Optical and electrical properties of aluminum-doped ZnO

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Optical and Electrical Properties of Aluminum-doped ZnO

CHAN Yu Wai, Ray

A thesis submitted for the requirement of candidate

for the degree of Master of Philosophy in Physics

Principal Supervisor: Prof. CHEAH Kok Wai

Hong Kong Baptist University

Department of Physics

Jun 2015
DECLARATION

I hereby declare that this thesis represents my own work which has been done after registration for the degree of M.Phil at Hong Kong Baptist University, and has not been previously included in a thesis, dissertation submitted to this or other institute for a degree, diploma or other qualification.

Signature:____________________

Date: June 2015
ABSTRACT

In the past few years, “green” technologies and touch screen technologies for portable devices has came to hot topic in consumer market. The demand for transparent conducting oxides (TCO) is increasing continuously. Therefore, the potential replacement of indium tin oxide (ITO), which is the most widely used TCO in industry, by aluminum zinc oxide (AZO) draws much attention in order to solve the problem of shortage of ITO one day due to the consisting of rare-earth element.

In this work, electrical and optical properties of AZO had been characterized according to different sputtering parameters such as oxygen contents, working pressures and gas flow ratios. Physics of electrical conduction and optical transparency of AZO films were revealed and analyzed in order to set up a more complete relationship between mechanism and performance. Meanwhile, a comparison of sensitivity between AZO and zinc oxide (ZnO) to sputtering environment had been made and behaviors of AZO at low temperature had been presented.

Optimum sputtering conditions for AZO had been established as a function of sputtering time and the film resistivity reached down to $7 \times 10^{-4} \Omega \cdot \text{cm}$ while film transmittance was above 85% when $t = 140$ mins having film thickness about 610 nm. Degradation of AZO had been investigated. Application of AZO in OLED fabrication had been carried out after film refinement and device performance had been given. Finally, simulation of OLED structure was done for better device performance.
ACKNOWLEDGEMENTS

I would like to send my wholehearted and deepest gratitude to my supervisor, Prof. K. W. CHEAH, for his kind advice and useful guidance during my study period of Master degree. In addition, I would like to thank my co-supervisor, Prof. S. K. SO, for his concern to my work. I also want to express my acknowledgements Mr. W. K. CHAN for his assistance of XRD measurement and Mr. P. L. TSE for his technical support of the laboratory equipment.

Heartfelt thank is presented to Mr. W. Y. LAM for the helpful discussions and encouragements. Sincere thanks are given to my other colleagues in IAM, namely Miss K. M. FUNG, Miss S. Y. CHING, Ms. Y. W. O, Ms. C. M. CHOW, Mr. K. C. TAM and Mr. C. CAI for the sharing of their knowledge. I would take this special chance to thank my family and my wife, Ms. Y. T. LEUNG, for every single word and support throughout my studies. Moreover, every encouragement, including from Mr. J. K. NGO, Mr. M. H. CHOI and other members of RED, given to me are appreciated.

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CHAPTER 1 INTRODUCTION TO ALUMINUM ZINC OXIDE

1.1 Transparent Conducting Oxide

In 1907, the first report of a transparent conducting oxide (TCO) was published by Badeker when he first prepared cadmium oxide (CdO) films by the thermal oxidation of sputtered cadmium film [1]. The films were transparent while remaining electrically conducting. Then, the commercial value of these thin films has been recognized, and thus, the list of potential TCO materials has expanded. Since the 1960s, the most widely used TCO for optoelectronic device applications has been tin-doped indium oxide (ITO). At present, ITO offers the best available performance in terms of conductivity and transmittance combining with excellent environmental stability, reproducibility and good surface morphology. The use of other TCOs is application-specific. There are both types of p-type TCOs, such as NGZO by co-doping zinc oxide (ZnO) with nitrogen (N) and Gallium (Ga), and n-type TCOs, such as aluminum-doped ZnO (AZO), available for designers’ toolbox.

1.1.1 History and Development of TCO

The history of TCO films can be traced back to 1907, when Badeker reported that Cd metal thin films deposited in a glow discharge chamber could be oxidized to CdO films that were both transparent and conducting [1]. There was huge interest in TCO films along with the advancement in optoelectronic technology after this discovery. Over the past few decades, many new TCO materials including tin oxide (SnO₂), indium oxide (In₂O₃), ITO, ZnO, etc. have emerged. Among the class of TCO films, ITO thin film is highly favored due to its combination of technologically
important properties such as low electrical resistivity, high luminous transmittance, high near-infrared reflectance, excellent substrate adherence, hardness and chemical inertness [2-8]. Meanwhile, a number of new techniques for the preparation of TCO films have also been developed.

