifting of the main peaks (i.e., (222) orientation) for ITO and Ti-doped ITO thin films annealed at 500 °C. The shifts of (222) toward lower 2θ value indicates distortion in the lattice structure takes place due to Ti additives, and thus leading to an expansion in calculated lattice parameters.
Figure 3.3 The annealing temperature dependent grain size

Figure 3.4 Peaks shift of (222) for the ITO and Ti-doped ITO thin films annealed at 500 °C
Table 3.1 Structural parameters for the ITO and Ti-doped ITO thin films at 2 at.% and 4 at.% Ti concentration and post annealed at different temperatures

<table>
<thead>
<tr>
<th>Ti at.%</th>
<th>T°C</th>
<th>2θ (in degrees)</th>
<th>d-spacing Å</th>
<th>(h k l)</th>
<th>Lattice constant Å</th>
<th>Crystallite size nm</th>
</tr>
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<tbody>
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<td>0 at.%</td>
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<td>30.56</td>
<td>2.921</td>
<td>(222)</td>
<td>10.12</td>
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<td>400</td>
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<td>10.13</td>
<td>31</td>
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<td></td>
<td>600</td>
<td>30.52</td>
<td>2.925</td>
<td></td>
<td>10.13</td>
<td>46</td>
</tr>
<tr>
<td>2 at.%</td>
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<td>30.52</td>
<td>2.925</td>
<td>(222)</td>
<td>10.13</td>
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<td></td>
<td>400</td>
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</tr>
<tr>
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<td>30.52</td>
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<td>2.923</td>
<td></td>
<td>10.15</td>
<td>60</td>
</tr>
<tr>
<td>4 at.%</td>
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<td>2.934</td>
<td>(222)</td>
<td>10.16</td>
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<td>2.942</td>
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<td></td>
<td>600</td>
<td>30.46</td>
<td>2.931</td>
<td></td>
<td>10.15</td>
<td>68</td>
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</tbody>
</table>

3.4.2. Surface Morphology Properties

The FESEM images of the synthesized ITO and Ti-doped ITO films as deposited (150 °C) and after being annealed at 400, 500 and 600 °C are presented in Figures 3.5 and 3.6. The surfaces of all the thin films are smooth, homogeneous, and composed of uniform coalesced clusters, and show a grain structure demonstrating the nanocrystalline features. However, the as deposited thin film of 4 at.% Ti shows a smoother surface and larger grains compared to those of pure ITO and 2 at.% Ti-doped ITO that may be due to the enhancement of crystallinity with Ti ratio. Also, increasing the annealing temperature up to 500 °C resulted in an increase in grain size and decreased grain boundaries which are in a good agreement with the results obtained from XRD measurements. As the annealing temperature was further increased to 600 °C, micro-cracks were formed on the surfaces of all the films due to induced stress resulting from possible different thermal expansions between the film and its substrate.
Figure 3.5 FESEM images of prepared and post annealed ITO thin films

Figure 3.6 FESEM images of Ti-doped ITO thin films, (a1-a4) for 2 at.% and (b1-b4) for 4 at.% Ti concentrations and post annealed at different temperatures
3.4.3. Electrical Properties

The dependence of electrical resistivity, carrier concentration and carrier mobility on Ti dopant concentration and thermal annealing temperature are shown in Figures 3.7 and 3.8 respectively. Figure 3.7 indicates that the resistivity for as deposited thin films with 4 at.% Ti content is lower than those for as deposited pure ITO and 2 at.% Ti thin films. This is most likely attributed to the level of Ti doping which contribute to a large number of electrons and hence increasing the number of free carries in the thin films. Furthermore, during the sol-gel spin coating process, the formation of both defects and oxygen vacancies (those are considered as electron donors) were introduced easily which also results in a decrease in the film resistivity. Additionally, the resistivity of the films decreased with increasing annealing temperature for both pure ITO and Ti-doped ITO at both Ti concentrations. The lowest resistivity values ($1.6 \times 10^{-4}$ $\Omega$·cm and $1.8 \times 10^{-4}$ $\Omega$·cm) were obtained from samples annealed at 500 °C with 4 at.%, 2 at.% Ti concentrations and pure ITO, respectively. These results are as good as that fabricated using vacuum sputtering techniques, e. g., $1.8 \times 10^{-4}$ $\Omega$·cm [363]. It was reported by Chopra et al. that the low resistivity and/or the high conductivity of the ITO films is related to carrier concentration, which is linked to the dopant level and/or oxygen vacancies [14, 342, 364]. The annealing temperature leads to enhanced substitution of indium atoms by titanium and tin atoms, yielding an increase in carrier concentration in the thin films. Moreover, increased annealing temperature assisted desorption of interstitial oxygen atoms at the grain boundaries which has led to improved crystal structure and reduced the grain boundaries of the films. Therefore, the trapped electrons at the grain boundaries were released which contributed to increase the carrier concentration, as well as conductivity. This is evident in Figure 3.8, where the carrier concentration and the Hall mobility increased to their maximum values of $(7 \times 10^{20}, 7.4 \times 10^{20}$ and $8.6 \times 10^{20}$) cm$^{-3}$ for pure ITO, 2 at.% and 4 at.% Ti concentrations, respectively. Similarly, the Hall mobility is strongly depended by the disordered of the crystallite structure, which can be manipulated by a number of approaches, such as doping and annealing temperature. It is interesting to note that, however, the as deposited film with 4 at.% Ti has a higher carrier concentration but lower Hall mobility compared with those of pure ITO and 2 at.% Ti thin films. This is probably attributed by the solubility limits of Sn and Ti dopants resulting in the increase of occupational random sites in the ITO matrix. With increasing the annealing temperature up to
500 °C, the highest Hall mobility values (39 cm²/Vs, 42 cm²/Vs and 49 cm²/Vs) and lowest resistivity were accomplished for all the films studied here.

As the annealing temperature was further increased to 600 °C, the resistivity increased while the carrier concentration and the carrier mobility decreased for both Ti concentrations. This behaviour is expected, due to oxygen chemisorbed on the sample surface [364, 365]. Also, all the thin films annealed at this temperature show some micro-cracks, see FESEM images above. These cracks may be due to the mismatch of thermal coefficients between films and substrates which causes a significant increase of compressive stress in the films. Eventually these micro-cracks increase resistivity of the films. A summary of electrical properties of these films are presented in Table 3.2.

![Graph](image1)

![Graph](image2)

**Figure 3.7** Electrical resistivity of pure ITO and Ti-doped ITO thin films for 2 at.% and 4 at.% Ti concentrations and post annealed at different temperatures
Figure 3.8 Variations of carrier concentration and Hall mobility of ITO and Ti-doped ITO thin films for 2 at.% and 4 at.% Ti concentrations with annealing temperature.
3.4.4. Optical Properties

The optical transmittance spectra of ITO and Ti-doped ITO thin films are shown in Figure 3.9. The optical transmittance of as deposited ITO and Ti-doped ITO thin films are very similar; however, the ITO film doped with 4 at.% Ti exhibits a higher optical transmittance of 87% over the entire wavelength range. This may be due to the enlargement of the grain size and Ti additive, as explained in the XRD and FESEM results (see section 3.4.1 and section 3.4.2). Moreover, decreasing the level of defects, which could act as scattering centres, may contribute to a higher optical transparency in the thin films. The highest optical transmittance of 92% was achieved for the thin film annealed at 500 °C. Higher annealing temperature leads to higher optical transmittance due to the improvement in the film quality through the increase in the crystallinity and grain size of the film (see the XRD results) as well as reduced grain boundaries. All these factors eventually reduce light scattering yielding better transmittance. It is also observed from Figure 3.9 that there is a shift in the absorption edge to shorter wavelengths as the annealing temperature is increased up to 500 °C which is related to the Burstein-Moss shift (shift of Fermi level due to increasing the carrier density in the conduction band) [366, 367]. This carrier concentration increment is comparable with the results obtained from electrical studies (section 3.4.3). Thus, the higher optical transmittance and the move of the optical absorption edge toward higher photon energy from Ti-doped ITO thin films essentially confirmed the overall improvement of the optical properties of TCO films.

To obtain the band gap energy \( (E_g) \) from the transmittance data, we used the relation:

\[
(ahv)^2 = A(hv-E_g)
\]

(3.1)

where \( a \) is the absorption coefficient, \( hv \) photon energy, \( A \) the proportionality coefficient. Plots of photon energy \( hv \) versus \( (ahv)^2 \) are shown in Figure 3.10. The energy band gap was obtained by extrapolating the straight line part of the plotted curves along the energy axis. Table 3.2 summarizes the optical and the electrical properties of pure ITO and Ti-doped ITO thin films at different annealing temperatures.
Figure 3.9  Optical transmittance of pure ITO and Ti-doped ITO thin films annealed at different temperatures
Table 3.2 The optical and electrical parameters of as prepared and post annealed ITO and Ti-doped ITO thin films for 2 at.% and 4 at.% Ti concentrations

<table>
<thead>
<tr>
<th>Ti at.%</th>
<th>T (°C)</th>
<th>T (%)</th>
<th>E_g (eV)</th>
<th>$\rho \times 10^4$ (Ω.cm)</th>
<th>$n \times 10^{20}$ (cm$^-3$)</th>
<th>$\mu$ (cm/Vs)</th>
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<td>0 at.%</td>
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<td>86.7</td>
<td>3.4</td>
<td>7.6</td>
<td>3.9</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>89</td>
<td>3.5</td>
<td>3.6</td>
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<td>1.8</td>
<td>7.4</td>
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<td></td>
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<td>3.62</td>
<td>3.2</td>
<td>6.4</td>
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</tr>
<tr>
<td>4 at.%</td>
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</tr>
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</tr>
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<td>3.7</td>
<td>2.87</td>
<td>6.8</td>
<td>32</td>
</tr>
</tbody>
</table>

Table 3.2 shows that the optical band gaps of as deposited (150 °C) ITO films in both pure and Ti-doped vary between 3.21 and 3.4 eV. Both pure and Ti-doped ITO thin films exhibit the largest optical energy band-gap after being annealed at the temperature of 500 °C, i.e., 3.7, 3.73 and 3.77 eV for pure ITO, 2 at.% and 4 at.% Ti dopant levels of ITO thin films, respectively. A gradual increase in the optical energy band gap due to the annealing temperature can be associated with the change of grain size and modified carrier concentration (as seen in XRD results) [368]. This can be explained by noting that free electrons are normally trapped in the grain boundaries and by increasing the annealing temperature the grain size increases and the volume of grain boundaries decreases. Consequently, fewer carriers may be trapped in the grain boundary regions leading to an overall increase in the free carrier concentration, and as a result, a higher electrical conductivity is obtained (see section 3.3). Furthermore, the enhancement of optical band gap can also be explained through the $(\Delta E_g^{BM})$ Burstein-Moss relation [369, 370]:

$$\Delta E_g^{BM} = \frac{1}{2m_{vc}} \left(3\pi^2 n\right)^{2}$$

(3.2)

where $m_{vc}$ is the electron effective mass calculated from $m_v$ and $m_c$. $m_v$ and $m_c$ are the effective electron mass in valance and conduction bands, respectively. $n$ is the carrier concentration. The results are consistent with the prediction given by equation (3.2), and in good agreement with Hall measurement results as well [244, 371].
Figure 3.10 Estimated optical band gaps of pure ITO and Ti-doped ITO thin films for 2 at.% and 4 at.% Ti concentrations post annealed at different
3.5. Conclusions

In this work, transparent conductive oxide thin films of pure ITO and Ti-doped ITO were fabricated on to soda-lime glass substrates using an efficient and low cost sol-gel spin coating technique. The effects of doping concentrations (i.e., 0 at.%, 2 at.% and 4 at.% Ti) and annealing temperature (ranging of 150 – 600 °C) on the structural, morphological, electrical and optical properties were studied. The conductivity and optical transparency of Ti doped ITO, particularly those for as deposited (i.e., at 150 °C), are acceptable for many applications such as flexible electronics. All these properties were improved as the Ti concentration was increased from 0% to 4% and the annealing temperature increased up to 500 °C. Increasing both Ti doping level and annealing temperature leads to an enhanced substitution of indium atoms by titanium and tin atoms, yielding an increase in carrier concentration in the thin films. Moreover, increased annealing temperature assists desorption of interstitial oxygen atoms at the grain boundaries which has led to improved crystal structure and reduced the grain boundaries of the films. Likewise, higher Ti ratio and annealing temperature can lead to a higher optical transmittance, due to the improvement in the film quality through the increase in the crystallinity and grain size.

The best performing Ti-doped ITO thin films were achieved with 4 at.% Ti concentration, annealed at 500 °C. In particular, these films exhibited low resistivity (1.6×10^{-4} Ω·cm), high carrier concentration and mobility of (8.63×10^{20} cm^{-3} and 48.7 cm^{2}/Vs, respectively), high transmittance (92%) and a high optical band gap (3.77 eV). These results confirm that high quality Ti-doped ITO thin films, suitable for various optoelectronic applications, can be synthesized by a simple sol-gel and spin coating process.
CHAPTER 4: Probing the Effects of Thermal Treatment on the Electronic Structure and Mechanical Properties of Ti-Doped ITO Thin Films

Paper II

4.1. Abstract

Titanium-doped indium tin oxide thin films were synthesized via a sol-gel spin coating process. Surface chemical bonding states and mechanical properties have been investigated as a function of titanium content (2 and 4 at.%) and annealing temperature ranging from 400 to 600 °C with increments of 100 °C. Raman analysis was performed to study the phonon vibrations for the prepared samples and the results revealed the existence of ITO vibrational modes. The elemental compositions, bonding states and binding energies of the film materials were investigated using X-ray photoelectron spectroscopy (XPS) technique. The XPS results indicated that the ratio of the metallic elements (In, Sn, Ti) to the oxygen on the surface of the thin film coatings decreased due to the increase of the oxide layer on the surface of the thin films. Also, by increasing the annealing temperature up to 600 °C, the Ti 2p and Cl 2p signals were no longer detected for both 2 and 4 at.% Ti contents, due to the thicker surface oxidation layer. Mechanical properties of the synthesized films were also evaluated using a nanoindentation process. Variations in the hardness (H) and the elastic modulus (E) were observed with different Ti at.% and annealing temperatures. The hardness is within the range of 6.3 - 6.6 GPa and 6.7 - 6.8 GPa for 2 and 4 at.% Ti content samples, respectively, while the elastic modulus is within the ranges of 137 - 143 and 139 - 143 GPa for 2 at.% and 4 at.% Ti contents samples, respectively. A combination of the highest H and E was achieved in the sample of 4% Ti content annealed at 600 °C. Furthermore, the H/E ratio ranges from 4.5× 10² to 5.0× 10² which reflects a reasonable level of wear resistance.
4.2. Introduction

Transparent conductive oxides (TCOs) receive widespread attention from researchers due to their unique combination of very low electrical resistivity and high optical transparency over the visible spectral region [336, 372-374]. They exhibit favorable properties which include high infrared reflection, good chemical stability and good mechanical properties along with low electrical contact resistance and high optical transparency in the visible light region. Indium oxide (In₂O₃) and/or indium tin oxide (ITO) based TCOs are the most commonly used transparent conductive oxides compared with zinc oxide (ZnO), aluminium doped zinc oxide (AZO), tin oxide (SnO₂), and cadmium oxide (CdO) [159, 367]. ITO-based TCO films can exhibit different electro-optical, mechanical, electronic structure and composition properties depending on manufacturing technique. Many deposition techniques are used to prepare TCO coatings such as Dc and/or RF sputtering, chemical vapour deposition, reactive evaporation, molecular beam epitaxy, sol-gel method, electron beam evaporation and pulsed laser deposition [193, 243, 259, 375-379]. However, the sol-gel technique has many advantages including cost effectiveness, short processing time, simplicity and the opportunity to fabricate coatings with high scalability along with the flexibility of fine-tuning coatings to have preferred shapes and surface areas [196, 347, 348, 380].

Novel ITO composites doped with 3-d and/or 4-d transition metals, such as (Ti, Ag, Cr, Mo, W, Ta and Cu), are being considered as potential candidates in a wide range of optoelectronic applications such as organic and inorganic solar cells, touch screens, organic light-emitting diodes, sensors and electro-chromic devices [153, 217, 335, 338, 381, 382]. In order to satisfy the demands for some of these applications, TCO composites with improved durability are required. The durability of ITO based coatings depends on their physical, mechanical and structural properties. Therefore, it is expected that the mechanical properties of ITO based films play a significant role in the performance of optoelectronic devices. It has been reported that the bare ITO films have a brittle surface and seem to be susceptible to cracking and delamination. So far, there has been scarce information on the mechanical properties of ITO thin films, particularly, their micro or nanostructure. The elastic modulus and the hardness of 240 nm thick sputtered ITO thin film coatings were reported by Chen et al. [20] to be 140 GPa and 12 GPa respectively. The hardness and elastic modulus were enhanced by introducing hydrogen into the
gas mixture during the deposition process [383]. We propose that incorporating a transition metal such as titanium into the ITO nanostructure may enhance the mechanical properties of this material. Therefore, the main objective of the present study is to evaluate the influence of variations in the Ti concentration and annealing temperature on the chemical bonding states and the mechanical properties, including Young’s modulus ($E$) and Hardness ($H$) of spin coated Ti-doped ITO thin films, technical aspects which have not been reported thus far, to the best of the authors’ knowledge.

4.3. Experimental Details

4.3.1. Thin Films Deposition

Hydrated indium nitrate ($\text{In(NO}_3\text{)}_3\cdot5\text{H}_2\text{O}$, purity 99.9%, Alfa Aesar) titanium(IV) isopropoxide ($\text{Ti[OCH(CH}_3\text{)_2]}_4$, purity 99.9%, Sigma Aldrich), and tin chloride dihydrate ($\text{SnCl}_2\cdot2\text{H}_2\text{O}$, purity 98%, Chem-supply) were used as received as precursors to produce Ti-doped ITO films via a sol-gel spin coating process. Absolute ethanol was used as a solvent and the ITO films were deposited onto soda-lime glass slides.

ITO solutions (0.1 M) were prepared by dissolving appropriate amounts of $\text{In(NO}_3\text{)}_3\cdot5\text{H}_2\text{O}$ and $\text{SnCl}_2\cdot2\text{H}_2\text{O}$ separately in absolute ethanol. The solutions were combined and stirred vigorously for 1 hour. Required amounts of ($\text{Ti[OCH(CH}_3\text{)_2]}_4$) were then dissolved in ethanol and added to ITO solutions in order to obtain solutions of Ti doped ITO with 2 and 4 at.% Ti contents, respectively. The resultant solutions were then refluxed at 85 °C for 1 hour and aged for 24 hours at room temperature. Since uniformity and homogeneity of the thin films mainly depends on the cleanness of the substrates, the glass substrates with (25×25 mm dimensions) were first washed with soap and rinsed repeatedly in deionized water. Then, the substrates were sonicated at 60 °C for 10 min in ethanol and DI water, respectively and dried in a vacuum drying oven at 100 °C, prior to the coating process. A Polos spin coater was used to fabricate Ti-doped ITO films based on three main spin steps. Firstly, the solution was dispensed on to the substrate at 300 rpm for 15 seconds followed by spreading at 2500 rpm for 20 seconds and finally dried at 4000 rpm for 20 seconds. The sample was calcined on a conventional hot plate at 150 °C for 10 minutes. These
steps were repeated until the desired coating thickness (300 – 400 nm) was achieved. Thermal annealing in air atmosphere was performed upon the fabricated samples at (400, 500 and 600) °C for 2h.

4.3.2. Characterization Techniques

Raman analysis was performed on a Nicolet 6700 Fourier transform infrared (FT-IR) spectrophotometer attached with an NXR FT-Raman module. Raman spectra were obtained by using the following settings: Helium-Neon (He-Ne) laser beam with excitation wavelength and operation power of 1064 nm and 0.204 W, respectively, InGaAs detector with 90° detection angle, optical velocity of 0.3165, CaF$_2$ beam splitter, gain of 1, aperture of 150, maximum peak to peak signal along with optimum focusing and side-to-side values, and 32 scans with resolution of 8 cm$^{-1}$ in the range of 0 - 4000 cm$^{-1}$. Information of elemental compositions, chemical structures and bonding states of the thin film coating surfaces were probed using a Kratos Axis Ultra-X-ray Photoelectron Spectrometer. The X-ray source was Al-Kα monochromatic radiation ($h\nu = 1486.6$ eV) with a power of 15 kV and 10 mA. The base pressure of the analysis chamber maintained at 2.9 × 10$^{-9}$ Torr. The XPS survey and high resolution scans were collected before etching. Typical high resolution XPS core level spectra were focused on the regions of In3d, Sn3d, Ti2p, O1s and C1s. The deconvolution of high resolution spectra was carried by employing the CASA XPS software (version 2.3.1.5) which provides information for the analyses of chemical bonding states.

The elastic modulus ($E$) and the hardness ($H$) of the coatings were measured using a nanoindentation workstation (Ultra-Micro Indentation System 2000, CSIRO, Sydney, Australia), equipped with a diamond Berkovich indenter [332]. The area function of the indenter tip was calibrated using a standard fused silica specimen. Load control method was used with a maximum loading of 200 nN. The low peak loading was based on the consideration that the maximum displacement during indentation should be no more than 10% of the coating thickness, and that high loading may result in micro-cracks in the coating, which is thought to be relatively brittle compared with metal coatings. To obtain good resolution, 15 measuring points were used during loading and 20 during unloading.
4.4. Results and Discussions

4.4.1. Raman Analysis

The structural and morphological properties of the synthesized and annealed Ti-doped ITO thin film coatings were characterized via x-ray diffraction (XRD) and field emission scanning electron microscopy (FESEM) techniques and were discussed in our previous work [384]. The XRD results confirm the formation of body centred cubic bixbyite structure with space group of \( Ia\overline{3}/cubic \) similar to \( \text{In}_2\text{O}_3 \) (JCPDS card 06-0416). The ionic radii of tin (\( \text{Sn}^{4+} \)), Titanium (\( \text{Ti}^{4+} \)) and indium (\( \text{In}^{3+} \)) are 0.07, 0.06 and 0.09 nm, respectively. The small ionic radii of \( \text{Sn}^{4+} \) and \( \text{Ti}^{4+} \) imply that the crystalline features of \( \text{In}_2\text{O}_3 \) and/or ITO frameworks should not change if these elements are used as dopants. Grain sizes increase with the introduction of Ti dopants along with increasing annealing temperature, reaching the maximum value of 80 nm for the film prepared with 4 at.% Ti concentration and post-annealed at 500 °C. Therefore, we propose that enhancing the crystal growth and the preferred orientation of the 3-d metal doped ITO thin films could be attributed to introduction of Ti as a dopant for these thin films.

The FESEM images of the synthesized ITO and Ti-doped ITO films as deposited (150 °C) and after being annealed at 400, 500 and 600 °C show that the surfaces of all the thin films are smooth, homogeneous, and composed of uniform coalesced clusters, and show a grain structure demonstrating nanocrystalline features. However, the as deposited thin film of 4 at.% Ti shows a smoother surface and possesses larger grains compared to those of pure ITO and 2 at.% Ti-doped ITO, which may be attributed to the enhancement of crystallinity with Ti ratio.