<table>
<thead>
<tr>
<th>Material</th>
<th>Year</th>
<th>Process</th>
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<td>CdO</td>
<td>1907</td>
<td>Thermally Oxidation</td>
<td>K. Badeker, Ann. Phys. (Leipzig) 22, 749 (1907)</td>
</tr>
<tr>
<td>CdO</td>
<td>1952</td>
<td>Sputtering</td>
<td>G. Helwig, Z. Physik, 132, 621 (1952)</td>
</tr>
<tr>
<td>SnO₂Cl</td>
<td>1947</td>
<td>Spray pyrolysis</td>
<td>H.A. McMaster, U.S. Patent 2,429,420</td>
</tr>
<tr>
<td>SnO₂Sb</td>
<td>1947</td>
<td>Spray pyrolysis</td>
<td>J.M. Mochel, U.S. Patent 2,564,706</td>
</tr>
<tr>
<td>SnO₂F</td>
<td>1951</td>
<td>Spray pyrolysis</td>
<td>W.O. Lytle and A.E. Junge</td>
</tr>
<tr>
<td>SnO₂Sb</td>
<td>1967</td>
<td>CVD</td>
<td>H.F. Dates and J.K. Davis, USP 3,331,702</td>
</tr>
<tr>
<td>InO</td>
<td>1947</td>
<td></td>
<td>M.J. Zunick, U.S. Patent 2,516,663</td>
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<tr>
<td>In₂O₃Sn</td>
<td>1951</td>
<td>Spray pyrolysis</td>
<td>J.M. Mochel, U.S. Patent 2,564,707 (1951)</td>
</tr>
<tr>
<td>In₂O₃Sn</td>
<td>1955</td>
<td>Sputtering</td>
<td>L. Holland and G. Siddall, Vacuum III</td>
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Table 1.1 Selected historical TCO references [9]
Table 1.1 clearly shows the wide diversity of a list of current TCO materials although not fully comprehensive [9]. From the table, the number of TCO materials had a significant and appreciable increase after 1995. The rate of development of new materials has been continuing. Transparent conductors now include thin metal films, sulphides, selenides, nitrides, nanotube composites, graphenes and polymers in addition to the traditional metal oxide based TCO.

Over the last 20 years, much of the material work on TCO has been empirical with a focus on minor variants of $\text{In}_2\text{O}_3$, $\text{SnO}_2$, ITO and ZnO. It was quite remarkable how dramatically this field has grown recently in both applied and basic science. This could be reflected in the thousands of paper published during this period of time. A very important realization is that there is still not a complete theoretical understanding of the materials nor an ability to reliably and precisely predict the properties of new materials.

The widespread use of ITO, particularly in high-growth and high-volume consumer markets, has over the last several years putting severe pressure on the availability of indium. The annual supply of indium is about 200 metric tons. Half of this amount is used as ITO in its application in the Far East. Over the last decades, indium supply from China is about 30-40 metric tons per year among which majority serves the Japanese market. A shortage in supply could soon happen in the near future if there is no market-driven planning by the mining industry. The development of alternative TCO composed of less-costly raw materials would solve this problem. In other words, work on improved or alternative TCOs suited for the manufacturing environment for any of the high-growth and high-value optoelectronic products that currently rely heavily on ITO is a particularly challenging material problem to solve.
The cost of producing a transparent conducting material depends on the cost of the materials and the deposition process. The cost of the raw materials generally increases in the following order:

\[ \text{Cd} < \text{Zn} < \text{Ti} < \text{Sn} < \text{Ag} < \text{In} \]

Although this ranking can only give a rough comparison, indium is a rare and expensive element that is obtained as a byproduct of the mining of ores for their content of other metals such as zinc and lead. There is no “indium mines” because its concentration in minerals is too low to allow economic extraction only for the value of indium. Thus, the supply of indium cannot be increased significantly. It is reflected known from the fact that ITO has become ten times more expensive over the last few years due to the diminishing of indium resources [10].

Hence, other TCO such as AZO may be one of the future prospects to solve this problem.

1.1.2 Characteristics of TCO

TCO is an essential part of technology that requires both large-area electrical contact and optical access in the visible light range. TCO, which is achieved by selecting a wide-bandgap oxide made degenerate through the introduction of native or substitutional dopants, has high transparency and also high electrical conductivity. The key features of a TCO material are that the transmittance should be higher than 80\% in the visible portion of light range, which is 400-700 nm, and the resistivity
should be lower than $10^{-4}$ Ωcm. Most of the useful oxide-based materials are n-type conductors that ideally have wide bandgap, a conduction band shape, which ensures the plasma-absorption edge lies in the infrared range, and the ability to be doped to degeneracy.

The three fundamental requirements for the electronic structure of a TCO material are outlined as follows [11]:

(1) Optical transparency in the visible region requires the bandgap of the TCO, which must be intrinsically insulating, to be greater than 3.1 eV.

(2) Electric current is transported by electron introduction to the conduction band and the conduction band must constitute an extended state so that doped electrons can migrate in the lattice under a weak applied electric field.

(3) Electron doping in the oxide crystals is obtained using methods such as substitution of cations/ anions or by the addition of oxygen vacancies/ excess cations.

Table 1.2 gives a summary list of the critical properties and some of the TCO materials [12]. This is driving the exploration of new and improved materials as well as the increasing emphasis on improved environmental properties.
### Applications of TCO

There are global societal drivers for the development of TCOs due to their critical role in the development of various energy related technologies. Fig.1.1, which shows the world energy consumption by region, makes very clear the rapid increasing energy consumption worldwide [13]. Total global energy consumption will continue to rise up rapidly. If there is no any other new energy source found or “green” technology studied, energy shortage may occur in the near future. Actually, TCOs relate to this global problem because they are the key elements in a number of “green” technologies. In particular, they are critical to low emissivity (low-e) and solar control windows, photovoltaics, organic light emitting devices (OLEDs) and vehicle heat management.

<table>
<thead>
<tr>
<th>Property application</th>
<th>Simple</th>
<th>Binary</th>
<th>Ternary</th>
</tr>
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<tbody>
<tr>
<td>Highest transparency</td>
<td>ZnO:F</td>
<td>Cd$_2$SnO$_4$</td>
<td></td>
</tr>
<tr>
<td>Highest conductivity</td>
<td>In$_2$O$_3$:Sn</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Highest plasma frequency</td>
<td>In$_2$O$_3$:Sn</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Highest work function</td>
<td>SnO$_2$:F</td>
<td>ZnSnO$_3$</td>
<td>Zn$<em>{0.45}$In$</em>{0.85}$Sn$_{0.66}$O$_3$</td>
</tr>
<tr>
<td>Lowest work function</td>
<td>ZnO:F</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Best thermal stability</td>
<td>SnO$_2$:F</td>
<td>Cd$_2$SnO$_4$</td>
<td></td>
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<tr>
<td>Best mechanical durability</td>
<td>SnO$_2$:F</td>
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<tr>
<td>Best chemical durability</td>
<td>SnO$_2$:F</td>
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<td></td>
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<tr>
<td>Easiest to etch</td>
<td>ZnO:F</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Best resistance to H plasmas</td>
<td>ZnO:F</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lowest deposition temperature</td>
<td>In$_2$O$_3$:Sn</td>
<td>a-InZnO</td>
<td></td>
</tr>
<tr>
<td>Least toxic</td>
<td>ZnO:F</td>
<td>SnO$_2$:F</td>
<td></td>
</tr>
<tr>
<td>Lowest cost</td>
<td>SnO$_2$:F</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TFT channel layer</td>
<td>ZnO</td>
<td>a-InZnO, a-ZnSnO</td>
<td>InGaO$_3$(ZnO)$_3$, a-InGaZnO</td>
</tr>
<tr>
<td>Highest mobility</td>
<td>CdO, In$_2$O$_3$:Ti</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Resistance to water</td>
<td>SnO$_2$:F</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1.2 TCO materials for different applications [12]
Fig. 1.1 Energy consumption against year by region [13]

Presently, TCO films are found in a host of optoelectronic, mechanical and architectural systems. These include flat panel displays, OLEDs [14-16], solar cells, heat mirrors, energy-efficient windows and gas sensors [2,3]. In flat panel displays, a TCO layer is needed to transmit the back light through the device to the viewers. In solar cells, a TCO layer is used as a transparent electrode or an n-type layer in the case of a p-n heterojunction system. In addition, a TCO layer coated on solar cells also serves as an antireflective coating. With increasing sophistication in the areas of optoelectronic applications such as large area flat panel displays, TCO thin films of
much lower resistivity are required. These display devices now utilize substrates such as polymers and organic color filter films that cannot survive temperatures over 200°C. Therefore, such a low resistivity should be achieved near room temperature.

**Flat Panel Displays**

One high profile and rapidly emerging area of TCO is thin film transistors (TFTs). Conducting TCO can be combined with amorphous semi-insulating high mobility TCO materials to create a feasible alternative to the conventional amorphous silicon (Si) TFTs currently used in flat panel displays. Fig. 1.2 shows a schematic image of TFT structure on Si substrate with indium zinc oxide (IZO) as the channel layer [17].