Raman spectroscopy was used to study the effect of Ti contents and annealing temperature on the electronic and mechanical properties of Ti doped ITO thin films. It is well known that ITO based materials have a body centred cubic structure that belongs to \( Ia\overline{3} \) space group, similar to that of \( \text{In}_2\text{O}_3 \). Two types of cation are present in the ITO based structure: (1) 8 \( \text{In}^{3+} \) with 3 sides symmetry at b-sites and (2) 24 \( \text{In}^{3+} \) with 2-fold point symmetry at d-sites. Moreover, the 48 oxygen atoms in this structure occupy general e-sites with no symmetry. Thus, six possible vibration modes may be identified [321]:

\[
4A_g + 4E_g + 14T_g + 5A_u + 5E_u + 16T_u
\]
The $A_g$, $E_g$ and $T_g$ symmetry vibrations are Raman active and infrared (IR) inactive modes; whereas, $T_u$ vibration modes are Raman inactive and IR active. The $A_u$ and $E_u$ vibration modes are inactive for both Raman and IR measurements. Figure 4.1 presents the results of Raman active modes for the Ti doped ITO thin films at 2% and 4% Ti concentrations after being annealed at the temperatures of 400, 500 and 600 °C. The observed vibrational modes correspond to 106, 135, 176, 275, 367, 432, 584, 633 and 704 cm$^{-1}$ which represent an unequivocal fingerprint for In$_2$O$_3$ and/or ITO cubic structure. These results are in good agreement with Raman active modes observed from In$_2$O$_3$ and ITO based materials [385, 386]. The peaks recorded at a wavenumbers below 500 cm$^{-1}$ are attributed by In-O stretching vibrational modes in the ITO matrix. However, the line at 633 cm$^{-1}$ is due to the overlapping of the contributions from In-O, Sn-O and O-Ti-O vibrational modes with frequencies of 630, 633 and 636 cm$^{-1}$ respectively. Indeed, these observed vibrational modes in Ti doped ITO structure may be ascribed to a good incorporation of Ti and Sn dopants into the In$_2$O$_3$ lattice. It is also noticed that, along with the increase in annealing temperature from 400 to 500 °C, the intensity of the high frequency peaks at 633 and 704 cm$^{-1}$ was gradually enhanced. However, the intensity of the low frequency peak at 175 cm$^{-1}$ decreased. For the sample annealed at 600 °C, the intensity of the high frequency peaks decreased and the low frequency peak at 135 cm$^{-1}$ disappeared. Increasing the annealing temperature up to 600 °C also led to the disappearance of the peaks at 367 and 432 cm$^{-1}$.
Figure 4.1 Raman shift of Ti-doped ITO films (a): 2 at % and (b): 4 at % of Ti, annealed at different temperatures.

4.4.2. Atomic Compositions and Surface Chemical Bonding States

The elemental compositions of Ti-doped ITO thin films were obtained via XPS survey scans. Figure 4.2 (a, b) shows the survey scan results for the synthesized Ti doped ITO thin films for both Ti contents. The photoelectron peaks for In 3d, Sn 3d, Ti 2p, O 1s, Cl 2p and C 1s in the binding energy range of 0 - 1200 eV were observed. The XPS survey spectra confirm the existence of the principal elements (In, Sn, Ti, Cl and O), as well as carbon, in the related sample.
coatings. Table 4.1 lists the atomic compositions of the Ti doped ITO thin films at 2% and 4% Ti concentrations after being annealed at 400, 500 and 600 °C. The results imply that the surface elemental composition of the film materials was significantly affected by annealing temperature. As the annealing temperature increased, the ratio of atomic percentages of the principal elements (In, Sn and Ti) to oxygen on the surface of the thin film coatings decreased for both levels of Ti doping. At 600 °C the Ti 2p and Cl 2p signals were completely absent for both 2 and 4 at % Ti concentrations, respectively, indicating that surface oxidation is taking place at high temperature. As the oxygen content becomes higher at high temperatures, the surface oxidation layer should become thicker. In order to compensate for any charge shifts, the XPS energy scale was calibrated by the C1s (C-H) line at 284.60 eV (bonding energy).

![Figure 4.2 XPS survey scans of Ti-doped ITO films (a): 2 at % and (b): 4 at % of Ti, annealed at different temperatures](image-url)
Table 4.1 Elemental compositions of Ti doped ITO thin films at 2 at.% and 4 at.% Ti concentrations after being annealed at different temperatures

<table>
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<tr>
<th>Ti Concentration</th>
<th>Annealing Temperature °C</th>
<th>Atomic percentage of the elements</th>
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</thead>
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<td></td>
<td>600</td>
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<tr>
<td>4 at.%</td>
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<td>600</td>
<td>6.6</td>
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</table>

The XPS spectra for these elements are shown in Figures 4.3 – 4.7. The surface chemical bonding states of the annealed Ti doped ITO films were characterised by de-convoluting the high resolution In 3d, Sn 3d, Ti 2p, Cl 2p and O 1s photoelectron lines using the Gaussian distribution, in order to appraise the possible chemical bonding states of these atoms in the composites. The parameters, derived from the analysis of the XPS spectra, are listed in Table 4.2 and include: the photoelectron lines, bonding states and their corresponding binding energies, full width at half maximum (FWHM) values and atomic percentages of the elemental compositions present in the films after being annealed at 400, 500 and 600 °C as evaluated from XPS curve fittings.

The de-convoluted curves of the high resolution XPS spectra of In 3d$_{5/2}$ photoelectron lines are shown in Figure 4.3 (a, b). It is clear that the de-convoluted In3d$_{5/2}$ spectrum is assigned to three different bonding states in the range of 443.6 - 445.4eV. The lower energy peaks placed within the range 443.6 – 443.8 eV (labelled i) is linked to In$^\circ$ bonding state, precisely In-In bonds, while the mid energy peaks located in the range 444.1 – 444.6 eV (labelled ii) corresponds to In$^{3+}$ bonding state from In$_2$O$_3$ [387, 388]. The higher energy peaks in the range 444.7 – 445.4 eV (labelled iii) could be attributed to the In-Cl bonds from InCl.
Figure 4.3 In 3d XPS spectra of Ti doped ITO films (a): 2 at % and (b): 4 at % Ti, annealed at different temperatures
Figure 4.4 (a, b) displays the de-convoluted curves of high resolution XPS spectra for Sn 3d$_{5/2}$ photoelectron lines. Three bonding states in the range of 485.6 - 487.2 eV have been allocated. The first components are obtained within the range 485.6 - 485.8 eV (labelled ‘i’) correspond to Sn$^{4+}$ in SnO$_2$, whereas the second features (labelled ‘ii’) observed in the range 486.0 - 486.5 eV are related to Sn$^{2+}$ from SnO. It has been reported by Fan and Goodenough that the Sn3d peak for Sn$^{2+}$ in SnO was seen at a binding energy around 0.5eV higher than that for Sn$^{4+}$ in SnO$_2$ [148, 389]. The SnO phase is thermodynamically less stable than the SnO$_2$ phase; therefore, the Sn$^{4+}$ is thought to be the predominant state in the ITO based materials. The last components (labelled ‘iii’) seen in the range 486.6 - 487.2 eV may be attributed to the SnCl$_2$ bonding state.

The Ti 2p photoelectron lines of Ti-doped ITO films are presented in Figure 4.5 (a, b). The curve fitting of Ti2p core level XPS spectra assigned three components within the energy range of 457.3-458.5 eV. The lower constituent in the energy range of 457.3 - 457.5 eV (labelled ‘i’) corresponds to Ti$^{3+}$ in Ti$_2$O$_3$ bonding state [390]. The second component within the energy range 457.9 - 458.0 eV could be attributed to TiCl$_3$; while the higher energy components in the range 458.4 - 458.5 eV correspond to Ti$^{4+}$ from TiO$_2$ [391].
Figure 4.4 Sn 3d XPS spectra of Ti doped ITO films (a): 2 at % and (b): 4 at % Ti, annealed at different temperatures
Figure 4.5 Ti 2p XPS spectra of Ti doped ITO films (a): 2 at % and (b): 4 at % Ti, annealed at different temperatures.
The de-convolution of O 1s spectra exhibits three sub-peaks within the energy range of 529.3 - 531.8 eV as shown in Figure 4.6 (a, b). The first components in the range of 529.3 - 529.6 eV correspond to O-In bonds and O-Ti bonds, in In$_2$O$_3$ and Ti$_2$O$_3$. The second components within the range 530.3 - 530.8 eV are attributed to TiO$_2$ and SnO$_2$ bonding states. Finally, the other components in the range of 531.4 - 531.8 eV could be due to the existence of O-Sn bonds [387, 388, 391]. For In$_2$O$_3$-based oxide semiconductors, the role of oxygen vacancies (Vo) on the electrical properties has inspired significant debate. Using first principle calculations and density function theory, Agoston et.al reported that the oxygen vacancies in indium oxide lattice are shallow, suitable for generating free electrons in the conduction band. Existence of oxygen vacancies in indium oxide system and its derivative materials indicate experimentally that these defects are the major source of $n$-type conductivity [392].

Figure 4.7 (a, b) shows the results from curve fitting of high resolution XPS spectra for Cl 2p photon lines. Here also three components were obtained in the range of 197.6 – 199.9 eV. The first components are observed in the energy range of 197.6 - 198.0 eV (labelled ‘i’) related to InCl bonding state [393], the second components within 198.5 - 198.7 eV (labelled ‘ii’) may be attributed to SnCl$_2$ bonding states, while the last components in the range of 199.6 – 199.9 eV (labelled ‘iii’) corresponds to TiCl$_3$ bonding states [391]. Table 3.2 details the de-convoluting results of the XPS data of spin coated Ti-doped ITO thin films as a function of Ti concentrations and annealing temperature.
Figure 4.6 O 1s XPS spectra of Ti doped ITO films (a): 2 at % and (b): 4 at % Ti, annealed at different temperatures
Figure 4.7 Cl 2p XPS spectra of Ti-doped ITO films (a): 2 at % and (b): 4 at % Ti, annealed at different temperatures
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<th>Photoelectrons lines</th>
<th>Bonding states</th>
<th>Binding energy (eV)</th>
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4.4.3. Mechanical Properties (Hardness, Young’s modulus and Wear resistance)

The thickness of the TCO films prepared for this study is within the range of 300 - 400 nm. It has previously been reported that the indentation depth should be less than 10% of the film thickness to avoid substrate effects. Therefore, in order to determine the hardness and elastic modulus values for our Ti-doped ITO thin films, the measurements were taken at a maximum indenter depth of around 13 nm, which is less than one-tenth our samples thickness.

Figure 4.8 (a, b) shows the load-displacement curves determined from the nanoindentation measurements corresponding to the Ti-doped ITO samples of both Ti contents and after being annealed. It was reported by Jian and co-worker that establishment of cracking in films underneath the nanoindentor resulted in a distinct discontinuity in the loading part of the loading displacement curve [394]. In this study, the experimental nanoindentation results presented in Figure 4.8 (a, b) confirmed that continuous loading curves were obtained for all the films, indicating that the phenomenon of cracking was absent in the Ti-doped ITO films at different Ti contents and annealing temperatures. Hardness and Elastic (Young’s) modulus can be calculated directly from the measurements of indentation load and penetration depth for both loading and unloading process. From a typical load-penetration depth (p-h) curve, maximum load, maximum displacement and unloading stiffness (also called contact stiffness S) can be determined. The value of how resistant solid matter is to deformation under an applied force is known as the hardness which was expressed by (Eq. 2.33). Young’s modulus can also be calculated from (Eq. 2.34) and (Eq. 2.35).
Figure 4.8 Load-displacement curves of Ti-doped ITO films (a): 2 at % and (b): 4 at % Ti, annealed at different temperatures
The hardness \( (H) \) and elastic modulus \( (E) \) values of the Ti-doped ITO films derived from nanoindentation experiments are shown in Figure 4.9 (a, b). A difference is observed between the trends in the hardness results of the two sets of samples. For the 2 at.% samples, the hardness decreased with increasing annealing temperature, changing from 6.6 to 6.3 GPa when the annealing temperature increased from 400 to 600 °C. In contrast, for the 4 at.% samples, the hardness seems to stabilise around 6.8 GPa after annealing at different temperatures, only showing a slight decrease after annealing at 500 °C. Overall, the results show that the ITO films with higher Ti concentrations have the highest average hardness. The hardness of the Ti-doped ITO thin films measured in the present study are generally consistent with those reported by Zeng et.al (6.5 ± 1.6 GPa) for 250 nm thick sputtered ITO thin films onto glass substrate using a Berkovich indenter with 6 mN load [395]. Similar trends were also observed by Yen et.al for ZnO thin films deposited by atomic layer deposition on Si substrates and then post annealed at different temperatures. They suggested that the decreasing hardness of the ZnO thin films with increasing annealing temperature can be related to the increment of the grain size with increasing temperature [396]. Therefore, it seems here that there is no effect of the grain size to the hardness of the films prepared with 4 at% Ti since they mostly possess the same hardness. However, the films prepared with 2 at% Ti show a slight improve in the hardness with decreasing their grain sizes (as seen in section 3.4.1). However they are still less hard than the 4 at.% samples. Also, the reduction in the hardness could be ascribed to the changes in elemental compositions resulting from the diffusion process in the coatings, softening of the substrate, stress relaxations and formation of new phases. As such, the decrease in the hardness of 2 at.% Ti-doped ITO films with increasing annealing temperature could be attributed to a number of different mechanisms.

In this work, the samples were annealed in atmospheric environment, so it was expected that the composition of the surfaces would change due to oxidation. Therefore, it is reasonable to assume that the change in the hardness of Ti-doped ITO samples is induced by the difference in the oxygen content on the surface of the film with increasing temperature, as proved in the XPS results (section 4.4.1). These results are in general agreement with those reported by Biswas and co-authors, which show that there is a relation between the hardness and the oxygen contents in the ITO film materials. They found that when the oxygen content increased from 6 to 10 wt% in the precursor solutions, the hardness of the corresponding ITO films decreased from 9.6 ± 0.9 GPa to 1.6 ± 0.1 GPa [397]. Barna et.al and Petrov et.al reported that, oxygen, impurities and other defects may lead to grain refinement and then change the morphology of the films [398,
As a summary, a higher annealing temperature leads to larger grain size (as mentioned previously in Section 4.4.1), which, when combined with substitutions, interstitials, and/or the formation of oxygen vacancies and other point defects, may cause a hardness decrement, although this effect is not so significant in our 4 at.% samples. In relation to the annealing temperature increment, the Young’s modulus of Ti-doped ITO films decreased for the films of 2 at.% Ti, while it increased for the films of 4 at.% as shown in Figure 4.9 (a and b). However, both thin films with 2 at.% and 4 at.% Ti contents present similar Young’s modulus in the range of 137 - 143 GPa, which is comparable to the reported results given by Zeng et.al (120 - 160 GPa) [38] and Chen and Bull (141 GPa)[383, 395].

Elastic modulus along with hardness of material can influence wear behaviour. The wear of a material coupled with elastic limit define the ability of this material to deform under an applied stress and regain its initial state without being deformed permanently [400]. The ratio, $H/E$, which is obtained from nanoindentation measurements can be used to evaluate the wear resistance of the coating. The larger this ratio is the higher the wear resistance will be [329]. The Ti-doped ITO thin films exhibited a decrease in $H/E$ values which are correlated to the reduction of wear resistance through high annealing temperature, as shown in Table 4.3. It is clear from Table 4.3 that both the hardness and Young’s modulus depends on the annealing temperature. As discussed previously, the prepared Ti-doped ITO thin films were annealed in air atmosphere resulting in changes of the composition of the sample surface due to an oxidation process. Thus, the decrease in the hardness of Ti-doped ITO samples along with increasing annealing temperature could be attributed to increasing the oxygen contents at the surface of the film. A similar trend for Young’s modulus was observed with increasing annealing temperature. Thus, it is possible to surmise that the annealing temperature exerts a negative effect on the mechanical properties of the Ti-doped ITO film coatings. The $H/E$ values in this study are in the range of $4.5 \times 10^{-2} - 4.6 \times 10^{-2}$ and $4.8 \times 10^{-2} - 5 \times 10^{-2}$, for the films of 2 at.% and 4 at.%, respectively. These values represent a reasonable level of wear resistance, which is even better than other metal oxide ceramics with $H/E$ values of $3 \times 10^{-2} - 4 \times 10^{-2}$ [401, 402].
Table 4.3 Mechanical properties of Ti doped ITO films after being annealed at different temperatures

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<td>600</td>
<td>6.8</td>
<td>143</td>
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</table>
4.5. Conclusions

Ti-doped ITO thin films were fabricated on glass substrates using a low cost and efficient sol-gel spin coating method. The effects of Ti concentrations (i.e., 2 at.% and 4 at.% Ti) and annealing temperature (ranging from 400 - 600 °C) on the phonon vibrational modes, surface chemical bonding states and mechanical properties of Ti doped ITO thin films were studied using Raman spectroscopy, XPS and nanoindentation techniques. Raman analysis revealed the existence of ITO and/or In$_2$O$_3$ vibrational modes. By increasing the annealing temperature some peaks were inversely altered. The XPS results show that the main component atomic percentages such as In, Sn and Ti decreased as the annealing temperature increased from 400 to 600 °C, while the O atomic percentages increased. Also, at 600 °C, the Ti2p and Cl2p signals were completely absent for 2 at % and 4 at % Ti concentration, respectively, indicating that surface oxidation takes place at high temperature.

The nanoindentation load-displacement curves confirmed that all the films exhibited continuous loading curves, indicating that the phenomenon of cracking was absent in the Ti doped ITO films at both Ti contents. Variations in the hardness ($H$) and the elastic modulus ($E$) were observed with different Ti at.% and annealing temperature. The hardness is within the range of 6.3-6.6 GPa and 6.7-6.8 GPa for 2 at.% and 4 at.% Ti content samples, respectively. In most cases the hardness values are negatively affected with increasing annealing temperature, and the films with higher Ti concentration in the ITO films possess the highest average hardness. Synthesized Ti-doped ITO thin films at different Ti contents show the same Young’s modulus values in the range of 137 - 143 GPa. A combination of the highest $H$ and $E$ were achieved in the sample of 4% Ti content annealed at 600 °C. All the Ti-doped ITO films appear to possess high wear resistance. Combining with optimised control over the doping and annealing processes, the results from this work are expected to help facilitate the engineering design of customizable Ti-doped ITO thin films for various industrial applications.
CHAPTER 5: Improved Mechanical Properties of Sol-Gel Derived ITO Thin Films via Ag Doping

Paper III

5.1. Abstract

In this work, indium tin oxide (ITO) and silver-doped ITO thin films at different Ag concentrations (i.e. 2, 4, 6 and 10 at. %) were fabricated via a sol-gel spin coating technique. The thin film coatings were post annealed at 500 °C. Structural, mechanical, surface morphology, electrical and optical characteristics of the ITO and Ag-doped ITO thin films were studied as a function of Ag concentrations. XRD results are consistent with the presence of body centered cubic structure of the indium oxide polycrystalline phase with a new peak for Ag at 2θ ≈ 38.2°, indicating that by introducing Ag atoms they do not remarkably change the structural characteristics of the ITO films. FESEM images display the formation of ITO and Ag-doped ITO nanocrystals and the average crystallite size increases after annealing treatment as well as the incorporation of Ag concentration. The mechanical properties of the thin films were characterised by nanoindentation technique, with significant improvement observed through a combination of Ag doping and annealing treatment, which helps enhancing the effectiveness of the grain boundary in obstructing the displacement movements. The observed improvement in $E$ and $H$ is 14% and 28% respectively, with the hardness and Young’s modulus finally reaching 6.7 GPa and 148 GPa, respectively. Load carrying capability and wear resistance are also enhanced by doping and annealing treatment. After annealing at 500 °C, the thin film coatings with the electrical resistivity of $2.4 \times 10^{-4} \, \Omega \cdot \text{cm}$, carrier concentration of $6.8 \times 10^{20} \, \text{cm}^{-3}$ and carrier mobility of $37 \, \text{cm}^2/\text{V} \cdot \text{s}$ were achieved when the Ag doping level was 4 at.%. On the other hand, the maximum optical transparency was found to be 92% for both ITO and 2% Ag-doped ITO thin films after being annealed at 500 °C. The variation of optical constants, such as absorption coefficient, refractive index and extinction coefficient with different Ag concentrations, were also studied.
5.2. Introduction

Transparent conductive films (TCFs) have received significant attention owing to their desirable optoelectronic characteristics such as high optical transparency and low electrical resistivity. So far, indium oxide (In$_2$O$_3$) and/or tin-doped In$_2$O$_3$ (ITO) are well-known materials that have been widely used as transparent conductive oxides (TCOs) in touch screens, solar cells, liquid crystal displays, smart windows, light emitting diodes (LEDs) and sensors [217, 403-409]. Other than possessing good electrical and optical properties, ITO thin films also have good chemical and thermal stability as well as great adhesion and etching characteristics, compared to other TCOs such as ZnO, TiO$_2$ and SnO$_2$ [199, 410-413]. Many techniques are used for manufacturing ITO based thin films such as, thermal evaporation, DC and RF magnetron sputtering, electron beam evaporation, pulsed laser deposition, screen printing, spray pyrolysis and sol-gel methods [26, 212, 414-419]. The most common fabricating methods are based on sophisticated equipment such as high vacuum systems combined with physical vapour deposition (PVD) processes supplied with high calcine temperature and complicated controlling unit. These complicated and harsh processes, which result in very high end products, have greatly encouraged the development of vacuum-free and low-cost techniques. The sol-gel method combined with a spin coating process has certain advantages such as cost effectiveness (no vacuum requirements), low temperature, easy control of the doping level, shorter processing time, and the possibility of producing coatings with high scalability along with the opportunity of fine-tuning the preferred shapes and surface areas has been widely used so far for fabricating TCFs [182, 261, 420-422]. To improve the performance of ITO thin films, numerous studies have been carried out to improve either their electrical conductivity or optical transparency. Introducing suitable foreign dopants such as Ti, Cr, Cu, Mo, Fe, Nb and Ag to the ITO matrix were found to be beneficial for improving both the electrical conductivity and optical transparency [423-425]. Among these dopants, silver (Ag) was found to be favoured due to its low electrical resistivity compared to other bulk materials [426-429]. However, there have been only limited efforts and attempts to improve the mechanical characteristics of ITO thin films. In this study, simple and low cost spin-coating derived ITO and Ag-doped ITO thin films were produced. The concentration of the ITO solution was fixed at 0.1 M, while the silver (additive) doping concentration varied (2%, 4% 6% and 10%). All the samples were post annealed at 500 °C. Owing to the brittle surface of ITO, it is thought that by introducing a foreign metal element with better mechanical properties than
Indium in ITO matrix may improve the mechanical properties of the thin films. A review of the literature indicated that both high Ag doping concentration (10%) and high annealing temperature (500 °C) for Ag-doped ITO thin films have not been investigated in detail. We assume that higher Ag concentration may result in enhancing the mechanical properties along with maintaining the optoelectronic characteristics of ITO thin films. Furthermore, based on our previous study [430], a better optoelectronic characteristic can be achieved by applying annealing process. Therefore, the main objective of the present investigation is to study the role of Ag additive and annealing temperature on the mechanical and optoelectronic properties of sol-gel synthesized Ag-doped ITO thin films.

5.3. Experimental Methods

5.3.1. Raw Materials

ITO and Ag-doped ITO solutions were prepared by using hydrated indium nitrate (In(NO$_3$)$_3$.5H$_2$O, Alfa Aesar, 99.9%), tin chloride dihydrate (SnCl$_2$.2H$_2$O, Chem-supply, 98%), Silver nitrate (AgNO$_3$, Chem-supply, 99.5%) and polyvinylpyrrolidone (PVP, M = 40000g/mol). All of these chemicals were used as received. Absolute ethanol was employed as a solvent and the ITO and Ag-doped ITO thin films were deposited on soda-lime glass substrates.

5.3.2. Sol-Gel and Thin Films Preparation

A 40 ml solution of ITO (0.1M) was prepared by separately dissolving the required amounts of In(NO$_3$)$_3$.5H$_2$O and SnCl$_2$.2H$_2$O into two separate beakers with 20 ml absolute ethanol. The two solutions were stirred for 1 hour, then mixed together and refluxed at 60 °C for 1 hour until a transparent solution was obtained. Then, the resultant solution was divided into five separate beakers each with 8 ml of ITO solution. The required amounts of AgNO$_3$ and PVP were then added to four of the previous ITO solutions to make Ag-doped ITO solutions with 2, 4, 6 and 10 at.% Ag concentrations then refluxed at 60 °C for 1 hour. The role of PVP is to provide a hydrophobic layer to prevent the agglomeration of Ag particles through the preparation of solutions. The final solutions were stored at room temperature for 24 hours prior to deposition processes. Soda-lime glass substrates (25×25 mm) were sonicated in absolute ethanol followed by milliQ water at 60 °C for 10 minutes, then dried under vacuum in a drying oven at 100 °C for
30 minutes. The deposition process included: (1) dispensing the solution at 300 rpm for 15 seconds, (2) spreading the solution at 2500 rpm for 20 seconds and (3) drying the solution at 4000 rpm for 20 seconds. After each deposition step, the sample was calcined at 150 °C for 10 minutes. These steps were repeated until the desired film thickness was achieved. Samples referred to as deposited samples were calcined but not annealed. The prepared samples were then annealed at 500 °C for 2 hours in air atmosphere.

5.3.3. Analysis Techniques

The crystallographic structure of the ITO and Ag-doped ITO thin films were examined by X-ray diffraction (XRD) analysis via a GBC EMMA diffractometer with CuKα radiation (λ=0.154nm). All the XRD measurements were carried out at a diffraction angle (2θ) in the range of 25° - 70° with a scanning rate of 2°/min and 2θ step size of 0.02°. The surface morphology was observed via Philips XL 20 SEM equipped with an electron dispersive X-ray (EDX) analysis column and a Zeiss Neon 40EsB Field Emission Scanning Electron Microscopy (FESEM). Prior to FESEM imaging, the samples were first mounted onto the substrates holder using carbon tape followed by coating with platinum (about 3nm thick) to minimize the charging effects. A 4-point probe (Dasol Eng. FPP-HS8) was used to measure the electrical properties of prepared films and the Hall-effect measurements were carried out on specimens of (10×10 mm) using ECOPIA HMS-2000 system at 0.9 Tesla of magnetic field and Polytec Bipolar Operation Power supplies (BPO). Au contacts were thermally evaporated on the coated samples in a system of four probes. The transmittance spectrum was obtained by using UV-VIS Perkin Elmer spectrometer in a wavelength range of 250 - 800 nm. The mechanical characterisation was performed using a nanoindentation workstation (Ultra-Micro Indentation system 2000, CSIRO, Sydney, Australia), equipped with a diamond Berkovich indenter. The area function of the indenter tip was calibrated using a standard fused silica specimen. The measurements were collected with maximum loading of 200 nN and maximum penetration depth less than one-tenth of the coating thickness. In order to attain better resolution, the number of measuring points has been increased to 15 during loading and 20 during unloading.
5.4. Results and Discussions

5.4.1. Crystallographic Structure Properties

In this investigation, the films prepared with 4 at.% and 6 at.% Ag concentration exhibit quite similar electro-optical characteristics. Therefore, only the results related to 4 at.% Ag are discussed in terms of structural, morphological, electrical and optical properties. Figures 5.1 and 5.2 show the XRD patterns for the as deposited (150 °C) and post annealed spin coated ITO and Ag-doped ITO thin films, respectively. The XRD data for all the samples are consistent with the presence of polycrystalline features of a body centred cubic bixbyite structure with space group of $la3/c$ cubic similar to In$_2$O$_3$ (JCPDS card 06-0416) with a lattice parameter of 10.118 Å. The main features for the prepared and post annealed thin films are assigned to be (222), (400), (411), (332), (440) and (622) ITO reflection directions of In$_2$O$_3$ as well as (111) Ag reflection direction located around ($2\theta \approx 38.2^\circ$) for the films of Ag-doped ITO at all Ag concentrations. These results confirm the observation that the polycrystalline feature of In$_2$O$_3$ may act as a network with a body centred cubic bixbyite structure and the Ag atoms are well incorporated in the ITO matrix without any observable changes in the crystal structure of the host. Furthermore, there aren’t any adulterated phases related to tin compounds observed in the XRD patterns of ITO and Ag-doped ITO thin films. Both as deposited ITO and Ag-doped ITO thin films show poor crystallinity due to the crystallization temperature of ITO to be in the range of 150-160 °C [68, 353]. Since the variation of Ag concentration has not altered the as-deposited crystalline structure for Ag-doped ITO samples, one XRD spectrum of the thin film with 4 at.% Ag was used as an example in Figure 5.2. After the annealing process, the increase of Ag concentration slightly enhanced the Ag phase (111) reflection direction as expected, see Figure 5.2. Mirzaee et al. [431] have proposed that doping of ITO with silver leads to formation of silver nanoparticles within the structure of In$_2$O$_3$. They suggest that the reduction of silver ions is facilitated by a redox reaction with tin as described in the following relation:

$$\text{Sn}^{2+} + 2\text{Ag}^+ \rightarrow \text{Sn}^{4+} + 2\text{Ag}^0 \quad (5.1)$$

It is also clear from Figures 5.1 and 5.2 that the ITO and Ag-doped ITO thin films had improved crystalline quality, evident by the intensity of the (222) peak as the annealing temperature (500
°C) was applied. However, there is a slight shift in the main peak (i.e., (222)) position toward smaller angle of 2θ for the synthesized thin films compared to the standard JCPDS of In$_2$O$_3$. This indicates that the occurrence of lattice expansion is possibly due to the substitution of In$^{3+}$ atoms by both Sn$^{4+}$ and Ag atoms having different atomic radii. The atomic radii for In, Sn and Ag are 0.09, 0.07 and 0.126 nm, respectively. This phenomenon can be attributed to the fact that electrons are thermally excited from the donor impurities bands to the conduction band after applying annealing temperature. These electrons are mainly characterized as Sn and Ag 5s state with a Sn-O and Ag-O anti-bonding character. The occupations in these anti-bonding states enhance the reduction of Sn and Ag, which is lower than the forces between Sn and O, Ag and O as well as the overall energy of the crystal structure, thus inducing the lattice expansion [432, 433]. With the combined effects of both ionic radii and occupations in the anti-bonding states, the lattice variation can impact the electronic band structure, thereby the electronic properties. Another consideration for this shift could be related to the strain effect due to thermal expansion misfit between the substrate and the thin film.

Figure 5.1 The XRD patterns of as deposited and annealed ITO thin films
Table 5.1 Structural parameters for as deposited and annealed ITO and Ag-doped ITO thin films

<table>
<thead>
<tr>
<th>Ag content (at.%)</th>
<th>2θ (in degrees)</th>
<th>d-spacing (Å)</th>
<th>(h k l)</th>
<th>Lattice constant (Å)</th>
<th>Crystallite size (nm)</th>
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<td>(411)</td>
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<td>26</td>
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<td>Annealed at 500°C</td>
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Figure 5.2 The XRD patterns of as deposited and annealed Ag-doped ITO films prepared at different Ag concentrations
Debye Scherrer equation (Eq. 2.26) was used to determine the crystallite size \( (D) \) from the full width at half maximum (FWHM) of the main peak (222).

Also, the lattice constant and the related inter-planar spacing (d-spacing) were calculated using Bragg's law and related standard Bravias lattice for cubic system (Eq. 2.25) and (Eq. 2.27), respectively. The calculated results are presented in Table 5.1.

From Table 5.1 and Figure 5.3, it is clearly shown that the calculated crystallite size of the ITO and Ag-doped ITO thin films at different Ag content is increased after being annealed at 500 °C. However, the Ag-doped ITO samples showed bigger crystallite sizes than those for pure ITO. This can be related to the effect of Ag additive that may act as nucleation centres, resulting in the formation of large crystallites. Also, by enlarging the crystallite sizes for ITO and Ag-doped ITO thin films along with applying annealing temperature suggest that annealing can improve the crystallization and enhance the substitution of \( \text{In}^{3+} \) by \( \text{Sn}^{4+} \) and Ag ions [61]. Furthermore, it has been reported that the Ag atoms may also vibrate resulting in an annealing effect in the ITO structure which promotes the nucleation process and growth of the thin film along the preferred direction [60]. We also note that crystallite sizes in our study are substantially larger than those reported by Mirzaee \textit{et al.} annealed at 350 °C [431]. Indeed, the average calculated lattice constants for all the as deposited and post annealed ITO and Ag-doped ITO thin films were estimated to be slightly larger than the reported value for un-doped indium oxide of 10.118Å. The variation in the lattice constants could be due to the size differences of the dopant atoms \( (i.e., \text{Sn and Ag}) \) as well as the induced stress near the film surface through both doping and annealing process. Furthermore, since Ag is an amphoteric dopant, it can be considered that some of these ions may occupy interstitial sites or become scattered or clustered centres in the ITO matrix.
5.4.2. Morphological and EDX Analysis

Figures 5.4 presents high magnification FESEM images of the synthesized ITO and Ag-doped ITO at (2, 4 and 10 at.% Ag content) thin films after being annealed at 500 °C. All thin films show uniform, dense, smooth and homogeneous surfaces with a grain structure indicating the nanocrystalline features. However, the Ag-doped ITO thin films prepared at different Ag contents have larger crystallite sizes compared to that of pure ITO. This can be related to the effect of Ag dopants that may agglomerate around the preferred orientation resulting in the formation of large crystallites, thereby improving the crystalline quality of Ag-doped ITO thin films as noticed previously in the XRD results. These results are in good agreement with those reported by Jeong et al. [434] for Ag doped ZnO. Figure 5.5 show the EDX analysis of the ITO and Ag- doped ITO thin films. The results reveal the existence of the main elements (In, Sn, Ag, and O) in each sample coatings.
Figure 5.4 FESEM images of annealed ITO and Ag-doped ITO thin films at different Ag concentrations

Figure 5.5 EDX analyses of annealed (a): ITO and (b): 4 at% Ag-doped ITO thin films
5.4.3. Electrical Properties

The electrical properties of ITO and Ag-doped ITO thin films were investigated by means of 4-point probes and Hall-Effect measurements. Figure 5.6 presents the variation of electrical resistivity and conductivity ($\sigma = 1/\rho$) with Ag concentration. The as deposited ITO thin film has a resistivity of $7.4 \times 10^{-4} \ \Omega \cdot \text{cm}$ with carrier concentration and mobility values of $2.8 \times 10^{20} \ \text{cm}^{-3}$ and $29 \ \text{cm}^2/\text{Vs}$, respectively, as shown in Figure 5.7a. The resistivity of as deposited Ag-doped ITO thin films decreased from 7.1 to $5.8 \times 10^{-4} \ \Omega \cdot \text{cm}$ as the Ag concentration increased from 2 at.% to 4 at.% respectively. Also, it is observed from Figure 5.6a that the resistivities for as deposited thin films with 2 at.% and 4 at.% Ag concentration were lower than that from pure ITO thin films. When Ag concentration increased to 10 at.%, the resistivity showed a rapid increase reaching its maximum value of $8 \times 10^{-4} \ \Omega \cdot \text{cm}$ as seen in Figure 5.6a. This increment in the electrical resistivity at higher Ag concentration is likely to be related to the solubility limits of Ag in the ITO matrix. Therefore, the Ag atoms may occupy random sites in the ITO structure, resulting in an increase of lattice distortion. Also, at higher Ag doping concentration, the increase of ionized impurities scattering and electron-electron scattering leads to increasing the resistivity of Ag-doped ITO as well [431]. Ag doping contributes a large number of electrons, thereby, increasing the carrier concentration in the thin film. This is seen in Figure 5.7a where the as deposited film of 4 at.% Ag concentration has a high carrier concentration of $3.9 \times 10^{20} \ \text{cm}^{-3}$. However, higher dopant concentration can impair the carrier mobility since these dopants may act as trapping centres for the free carriers. Therefore, the carrier concentration and mobility were found to be lower than expected for the film prepared with higher Ag doping rate [435]. This suggests that a portion of these dopants may remain electrically inactive, hence, the carrier concentration and the mobility of the as deposited film of 10 at.% Ag content decreased to values of $3.5 \times 10^{20} \ \text{cm}^{-3}$ and $22 \ \text{cm}^2/\text{Vs}$, respectively, as seen in Figure 5.7a.

When the annealing temperature was applied on the fabricated samples, the resistivity for ITO film decreased to $2.7 \times 10^{-4} \ \Omega \cdot \text{cm}$, while the carrier concentration and the mobility increased to $6.5 \times 10^{20} \ \text{cm}^{-3}$ and 35 cm$^2$/Vs, respectively. The Ag-doped ITO samples showed the lowest resistivity value of $2.4 \times 10^{-4} \ \Omega \cdot \text{cm}$ for the film of 4 at.% Ag content as shown in Figure 5.6b. Annealing temperature leads to an improvement in the crystalline quality along with increasing the crystallite size of fabricated samples as evident in the XRD results. As a result, the grain
boundaries decreased and the trapped electrons were released which led to an increase in the carrier concentration. For the films of Ag-doped ITO, increasing the crystallite size after annealing treatment may be due to the growth of the coalescence of Ag particles in the film matrix, which may provide effective conducting paths for free carriers [179, 436]. Moreover, annealing treatment enhances substitution of indium atoms by tin and silver atoms, yielding an increase in carrier concentration as well as conductivity in the thin films. This is evident in Figure 5.7b where the carrier concentration and the mobility of Ag-doped ITO thin films increased especially for that of 4 at.% Ag contents reaching their maximum values of 6.8×10^{20} cm^{-3} and 37 cm^{2}/Vs, respectively. The film with 10 at.% Ag content exhibits an increase in the carrier concentration reaching 6.3×10^{20} cm^{-3} after being annealed at 500 °C, compared with 6.0×10^{20} cm^{-3} obtained from the 2 at.% Ag sample. Meanwhile, in the former thin film the carrier mobility decreased to 22 cm^{2}/Vs due to the increase of electron-electron scattering and impurities scattering, as discussed before which in turn reduced the conductivity. It is interesting to notice that, the film with 10 at.% Ag content has a higher carrier concentration; however, it also has a higher electrical resistivity compared to that prepared with 2 at.% Ag content. This is because the lower resistivity and/or the higher conductivity—basically depends on both carrier concentration (N) and mobility (μ) based on the relation of \( \sigma = N e \mu \).

Table 5.2 Electrical and optical properties for as deposited and annealed ITO and Ag-doped ITO thin films

<table>
<thead>
<tr>
<th></th>
<th>Ag (at.%)</th>
<th>T (%)</th>
<th>( E_g ) (eV)</th>
<th>( \rho \times 10^{-4} ) (Ω·cm)</th>
<th>( n \times 10^{20} ) (cm^{-3})</th>
<th>( \mu ) (cm/Vs)</th>
<th>( \Phi \times 10^{-3} ) (Ω^{-1})</th>
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</table>
Figure 5.6 Electrical resistivity and conductivity of ITO and Ag-doped ITO thin films with different Ag concentration, (a): as deposited and (b): annealed
Figure 5.7 Mobility and carrier concentration of ITO and Ag-doped ITO thin films with different Ag concentration, (a): as deposited and (b): annealed
5.4.4. Optical Properties

The transmittance spectra of as deposited and annealed pure ITO and Ag-doped ITO thin films prepared at different Ag content (i.e., 2, 4, and 10) at.% are shown in Figure 5.8. The optical transparency of as deposited ITO thin film was found to be 88%. When the Ag dopants were introduced to the ITO film materials, the optical transparency of as deposited Ag-doped ITO thin film with 2 at.% Ag content was slightly enhanced achieving 88.5% due to the enlargement of the crystallite size. This is proved by the XRD and FESEM results while, the film with 4 at.% Ag appears to have the same transparency as the ITO thin film. However, with further increase of the Ag content to 10 at.%, the optical transparency of Ag-doped ITO thin film decreased to a value of 85% as seen in Figure 5.8a, which could be related to increasing both the electrons and impurities scattering along with increasing the lattice distortion at high doping concentrations. When the annealing temperature of 500 °C was applied on the deposited ITO and Ag-doped ITO thin film, the transparency was increased in all of the samples reaching its maximum value of 92% for both pure ITO and 2 at.% Ag-doped ITO thin films (Figure 5.8b). Higher annealing temperature leads to an improvement of the crystalline quality of the prepared samples through increasing the crystallite size and decreasing the grain boundaries (as noticed previously in the XRD analysis), and then higher optical transparency. It is also observed from Figure 5.8 that the transmittance threshold for as deposited and annealed Ag-doped ITO thin films shift to lower energy compared with that for pure ITO spectra. This can be related to the Burstein-Moss shift (shift of Fermi level due to high carrier concentration in the conduction band) [437, 438].
Figure 5.8 Transmittance spectra of ITO and Ag-doped ITO thin films with different Ag concentration, (a): as deposited and (b): annealed
The band gap energy \((E_g)\) was obtained from the transmittance data using (Eq. (3.1)).

The Tauc Plot of photon energy \(hv\) versus \((ahv)^2\) was used to obtain the band gap energies of the synthesised ITO and Ag-doped ITO thin films by extrapolating the linear part of the plotted curves along with \((ahv = 0)\).

The estimated energy band gap of ITO and Ag-doped ITO thin films for both as deposited and after being annealed at 500 °C are presented in Figure 5.9. The results show that the as deposited ITO and Ag-doped ITO thin films have smaller energy band gaps than those annealed at 500 °C indicating a band gap broadening occurring after thermal treatment. The energy band gap increment is possibly due to the improvement of crystalline structure and increasing the crystallite size, as well as carrier concentration, in the films. The optical band gap energy for ITO thin film increased from 3.69 eV for as deposited film to 3.74 eV after being annealed at 500 °C.

Thin film with lower Ag concentration, such as 2 at.% , exhibits slightly larger energy band gap than that of ITO, \(i.e.,\) 3.71 eV and 3.75 eV for as deposited and annealed thin films, respectively. However, with the increase of Ag concentration, the optical band gap decreased due to the increase of electron and ion impurities scattering at high doping concentration (Burstein-Moss effect) [162, 439]. The films with 10 at.% Ag content appears to have the lowest optical band gap energy of 3.67 eV for both as deposited and after being annealed at 500 °C. Relevant optical properties are listed in Table 5.2.
Figure 5.9 Optical band gap of ITO and Ag-doped ITO thin films with different Ag concentration, (a): as deposited and (b): annealed.
The absorption coefficient ($\alpha$) of the ITO and Ag-doped ITO thin films was calculated by using the formula as below [440]:

$$\alpha = \frac{1}{t} \ln \left( \frac{1}{T} \right)$$  \hspace{1cm} (5.2)

where $t$ is the film thickness and $T$ is the transmittance value.

Variation of the absorption coefficient for as deposited and annealed thin films with respect to wavelength in the range of (350-800) nm is presented in Figure 5.10. From Figure 5.10, it is seen that the absorption edge for Ag-doped ITO films shifts to longer wavelength and the thin films show higher absorption coefficient compared to pure ITO samples. This phenomenon suggests that the increase of Ag doping level enhances the absorption in the UV – Deep-UV region. Thus, as noticed previously in the optical band gap calculations, the as deposited and annealed Ag-doped ITO thin films show larger absorption coefficient, especially, those prepared with 4 % and 10 at.% Ag concentrations.

The performance of our ITO and Ag-doped ITO thin films as transparent conductive materials was further evaluated by means of figure of merit ($\Phi$). The figure of merit is related to the sheet resistance and the transmittance of the synthesized transparent conductive thin films, which also indicates the optimum cooperation of these two values in the performance of the film. The figure of merit was defined as $T^{10}/R_s$ by Haacke [441], and/or $T/R_s$ by Fraser and Cook [442], where $R_s$ is the sheet resistance and $T$ is the transmittance of the film. The higher the figure of merit value, the better the performance of the transparent conductive device. In this study, the ‘$T$’ value was selected at a wavelength of 550 nm for all the samples, the results are presented in Table 5.2. The highest values of $\Phi$ for as deposited and annealed thin films were found to be $16\times10^{-3}$ and $56\times10^{-3}$ for 4 at.% Ag and ITO thin films respectively. These results are comparable with those reported previously [355, 443].
5.4.5. Determination of Optical Constants

The optical constants of thin film materials such as refractive index ($n$) and extinction coefficient ($k$) are very important aspects for achieving good performance in optoelectronic devices. For instance, the refractive index of a material is believed to be a measure of its transparency to incident radiation within a certain area of light spectra. The assessment of the refractive index is notably very important in integrated optoelectronic devices [444]. The extinction coefficient $k$ of
ITO and Ag-doped ITO thin films was calculated from (Eq. 2.19), while the refractive index \( n \) was calculated from the following formulae:

\[
  n = \left( \frac{1+R}{1-R} \right) + \sqrt{\frac{4R}{(1-R)^2} - k^2}
\]  

(5.3)

where \( R \) is reflectance and \( k \) is the extinction coefficient.

Figure 5.11 shows the variation of refractive index of as deposited and annealed ITO and Ag-doped ITO thin films. It is seen in Figure 5.11 that the average value of refractive index for Ag-doped ITO samples is higher than that for pure ITO. This could be due to increasing the carrier concentration in the Ag-doped ITO thin films along with increasing the Ag concentration. Increasing carrier concentration at high Ag doping level leads to the formation of Ag clusters along with defects, which hinders the optical transparency. Chiou and Tsai [445] reported similar results from antireflective sputtered ITO thin films on glass substrates. Also, Cao *et al.*, [446] concluded that the increase of the doping level results in the enhancement of the average value of \( n \) for Ag-doped ITO thin films. The average value of \( n \) decreased for annealed ITO and Ag-doped ITO thin films. However, all the as deposited and annealed samples have large average refractive index indicating that these types of coatings may become the ideal replacement for the common antireflection coating.

The extinction coefficient of the as prepared and annealed ITO and Ag-doped ITO thin films is presented in Figure 5.12. The extinction coefficient of all samples initially decreases in the near ultraviolet (NUV) region. However, Ag-doped ITO samples show higher average extinction coefficient values than that of pure ITO which is related to increasing light absorption by Ag atoms. The extinction coefficients gradually increase in the visible range. This behaviour of Ag-doped ITO thin films can be useful in the applications of visible light transmittance and UV light interception. Also, the average extinction coefficient values obtained in this study are of low order over the entire range of studied wavelength indicating the homogeneity of the samples and smoothness of the surfaces [447].
Figure 5.11 Variation the refractive index of ITO and Ag-doped ITO thin films with different Ag concentration, (a): as deposited and (b): annealed
In this study, the thickness of fabricated ITO and Ag-doped ITO thin films is around 350 nm; therefore, it is essential to use a suitable indentation depth to avoid any influence from the substrate that may affect the nanoindentation measurements. It is well known that the nanoindentation measurements should be performed on an indentation depth less than 10 at.% of the film thickness to assure that the obtained results only reflect the mechanical properties of the film coating. In order to obtain accurate values of both the hardness $H$ and the elastic (Young’s)
modulus $E$ for the ITO and Ag-doped ITO films, the nanoindentation measurements were
collected at a maximum indenter depth of 13 nm which is less than one-tenth the thickness of the
fabricated ITO and Ag-doped ITO thin film.

Since it shows high mechanical properties, the results of the film with 6% Ag concentration have
been included in this section. Figure 5.13 (a) and (b) shows the typical load-displacement ($p-h$)
curves determined from the nanoindentation measurements for the as deposited and annealed
ITO/Ag-doped ITO samples, respectively. These curves reflect the deformation history of the
synthesized thin films throughout penetration of the Berkovich indenter load with continuous
contact stiffness measurements mode. It was reported by Jian and Lee that establishment of
cracking in films underneath the nanoindentor resulted in a distinct discontinuity in the loading
part of the loading displacement curve [394]. In this study, the experimental nanoindentation
results presented in Figure 5.13 (a) and (b) confirmed that continuous loading curves were
obtained for all the films, indicating that no cracking occurred during indentation for all the
samples being studied.

Both $H$ and $E$ were evaluated from the measurements results of indentation obtained during the
loading and unloading process. Maximum load, maximum depth and the stiffness ($S$) can be
determined from the load-displacement ($p-h$) curve. Hardness is defined as a measure of how
well the surface of a solid specimen can withstands deformation under an applied force.
Hardness and Young’s modulus of as deposited and annealed ITO and Ag-doped ITO thin films
were calculated based on (Eq. 2.33), (Eq. 2.34) and (Eq. 2.35).