![Fig. 1.2 Schematic image of IZO based TFT structure on Si substrate [17]](image)
Flat panel displays are found in a wide variety of display applications such as instrument panels for airplanes and automobiles, televisions, mobile phones, displays for home appliances and displays with specialty requirements for the medical and military markets. Some of the applications are shown in Fig. 1.3 [18]. The list is extensive and the demand is large. These diverse applications have different display requirements that are met by a combination of different device design and optical enhancements. The role of TCO in all of these devices is as transparent conducting electrodes addressing each pixel or larger zone on the display screen. TCO remains essentially the same and important while display types may vary from a wide range. A higher level of display performance is offered by active-matrix displays which TCO pixel electrodes respond is isolated to the TFT switches and to row-and-column arrays instead of sequenced and pulsed signals. TCO can be used for the row-and-column bus lines in these configurations.
Solid-State Lighting

TCO is widely used in organic light emitting diode (OLED) as a transparent electrode. Normally, it is coated onto glass substrate and appears as the anode of OLED. Fig. 1.4 depicts a typical structure of OLED [19].

![OLED Structure](image)

**Fig. 1.4 Typical structure of OLED [19]**

OLED contributes to the solid-state lighting application owing to the performance characteristics of OLED which can achieve high luminance of 1000cd/m² and stay with a long lifetime of over 5000 hours. Therefore, it favors the lighting application due to its low power consumption. Since OLED can be fabricated on flexible substrates, it can be bent into any shape for lighting. Fig.1.5 shows some solid-state lighting designs [20-21].
In 2010, Konica Minolta started mass production of world first flexible OLED lights. They received the manufacturing technology from GE which uses TCO, a polymer light emitting materials and printing technologies. Fig. 1.6 is the world first flexible OLED light under mass production [21].
Functional Glass

Functional glass for window applications can be categorized into two groups, passive application and active application.

Passive applications of TCO are used for thermal management in architectural, automotive and aircraft window glass. For passive window application, the TCO is used as a filter that reflects in the infrared region while remaining transparent in the visible. In cold climates, TCO-coated windows can be used to reflect heat back into residential space while they can reflect heat of sunlight from residential space in hot climates. It is also called heat-efficient window application and the glass is called low-emissivity (low-e) glass. Low-e glass is very cost-effective. It has advantages in thermal management, demisting and deicing. Fig. 1.7 depicts the basic principle of low-e glass [22].

Fig. 1.7 Basic principle of low-e glass [22]
Active applications of TCO are used in electrically activated structures such as electrochromic (EC) windows, which have been appearing as a commercial product over the last 10 years. It was first found application in the automotive area for self-dimming and then smart rear view mirrors as well as in smart windows with electronically adjustable transmission for building applications [23-25]. EC window is used for privacy. It has electrically controllable change in color and light transmission due to the electrically induced reduction or bleaching of TCO. This effect can be used in the design of smart windows of which the passage of a small current causes a change in color. Fig. 1.8 demonstrates a change of color of smart glass [26].
For active window application, either one of the TCO layer is used for reflective purpose. Two TCO layers are needed for transmission purpose. The two figures above show the schematic structure and working principle of an EC smart window. Fig. 1.9 reveals the diagram when the circuit of an EC smart window is open while Fig. 1.10 reveals the diagram when the circuit of an EC smart window is closed [27].
1.2 Aluminum-Doped Zinc Oxide

In 1971, aluminum-doped zinc oxide (AZO) film prepared by RF magnetron sputtering was first reported [28]. It had the properties of typical TCOs that were both electrically conducting and optically transparent in visible light range. It was a degenerated oxide having wide band gap. Recently, AZO has been used to fabricate organic photovoltaics (OPV) after decades of research in its own properties and its application in devices.