The hardness and Young’s modulus values of as deposited as well as annealed ITO and Ag-
doped ITO thin films are presented in Figure 5.14. From Figure 5.14a, several as deposited thin
films (i.e., 0 at.%, 2 at.% and 4 at.% Ag-doped ITO thin films) show similar hardness and
Young’s modulus values, around 5.3 GPa and 129 GPa, respectively. In contrast, the as
deposited thin films with 6 at.% and 10 at.% Ag show higher hardness and Young’s modulus
values, which were calculated to be 5.9 GPa, 5.7 GPa and 133 GPa, 134 GPa, respectively. The
high values of $H$ and $E$ for the films prepared with 6 at.% and 10 at.% Ag concentration could be
attributed to metallic Ag cluster formation. Therefore, it may be naturally postulated that
increased Ag concentration within the ITO matrix frame above a certain level would help to
enhance both the $H$ and $E$ values.
Figure 5.13 Typical load-displacement curves of ITO and Ag-doped ITO thin films with different Ag concentration, (a): as deposited and (b): annealed

Figure 5.14b presents the variations of both the hardness and Young’s modulus of the annealed ITO and Ag-doped ITO thin films. By applying annealing on the prepared samples at 500 °C, the $H$ and $E$ values are significantly improved, with the 6 at.% Ag sample reaching the maximum values of 6.8 GPa and 146 GPa, respectively. It is clear, from Table 5.3 that there is improvement in the mechanical properties for Ag doped films over Ti-doped ITO films, which
were reported in our previous study [448]. It has been proposed that, the main factors governing mechanical characteristics of nanostructure materials include: the chemical and physical nature, and the structural composition [449]. The surface morphology of the thin films (as seen in previous morphological and EDS analysis section) seems also to be linked to the mechanical characteristics, which is reflected in the fact that the denser and smoother the surface is, the higher the mechanical parameters $H$ and $E$. Also, the as-deposited samples show lower degree of crystallinity as proved by XRD measurements. While annealed ITO and Ag-doped ITO thin films show improvement in the crystalline structure, which positively affects the mechanical properties of the samples. As mentioned previously, the film with higher Ag concentration shows improved mechanical properties, which could be related to the formation of smaller crystallite size compared to other thin films (as confirmed in section 5.4.1). Variations in $H$ and $E$ were also reported by Yen and co-authors [396] for ZnO thin films fabricated on silicon substrates via atomic layer deposition and then post annealed at different temperatures. In their study, the increase of the crystallite size of ZnO thin films along with increasing annealing temperature results in the reduction in the mechanical properties.

Table 5.3 Mechanical properties for as deposited and annealed ITO and Ag-doped ITO thin films

<table>
<thead>
<tr>
<th>T°C</th>
<th>Ag%</th>
<th>Hardness (GPa)</th>
<th>Young’s modulus (GPa)</th>
<th>Wear resistance $(H/E \times 10^2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>As deposited</td>
<td>0</td>
<td>5.3</td>
<td>128</td>
<td>4.1</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>5.3</td>
<td>130</td>
<td>4.0</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>5.4</td>
<td>129</td>
<td>4.1</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>5.9</td>
<td>133</td>
<td>4.4</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>5.7</td>
<td>134</td>
<td>4.2</td>
</tr>
<tr>
<td>Annealed at 500°C</td>
<td>0</td>
<td>6</td>
<td>134</td>
<td>4.4</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>6</td>
<td>136</td>
<td>4.4</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>6.4</td>
<td>141</td>
<td>4.5</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>6.8</td>
<td>146</td>
<td>4.6</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>6.7</td>
<td>148</td>
<td>4.5</td>
</tr>
</tbody>
</table>
Figure 5.14 Variation the hardness and Young’s modulus of ITO and Ag-doped ITO thin films with different Ag concentration, (a): as deposited and (b): annealed
The dependence of material hardness on the grain size may be described by the Hall-Petch formula [450]:

\[
H(D) = H_0 + K_{H-P} D^{-1/2}
\]

(5.4)

where \(H_0\) denotes the lattice friction stress, \(K_{H-P}\) is the Hall-Petch constant and \(D\) is the grain size.

Figure 5.15 (a and b) presents the variation of hardness with \(D^{-1/2}\) of as deposited and annealed ITO/Ag-doped ITO thin films prepared at various Ag concentrations. Although this analysis does not show strong correlation between hardness and particle size, it facilitates the calculation of other parameters. Two sets of different values, \(i.e.,\) lattice friction stress (4.5722, 3.7285) GPa and Hall-Petch constant (4.8135, 17.148) GPa.m\(^{1/2}\) for as deposited and annealed samples respectively, were derived. The obtained average \(H_0\) value is over the reported value of intrinsic stress for ITO (ca. 2.1 GPa) [451]. The Hall-Petch values also indicate the effectiveness of the grain boundary in obstructing the displacement movements. In this case, the annealed samples demonstrated a larger \(H_0\) value, indicating that here the decrease in grain size has a stronger influence in enhancing the hardness.

The wear resistance of the specimen can be predicted from the \(H\) and \(E\) values. The \(H/E\) value is considered to be a significant factor for predicting wear resistance, and the larger this ratio the higher the wear resistance will be [329]. The obtained \(H/E\) values for as deposited and annealed ITO and Ag-doped ITO thin films were in the range of \((4.0\times10^{-2} - 4.2\times10^{-2})\) and \((4.4\times10^{-2} - 4.6\times10^{-2})\), respectively, indicating a higher level of wear resistance for the annealed films over the as-deposited samples, and Ag-doped samples over the pure ITO thin films.
To compare the load carrying capability of the samples under investigation, finite element modelling (FEM) has been performed on as-deposited ITO, as-deposited 6 at.% Ag-doped ITO, and annealed at 500 °C 6 at.% Ag-doped ITO. A spherical indenter of 5 µm in radius loaded onto a film of 2 µm thickness, with a maximum indentation depth of 0.2-0.6 µm, is modelled. Note that this thickness, which is different from those of our experimental samples, is used here for a general evaluation and comparison between the type of films with different Ag concentration and
heat treatment. The consideration here is that, under real application environments, loadings with a dimension in the order of μm are more realistic than smaller and sharper ones. Hence, the thickness used in the modelling work is designed to match the loading conditions.

The Young’s modulus for the films is taken from Table 5.3, while that of the substrate (glass) is 90 GPa. Comsol software was used in the modelling, and more details of the modelling can be found in our previous work [452]. The load carrying ability of the films was assessed by the equivalent stress, or von Mises stress, which is a measure of the severity for potential damage to the film, and can be expressed by:

\[
 s_{\text{equiv}} = \left\{ 0.5 \left[ (s_{xx} - s_{yy})^2 + (s_{yy} - s_{zz})^2 + (s_{zz} - s_{xx})^2 + 6(s_{xy} + s_{yz} + s_{zx}) \right] \right\}^{1/2} \tag{5.5}
\]

where \( s_{\text{equiv}} \) represents the equivalent stress, \( s_{xx}, s_{yy}, s_{zz}, s_{xy}, s_{yz}, s_{zx} \) are the corresponding stress tensor components, respectively.

The FEM modelling result of von Mises stress distribution in a 2 μm as-deposited ITO film under a spherical indentation of 0.4 μm depth along with the displacement along the axial symmetry line from the surface of the film to the interface between the film and the substrate under a loading of 58 mN for pure ITO and 6 at.% Ag-doped ITO thin films are presented in Figure 5.16.

Figure 5.16 (a) shows the modelling image of as-deposited ITO thin film. At an indentation depth 0.4 μm, the maximum of the von Mises stress is found at the interface between the film and the substrate, immediately below the centre of the indenter, with the value being 11 GPa. Such a load resulted in a vertical displacement in the film close to the indenter. Figure 5.16 (b) shows a comparison of displacement in two different films under study, top: ITO with 6 at.% Ag and bottom: pure ITO. The displacements are plotted along the centre (axial symmetric) line, from the surface of the film to the interface between the film and the substrate. When the indentation loading is kept at 58 mN, the z-displacement was reduced by 10%, within the Ag doped and annealed film. This reduced the possibility of delamination at the interface between the film and the substrate.
In summary, our experimental results show that, the doping of 6 at.% Ag into ITO film resulted in an increase of 4% and 11% in $E$ and $H$, respectively. After the films were annealed at 500 °C, further increases of 9% and 13% respectively in $E$ and $H$ were observed. Taking both changes into account, the improvement is 14% and 28% for $E$ and $H$, respectively. Combining Ag doping and annealing also helps enhancing the effectiveness of the grain boundary in obstructing the displacement movements. At the same loading smaller deformation will be induced in the Ag-doped film, hence this film has higher load carrying capability. Wear resistance can also be enhanced by doping of Ag, as well as by annealing at 500 °C.
Figure 5.16 (a): FEM modelling result of von Mises stress distribution of as-deposited ITO film and (b): a comparison of displacement in two different films under study, top: ITO with 6 at.% Ag film and bottom: pure ITO film.
5.5. Conclusions

ITO and Ag-doped ITO thin films were successfully fabricated onto glass substrates via a sol-gel spin coating technique. The effects of Ag concentrations (e.g., 2, 4, 6 and 10 at.% in this study) on the structural, surface morphology, mechanical and optoelectronic characteristics of ITO and Ag-doped ITO thin films were studied by means of XRD, FESEM, nanoindentation, UV-VIS spectroscopy and Hall Effect measurements. Introducing Ag atoms to the ITO matrix did not strongly alter the ITO structure. However, Ag phase appears at (2θ ≈ 38.2°) for Ag-doped ITO thin films. The films of Ag-doped ITO showed larger particle size than that of ITO which are further enlarged after annealing at 500 °C. Variations in $H$ and $E$ values of ITO and Ag-doped ITO thin films were observed as a function of Ag concentration. The hardness for as deposited and annealed thin films were within the range of (5.3 – 5.7) GPa and (6.0 – 6.7) GPa respectively. While the Young’s modulus values for as deposited and annealed samples were in the range of (128 – 134) GPa and (134 – 148) GPa respectively. The variation in Ag concentration exerts a positive effect on both the hardness and Young’s modulus values. A combination of the highest $H$ and $E$ (6.7 GPa and 148 GPa, respectively) were achieved in the sample with highest Ag concentration (i.e., 10 at.% Ag) and annealed at 500 °C. Evaluated by means of comparison, doping of 6% Ag into ITO film resulted in an increase of 4% and 11% in $E$ and $H$, respectively, while annealing the films at 500 °C further increases $E$ and $H$ 9% and 13% respectively. Taking both changes into account, the improvement is 14% and 28% for $E$ and $H$, respectively. Wear resistance can also be improved by both doping of Ag and thermal treatment (i.e., annealing at 500 °C). It has also been shown that combining Ag doping and annealing helps enhance the effectiveness of the grain boundary in obstructing the displacement movements. FEM modelling results indicate that at the same loading, smaller deformation will be induced in the Ag-doped film; hence this film has higher load carrying capability. Furthermore, improved wear resistance over pure ITO thin films was also observed for the samples being studied, indicated by the higher $H/E$ values.

FESEM images show the formation of uniform, dense, smooth and homogeneous surfaces with a grain structure indicating the nanocrystalline features, and the Ag-doped ITO thin films prepared at different Ag contents have larger crystallite sizes compared to that of pure ITO. The electrical resistivity of all samples decreased after applying annealing temperature, and the
lowest values were assigned to be $2.7 \times 10^{-4} \ \Omega \cdot \text{cm}$ and $2.4 \times 10^{-4} \ \Omega \cdot \text{cm}$ for pure ITO and 4 at.% Ag-doped ITO thin films, respectively. The maximum optical transparency in the visible region was found to be 92% for both ITO and 2 at.% Ag-doped ITO thin films, while, the highest optical band gap energy of 3.76 eV was obtained for the film of 2 at.% Ag content. The optical constants such as refractive index and extinction coefficient of the prepared samples were extracted from the transmittance data. The refractive index values for ITO and Ag-doped ITO thin films indicate that they can be used as an antireflection coating in optoelectronic applications. Moreover, Ag doping dramatically enhanced the extinction coefficient of ITO samples in the absorption UV region. With an optimised doping and annealing process, the results from this work are expected to facilitate the engineering design of customizable Ag-doped ITO thin films for various industrial applications.
CHAPTER 6: Novel Approach for Fabricating Transparent and Conducting SWCNTs/ITO Thin Films for Optoelectronic Applications

Paper IV

6.1. Abstract

Single walled carbon nanotubes (SWCNTs) incorporated in indium tin oxide (ITO) was developed to fabricate transparent conductive thin films \textit{via} a sol-gel spin coating technique. The fabricated thin films were annealed at 350 °C. The effects of incorporating SWCNTs and varying film thickness on crystal structure were systematically investigated by Raman shift, surface elemental compositions, surface topography and roughness, optoelectronic characteristics and mechanical properties. X-ray diffraction (XRD) results confirmed the body centered cubic structure of indium oxide polycrystalline phase, indicating that the structural properties of the ITO films were not significantly altered by incorporating CNTs. The presence of CNTs in the ITO matrix was confirmed by analyses of Raman spectroscopy, x-ray photoelectron spectroscopy (XPS) and energy dispersive x-ray spectroscopy (EDX). FESEM images revealed the formation of SWCNTs/ITO nanoparticles, and the average crystallite size increased along with increasing film thickness. Electrical characteristics also improved as the film thickness increased. The lowest electrical resistivity ($4.6\times10^{-4}$ Ω·cm), as well as the highest carrier concentration ($3.3\times10^{20}$ cm$^{-3}$) and carrier mobility (41 cm$^2$/V·s) were achieved from the 320 nm thick film. However, the optical transparency decreased from 91% to 87.5% as the film thickness increased from 150 to 320 nm. The hardness and Young’s modulus of the prepared samples improved, with the increase of SWCNTs doping level, and achieved the maximum values of 28 GPa and 306 GPa, respectively.
6.2. Introduction

Over recent years, the demand for transparent conductive materials (TCMs) has been continuously growing, mainly driven by the significant increase in the volume of components used in optoelectronic devices. However, strict requirements need to be met before a new material is qualified for a wide range of optoelectronic applications, particularly, high quality TCMs should have very high UV/Vis optical transparency with extremely low electrical resistivity [153, 182]. Transparent conductive oxides (TCOs) are the most common type of TCMs due to their unique combination of optical transparency and electrical conductivity. Indium oxide (In$_2$O$_3$) and indium tin oxide (ITO) based TCOs still represent the major TCM in numerous optoelectronic applications including touch screens, liquid crystal displays, solar cells, light emitting diodes, functional glasses and sensors [183, 336, 338, 381, 453]. However, one of the major drawbacks of ITO coatings is their cost due to the scarcity of indium concentration and fabrication efficiency [454].

Another shortcoming of ITO films is their brittleness which can lead to the formation of micro-cracks under an applied strain which results in increased electrical resistivity. Incorporating a hard conductive material in the ITO matrix can reduce the brittleness of the coating [455, 456]. Carbon-based materials (graphene, carbon nanotubes), metal grids and conducting polymers have good electrical characteristics and can be formed into pure transparent conducting thin films [457-460]. However, in pure form they have several limitations. Graphene has high charge carrier mobility ($\mu$) and low electrical resistivity, but it should be completely reduced from graphene oxide to exhibit suitable electrical characteristics [461]. Metal grids have the disadvantage of sensitivity of their surfaces to photon scattering and oxidation [462]. Alternatively, the electrical instability to thermal and chemical strain is the main disadvantage of conducting polymers [463]. Despite relatively low transparency over the visible region, the electrical, optical, mechanical and chemical characteristics of CNTs make them a favourable applicant for TCMs [464]. It is known that the electrical conductivity is directly correlated to charge carrier concentration and mobility [370, 465] and CNTs are considered to have a higher carrier mobility than ITO [466]. Also, CNTs exhibit electrical properties higher than typical metals such as copper and aluminium [467] as well as a high Young’s modulus of approximately 1-2 TPa [468]. So far, CNTs have mostly been used in multilayer structures and/or combined
with conductive polymers such as PEDOT:PSS [469-471]. Although efforts have been made to increase the carrier concentration for ITO thin films by using dopant atoms, this can potentially exert a negative effect on the conductivity, since these dopant atoms may act as scattering points. As an alternative, enhancing the carrier mobility of ITO films by introducing CNTs could be beneficial for improving the electrical conductivity. Inclusion of CNTs into an ITO film may also improve the mechanical properties of the film.

In order to fully exploit the advantages of incorporating the reinforced materials into the ITO coatings, a suitable technique needs to be developed. Numerous techniques are employed for fabricating ITO based TCOs such as, chemical vapour deposition, RF and DC sputtering, pulsed laser deposition, electron beam evaporation, molecular beam epitaxy and sol-gel method [193, 243, 259, 375-379]. However, most of these techniques are not easily adapted to incorporate intact nanotubes into an ITO coating. The advantages of using a sol-gel process for fabricating TCMs are (1) normal ambient wet-chemistry lab conditions, (2) less processing time, (3) lower cost and (4) high yields [63, 64, 347, 348]. Therefore, in this study, a sol-gel method combined with spin coating was employed to incorporate CNTs in an ITO matrix. The main objective of this work is to enhance the characteristics of ITO films through its combination with SWCNTs which could also potentially reduce the consumption of costly indium and enhance the mechanical and surface morphology characteristics of ITO thin films.

6.3. Experimental Section

6.3.1. Raw Materials

Hydrated indium nitrate (In(NO₃)₃.5H₂O, Alfa Aesar, 99.9%), tin chloride dihydrate (SnCl₂.2H₂O, Chem-supply, 98%), graphene oxide (GO) solution, single walled carbon nanotubes (SWCNTs) Sigma Aldrich, carbon > 90%, carbon + SWCNTs ≥ 70%, nitric acid (HNO₃) and sulphuric acid (H₂SO₄) (chem-supply 98%), absolute ethanol (EtOH, Merck, 99.5%), and milliQ water, were used as supplied.
6.3.2. SWCNTs/ITO Sol Preparation and Samples Deposition

In(NO$_3$)$_3$.5H$_2$O and SnCl$_2$.2H$_2$O were dissolved separately in absolute ethanol and refluxed for 1 hour at 85 °C. The two solutions were mixed and refluxed for another 1 hour at 85 °C resulting in (0.2 M) ITO solution. To be suitable for the incorporation process, SWCNTs were first ultrasonicated in a mixture of concentrated nitric acid and sulphuric acid (HNO$_3$: H$_2$SO$_4$= 3:1) for 30 minutes. This acidic treatment process is important to enhance the formation of carboxylic acid functional groups and break down the nodules in agglomerate SWCNTs, rendering the SWCNTs hydrophilic and prevents re-bundling when mixed with the ITO solution. Also, it has been reported that the nitric acid treatment not only reduces the CNT-CNT junction’s resistance but also facilitates the removal of amorphous carbon and other carbonaceous impurities in these junctions. All these eventually result in improving the tunnelling contacts between CNTs [216, 472, 473]. The SWCNTs were then washed with milliQ water and centrifuged 5 times to remove any traces of anions. The resultant functionalized SWCNTs were then dried for 24 hours at 60 °C in a vacuum oven prior to incorporation with the ITO sol. 0.25 wt% SWCNTs was added to 2 ml of GO and sonicated for 2 hours, then mixed with ITO sol and stirred for 1 hour. The resultant solution was aged for 24 hours at room temperature prior to deposition. Soda-lime glass substrates (25×25 mm) were cleaned by detergent and washed with milliQ water. Then the substrates were subjected to ultrasonication in ethanol for 15 minutes, and milliQ water washing was repeated. Finally, the substrates were dried under vacuum in a conventional drying oven at 100 °C for 60 minutes. A Polos spin coater was used for depositing the SWCNT/ITO sol onto the glass substrates. The spin coating parameters are described below: (1) dispensing the solution on to the substrate at 300 rpm for 20 seconds, (2) spreading the solution at 2000 rpm for 30 seconds, and (3) finally drying the solution at 3500 rpm for 30 seconds. Subsequently, the sample was dried at 100 °C for 15 minutes on a hot plate. The coating and calcination steps were repeated until the desired film thickness was achieved. All samples were then annealed at 350 °C for 2 hours in an air atmosphere. SWCNTs/ITO coatings with different films thicknesses (i.e. 150, 210, 250 and 320) ± 5 nm were synthesized in this study. In order to estimate the errors of the measured quantities 4 samples were prepared for each thickness. A thicker film around 370 ± 5 nm was fabricated, but it exhibited a significant drop in the optical transparency (~ 82%) while its electrical properties were very close to those of the 320 nm film thickness. Thus, the results of the thicker film (i.e. 370 nm) were not considered and presented in this investigation.
6.3.3. Analysis Techniques

The crystallographic structures of the SWCNTs/ITO thin films were examined via X-ray diffraction (XRD) analysis using a GBC EMMA diffractometer with Cu-Kα emission line (λ=0.154 nm). The diffraction angle 2θ = 20 - 70° was scanned at 2 °/min with a step increment of 0.02°. The analysis was carried out with beam acceleration of 35 kV/28 mA. Information on elemental compositions, binding energies and chemical bonding states for the outmost 5 nm of the surfaces were obtained using X-ray photoelectron spectroscopy (XPS) technique. The XPS analysis was performed using a Kratos axis ultra-X-ray photoelectron spectrometer operating at 15 kV and 10 mA with an Al-Kα monochromatic radiation source (hv = 1486.6 eV). The specimens were mounted onto a steel sample holder using carbon tape and analysed under ultrahigh vacuum (2.9 × 10⁻⁹ torr). The XPS data for both survey and high resolution scans were collected without surface etching. Typical high resolution XPS scans of SWCNTs/ITO thin films displayed In3d, Sn3d, Ti2p, O1s and C1s energy regions. Curve fitting of the high-resolution scans were carried out using CASA XPS software (version 2.3.1.5) which affords information about the presence of elemental compositions and chemical bonding states for the analysed samples. Surface topographic images of the fabricated thin films were obtained via a Bruker Dimension (Santa Barbara, California, USA) fast scan atomic force microscope (AFM). The samples were mounted on adhesive tape prior to AFM scans and the images were recorded in Tapping Mode using a standard Tapping Mode probe (type NCHV, resonant frequency 300 kHz, spring constant 40N/m.

Raman analysis was conducted using a Nicolet 6700 Fourier transform infrared (FTIR) spectrophotometer equipped with NXR FT-Raman module. Raman spectra were collected using a Helium-Neon (He-Ne) monochromatic laser with 1064 nm excitation wavelength and 0.204 W operation power, CaF₂ beam splitter, InGaAs detector with 90° detection angle, optical velocity of 0.3165, gain of 1, aperture of 150, and 16 scans with resolution of 8 cm⁻¹ in the range of 0-4000 cm⁻¹. Field emission scanning electron microscopy (FESEM) (Zeiss Neon 40EsB) was used to investigate the surface morphology and the EDX analysis of SWCNT/ITO provided the distributions of elemental concentration. The samples were first assembled onto a steel holder using carbon tape and then coated with platinum (3nm thick) to decrease the charging effects before FESEM imaging. The electrical properties of prepared SWCNTs/ITO thin films were
evaluated by a 4-point probe method using (Dasol Eng. FPP-HS8 system). Hall-effect measurements were carried by a system of four Au deposited probe contacts on the coated samples (10×10 mm). In this measurement the applied magnetic field was 0.9 Tesla via ECOPIA HMS-2000 system combined with Polytec Bipolar Operation Power supplies (BPO). The optical properties were measured within the wavelength range of 250 - 800 nm via a UV-VIS Perkin Elmer spectrometer. The mechanical characteristics of the synthesized samples were performed using a nanoindentation workstation (Ultra-Micro Indentation system 2000, CSIRO, Sydney, Australia), equipped with a diamond Berkovich indenter. The area function of the indenter head was calibrated by a standard fused silica specimen. The measurements were collected with maximum loading of 200 nN and maximum penetration depth less than one-tenth of the coating thickness. In order to attain better resolution, the number of measuring points was increased to 15 during loading and 20 during unloading.

6.4. Results and Discussions

6.4.1. Structural Properties

Figure 6.1 shows the XRD patterns of prepared SWCNTs/ITO coatings with different film thickness. The XRD results revealed the formation of a body centred cubic bixbyite structure of indium oxide (In$_2$O$_3$) with space group of $Ia\overline{3}$ according to (JCPDS 06-0416) for all SWCNTs/ITO thin films. No effect from the SWCNTs was observed on the orientation direction and peak position of the ITO matrix. However, two small peaks where observed at 26.5° and 43.5° which are related to the reflection planes of (002) and (101) respectively of CNTs. It has been reported that the (002) and (101) reflection planes of CNTs are normally featured as weak and broadened peaks with low intensity [474]. The first peak at 26.5° indicates the formation of a hexagonal-like graphene structure, while the second peak at 43.5° is due to in-plane reflection. The preferred orientations for the SWCNTs/ITO thin films are identified as (222), (400), (411), (332), (440) and (622) planes similar to those for In$_2$O$_3$, as well as (002) and (101) of CNTs. It is interesting to notice that both the (332) orientation with a reflection line featured at 43° for ITO and the (101) orientation with a reflection line featured at 43.5° for SWCNTs overlapped and formed a weak and broadened peak around 43.4°. Also, it is clear from Figure 6.1 that as the film thickness increased the preferred orientation plane of (222) and the shape and peak intensity improved. This phenomenon indicates an enhancement of the degree of crystallinity of the thin
films as their thickness increased, which could be a result of an increasing number of SWCNTs that accumulate along the preferred orientation plane (222).

Figure 6.1 XRD pattern of SWCNT/ITO thin films prepared at various thicknesses and annealed at 350 °C

The crystallite sizes ($D$) for the SWCNTs/ITO thin films were calculated based on Scherrer equation (Eq. 2.26) from the values of full width at half maximum (FWHM) of the preferred orientation peak (222).

Figure 6.2 displays the variation of the crystallite size with respect to the film thickness. It is clear that the crystallite size of the SWCNTs/ITO thin films increased with increasing film thickness, due to the improvement in the crystal quality. The maximum crystallite size of 43 nm was obtained for the thickest film of 320 nm compared with the minimum size of 23 nm for the film of 150 nm thickness (Table 6.3). The lattice constant ($a$) value of the SWCNTs/ITO thin films (10.13 – 10.17) were calculated which is slightly larger than that reported so far for undoped indium oxide of 10.118 Å [475]. This variation in the lattice parameters can be related to increasing the number of oxygen vacancies along with the incorporation of SWCNTs into the film. These effects will result in stress being developed near the film surface [360], which may
be due to the thermal expansion coefficient mismatch between the film and the substrate [361, 362].

![Graph showing grain size vs. thickness](image)

**Figure 6.2** Effect of film thickness on the grain crystallite size of SWCNTs/ITO thin films

### 6.4.2. Elemental Compositions and Surface Chemical Bonding States

Figure 6.3 displays the XPS survey scan results for the prepared and annealed SWCNTs/ITO thin films, at various films thicknesses, in the binding energy range of (200 - 600) eV. The expected elements with their photoelectron peaks for In 3d, Sn 3d, O 1s and C 1s were confirmed by wide XPS spectra. The observed results show that the atomic compositions of SWCNTs/ITO samples were altered with the increase in film thickness. The atomic percentages of the main elements (In and Sn) as well as O were increased as the film thickness increased; while, the carbon percentage was decreased. The increasing oxygen ratio with increasing film thickness indicates that surface oxidation occurred during the calcination process, following each deposition step. Table 6.1 summarizes the atomic compositions of the as prepared and post
annealed SWCNTs/ITO thin films as a function of film thickness. Note that in all of the discussions, the analysed XPS results were calibrated with respect to the binding energy of C1s from C-H bonding state at 284.5 eV to recover any charge shift.

Table 6.1 Elemental compositions of SWCNTs/ITO thin films annealed at 350 °C

<table>
<thead>
<tr>
<th>$t$(nm) (± 5nm)</th>
<th>Atomic percentage of the elements %</th>
<th>In</th>
<th>Sn</th>
<th>O</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>12.1 ± 0.1</td>
<td>1.4 ± 0.1</td>
<td>41.4 ± 0.1</td>
<td>45.1 ± 0.1</td>
<td></td>
</tr>
<tr>
<td>210</td>
<td>11.6 ± 0.1</td>
<td>1.3 ± 0.1</td>
<td>43.5 ± 0.1</td>
<td>43.6 ± 0.1</td>
<td></td>
</tr>
<tr>
<td>250</td>
<td>16.0 ± 0.2</td>
<td>1.8 ± 0.1</td>
<td>51.0 ± 0.1</td>
<td>31.2 ± 0.1</td>
<td></td>
</tr>
<tr>
<td>320</td>
<td>17.3 ± 0.3</td>
<td>1.9 ± 0.1</td>
<td>51.9 ± 0.1</td>
<td>28.9 ± 0.1</td>
<td></td>
</tr>
</tbody>
</table>

Figure 6.3 XPS wide scans of SWCNTs/ITO thin films prepared at various thicknesses and annealed at 350 °C
The surface chemical bonding states of the prepared and post annealed SWCNTs/ITO thin films were investigated by de-convoluting the high resolution In 3d, Sn 3d, O 1s and C 1s peaks to evaluate the contributions of metal oxides and/or compounds to the film materials (Figure 6.4).

Figure 6.4a shows the fitting curves of high resolution XPS spectra for In 3d$_{5/2}$ photoelectron lines. Two bonding states allocated at 443.99 and 444.69 eV were identified. The lowest binding energy related to In$^\circ$ bonding state, specifically In-In bonds, while the highest binding energy is attributed to In$^{3+}$ bonding state from In$_2$O$_3$ [387, 388]. The fitting curves of high resolution XPS spectra for photoelectron peaks of Sn 3d$_{5/2}$ photoelectron peaks are presented in Figure 6.4b. In the fitting curves, two sub peaks are assigned around 485.99 and 486.54 eV. The first peak at 485.99 eV can be attributed to Sn$^{4+}$ in SnO$_2$ while the second peak at 486.54 eV is linked to Sn$^{2+}$ in SnO [389]. Fan and Goodenough [148] reported that the Sn3d peak for Sn$^{4+}$ from SnO$_2$ has a binding energy around 0.5 eV lower than that for Sn$^{2+}$ from SnO. The SnO$_2$ feature is thermodynamically more stable than the SnO feature and is predicted to be the major phase between the Sn components in the ITO based surface coatings. The de-convoluted curves for O 1s core level exhibit two different peaks located at 529.64 and 531.34 eV (Figure 6.4c). The first feature around 529.64 eV is contributed to In-O bonds from In$_2$O$_3$, and the second feature at 531.34 corresponds to Sn-O bonds from both SnO and SnO$_2$ [391].

The chemical bonding of CNTs is comprised entirely of $sp^2$ bonds, similar to those of graphite and these bonds provide CNTs with their unique mechanical properties. The de-convoluted curves of high resolution XPS spectra for C 1s photoelectron lines are shown in Figure 6.4d. The C1s photoelectron peaks can be split up into three sub-peaks allocated at the binding energy range of 284.5 eV-288.4 eV. The first peak with the lowest binding energy around 284.5 eV has a high contribution of 66.8% and can be assigned to pure $sp^2$ hybridized graphitic carbon atoms of (C=C and C=C bonds), and carbon atoms bounded to hydrogen (C-H bonds).

The second peak originated at the binding energy 285.4 eV with a contribution of 17% is attributed to hybridized $sp^3$ carbon atoms (C-C bonds) which indicates that defects have been introduced to SWCNTs surfaces. While, the third peak allocated at 288.4 eV with the lowest contribution of 16.2% corresponds to carbon atoms bounded to oxygen atoms either by single bonds (C-O) or double bonds (C=O) which are caused by high temperature oxidation of SWCNTs [476, 477].
As noted above in the XRD results, the SWCNTs/ITO has a cubic bixbyite structure with $Ia3$ space group similar to $\text{In}_2\text{O}_3$. The structure consists of two types of cations where 8 In$^{3+}$ ions with side symmetry are located at b-sites and 24 In$^{3+}$ ions with point symmetry at d-sites. Furthermore, 48 oxygen atoms have general C1 site symmetry. Therefore, the following phonon vibrational modes are expected:

$$4A_g + 4E_g + 14T_g + 5A_u + 5E_u + 16T_u$$

6.4.3. Raman Studies

As noted above in the XRD results, the SWCNTs/ITO has a cubic bixbyite structure with $Ia3$ space group similar to $\text{In}_2\text{O}_3$. The structure consists of two types of cations where 8 In$^{3+}$ ions with side symmetry are located at b-sites and 24 In$^{3+}$ ions with point symmetry at d-sites. Furthermore, 48 oxygen atoms have general C1 site symmetry. Therefore, the following phonon vibrational modes are expected:

$$4A_g + 4E_g + 14T_g + 5A_u + 5E_u + 16T_u$$

Figure 6.4 High resolution scans of (a) In3d, (b) Sn3d, (c) O1s and (d) C1s of SWCNTs/ITO thin films
The phonon vibrational modes with $A_g$, $E_g$ and $T_g$ symmetry are known to be Raman active but infrared inactive. The $T_u$ vibrational mode is infrared active and Raman inactive, while the others ($A_u$ and $E_u$) are inactive for both Raman and infrared. Figure 6.5 displays the Raman spectra of sol-gel derived SWCNTs/ITO thin film. The peaks seen at 109.8, 269.7, 312.5, 368, 433.3, 558.9, 631.6 and 703.5 cm$^{-1}$ belong to the cubic structure of In$_2$O$_3$ [68, 386]. The small peaks featured at 171.7 and 239.7 cm$^{-1}$ belong to Sn-O vibrational modes within the ITO structure [385]. The peaks seen at 1292.4 and 1594.6 cm$^{-1}$ are the D-band and G-band for SWCNTs. The D-band at 1292.4 cm$^{-1}$ is attributed to the defect in the SWCNTs, which could result in single and/or double phonon vibrational modes for Raman scattering processes. While, the G-band at 1594.6 cm$^{-1}$ is related to a carbon atom vibrational mode along the SWCNT axis with a frequency very sensitive to the transition of charge carriers from dopants to SWCNTs [478]. Also, the G-band is characteristic of $sp^2$ graphitic material, which is a signature of the existence of SWCNTs in the ITO matrix [479].

![Raman spectra of SWCNTs/ITO thin film](image)

Figure 6.5 Raman spectra of SWCNTs/ITO thin film

### 6.4.4. Surface Morphology and Topography

The FESEM images of the prepared and annealed SWCNTs/ITO thin films at various thicknesses are presented in Figure 6.6. It is evident from Figure 6.6 that all the SWCNTs/ITO thin films have dense and homogeneous surfaces, with grain features demonstrating the
nanocrystalline structure. No cluster of SWCNTs was identified in the FESEM images, indicating that they are well dispersed in the ITO films. However, the surface roughness of the coatings was affected by SWCNTs incorporation. It is also seen from Figure 6.6 that by incorporating SWCNTs in the ITO matrix, it reduces the surface micro-cracks and improves the surface roughness especially for the films of 150 nm and 210 nm thickness which could be due to elasticity and one-dimensional nature of SWCNTs. Nevertheless, the films of higher thicknesses (i.e., 250 and 320 nm) demonstrate the formation of some micro-cracks. This is possibly related to increasing the film thickness along with repeating the film drying (or thermal treatment) during the fabrication process. Furthermore, higher film thickness led to a greater grain size, which is consistent with the XRD results (section 6.4.1).

Figure 6.6 FESEM images of SWCNTs/ITO thin films prepared at various thicknesses and annealed at 350 °C
EDX analysis confirms the presence of the main elements (i.e., indium, tin, oxygen as well as carbon) in the thin films (Figure 6.7). The carbon ratios were observed to be higher in thicker films, which suggest higher concentration distribution of carbon within these films. However, metal to oxygen and carbon ratios could not be established conclusively since the EDX analysis was focused on selected areas of the samples, and the presence of some other elements related to glass substrate in the EDX spectra. Interestingly, while the In and Sn atomic percentages appear to be close to values obtained from XPS measurements, carbon percentage increased along with increasing film thickness. This is in contrast with the results obtained from XPS analysis since the XPS measurements were performed on a maximum depth of ~10 nm from the sample surface, in which measurements could be affected by the existence of carbon from the external environment and/or the oxidation process of the top surface layer of the sample.

AFM scans were used to complement the FESEM imaging which provided further information about the thin films’ roughness. Figure 6.8 shows the AFM images of the fabricated samples.
Analysis of the images indicates that these samples possess smooth surfaces with low average root mean square roughness values of approximately 4 nm. This root mean square (RMS) value is lower than a previously reported study especially for doped ITO and ITO modified CNTs transparent films [469]. Additionally, Figure 6.8 shows that the surfaces of thicker SWCNTs/ITO films have rougher characteristic (with higher RMS values), but they also possess a relatively homogeneous morphology compared to the thinner films due to increasing concentration of SWCNTs in the film network. This homogeneous morphology may heighten the intimate contact of the grains/crystallites through decreasing the density of the grain boundaries within the ITO framework [480]. This might also be attributed to the improvement in the films quality through enhancing nucleation, coalescence and continuous films growth with increasing film’s thickness. This is evident in the XRD and FESEM results where thicker film exhibits more prominent crystalline structure and larger grain size. This is consistent with the established notion that changing the grain size and clusters significantly affects the surface roughness of the films.

Figure 6.8 AFM images of SWCNTs/ITO thin films annealed at 350 °C
6.4.5. Electrical Properties

In this work, the roles of both high carrier concentration of ITO ($\sim 10^{20}$ /cm$^3$) and high carrier mobility for CNTs ($\sim 100$ cm$^2$ Vs$^{-1}$) on the electrical properties was considered. It is stated that the electrical conductivity of transparent conductive materials depends on both carrier concentration ($N$), carrier mobility ($\mu$) and electron charge ($e$) based on the relation of $\sigma = Ne\mu$.

We assumed that increased film thickness results in more SWCNTs which should increase the level of carrier mobility in the film material. Therefore, the effect of incorporating SWCNTs on the electrical properties of ITO thin films was studied in terms of the film thickness. Figure 6.9 summarizes the dependence of electrical resistivity and conductivity, carrier concentration and Hall carrier mobility of the SWCNTs/ITO thin films on film thickness. From Figure 6.9a, the electrical resistivity decreased with increasing film thickness, reaching the lowest value of $4.6\times10^{-4}$ $\Omega$-cm for the film of $320 \pm 5$ nm. This value for electrical resistivity is lower than that reported previously by Golobostanfard and co-authors ($4.1\times10^{-3}$ $\Omega$-cm) for a dip coated SWCNTs/ITO thin film prepared with 0.28% of SWCNTs.[481] This could be related to the better uniformity and homogeneity of these thin films. Incorporation of SWCNTs in the ITO matrix not only decreased micro-crack formation and enhanced the elasticity of ITO, but also may have provided conducting bridges in the ITO matrix for the free charge carriers if their concentration was sufficient enough to create these low resistance conducting bridges. This is consistent with the results obtained by Ji et al. [222] for the conductivity enhancement of PEDOT:PSS after incorporated with solfonated CNTs. The authors proposed that the highly conductive sulfonated CNTs may provide direct charge transport templates and form bridges or networks to connect the distinct PEDOT islands in the composites, resulting in a great improvement in the conductivity.

It is known that the electronic characteristics of SWCNTs based transparent conductive system are strongly dependent on the number of nanotubes in a system. As such, it may be assumed that the large amount of SWCNTs in the films can be obtained by increasing the thin film thickness. Increasing the film’s thickness has also improved the degree of crystallinity and increased the grain size. Therefore, the mean free path of the charge carriers improved, which minimizes charge scattering and hence reduces the electrical resistivity. It has previously been reported that the reduction of electrical resistivity of TCO thin films is linked to an increase in the carrier
concentration (i.e., dopants and oxygen vacancies) [342, 364, 372]. However, this phenomenon can be limited, especially for films synthesized by sol-gel method, since the drying process following each deposition step affects the oxygen vacancies and leads to the formation of micro-cracks for a thick film, which, in turn, generally increases the electrical resistivity [482]. However, SWCNTs could reduce the elimination of oxygen vacancies in the film material due to their strong reduction ability and hence decrease the electrical resistivity. Indeed, the SWCNTs have a higher work function (5.0 eV) [483] compared with ITO (ca. 4.3 - 4.7 eV) which may provide a greater carrier injection into the ITO matrix due to the difference in the work functions [484]. All these features enhance the carrier concentration in thicker SWCNTs/ITO thin film. It has also been reported by Ho et al. [485] that the work function of ITO thin films improved from 4.68 to 5.25 eV by increasing V⁺⁴ doping concentration, and this resulting work function was stable over a long period of time, and demonstrates potential to offer good reliability and long-term stability in industrial applications. Figure 6.9b presents the variation of the free carrier concentration and Hall mobility of SWCNTs/ITO thin films for different film thickness. The carrier concentration increased from 1.9×10²⁰ to 3.3×10²⁰ cm⁻³ when the film thickness increased from 150 ± 5 to 320 ± 5 nm. Likewise, the Hall mobility also increased from 30 to 41 cm²/Vs with increasing film thickness. These results reflect the advantages of combining the high carrier concentration of ITO and the high carrier mobility of SWCNTs in a thin film.

Table 6.2 Electrical properties of SWCNTs/ITO, pure ITO and Ti-doped ITO thin films

<table>
<thead>
<tr>
<th>Coating</th>
<th>t (nm) (± 5 nm)</th>
<th>ρ×10⁻⁴ (Ωcm)</th>
<th>σ (S/cm)</th>
<th>N×10²⁰ (cm⁻³)</th>
<th>μ (cm/Vs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWCNTs/ITO</td>
<td>150</td>
<td>11.0 ± 0.4</td>
<td>922 ± 70</td>
<td>1.9 ± 0.1</td>
<td>30 ± 1</td>
</tr>
<tr>
<td></td>
<td>210</td>
<td>8.6 ± 0.3</td>
<td>1198 ± 62</td>
<td>2.1 ± 0.2</td>
<td>35 ± 1</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>6.3 ± 0.2</td>
<td>1480 ± 81</td>
<td>2.5 ± 0.1</td>
<td>37 ± 1</td>
</tr>
<tr>
<td></td>
<td>320</td>
<td>4.6 ± 0.2</td>
<td>2157 ± 76</td>
<td>3.3 ± 0.1</td>
<td>41 ± 1</td>
</tr>
<tr>
<td>Pure ITO</td>
<td>350</td>
<td>3.6</td>
<td>2320</td>
<td>5.8</td>
<td>25</td>
</tr>
<tr>
<td>Ti-doped ITO</td>
<td>350</td>
<td>3.78</td>
<td>2592</td>
<td>6.0</td>
<td>27</td>
</tr>
</tbody>
</table>
Grain boundaries in the film structure can act as trapping centres for free charge carriers thereby negatively affecting both the carrier mobility and carrier concentration [486]. Also, these trapping centres may generate a potential barrier which hinders the drift of the free carriers and hence decreases the electrical conductivity [487]. The enhancement in the electrical properties of our SWCNTs/ITO thin films with increasing thickness can be linked to the improvement in the crystalline quality (increasing the grain size and decreasing the grain boundaries) as seen previously in the XRD and FESEM results. This effect reduces the scattering of the free carrier due to decrease in grain boundaries. The density of grain boundaries in thinner films is higher than those in thicker films. Therefore, with increasing SWCNTs/ITO film thickness, the number of SWCNTs that segregate in the grain boundary regions will increase, thereby, forming effective conducting paths in the SWCNTs/ITO matrix as discussed previously (see Figure 6.10). Golobostanfard and co-authors reported the same tendency of forming low resistance transport bridges in their ITO-CNT thin film network [488]. The electrical properties of thin SWCNTs/ITO films due to film thickness are presented in Table 6.2.
Figure 6.9 Variations of (a) electrical resistivity and conductivity, (b) mobility and carrier concentration of SWCNTs/ITO thin films with film thickness.
6.4.6. Optical Properties

The transmittance spectra of the synthesized and annealed SWCNTs/ITO thin films are compared in Figure 6.11. It can be seen that the films exhibit a transmittance around 91% for the film of $150 \pm 5$ nm in the visible region ($\sim 550$ nm). However, the SWCNTs/ITO thin films show a higher transmittance toward the near infra-red (NIR) region than in the visible region due to higher transparency of SWCNTs in this region. SWCNTs also exhibit Van Hove singularities in the density of states (i.e., $S_1 \sim 0.68$ eV, $S_2 \sim 1.2$ eV and $M_1 \sim 1.8$ eV) resulting in chirality (metallic to semi-conductive ratio) dependent emission and absorption. Furthermore, the transmittance of the prepared thin films slightly decreased with increasing film thickness, reaching a value of 87.5% at 550 nm for the film of $320 \pm 5$ nm. This can be explained by the fact that, increasing the film thickness results in an increase in both the free carrier concentration (section 6.4.5) and the number of SWCNTs that distribute in the film matrix. It must be realized that CNTs in general, are very strong electromagnetic (EM) radiation absorbers in the visible region.
region of the electromagnetic spectrum [489]. As a result, more light is absorbed, and hence the optical transparency decreased [343, 490].

![Optical transmittance spectra of SWCNT/ITO thin films annealed at 350 °C](image)

Figure 6.11 Optical transmittance spectra of SWCNT/ITO thin films annealed at 350 °C

The absorption coefficient ($\alpha$) of the SWCNTs/ITO thin films can be computed from (Eq. 5.2). The plot for absorption coefficient versus wavelength is presented in Figure 6.12. It is found that there is a shift in the UV absorption edge towards higher wavelengths with increasing film thickness.

![Absorption coefficients of SWCNT/ITO thin films annealed at 350 °C](image)

Figure 6.12 Absorption coefficients of SWCNT/ITO thin films annealed at 350 °C
The band gap energy ($E_g$) for the prepared SWCNTs/ITO thin films was obtained from the transmittance data using (Eq. 3.1).

Figure 6.13 presents the Tauc plot of SWCNTs/ITO thin films for all the four different film thickness studied. The optical band gap ($E_g$) value of SWCNTs/ITO thin films was obtained by extrapolating the linear sections of the plotted curves to the x-axis [491]. It is clear from Figure 6.13 that the band gap energy of SWCNTs/ITO thin films decreased from 3.70 eV to the lowest value of 3.66 eV, with increasing film thickness from 150 to 320 nm. Indeed, there is a shift in the absorption edge towards the long wavelength side as the film thickness increases, resulting from band gap narrowing due to the high optical absorption of SWCNTs in the visible region as discussed previously, and explained by a Burstein-Moss shift [337]. This behaviour is in good agreement with the electrical properties presented in the previous section. The electrical and optical characteristics in this investigation are comparable with those from pure and doped ITO thin films fabricated under the same conditions in our previous investigations [430]. Table 6.3 summarizes and compares the structural and optical properties of SWCNTs/ITO thin films (this study) along with the properties of pure ITO and Ti-doped ITO thin films (previous study).

Table 6.3 Structural, and optical properties of SWCNTs/ITO, pure ITO and Ti-doped ITO thin films

<table>
<thead>
<tr>
<th>Coating</th>
<th>$t$ (nm)</th>
<th>D (nm)</th>
<th>$\alpha$ (Å)</th>
<th>$T$ (%)</th>
<th>$E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWCNTs/ITO</td>
<td>150</td>
<td>23 ± 1</td>
<td>10.13 ± 0.01</td>
<td>91 ± 0.5</td>
<td>3.70 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>210</td>
<td>31 ± 1</td>
<td>10.15 ± 0.01</td>
<td>90 ± 0.2</td>
<td>3.69 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>35 ± 1</td>
<td>10.16 ± 0.01</td>
<td>89 ± 0.5</td>
<td>3.68 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>320</td>
<td>43 ± 1</td>
<td>10.17 ± 0.01</td>
<td>88 ± 0.2</td>
<td>3.66 ± 0.02</td>
</tr>
<tr>
<td>Pure ITO</td>
<td>350</td>
<td>31</td>
<td>10.13</td>
<td>89.0</td>
<td>3.50</td>
</tr>
<tr>
<td>Ti-doped ITO</td>
<td>350</td>
<td>38</td>
<td>10.14</td>
<td>88.9</td>
<td>3.54</td>
</tr>
</tbody>
</table>
6.4.7. Mechanical Characteristics

The thickness of SWCNTs/ITO thin films fabricated in this work is varied within the range of 150 - 320 nm; therefore, it is crucial to select a suitable range of indentation displacement to avoid any influence from the substrate that may affect the nanoindentation measurements. It is well known that the nanoindentation measurements should be performed on an indentation depth less than 10% of the thin film thickness to ensure that the obtained results are only related to the film coating. In order to determine both the hardness $H$ and the elastic (Young’s) modulus $E$ values for SWCNTs/ITO thin films, the nanoindentation measurements were performed at a maximum indenter depth of 13 nm which is less than one-tenth of the thickness of the thinnest film.

Both the hardness and elastic modulus can be determined from the measurements of indentation load and displacement for both loading and unloading process. Maximum load, maximum displacement and stiffness ($S$) can be calculated from a typical load-displacement ($p-h$) curve. Hardness is a measure of the resistance from a solid surface to deformation under an applied

Figure 6.13 Tauc plot of SWCNT/ITO thin films annealed at 350 °C
force. Hardness and Young’s modulus can be determined from (Eq. 2.33), (Eq. 2.34) and (Eq. 2.35).

The hardness and Young’s modulus values of the prepared and annealed SWCNTs/ITO thin films are shown in Figure 6.14. It is expected that along with increasing the film thickness, the number of SWCNTs in the film material is also increases. As noticed from Figure 6.14, the level of resistance to deformation and the Young’s modulus of our sol-gel derived SWCNTs/ITO thin film coatings increase along with rising thin film thickness, and the film of the highest thickness \(i.e.,\) 320 nm exhibits the highest resistance to deformation and Young’s modulus \(ca.\) to be 28 GPa and 306 GPa, respectively. The obtained hardness and Young’s modulus values for the samples in the present study are higher than those obtained from our previous study of Ti-doped ITO thin films [448]. The high values of hardness and Young’s modulus of our SWCNTs/ITO thin films can be ascribed to uniformly incorporating SWCNTs in the ITO matrix. Winarto \textit{et al.} reported a similar effect from inclusion of CNTs in an alumina matrix [492]. An and co-worker showed in their study on CNTs-alumina-iron samples that the hardness of the fabricated samples was increased by 33\% with the increase in the CNTs ratio compared to the sample with 0\% CNTs [493]. It has been reported that CNTs have hardness and Young’s modulus values of 55 GPa and 1-2 TPa respectively [494]. This high strength of CNTs is attributed to the covalent \(sp^2\) bonds formed between the individual carbon atoms (C-C bonds). The \(sp^2\) bonds are among the strongest chemical bonds, resulting in a unique structure which is electrically stable, chemically inert and mechanically robust. Therefore, we propose that enhancing the mechanical characteristics of our SWCNTs/ITO thin films is attributed to the high contribution of \(sp^2\) bonds (66.8\% as seen in XPS analysis). The improved mechanical properties may also arise from the improvement of the crystal quality for thicker thin films.

The wear resistance of a solid material coupled with elastic limit describe how this material will withstand deformation under an applied force and recover its initial state without permanent deformation once the external loading is removed. The wear resistance can be calculated from the values of hardness and young’s modulus using the relation \(H/E\). The larger this ratio the higher the wear resistance will be. The SWCNTs/ITO thin films in this study exhibited an increase in the wear resistance, which correlates to the increasing of \(H/E\) values, with increasing film thickness. The obtained \(H/E\) values, in the range of \(8.7\times10^{-2} – 9.3\times10^{-2}\), indicate a higher
level of wear resistance than that for pure ITO thin films [448]. The mechanical properties of the SWCNTs/ITO thin films in this study are superior in comparison with our previously published results from Ti-doped ITO thin films see Table 6.4.

<table>
<thead>
<tr>
<th>Coating</th>
<th>t (nm) (± 5 nm)</th>
<th>Hardness, H (GPa)</th>
<th>Young’s modulus, E (GPa)</th>
<th>Wear resistance (H/E × 10⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWCNTs/ITO</td>
<td>150</td>
<td>22.4 ± 0.6</td>
<td>254.4 ± 11</td>
<td>8.8</td>
</tr>
<tr>
<td></td>
<td>210</td>
<td>24.2 ± 0.6</td>
<td>269.2 ± 8</td>
<td>9.0</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>25.7 ± 0.9</td>
<td>278.6 ± 9</td>
<td>9.2</td>
</tr>
<tr>
<td></td>
<td>320</td>
<td>28.0 ± 1.2</td>
<td>306.0 ± 12</td>
<td>9.3</td>
</tr>
<tr>
<td>Ti doped ITO</td>
<td>350</td>
<td>6.6 ± 1.2</td>
<td>143 ± 8</td>
<td>4.6</td>
</tr>
</tbody>
</table>

Figure 6.14 Hardness and Young’s modulus of SWCNTs/ITO thin films annealed at 350 °C

Table 6.4 Mechanical properties of SWCNTs/ITO thin films annealed at 350 °C and Ti-doped ITO thin film annealed at 400°C
6.5. Conclusions

In this study, a thin film transparent conductive oxide with dispersed single-walled carbon nanotubes (SWCNTs/ITO) was successfully produced via a low cost and efficient sol-gel spin coating technique onto soda-lime glass substrates. The effects of incorporating SWCNTs into the ITO matrix and variation of film thickness (i.e., 150, 210, 250 and 320 nm) were investigated by FESEM and EDX measurements, AFM imaging, elemental compositions, Raman shifts, morphological, electrical, optical, and nanoindentation measurements. Adding the SWCNTs into the ITO matrix did not alter the crystalline structure, as shown by the lattice constant and preferred orientation directions. The FESEM images show that the SWCNTs/ITO thin film surface possesses dense and homogenous features. While micro-cracks were absent in the thinnest 150 nm film, thicker films exhibited some cracks on their surfaces. The EDX and XPS results confirmed the presence of all the main elements in the film coatings, while the AFM imaging shows that the surfaces of thicker SWCNTs/ITO films show rougher but homogeneous morphology compared to thinner films. The Raman spectra showed the expected peaks for the $\text{In}_2\text{O}_3$ structure as well as the D and G bands for SWCNTs. With the increase of the film thickness from 150 to 320 nm, the resistivity decreased from $11.2 \times 10^{-4}$ to $4.6 \times 10^{-4}$ $\Omega$ cm, while the carrier concentration and Hall mobility increased, reaching their highest values of $3.3 \times 10^{20}$ cm$^{-3}$ and 41 cm/V s respectively. The maximum of both optical transmittance, in the visible region, and band gap energy were found to be 91% and 3.7 eV, respectively for the 150 nm film. As the film thickness increased to 320 nm, the minimum values for visible optical transparency and band gap energy dropped to 87.5% and 3.64 eV, respectively. The hardness of the different SWCNTs/ITO films were in the range of 22.4 - 28.0 GPa and the Young’s modulus values were in the range of 254.4 – 306.0 GPa. The film thickness and the annealing temperature exerted a positive effect on both the hardness and Young’s modulus values. A combination of the highest $H$ and $E$ were achieved in the sample with highest thickness and annealed at 350 °C. All the synthesized thin films appeared to possess very high wear resistance. Combining the high order of carrier concentration for ITO and the high order of both carrier mobility and mechanical characteristics of SWCNTs, the results from this study are expected to help facilitate the engineering design of customizable SWCNTs/ITO thin films for various industrial applications.
CHAPTER 7: ITO-Based Bi-Layer and Tri-Layer Thin Film Coatings

7.1. Abstract

In this investigation, ITO-based bi-layer and tri-layer thin film coatings (~ 130 nm) were synthesized via a sol-gel spin-coating process and annealed at 500 °C. Thin layers of Au, Au-NPs, Ag-NPs and AgO were inserted underneath ITO films to form bi-layer thin film systems and/or encapsulated between two thin ITO layers to form tri-layer thin film systems. Thin film architectures included Au/ITO (AuI), Au-NPs/ITO ((Au)ₙI), Ag-NPs/ITO ((Ag)ₙI) and AgO/ITO ((AgO)I) for bi-layer coatings and ITO/Au/ITO (IAuI), ITO/Au-NPs/ITO (I(Au)ₙI), ITO/Ag-NPs/ITO (I(Ag)ₙI) and ITO/AgO/ITO (I(AgO)I) for tri-layer coatings. The effects of incorporating these layers with ITO thin films were investigated by X-ray diffraction, X-ray photoelectron spectroscopy (XPS), field emission scanning electron microscopy (FESEM), UV-Vis spectroscopy, four-point probes and Hall-Effect. XRD results confirmed the presence of a body-centred cubic structure of indium oxide. The existence of main elements (In, Sn and O) in the film surface materials were detected by XPS scans. FESEM images of all fabricated films revealed formation of dense surfaces with grain-like morphologies indicating the formation of a polycrystalline structure of ITO. Optical studies on the Ag-NPs and Au-NPs colloidal solutions resulted in absorption peaks featured at wavelengths 405 and 531 nm, indicating the formation of 10 – 14 nm and 48 nm Ag and Au nanoparticles, respectively. The highest optical transparency and band gap energy were found to be ~ 91.5% and 3.75 eV for both (AgO)I and (I(AgO)I) thin films. The lowest electrical resistivity of (1.2×10⁻⁴ Ω·cm), along with the highest carrier concentration (11.4×10²⁰ cm⁻³) and mobility (40 cm²/V s) were obtained from the IAuI thin film. An improvement in the power conversion efficiency (PCE) from 3.8 to 4.9% was achieved in an organic solar cell by replacing the conventional pure ITO electrode with the (I(AgO)I) electrode.
7.2. Introduction

Recently, transparent conductive materials (TCMs) exhibiting favourable optoelectronic characteristics of high optical transparency and good electrical conductivity have attracted considerable research interest due to their potential applications as flat panel displays, touch screens, solar cells, smart windows, sensors and storage devices [495-497]. As part of these TCMs, transparent conductive oxides (TCOs) have become the most common TCMs used as electrodes in optoelectronic devices. Single thin films of metal oxides such as indium oxide (In$_2$O$_3$), zinc oxide (ZnO), tin oxide (SnO$_2$), aluminium doped zinc oxide (AZO) and indium tin oxide (ITO) are widely used as transparent conductive materials [77, 110, 498]. In$_2$O$_3$ and ITO based TCO thin films have been considered the prime candidates among TCOs due to their numerous favourable characteristics including good thermal and chemical stability, high film-substrate adhesion and good etching properties [153, 336]. Nevertheless, the scarcity of indium along with its expensiveness influence the replacement of ITO by other materials having comparable optoelectronic characteristics, or the reduction of indium consumption in the thin films production. The typical thickness of ITO thin films used as transparent electrodes lies in the range of 150 - 700 nm. However, the lower thickness of 150 nm has major drawbacks related to the brittleness and weakness of this material resulting in increased electrical resistivity [499]. Growing industrial demands for the next generation of optoelectronic devices inspire current researchers to discover more novel materials and structures having higher optical transparency and lower electrical resistivity.

Oxide/metal/oxide (OMO) multilayer structures have received much attention as potential alternatives along with graphene [500], carbon nanotubes [211], metal oxide based nanowires [501] and metal nanowires [502], to replace single ITO coatings in a variety optoelectronic devices, owing to their good mechanical properties as well as high electrical conductivity and optical transparency in the visible region [503, 504]. Similar to single In$_2$O$_3$ and ITO-based TCO thin films, ITO/metal/ITO multilayers systems have also been proposed in optoelectronic devices. Different metals such as Au, Ag, Cu, Pt, and Ni were adopted to fabricate a thin layer encapsulated between two dielectric thin films in OMO hybrid systems [505]. Conventional ITO thin films are usually fabricated at a temperature higher than 300 °C to obtain good film crystalline quality with high electrical conductivity and optical transparency. For flexible
applications of ITO thin films, high annealing temperature should be avoided due to the lower thermal resistance the flexible substrates possess. Therefore, OMO systems fabricated at room temperature are of interest for these applications. Kim and co-researchers [175] studied the effects of Ag film thickness on the optoelectronic properties of ITO/Ag/ITO coatings. They reported that the ITO/Ag/ITO (43 nm/16 nm/43 nm) film exhibited a sheet resistance and transparency of 8.9 Ω/sq and 79.4%, respectively. ITO/Ag/ITO thin films deposited on PET substrates exhibited a sheet resistance of 6.7Ω/sq and optical transparency of 83% [506]. The effect of annealing temperature (200 °C) and radio frequency (RF) power of deposited ITO/Ag/ITO thin film were investigated by Choi and co-researchers [507]. They produced a film with sheet resistance and transparency of 4 Ω/sq and 90%, respectively. Yang and co-researchers [168] studied the effects of Au layer thickness on the structural and optoelectronic characteristics of Ga-doped ZnO (GZO)/Au/(GZO) thin films. The Au layer thickness was varied in the range from 3 to 12 nm. A GZO/Au/GZO thin film with Au interlayer thickness of 9 nm exhibited the highest transparency of 81.9% and the lowest resistivity of 6.63 × 10^{-5} Ω cm, along with relatively high figure of merit of 15.4 × 10^{-3} Ω^{-1}. Most of the OMO systems were synthesized via a sputtering technique. An interlayer film < 20 nm is the key aspect for obtaining high performance in OMO thin films to avoid strongly reflecting incident radiation in the visible and near-infrared regions. High reflection by the metal layer, which results in a substantial reduction in the optical transparency of the multi-layer thin films, is an intrinsic characteristic of the metal.

In this investigation, a simple and low cost sol-gel spin-coating process was used to synthesize bi-layer and tri-layer ITO-based thin films. Silver (–oxide and –nanoparticles) and gold (–film and –nanoparticles) layers were combined with ITO thin films in these bi-layer and tri-layer coatings to improve the optical transparency while maintaining the electrical properties of such coatings. To the best of the author’s knowledge, sol-gel spin-coated ITO-based bi-layer and tri-layer thin films combined with metal, metal oxide and metal nanoparticles layers have not been previously reported.
7.3. Experimental Details

7.3.1. Sol Preparation

Sol-gel derived ITO, silver oxide, silver nanoparticle and gold nanoparticle thin films along with sputtered gold coatings were synthesized. To prepare these thin films, the raw materials used were hydrated indium nitrate (In(NO$_3$)$_3$·5H$_2$O, purity 99.9%, Alfa Aesar), tin chloride dihydrate (SnCl$_2$·2H$_2$O, purity 98%, Chem-supply), Silver nitrate (AgNO$_3$, Chem-supply, 99.5%), hydrogen tetrachloroaurate (III) trihydrate (HAuCl$_4$·3H$_2$O) Sigma Aldrich, 99.99%, polyvinylpyrrolidone (PVP, M = 40000g/mol), sodium borohydride (NaBH$_4$, Sigma Aldrich, 99.7%), tri-sodium citrate dihydrate (Na$_3$C$_6$H$_5$O$_7$·2H$_2$O) Sigma Aldrich, 99.97%, pure gold target (purity 99.9%), absolute ethanol and milli-Q water. All precursors were used as received. An ITO solution with a concentration of 0.1M was used in this study. To prepare the ITO solution, the required amounts of In(NO$_3$)$_3$·5H$_2$O and (SnCl$_2$·2H$_2$O) were dissolved separately in absolute ethanol and stirred for 1 hour. The resultant solutions were then mixed and refluxed at 85 °C for 1 hour. A 0.2M Ag nanoparticle solution was prepared by dissolving the required amount of AgNO$_3$ in 10 ml of milliQ water. A large excess of NaBH$_4$ solution is needed to reduce the ionic silver and stabilize the formation of Ag-NPs. A 2mM sodium borohydride solution was prepared by dissolving a required amount of NaBH$_4$ in 30 ml milli-Q water and stirred until the chemical was completely dissolved. The resultant sodium borohydride solution was chilled in an ice bath and the silver nitrate solution was added drop-wise. The mixture was stirred vigorously on a magnetic stirrer plate until the solution turned light yellow after adding all of the silver nitrate solution. Then, the stirring was stopped and the stir bar removed. The resultant clear yellow silver solution is stable at room temperature. Silver oxide (AgO) sol with concentration 0.1M was prepared by dissolving the required amounts of AgNO$_3$ and PVP in 10 ml of absolute ethanol and stirred vigorously for 60 minutes at 85 °C on a hot magnetic stir plate. To prepare Au nanoparticle solution, 20 ml of Na$_3$C$_6$H$_5$O$_7$·2H$_2$O (0.5 wt%) was added to 20 ml of an aqueous solution of HAuCl$_4$·3H$_2$O and PVP (1mM). The solution turned dark grey after less than 30 minutes indicating the formation of Au-NPs solution.
7.3.2. Substrate Cleaning

Microscope glass substrates (Soda-lime silicate substrates with 25×25 mm dimensions) were used in this study. The substrates were first cleaned with detergent and rinsed in milli-Q water. Then, the substrates were sonicated in absolute ethanol at 60 °C for 10 min and washed vigorously with milli-Q water. After that, the substrates were sonicated in milli-Q water at 60 °C for 10 min followed by drying in high purity nitrogen stream. All glass substrates were dried in a conventional vacuum drying oven at 100 °C for 30 min prior to coating process.

7.3.3. Thin Films Depositions

The resultant solutions were deposited onto glass substrates in the form of bi-layer and tri-layer systems using a Polos spin-coater system. These coatings were: Au/ITO (AuI), Au-NPs/ITO ((Au)nI), Ag-NPs/ITO ((Ag)nI), and AgO/ITO ((AgO)I), and ITO/Au/ITO (IAuI), ITO/Au-NPs/ITO (I(Au)nI), ITO/Ag-NPs/ITO (I(Ag)nI) and ITO/AgO/ITO (I(AgO)I) for bi-layer and tri-layer thin films, respectively. The spin-coating procedure for thin film deposition was: (1) dispensing the solution at 300 rpm for 15 seconds, (2) spreading the solution at 2500 rpm for 20 seconds, (3) drying the solution at 4000 rpm for 20 seconds, and (4) heat treatment on a hot plate at 150 °C for 10 minutes. To fabricate the bi-layer thin films, single layers of Ag-NPs, Au-NPs and AgO solutions were deposited separately onto the glass substrates, followed by drying on a hot plate and annealing at 300 °C for 1h. Au layer was also sputtered onto glass substrates and annealed at 300 °C for 1h. ITO thin films were then deposited sequentially four times onto the surfaces of Au, Ag-NPs, Au-NPs and AgO layers and annealed at 300 °C. In the case of tri-layer thin films, ITO thin films were first deposited as bottom-layers onto the glass substrates following a similar deposition described above prior to depositing the metal based mid layer and top ITO layers. The resultant thin films were then annealed at 500 °C for 2 h.

7.3.4. Fabrication of Organic Solar Cells (OSCs)

Two thin films with the highest optoelectronic performance in this study were adopted as electrodes combined with a low band gap photoactive polymers to fabricate organic solar cells (OSCs). A photoactive layer of 100 nm thickness was prepared using 25 mg/mL of both poly(3hexylthiophene) (P3HT) and [6,6]-phenyl-C61-butric acid methyl ester (PCBM) dissolved separately in 1,2-dichlorobenzene and stirred at 50 °C under nitrogen atmosphere in dark glove
box for 8h. The resultant solutions were then mixed and further stirred for 4h prior to deposition. A buffer layer of poly(3,4-ethylenedioxythiophene):poly-(styrenesulfonate) (PEDOT:PSS) (~50 nm thick) was prepared by diluting a solution of PEDOT:PSS with isopropyl alcohol at a ratio being 1:2. This buffer layer which acts as a hole transport layer was spin-coated on the fabricated ITO, AgOI and IAgOI electrodes (3000 rpm for 30s) followed by drying at a temperature of 100 °C for 10 min in a conventional vacuum oven. The solution of P3HT and PCBM was spin-coated (1500 rpm for 40s) on the top of the PEDOT:PSS layer and stored to dry in the dark glove box at room temperature for 24h. A layer of Al (100 nm) thick used as a cathode was evaporated on the photoactive layer using a mask of an active area of (0.4 cm²).

7.3.5. Characterization Techniques

The crystallographic structure of the synthesized thin films were examined by X-ray diffraction (XRD) analysis via a GBC EMMA diffractometer with CuKα radiation (λ=0.154nm). All the XRD measurements were carried out at a diffraction angle (2θ) in the range of 25° - 70° with a scanning rate of 2°/min and 2θ step size of 0.02°. The phase identification of the thin film was confirmed by comparing observed diffraction peaks with those of the standard database. Information on elemental compositions and chemical bonding states for the outmost 5 nm of the synthesized thin film surfaces were obtained using a Kratos axis ultra-X-ray photoelectron spectrometer (XPS) operating at 15 kV and 10 mA with an Al-Kα monochromatic radiation source (hν = 1486.6 eV). The specimens were mounted onto sample holders using carbon tape and analysed under ultrahigh vacuum (2.9 × 10⁻⁹ torr). The XPS data for both survey and high resolution scans were collected without surface etching. Information about the presence of elemental compositions and chemical bonding states for the analysed specimens were obtained by de-convoluting the high-resolution scans of the In3d, Sn3d and O1s photoelectron lines using CASA XPS software (version 2.3.1.5). In order to compensate for any charge shifts, the XPS energy scale was calibrated by the C1s (C-H) line at 284.60 eV (bonding energy).

The surface topography was obtained using a Philips XL 20 SEM equipped with electron dispersive X-ray (EDX) analysis column and a Zeiss Neon 40EsB field emission scanning electron microscopy (FESEM). Prepared thin films were first mounted on the substrate holders using double-sided carbon tape followed by coating with (3nm thick) platinum to minimize the charging effects prior to FESEM imaging. The optical properties were determined by means of
transmittance spectra using UV-Vis Perkin Elmer spectrometer in a wavelength range of 250 - 800 nm. A 4-point probe (Dasol Eng. FPP-HS8) was used to observe the electrical properties (i.e., resistivity and sheet resistance) of the prepared thin films and the Hall-effect measurements were performed on specimens of (10×10 mm) via ECOPIA HMS-2000 system at 0.9 Tesla of magnetic field and Polytec Bipolar Operation Power supplies (BPO). Au contacts were thermally evaporated on the coated thin films in a system of four probes. The current density-voltage (J-V) characteristics of the fabricated OSCs were measured via a Keithly 2400 source meter measurements unit under simulated AM 1.5G illumination with an irradiance of 100 mW cm⁻².

7.4. Results and Discussions

7.4.1. Characterizations of Au-NPs and Ag-NPs Colloidal Solutions

The chemical reactions for reducing silver nitrate by sodium borohydride to produce a colloidal solution of Ag-NPs, and hydrogen tetrachloroaurate (III) trihydrate by tri-sodium citrate dehydrate to produce a colloidal solution of Au-NPs are as the follows:

\[ 2AgNO_3 + 2NaBH_4 \rightarrow 2Ag + H_2 + B_2H_6 + 2NaNO_3 \] (7.1)

\[ 2HAuCl_4 + 4Na_3C_6H_5O_7 \rightarrow 2Au + 4CO_2 + 4NaC_6H_5O_5 + 8NaCl + H_2 \] (7.2)

The reduction of ionic silver by sodium borohydride and the growth of the silver particles follow three distinct stages. The early stage of reduction occurs rapidly upon mixing of the reactant solutions, and the reaction results in the formation of small particles (~ 2 – 3 nm). In the second stage as the reaction proceeds, the resultant particles enlarge, reaching sizes of (~ 8 – 20 nm) within a time range of (20 – 60 min). In the last stage of the reaction, the majority of borohydride is consumed, resulting in the loss of the stabilizing BH₄⁻ and the solution switching from a reducing to an oxidizing environment [508]. The changes in the values of surface potential of the Ag particles and adsorbed borohydride enhance the aggregation of the Ag particles. Also, the adsorbed borohydride plays a key role in stabilising the growing Ag nanoparticles by offering a particle surface charge.
In contrast to the reduction of ionic silver, it has been reported that the preliminary reaction of the reduction of HAuCl$_4$ by Na$_3$C$_6$H$_5$O$_7$.2H$_2$O creates large clusters (~100 – 200 nm) which shrink in size as the reaction continues until a final cluster size of (~15 – 20 nm) is achieved [509]. Due to the absorption and scattering properties of gold nanoparticles, the shrinking process of the particles is continued along with a change in the colloidal solution colour from black to red. This phenomenon could be attributed to competitive adsorption between AuCl$_4^-$ ions and citrate ions which reflects different surface charges. Also, initially in the reaction, AuCl$_4^-$ binds and exhibits a low surface potential, resulting in weakly attractive inter-particle forces. Accordingly, small particles combine reversibly. With the progression of the reaction, AuCl$_4^-$ is consumed and the citrate binds to the resultant particle surfaces. Hence, the particle charge increases, and the pair potential becomes repulsive. Clusters then collapse to produce the final particle size distribution [510].

The distinctive colours of the prepared colloidal solutions of Ag-NPs and Au-NPs are attributed to plasmon absorbance, where the incident light produces oscillations in conduction electrons at the surface of the metal nanoparticles and the electromagnetic radiation is absorbed [511, 512]. The prepared colloidal solutions were first characterized by means of their absorbance spectra via the UV-Vis spectrophotometer. Figure 7.1 shows the absorbance spectra of both Ag-NPs and Au-NPs. From Figure 7.1, the absorption peak of Ag-NPs colloidal solution was observed at 405 nm while the absorption peak of Au-NPs colloidal solution was detected at 531 nm. The wavelength of the plasmon absorption maximum of the colloidal solution can be used to estimate the particle size of metal nanoparticle. It is well-known that the position and shape of the plasmon absorption maximum of metal nanoparticles is strongly dependent on the surface adsorbed species, particle size and dielectric medium [513]. It has previously been reported a plasmon absorption maximum for a silver nanoparticle colloidal solution at 405 nm corresponds to a particle size of (10 – 14) nm, while for a gold nanoparticle colloidal solution an absorption maximum around 531 nm corresponds to a particle size of 48 nm [511].
7.4.2. XRD Analysis of The Thin Films

The XRD patterns of annealed bi-layer (AuI), ((Au)_nI), ((Ag)_nI) and ((AgO)I) and tri-layer (IAuI), (I(Au)_nI), (I(Ag)_nI) and (I(AgO)I) thin films are presented in Figure 7.2 (a, b). All the thin films show pattern which are consistent with the growth of polycrystalline body centred cubic bixbyite structures similar to In$_2$O$_3$, with a space group of Ia3/cubic and lattice parameter of 10.118 Å (JCPDS card 06-0416). The main peaks for the synthesized thin films are linked to (222), (400), (411), (332), (440) and (622) reflection orientations similar to In$_2$O$_3$. There is no impure phase related to tin complexes in the ITO matrix for the bi-layer thin films, which confirms the investigations that the polycrystalline structure of thick top layer of ITO for this system can act as a network with a cubic structure and the tin atoms are well integrated. However, both (I(Ag)$_n$I) and (I(AgO)I) thin films show the existence of (110) reflection line featured at 2θ ~ 26.6° which reflects the presence of an SnO$_2$ phase (Figure 7.2b). This new phase can possibly be attributed to the coalescence and agglomeration of Sn atoms at the grain boundaries of the ITO structure. It is also noticed that the (IAuI) thin film shows a small peak featured around 33.3° indicating the formation of an AuInO$_2$ crystalline structure phase. This could be explained based on the fact that, some of Au ions possibly diffused throughout the ITO.
matrix, and some of them substituted indium atoms on their sites or scattered and/or agglomerated at the grain boundaries of the ITO system. However, no Au and/or Ag lines were observed in the bi-layer thin films (Figure 7.2a) which might be attributed to the growth of thicker ITO films compared to the tri-layer systems. Both the (AuI) and (IAuI) thin films exhibit the best crystalline quality among the thin films due to uniformity, continuity and enhanced crystallinity of the Au layers. Annealing temperature also has a potential effect on improving the crystalline quality of the fabricated thin films by providing sufficient energy to the particles to accumulate and grow uniformly along the preferred orientations. Compared to the peak positions of the standard card (JCPDS card 06-0416) of indium oxide, all the synthesized thin films exhibited a shift toward lower 2θ values indicating crystalline distortion has taken place.

The Debye-Scherrer formula (eq. 2.26) was used to calculate the grain sizes ($D$) of the synthesized thin films using the full width at half maximum (FWHM) of the main peak (222) of the ITO profile. In addition, the lattice parameter ($a$) and its corresponding inter-planar spacing (d-spacing) for fabricating thin films were calculated using the standard Bravias lattice for a cubic system (Eq. 2.27) and Bragg’s law (Eq. 2.25), respectively.

Table 7.1 presents the grain size and lattice constant values of the fabricated bi-layer and tri-layers thin films. As estimated from the XRD profiles of the synthesized thin films, all the thin films have larger lattice constants than In$_2$O$_3$ as shown by the shift in the main peak (i.e., (222)) position toward smaller 2θ (JCPDS of (10.118 Å)). The average value of the grain size of the tri-layer thin films (~ 29 nm) was found to be smaller in relation to the average value for bi-layer thin films (~ 31 nm), but both are larger than the value of pure ITO reported in our previous work [430]. The (IAuI) thin film shows the highest values of both $D$ and $a$ assigned to be 33 nm and 10.16 Å, respectively. This could possibly relate to the substitution of In atoms by Sn and Au atoms having different atomic radii. On the other hand, the annealing process can not only enhance the substitution of In by other atoms but also provide the particles of ITO, Au and Ag with sufficient energy to accumulate and grow uniformly along the preferred orientation of (222). Both these effects result in increasing the grain sizes along with reducing the level of the grain boundaries, thereby improving the crystalline structure of the synthesized thin films. The variation in the lattice constants could also be due to the induced stress near the film surface through the inter-diffusion of bottom- or mid- layer atoms to the ITO matrix, and thermal
expansion misfit between the glass substrates and the thin films [514]. The Au and Ag atoms may substitute either In and/or O atoms. Since both atoms have larger radii than In and O atoms, the increase of lattice space and bond length eventually enlarge the lattice constant.

Figure 7.2 XRD patterns of (a) bi-layer and (b) tri-layer thin films annealed at 500 °C
Table 7.1 Structural parameters of the fabricated bi-layer and tri-layer thin films

<table>
<thead>
<tr>
<th>System</th>
<th>Coatings</th>
<th>$D$ (nm)</th>
<th>$\alpha$ (Å)</th>
<th>$d$-spacing (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi-layer</td>
<td>AuI</td>
<td>32.45 ± 0.55</td>
<td>10.15 ± 0.01</td>
<td>2.931</td>
</tr>
<tr>
<td></td>
<td>(Ag)nI</td>
<td>29.32 ± 0.60</td>
<td>10.12 ± 0.01</td>
<td>2.921</td>
</tr>
<tr>
<td></td>
<td>(Au)nI</td>
<td>30.50 ± 0.56</td>
<td>10.12 ± 0.01</td>
<td>2.921</td>
</tr>
<tr>
<td></td>
<td>(AgO)I</td>
<td>32.66 ± 0.58</td>
<td>10.14 ± 0.01</td>
<td>2.925</td>
</tr>
<tr>
<td>Tri-layer</td>
<td>IAuI</td>
<td>33.40 ± 0.47</td>
<td>10.16 ± 0.01</td>
<td>2.934</td>
</tr>
<tr>
<td></td>
<td>I(Ag)nI</td>
<td>27.71 ± 0.51</td>
<td>10.12 ± 0.01</td>
<td>2.921</td>
</tr>
<tr>
<td></td>
<td>I(Au)nI</td>
<td>25.56 ± 0.50</td>
<td>10.14 ± 0.01</td>
<td>2.925</td>
</tr>
<tr>
<td></td>
<td>I(AgO)I</td>
<td>30.42 ± 0.52</td>
<td>10.14 ± 0.01</td>
<td>2.925</td>
</tr>
</tbody>
</table>

7.4.3. Surface Morphology

A comparison of the morphological properties of bi-layer and tri-layer thin films annealed at 500 °C was investigated using the FESEM images and the results are shown in Figure 7.3. All the fabricated bi-layer and tri-layer thin films appear as dense surfaces with grain-like morphologies indicating the formation of a polycrystalline structure of ITO. Since the whole thickness for bi-layer and tri-layer coatings is (~ 130 nm) as proved by cross sectional image, we may assume that each ITO layer in tri-layer system is (~ 60 nm), while that for bi-layer one it is (~ 120 nm). Thin films deposited on Au and AgO layers show larger grains along with significant improvement in the morphology of the top ITO layer compared with other thin films, due to the high degree of crystallinity that the former films possess. These results are consistent with those observed from the XRD measurements (section 3.2). Although other thin films grown on (Au)$_n$ and (Ag)$_n$ layers show granular morphology surfaces, few micro-cracks, grain boundaries and pinholes were observed between the granules of the top ITO thin films. This possibly indicates that both the Au-NPs and Ag-NPs coatings covered the substrates (for bi-layer systems) and bottom ITO films (for tri-layer systems) incompletely as seen in Figure 7.4. These undesirable morphologies seem to be an inherent property when ITO is deposited onto a discontinuous layer. Cross-section imaging was performed on two of the ITO thin films with encapsulating Au and An-NPs layers and the results are seen in Figure 7.3c. Both Au and Au-NP layers possess thicknesses of ~ 10 nm. Thus, we may assume that AgO and Ag-NPs insertions possess similar thicknesses since they are all fabricated with similar deposition conditions. It is clearly seen that the Au layer covered the bottom ITO film completely, while Au-NP layer exhibited a distinct
island-like structure. The discontinuity and granularity of Au-NP and Ag-NP coatings explain the morphological differences between these thin films and other thin films grown on Au and AgO layers. The formation of island-like structures in the Au-NPs and Ag-NPs coatings for bi-layer and tri-layer thin films restricted the lateral expansion of the top ITO granules due to the large numbers of voids and grain boundaries these layers possess. Consequently, there was a delay in the coalescence of neighbouring ITO particles, resulting in discontinuous film formation. However, this is not so significant in our bi-layer thin films due to the thicker ITO films compared to tri-layer thin films as noted in Figure 7.4 (b1 – b4).

Figure 7.3 Top-view images of bi-layer (a1 – a4) and tri-layer (b1 – b4) thin films. Cross-sectional images for (c1) - IAuI and (c2) - I(Au)ₙI thin films
7.4.4. Atomic Compositions and Surface Chemical Bonding States

The elemental compositions of the synthesized bi-layer and tri-layer thin films were obtained via XPS survey scans and the results are presented in Table 7.2. All the synthesized thin films show the presence of the photoelectron peaks for In 3d, Sn 3d, O 1s, and C 1s in the binding energy range of 200 - 600 eV, while no peaks related to Au and/or Ag. This was mainly because the XPS scans were performed on a maximum depth of ~ 10 nm from the top surfaces of the thin film. It is noticed from Table 7.2 that the atomic percentage of O 1s photoelectron line is higher than the other photoelectron lines due to the formation of a thick oxide layer owing to both the wet chemical process and annealing temperature. Also, the ratio of the atomic percentages of In to Sn obtained from XPS measurements is consistent with the mixed ratio ($\text{In:Sn} = 90:10 \text{ at.\%}$) for preparing the ITO solution.

Table 7.2 Variation of the atomic percentage of the main elements for bi-layer and tri-layer thin films

<table>
<thead>
<tr>
<th>Coating</th>
<th>Atomic percentage of the elements %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>In</td>
</tr>
<tr>
<td>Bi-layer</td>
<td>$16.12 \pm 0.11$</td>
</tr>
<tr>
<td>Tri-layer</td>
<td>$13.51 \pm 0.15$</td>
</tr>
</tbody>
</table>

Figure 7.4 Schematic diagram shows the differences in the formation of the mid-layer thin film coatings.
Since all fabricated bi-layer and tri-layer thin films exhibit similar photoelectron lines along with their corresponding binding energies, the surface chemical bonding states of one thin film (i.e., I AuI) coating were investigated by de-convoluting the high resolution In 3d, Sn 3d and O 1s peaks to evaluate the contributions of metal oxides and/or compounds to the film materials (Figure 7.5).

The fitting curves of high resolution XPS spectra for In 3d$_{5/2}$ photoelectron line are seen in Figure 7.5a. Two bonding states with their corresponding binding energies assigned at 444.08 and 444.78 eV were identified and they are attributed to In$^\circ$ bonding state, specifically In-In bonds, and In$^{3+}$ bonding state from In$_2$O$_3$, respectively [387, 388]. Figure 7.5b shows the fitting curves of high resolution XPS spectra of Sn 3d$_{5/2}$ photoelectron peaks. Two sub peaks are identified in the fitting curves around 486.38 and 487.45 eV. The first peak with the lowest binding energy of 486.38 eV can be linked to Sn$^{4+}$ in SnO$_2$ while the second peak with the highest binding energy of 487.45 eV is attributed to Sn$^{2+}$ in SnO. It has previously been reported that the Sn 3d peak for Sn$^{4+}$ from SnO$_2$ has a binding energy around 0.5 eV lower than that for Sn$^{2+}$ from SnO. Also, the SnO$_2$ phase is thermodynamically more stable than the SnO phase and is expected to be the major phase between these Sn components in the ITO-based surface coatings [148, 389]. The de-convoluted fitting curves for O 1s core level show two different peaks allocated at 529.70 and 531.20 eV, which correspond to In-O bonds from In$_2$O$_3$ and Sn-O bonds from both SnO and SnO$_2$, respectively (Figure 7.5c) [387]. Oxygen vacancies were found to be a key aspect in enhancing the electrical properties of In$_2$O$_3$-based thin film coatings through contributing free carriers to the In$_2$O$_3$ matrix. A theoretical study carried out by Agoston and co-authors [392] using density function theory (DFT) and first principle calculations, confirmed that the oxygen vacancies are shallow in the In$_2$O$_3$ matrix and its derivative materials, which facilitate the production of free electrons (which are the major source of $n$-type conductivity in In$_2$O$_3$-based thin film coatings) in the conduction band.
Electrical Properties

The electrical characteristics of bi-layer and tri-layer thin films represented by electrical resistivity, conductivity, carrier concentration and mobility are shown in Table 7.3. The well-structured morphology of both (IAuI) and (I(AgO)I) thin films fully accounted for the fact that the values of electrical resistivity of these tri-layer thin films are much lower compared with their relative thin films. The (IAuI) thin film shows the lowest electrical resistivity along with highest carrier concentration and mobility assigned to be $1.2 \times 10^{-4} \ \Omega\cdot\text{cm}$, $11.4 \times 10^{20} \ \text{cm}^{-3}$ and $40 \ \text{cm}^2/\text{Vs}$, respectively, while the (I(AgO)I) thin film displays electrical resistivity, carrier concentration and mobility of $1.6 \times 10^{-4} \ \Omega\cdot\text{cm}$, $9.4 \times 10^{20} \ \text{cm}^{-3}$ and $38 \ \text{cm}^2/\text{Vs}$, respectively. The resistivity for (IAuI) thin film is lower than that obtained in our previous report for 350 nm ITO and Ti-doped ITO thin films [430]. The superior electrical characteristics of the (IAuI) thin film are possibly attributed to the uniformity and continuity of the metal Au mid-layer which

Figure 7.5 High resolution scans of (a)- In 3d, (b)- Sn 3d and (c)- O 1s of IAuI thin film
restricted the scattering of the free carriers at the interface between this mid-layer and the top ITO layer, thereby enhance the carrier mobility. The inter-diffusion process of Au atoms to the top ITO layer may also have increased the carrier concentration of the thin film. In general, metals have high free carrier concentration of the order of $10^{22} - 10^{23}$ cm$^{-3}$, and Au was also found to have a high work function ($ca. 5.1-5.47$ eV), which makes it a good electron injector. Therefore, it is reasonable for the (IAuI) thin film to have a high carrier concentration due to efficient carrier injection from the Au layer to ITO matrix. Carrier scattering might be less significant at the interface between the Au mid-layer and ITO layer due to a decrease in the contact area between these layers when the Au layer formed a continuous film with larger particles owing to the fast coalescence of its atoms. Annealing also enhances both the diffusion process and the substitution of In atoms by Au and Ag atoms resulting in improved level of carrier concentration. (I(Au)$_n$I) and (I(Ag)$_n$I) thin films show significantly higher electrical resistivity assigned to be $11.4 \times 10^{-4}$ Ω·cm and $8.7 \times 10^{-4}$ Ω·cm, respectively. This could be related to the formation of distinct Au-NP and Ag-NP mid-layer coatings with agglomeration of these nanoparticles in the form of island like-structure as discussed previously. Moreover, the scattering of the free carriers at the interfaces between Au-NP or Ag-NP mid-layer coatings and ITO films, as well as the grain boundaries noticed in the top ITO layers of the (I(Au)$_n$I), (I(Ag)$_n$I) and (I(AgO)I) thin films, could be the main reasons that the mobility and carrier concentration of these thin films were less than that of the (IAuI) thin film. In the case of bi-layer thin films, the ITO film grown onto an Au layer exhibits the lowest electrical resistivity and the highest carrier concentration at $3.1 \times 10^{-4}$ Ω·cm, $6.8 \times 10^{20}$ cm$^{-3}$,respectively, while its carrier mobility (29 cm$^2$/Vs) is similar to that of ITO grown onto an AgO layer. It might be surmised that the electrical properties of the bi-layer coatings mainly depend on the ITO thin films rather than the bottom layers. The formation of quite thick ITO coatings for the bi-layer thin films compared to thin top ITO coatings for tri-layer thin films results in better surface morphologies. This shows that the differences in the electrical properties of bi-layer thin films are not as high as for the tri-layer thin films. For instance, the ITO coatings grown on Ag- and Au- nanoparticles layers show only a slight decrease in the electrical properties in comparison with those for tri-layer ones grown on similar Ag- and Au- nanoparticle mid-layers. This is because thicker ITO coatings for the bi-layer thin films compensate for the shortcomings of discontinuity of Ag- and Au-nanoparticle layers through early coalescence and agglomeration of ITO nanoparticles.
Table 7.3 Electric properties of fabricated bi-layer and tri-layer thin films

<table>
<thead>
<tr>
<th>System</th>
<th>Coatings</th>
<th>$\rho \times 10^{-4}$ (Ωcm)</th>
<th>$\sigma$ (S/cm)</th>
<th>$n \times 10^{26}$ (cm$^{-3}$)</th>
<th>$\mu$ (cm/Vs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi-layer</td>
<td>AuI</td>
<td>3.1 ± 0.39</td>
<td>3155.66 ± 140</td>
<td>6.8 ± 0.31</td>
<td>29.4 ± 0.93</td>
</tr>
<tr>
<td></td>
<td>(Ag)nI</td>
<td>5.0 ± 0.25</td>
<td>1856.12 ± 120</td>
<td>5.8 ± 0.27</td>
<td>20.3 ± 0.70</td>
</tr>
<tr>
<td></td>
<td>(Au)nI</td>
<td>7.5 ± 0.24</td>
<td>1270.10 ± 95</td>
<td>4.4 ± 0.28</td>
<td>18.5 ± 0.77</td>
</tr>
<tr>
<td></td>
<td>(AgO)I</td>
<td>3.8 ± 0.24</td>
<td>2598.72 ± 144</td>
<td>5.6 ± 0.30</td>
<td>29.96 ± 0.85</td>
</tr>
<tr>
<td>Tri-layer</td>
<td>I(Au)I</td>
<td>1.2 ± 0.15</td>
<td>7296.55 ± 190</td>
<td>11.4 ± 0.28</td>
<td>40.29 ± 0.82</td>
</tr>
<tr>
<td></td>
<td>I(Ag)nI</td>
<td>8.7 ± 0.31</td>
<td>1125.21 ± 105</td>
<td>3.0 ± 0.24</td>
<td>24.41 ± 0.68</td>
</tr>
<tr>
<td></td>
<td>I(Au)nI</td>
<td>11.4 ± 0.28</td>
<td>874.77 ± 0.91</td>
<td>2.6 ± 0.27</td>
<td>21.33 ± 0.75</td>
</tr>
<tr>
<td></td>
<td>I(AgO)I</td>
<td>1.6 ± 0.20</td>
<td>5720.28 ± 200</td>
<td>9.4 ± 0.33</td>
<td>38.48 ± 0.92</td>
</tr>
</tbody>
</table>

7.4.6. Optical Properties

Despite their high degree of crystallinity, (AuI) and (IAuI) films exhibit lower optical transparency than ITO and Ag-doped ITO thin films reported in our previous investigation [514] due to the reflectance losses that the metal layer introduces in the visible region. Figure 7.6 (a, b) presents the transmittance spectra of the fabricated bi-layer and tri-layer thin films. (AuI) and (IAuI) thin films have optical transparency of 85% and 82.5% respectively. In comparison, both ((AgO)I) and (I(AgO)I) thin films show high transmittance (~ 91.5%) owing to the oxidation of Ag, which results in tuning the refractive index of these films. A similar effect has been reported through increasing the oxygen to argon partial pressure level in a sputtering system [515, 516]. Despite the (AuI) and (IAuI) thin films having similar thicknesses, their optical transmittances were different. The high transparency of the (AuI) thin film can be possibly related to decrease light scattering. The bi-layer (AuI) thin film consists of two media with different refractive indices. For the tri-layer (I(Au)I) thin film, light scattering will occur from the interfaces between ITO and the Au layer. It is interesting to notice that both the (AuI) and (IAuI) thin films exhibit their maximum transparencies around 500 nm, while the other thin films exhibit their maximum transparency at a wavelength around 550 nm. However, the (IAuI) thin film shows a second maximum transmittance (83.5%) at a wavelength around 750 nm. This high transparency at longer wavelength can enhance the optoelectronic properties of the thin film especially for
producing a high level of photocurrent at this wavelength. Although the films grown on Au-NP and Ag-NP layers show high transmittances (~88%), they are still lower than those for ((AgO)I) and (I(AgO)I) thin films. This is possibly attributed to the discontinuity of Au-NP and Ag-NP layers that act as scattering centres for incident radiation.

The transmittance data were used to calculate the absorption coefficient and the optical band gap energy of the synthesized bi-layer and tri-layer thin films. The absorption coefficient ($\alpha$) was calculated using (Eq. 5.2).

Variations of the absorption coefficient for bi-layer and tri-layer thin films in the range of 350-800 nm are presented in Figure 7.7. It is seen that the AuI and IAuI thin films show the highest average absorption coefficient among other fabricated thin films. The I AuI thin film exhibits a shift in the absorption edge to longer wavelength, while the absorption edge of AuI thin film shifts to shorter wavelength.

The absorption coefficient for the direct allowed transition can be described as a function of photon energy using (Eq. 3.1). The optical band gap energies of the synthesized thin films were obtained by extrapolating the linear parts of the plotted curves to the $x$-axis.
Figure 7.6 Transmittance spectra of (a)- bi-layer and (b)- tri-layer thin films
Figure 7.7 Absorption coefficient of (a)- bi-layer and (b)- tri-layer thin films

Figure 7.8 (a, b) shows the variations of the band gap energies of the bi-layer and tri-layer thin films. The band gap energy between the top of the valence band and the lowest empty state in the conduction band was found to be proportional to the variations in the grain size, the internal stress and/or the free carrier concentration ($N$) \[517-519\], and it can be increased along with increasing $N$ due to filling of the lowest energy levels in the conduction band with a broadening proportional to $N^{2/3}$ (Burstein–Moss relation) (Eq. 3.2) \[370\]:
Despite the high $N$ values, the optical band gap energies of (AuI) and (IAuI) thin films were estimated to be low compared to the other thin films in this study. This could be mainly related to the reflectance losses of the Au layer and the introduction of some defects that create localized states in the $E_g$ [179]. The $E_g$ for the (AuI) and (IAuI) thin films were 3.73 eV and 3.5 eV, respectively, due to high optical transparency in the visible region, and the shift of the absorption edge towards shorter wavelength for the AuI thin film. The highest optical band gap energy (3.75 eV) was observed for both AgOI and IAgOI thin films. This high value of $E_g$ is mainly attributed to high optical transparency owing to the decrease in the light scattering, improved crystalline quality, enlarged crystallite size and the release of internal stress. Other fabricated bi-layer and tri-layer thin films on Au and Ag nanoparticle layers exhibit energy band gaps within the range of (3.65 – 3.72) eV.

The performance of the synthesized bi-layer and tri-layer thin films as transparent conductive coatings was further appraised through determination of the figure of merit (FOM) of these thin films. The FOM was pertinent to both the sheet resistance ($R_{sh}$) and transmittance ($T$) (at a wavelength of 550 nm) of the thin film, and can be expressed by the following relation: $FOM = T^{10}/R_{sh}$. A comparison of the FOM of the fabricated and annealed bi-layer and tri-layer thin films is presented in Table 7.4. It is known that a higher value of FOM suggests better performance for a transparent conducting thin film. The highest values of FOM were calculated to be $31 \times 10^{-3}$ and $13 \times 10^{-3}$ $\Omega^{-1}$ for (I(AgO)I) and (AgO)I thin films, respectively. These high values can be mainly attributed to high optical transparency of the (I(AgO)I) and (AgO)I films.

Table 7.4 Optical, sheet resistance and FOM values of synthesized thin films

<table>
<thead>
<tr>
<th>System</th>
<th>Coating</th>
<th>$T$ (%)</th>
<th>$E_g$ (eV)</th>
<th>$R_{sh}$ (Ω/sq)</th>
<th>$\Phi\times10^{-3}$ ($\Omega^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi-layer</td>
<td>AuI</td>
<td>85.0 ± 0.7</td>
<td>3.73 ± 0.01</td>
<td>23.80 ± 2.1</td>
<td>7.3 ± 0.2</td>
</tr>
<tr>
<td>Bi-layer</td>
<td>(Ag)nI</td>
<td>87.5 ± 0.4</td>
<td>3.65 ± 0.02</td>
<td>38.45 ± 1.8</td>
<td>6.4 ± 0.2</td>
</tr>
<tr>
<td>Bi-layer</td>
<td>(Au)nI</td>
<td>88.0 ± 0.2</td>
<td>3.70 ± 0.01</td>
<td>57.70 ± 2.2</td>
<td>4.8 ± 0.2</td>
</tr>
<tr>
<td>Bi-layer</td>
<td>(AgO)I</td>
<td>91.5 ± 0.2</td>
<td>3.75 ± 0.01</td>
<td>29.23 ± 2.4</td>
<td>13.0 ± 0.1</td>
</tr>
<tr>
<td>Tri-layer</td>
<td>IAuI</td>
<td>82.5 ± 0.5</td>
<td>3.51 ± 0.02</td>
<td>9.23 ± 1.2</td>
<td>9.0 ± 0.2</td>
</tr>
<tr>
<td>Tri-layer</td>
<td>I(Ag)nI</td>
<td>88.5 ± 0.2</td>
<td>3.72 ± 0.01</td>
<td>66.92 ± 3.1</td>
<td>4.1 ± 0.2</td>
</tr>
<tr>
<td>Tri-layer</td>
<td>I(Au)nI</td>
<td>87.5 ± 0.3</td>
<td>3.65 ± 0.03</td>
<td>87.70 ± 2.7</td>
<td>2.8 ± 0.1</td>
</tr>
<tr>
<td>Tri-layer</td>
<td>I(AgO)I</td>
<td>91.5 ± 0.3</td>
<td>3.75 ± 0.01</td>
<td>12.30 ± 0.9</td>
<td>31.0 ± 0.4</td>
</tr>
</tbody>
</table>
The optical constants including refractive index ($n$) and extinction coefficient ($k$) of the thin film are considered key aspects for achieving good performance in optoelectronic applications. The refractive index of a thin film is a measure of its transparency to incident radiation within a specific region of studied wavelength. The valuation of the refractive index is very important in

Figure 7.8 Variations of the band gap energy of (a)- bi-layer and (b)- tri-layer thin films
integrated optoelectronic devices. The $n$ and $k$ values of the bi-layer and tri-layer thin films were calculated based on (Eq. 5.3) and (Eq. 2.19), respectively.

Figure 7.9 (a, b) shows the variation of the refractive indices of the fabricated bi-layer and tri-layer thin films. It can be seen in Figure 7.9 that the refractive indices of all thin films decreased with increasing the wavelength, and the average values of $n$ for both AuI and IAuI thin films are higher than that for other thin films fabricated in this study. This could be attributed to the high carrier concentration and reflectivity that the AuI and IAuI thin films possess. Increasing carrier concentration might result in the formation of some light scattering centres, which hinders the optical transparency.

As seen in Figure 7.10 (a, b), the extinction coefficients of all the fabricated bi-layer and tri-layer thin films initially decrease in the near ultraviolet (NUV) region and then gradually increased in the visible region. The AuI and IAuI thin films exhibit the highest average extinction coefficient values in the visible region compared with the other thin film coatings, which could be also related to increased reflection of light by Au layer.
Figure 7.9 Refractive index spectra of (a) bi-layer and (b) tri-layer thin films
Figure 7.10 Extinction coefficient spectra of (a) bi-layer and (b) tri-layer thin films
7.4.7. Characteristics of OSCs

The favourable performance of AgOI and IAgOI identified these thin films for further investigation in organic solar cells (OSCs) using these thin films as electrodes combined with a low band gap photoactive polymers. The OSCs configuration: glass\electrode\PEDOT:PSS\P3HT:PCBM\Al is shown in Figure 7.11a. Characteristics of the OSCs fabricated with AgOI and IAgOI electrodes were compared with OSC fabricated with an ITO electrode reported in our previous study [430]. The power conversion efficiency (PCE) of the OSC is defined by the following formula:

\[
PCE = \frac{FF \times V_{oc} \times J_{sc}}{P_i}
\]  \hspace{1cm} (7.3)

where \(V_{oc}\), \(J_{sc}\) and \(P_i\) are the open circuit voltage, short-circuit current density and the input power of the solar irradiance, respectively. \(FF\) is the fill factor which is defined as:

\[
FF = \frac{J_m V_m}{J_{sc} V_{oc}}
\]  \hspace{1cm} (7.4)

where \(J_m\) and \(V_m\) are the maximum current density and maximum voltage, respectively.

A comparison of the \((J-V)\) characteristics of the fabricated OSCs based on ITO, AgOI and IAgOI electrodes showed that the short-circuit current density \(J_{sc}\) and fill factor \(FF\) values of the solar cell with IAgOI electrode were observably higher than those of AgOI and ITO electrodes as seen in Figure 7.11b and Table 7.5. Since the configuration of the fabricated OSCs is identical, all the OSCs showed similar open circuit voltage \(V_{oc}\). The higher value of \(J_{sc}\) and \(FF\) of the OSC fabricated with IAgOI electrode could be associated with the higher incident-photon to current conversion efficiency, owing to the higher optical transparency of the IAgOI electrode in the wavelength range of 400 – 800 nm, and the lower sheet resistance compared to AgOI and ITO electrodes. Series resistance \(R_s\) of an electrode has no effect on its \(V_{oc}\) value, yet it decreases the \(J_{sc}\) value of the electrode [20]. The power conversion efficiency \(PCE\) of the OSC fabricated with IAgOI electrode is greater than those OSCs fabricated with ITO and AgOI electrodes, despite similar optical transparency. This high \(PCE\) value observed in the OSC fabricated with IAgOI electrode is the result of the increase in the photocurrent production due to both low \(R_{sh}\) value, and high optical transparency in the wavelengths between 400 and 800 nm.
Table 7.5 Photovoltaic performance parameters of fabricated OSCs

<table>
<thead>
<tr>
<th>Electrode</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF (%)</th>
<th>$R_{sh}$ (Ω cm$^2$)</th>
<th>$R_s$ (Ω cm$^2$)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IAgO (I)</td>
<td>12.5</td>
<td>0.64</td>
<td>61.25</td>
<td>565.68</td>
<td>7.4</td>
<td>4.9</td>
</tr>
<tr>
<td>AgO (I)</td>
<td>11.53</td>
<td>0.64</td>
<td>57.70</td>
<td>731.74</td>
<td>10.1</td>
<td>4.2</td>
</tr>
<tr>
<td>ITO</td>
<td>10.63</td>
<td>0.64</td>
<td>56.10</td>
<td>829.31</td>
<td>14.5</td>
<td>3.8</td>
</tr>
</tbody>
</table>

7.5. Conclusions

In the present study, thin (Au\(I\)), (Au)$_n$\(I\), (Ag)$_n$\(I\), (AgO)\(I\), (IAu)\(I\), (I(Au)$_n$I), (I(Ag)$_n$I) and (I(AgO)\(I\) film coatings were successfully fabricated via a low cost, efficient and environmentally friendly sol-gel spin-coating method onto soda-lime glass substrates, and annealed at 500 °C. The effects of inserting thin Au, Au-NP, Ag-NP and AgO layers in bi-layer and tri-layer ITO-based thin films were investigated by means of structural, morphological, elemental composition, optical and electrical characteristics. XRD results confirmed the formation of a body-centered cubic structure of polycrystalline indium oxide. XPS scans show the existence of the main elements (In, Sn and O) in the film materials, and the contributions of the element compounds were estimated by de-convoluting the high resolution In 3d, Sn 3d and O 1s photoelectron lines via a Gaussian distribution. FESEM images revealed the development of dense surfaces with grain-like morphologies indicating the formation of polycrystalline features of ITO. Optical studies
revealed absorption peaks at wavelengths of 405 nm and 531 nm for Ag-NP and Au-NP colloidal solutions, respectively, which were attributed to the formation of 10 – 14 and 48 nm Au and Ag particles, respectively. The maximum transmittance in the visible region and band gap energy were found to be ~ 91.5% and 3.75 eV for both (AgO)I and (I(AgO)I) thin films. The IAuI thin film showed the lowest electrical resistivity of \(1.2 \times 10^{-4} \, \Omega \cdot \text{cm}\), along with the highest carrier concentration \(11.4 \times 10^{20} \, \text{cm}^{-3}\) and mobility \(40 \, \text{cm}^2/\text{V s}\). These results are better than those obtained from 350 nm pure ITO and doped-ITO films. An improvement in the power conversion efficiency \(PCE\) from 3.8 to 4.9% is achieved in an organic solar cell by replacing the conventional pure ITO electrode with an \((I(AgO)I)\) electrode.
CHAPTER 8: Conclusions and Recommendations

8.1. Conclusions

An efficient, low-cost and environmentally friendly sol-gel spin-coating method was adopted to synthesize ITO-based transparent and conducting thin films on soda-lime glass substrates. An alternative to high energy and vacuum techniques, high crystalline quality sol-gel derived ITO-based thin films combined with 3d transition metals including Ti and Ag, SWCNTs and metal nanoparticles were successfully prepared and characterized for their optoelectronic properties by means of XRD, XPS, FESEM, EDX, AFM, Raman analysis, UV-Vis, four point probes, Hall-Effect, and nanoindentation measurements. The structural, morphological, optoelectronic and mechanical properties were investigated for a range of variables including Ti (2 and 4 at.%) and Ag concentrations (2, 4, 6 and 10 at.%) for 350 nm Ti- and Ag- doped ITO film thickness, respectively, film thickness (150, 210, 250 and 320 nm) for SWCNTs (0.25 wt%) incorporated ITO thin films. Three different ITO-based film geometries (single-, bi- and tri- layers) were synthesized in this study. Single ITO coatings include ITO, Ti- and Ag- doped ITO and CNT incorporated ITO. While, bi-layer and tri-layer ITO stacks consisted of: Au/ITO (AuI), Au-NPs/ITO (Au)_nI, Ag-NPs/ITO (Ag)_nI and AgO/ITO (AgO)I for bi-layer coatings and ITO/Au/ITO (IAuI), ITO/Au-NPs/ITO (I(Au)_nI), ITO/Ag-NPs/ITO (I(Ag)_nI) and ITO/AgO/ITO (I(AgO)I) for tri-layer coatings. All the synthesized ITO-based thin films were fabricated using a pre-ITO solution of (In:Sn = 90:10 at.%), and post annealed in the range (350 – 600) °C.

XRD results confirmed that all the fabricated ITO-based thin films exhibited the presence of a body-centered cubic bixbyite structure similar to In_2O_3 with a space group of Ia3. The crystalline quality of the fabricated thin films was improved along with enlarging grain sizes and lattice constants by Ti, Ag and CNTs additives, annealing temperature and depositing ITO layers on continuous Au and AgO layers. A Thin ITO film prepared with 4 at.% Ti and annealed at 500 °C exhibited the largest crystallite size of 80 nm compared to other doped ITO-based thin films with crystallite size in the range of (50 – 65) nm. XRD results also showed the presence of Ag and C phases for Ag-doped ITO and SWCNTs/ITO thin films, respectively, which were also confirmed by EDX and Raman analysis. EDX results showed the presence of Ag and CNTs in ITO film materials, while Raman analysis performed on SWCNT/ITO thin films revealed the existence of both D- and G-bands for carbon. The D-band seen at 1292.4 cm⁻¹ is related to the defect in the
SWCNTs, while the G-band seen at 1594.6 cm$^{-1}$ is characteristic of $sp^2$ graphitic material, which is attributed to a carbon atom vibrational mode along the SWCNT axis. XPS results of SWCNTs/ITO thin films are consistent with Raman analysis. By de-convoluting the C1s photoelectron lines, a high contribution of 66.8% observed at the lowest binding energy around 284.5 eV was assigned to pure $sp^2$ hybridized graphitic carbon atoms of (C-C and C=C bonds), and carbon atoms bounded to hydrogen (C-H bonds). These $sp^2$ bonds provide CNTs with their unique mechanical properties.

The surface morphology of the synthesized ITO-based thin films was characterized by FESEM imaging. All the thin films showed dense and homogeneous surfaces with grain-like structures demonstrating the nanocrystalline structure. Incorporation of Ti, Ag and CNTs in ITO film materials resulted in enhancing the surface morphologies of these thin films along with enlarging their grains. These findings are consistent with the results obtained from the XRD results. Annealing temperature up to 500 °C enhanced the morphologies of the synthesized thin film. However, further increase in the annealing temperature up to 600 °C resulted in the formation of some cracks on the surfaces of ITO and Ti-doped ITO thin films. Also, thicker films (i.e., 250 and 320 nm) for SWCNTs/ITO coatings showed the formation of some cracks on their surfaces compared to thinner films of the same coating. These cracks significantly affected the surface topography of thicker SWCNTs/ITO films that displayed RMS values of 4.08 and 4.65 nm for 250 and 320 nm, respectively, compared to 3.36 and 3.49 nm for thinner films (150 and 210 nm, respectively) as proven by AFM scan results. FESEM images of bi-layer and tri-layer ITO-based thin film coatings revealed that the films deposited on continuously formed Au and AgO layers are dense, smooth and homogeneous, while those deposited on Au- and Ag- nanoparticles layers displayed a few micro-cracks, grain boundaries and pinholes due to discontinuous island-like structures these coatings possess. These continuous and distinct Au and Au-NPs layers were confirmed by cross-sectional FESEM images performed on ITO/Au ITO and ITO/Au-NPs/ITO thin films, respectively.

It is believed that improving the crystalline quality and surface morphology of ITO-based thin films resulted in enhancing their optoelectronic properties. The highest optical transparency (~92%) was for ITO, 4 at.% Ti-doped ITO and 2 at.% Ag-doped ITO thin films. This high optical transparency resulted from the broadening of the optical band gap energy calculated to be
(3.74, 3.77 and 3.75 eV) for the former thin films, respectively. Since the optical constants including absorption coefficient, complex refractive index and extinction coefficient are very important parameters for achieving good performance in optoelectronic devices, these parameters were also calculated in this work for different synthesized thin films. It is noted that increasing the Ag level in Ag-doped ITO thin films, and the film thickness of SWCNTs/ITO thin films resulted in a shift in the absorption edge to longer wavelength regions and the thin films showed higher absorption coefficient values compared to pure ITO films. Similarly, increasing the Ag level in Ag-doped ITO thin films resulted in increasing the average values of both refractive index and extinction coefficient. In relation to bi-layer and tri-layer ITO based thin films, both Au/ITO and ITO/Au/ITO stacks revealed the highest values of both refractive index and extinction coefficient compared to other stacked thin films.

Incorporating Ag, Ti and CNTs in ITO matrix resulted in improving the electrical and mechanical properties of ITO thin films. ITO thin films prepared with 4 at.% Ti concentration and annealed at 500 °C showed an improvement in the electrical resistivity of 1.6×10^{-4} \, \Omega \cdot \text{cm} along with carrier concentration and carrier mobility of 8.6×10^{20} \, \text{cm}^3 and 49 \, \text{cm}^2/\text{Vs}, respectively, compared with pure ITO film with resistivity, carrier concentration and mobility of 2.2×10^{-4} \, \Omega \cdot \text{cm}, 7.0 \times 10^{20} \, \text{cm}^3 and 39 \, \text{cm}^2/\text{Vs}, respectively. Similarly, the ITO film prepared with 4 at.% Ag concentration showed improved electrical properties among other Ag-doped ITO thin films. Additionally, increasing the thickness of SWCNTs/ITO thin films resulted in improving their electrical properties and slightly decreasing the optical transparencies. The thickest film (i.e., 320 nm) annealed at 350 °C exhibited electrical resistivity, carrier concentration and mobility of 4.6×10^{-4} \, \Omega \cdot \text{cm}, 3.3 \times 10^{20} \, \text{cm}^3 and 41 \, \text{cm}^2/\text{Vs}, respectively. However, the lowest electrical resistivity achieved in this study was 1.2 \times 10^{-4} \, \Omega \cdot \text{cm}, related to ITO/Au/ITO along with carrier concentration and mobility of 11.4 \times 10^{20} \, \text{cm}^3 and 40 \, \text{cm}^2/\text{Vs}, respectively.

Improvement in the mechanical properties of the thin films was attributed to crystalline quality, chemical and electronic states of the thin films. The contributions of Ti, Ag and CNT in improving the mechanical characteristics of the synthesized ITO-based thin films were estimated from the nanoindentation measurements. ITO thin films prepared with the highest levels of both Ti and Ag and annealed at 500 °C revealed a hardness and Young’s modulus in the range (6.7 -
6.8) and (143 – 148) GPa, respectively. Due to the high contribution of $sp^2$ bonds (66.8%) obtained from the XPS analysis, significant improvement in the mechanical properties was noted by incorporating robust SWCNTs in ITO matrix, with a hardness and Young’s modulus of 28 and 306 GPa, respectively, compared to 6.6 and 143 GPa for ITO thin film. These distinctive mechanical properties of SWCNT/ITO films resulted in a slight drop in their optical transparencies. However, these values of optical transparency are still acceptable in optoelectronic applications.

The performance of ITO-based thin film coatings was examined through fabricating OSCs with ITO, AgO\ITO and ITO\AgO\ITO electrodes. The resultant OSCS have the configuration: glass|electrode|PEDOT:PSS|P3HT:PCBM|Al. The power conversion efficiencies of 4.9%, 4.2% and 3.8% were obtained for ITO\AgO\ITO, AgO\ITO and ITO thin film coatings, respectively.

Increasing demands for the next generations of optoelectronic devices inspires researchers in the field of TCMs to develop new low-cost materials or use simple and low-cost techniques to fabricate these kinds of thin films. The sol-gel spin-coating process adopted in this research work has proven itself to compete with other, more expensive and more complicated methods in synthesizing high performance ITO-based transparent and conductive films.

Table 8.1 A comparison of the best achieved results of ITO-based TCOs thin films fabricated in this study

<table>
<thead>
<tr>
<th>Coating</th>
<th>$\rho \times 10^{-3}$(Ω.cm)</th>
<th>$n \times 10^{20}$(cm$^{-3}$)</th>
<th>T%</th>
<th>Hardness</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITO</td>
<td>2.2</td>
<td>7.0</td>
<td>90.5</td>
<td>6</td>
</tr>
<tr>
<td>Ti-doped ITO</td>
<td>1.6</td>
<td>8.6</td>
<td>92</td>
<td>6.8</td>
</tr>
<tr>
<td>Ag-doped ITO</td>
<td>2.4</td>
<td>6.8</td>
<td>92</td>
<td>6.8</td>
</tr>
<tr>
<td>SWCNTs/ITO</td>
<td>4.6</td>
<td>3.3</td>
<td>88</td>
<td>28.0</td>
</tr>
<tr>
<td>Au/ITO</td>
<td>3.1</td>
<td>6.8</td>
<td>80</td>
<td>-</td>
</tr>
<tr>
<td>AgO /ITO</td>
<td>3.8</td>
<td>5.6</td>
<td>85</td>
<td>-</td>
</tr>
<tr>
<td>ITO/Au/ITO</td>
<td>1.2</td>
<td>11.4</td>
<td>80</td>
<td>-</td>
</tr>
<tr>
<td>ITO/AgO/ITO</td>
<td>1.6</td>
<td>9.4</td>
<td>88</td>
<td>-</td>
</tr>
</tbody>
</table>
8.2. Recommendations

The scientific works embodied in this thesis have led to an intriguing opportunity for further investigations in improving the optoelectronic and mechanical properties of ITO-based thin film coatings. The next paragraphs discuss a few suggestions for potential future works.

Since the ITO properties have been improved by doping with Ti and Ag in this dissertation and annealing, co-doping of ITO thin films can be an efficient new strategy to further improve its optoelectronic characteristics. Investigation of alternative elements with suitable concentrations to dope ITO thin films without altering their crystallite structure will be beneficial for this purpose.

Mechanical properties are very important aspects in determining favorable performance from ITO-based thin films, especially for flexible applications. The surface of an ITO film is brittle, weak, and seems to be susceptible to delamination and cracking under an applied strain. In this study, CNTs incorporated with ITO showed good mechanical characteristics despite the reduction of the optical transparency. Therefore, developing new materials and/or elements to improve the mechanical properties of a brittle ITO while maintaining its optoelectronic properties, is important to commercialize ITO for the next generation of flexible optoelectronic devices.

Stacked thin films including ITO/metal/ITO have been investigated previously. However, a metal oxide layer encapsulated between two ITO layers adopted in this research study exhibited improved optical properties compared to pure metal layer. Further investigation is still needed to replace a metal layer which has high reflectivity with other metal oxide layers. Another suggestion is to fabricate ITO with other TCO thin films such as ZnO, SnO₂, TiO₂, etc.

Graphene and metal nanowires including Ag-, Cu-, and Ni- nanowires are of great interest in the field of transparent conducting materials. But, they still have some drawbacks related to high absorption by graphene in the visible region, and the oxidation issue of metal nanowires. Combining ITO thin films with graphene and metal nanowires can overcome their shortcomings.
References


electrical properties of indium tin oxide nanocolumns prepared by radio frequency (RF) magnetron sputtering, Superlattices Microstruct, 72 (2014) 140-147.


[419] Q. Liu, F. Jin, J. Dai, B. Li, L. Geng, J. Liu, Effect of thickness on the electrical and optical properties of epitaxial (La 0.07 Ba 0.93) SnO 3 thin films, Superlattices Microstruct, 96 (2016) 205-211.