1.2.1 History and Development of AZO

Transparent conducting aluminum-doped zinc oxide (AZO) films prepared by RF magnetron sputtering and undoped zinc oxide (ZnO) by spray pyrolysis were reported by Wasa et al. in 1971 [28] and Aranovich et al. in 1979 [29] respectively. In 1982, undoped ZnO films were found unstable in temperatures above about 150°C even though they had good electrical conductivity such that they could reach very low resistivity [30]. Moreover, transparent conducting impurity-doped ZnO films were reported to achieve a low resistivity in the order of $10^{-4} \ \Omega \text{cm}$ in 1983 by Chorpa et al. [31]. These films were ZnO films prepared by impurity doping with a Group III element [32], such as Al, Ga, In and B, or a Group IV element [33], such as Si, Ge, Ti, Zr and Hf, or a Group VII element, such as F [34]. In impurity-doped ZnO films, some atoms of Group III or Group IV element substituted into the sites of Zn atoms while atoms of Group VII element substituted into the sites of O atoms. In 1984, for the purpose of improving the stability of impurity-doped ZnO films at high temperatures, Minami et al. reported that AZO films prepared by RF magnetron
sputtering with a resistivity of the order of $10^{-4} \, \Omega\text{cm}$ were stable in terms of humidity and oxygen at the temperatures as high as 400$^\circ$C [35]. The effect of doping concentration in AZO films has been extensively investigated using different deposition methods. In the late 1990s, some ZnO films prepared by doping with a rare-earth element, such as Sc or Y to substitute to a Zn atom site, were reported [36].

### 1.2.2 Characteristics of AZO

AZO is an n-type oxide-based material, which belongs to the family of TCO. It has bandgap that is greater than 3.1 eV and migration of doped electrons in the lattice under a weak applied electric field. AZO also has the key features of TCO that are having high electrical conductivity and high optical transparency. The material cost and toxicity of AZO thin films are lower comparing to that of ITO thin films. It is believed that AZO thin films have high physical and chemical stabilities in such a way that they are more air-stable and moisture-stable.

Electron doping in AZO is obtained using methods such as substitution of zinc ions in ZnO by aluminum ions. Al dopant concentration in AZO varied from 0.8% to 5% from time to time since 1971 when AZO thin films were prepared and first reported. Taking all in all, 2 at% of Al in AZO have been considered to have better performance in both electrical and optical areas by most researchers. In addition, the composite ceramic ZnO:Al$_2$O$_3$ (98:2) is the most common commercial AZO target found in the market.
1.2.3 Applications of AZO

After decades of years of research in the properties of AZO films in both electrical and optical aspects, its performance improved a lot and was getting better and better. AZO became compatible with ITO as the electrical and optical performance difference between them has narrowed down. Recently, AZO was grown via magnetron sputtering as a low cost alternative to ITO for OPVs.

OPV has drawn increasing attention to capture sunlight as a low cost environmental-friendly renewable energy source. Power conversion efficiency of OPV has constantly been increasing since Tang first introduced the donor-acceptor device in 1986 [37]. OPV requires the use of transparent conducting material as the electrode in order to admit light into the active region as well as to collect charge. AZO is well suited to OPV applications due to its high electrical conductivity and excellent optical transparency in the near-infrared and visible regions. It can be an effective ITO replacement for double heterojunction phthalocyanine-based devices.

Fig. 1.11 Typical structure of OPV [38]
1.2.4 Review in Film Formation of AZO by Different Methods

Researchers have studied film formation of AZO thin films from different methods such as electron beam deposition, RF and DC sputtering, sol-gel process and chemical vapor deposition. In this section, electrical and optical properties of AZO obtained by methods would be discussed.

In the area of physical vapor deposition, AZO has been studied through electron beam deposition and sputtering. Crystal structure, optical and electrical properties of electron beam deposited AZO were studied. AZO films with thickness around 300 nm were prepared on quartz by co-deposition of ZnO and Al₂O₃ sources by electron beam fabricated N. Yamaguchi [106]. XRD showed AZO films were weakly c-axis oriented [106]. Transmittance of AZO films in the visible range was over 80% and high reflectance was found in the near infra-red region [106]. The resistivity was as low as 3.05 x 10⁻⁴ Ω·cm [106]. S. H. Jeong prepared AZO films by RF magnetron sputtering on glass substrates containing different amounts of Al(OH)₃ powder as doping source [107]. Average transmittance of was found higher than 85% in the visible region [107]. Resistivity of the film from a 4 wt. % Al-doped content was approximately 9.8 x 10⁻² Ω·cm [107].

The plasma-enhanced chemical vapor deposition of AZO has been demonstrated for the first time at 800 Torr and under 250°C by M. D. Barankin’s group [108]. AZO film resistivity of 3 x 10⁻² Ω·cm and a transparency of 95% from 375 - 2500 nm was obtained [108]. The maximum deposition rate was 72 nm/min [108].

Formation of AZO by sol-gel process was done by M. U. Shahid [109]. The doping of Al at 1% produced more regular shaped crystallites by sol-gel process. The
lowest resistivity \( (4.27 \times 10^{-3} \, \Omega \cdot \text{cm}) \) was achieved with film thickness of about 12 µm in 1 at% Al doping in ZnO [109].

1.2.5 Research Focus

AZO has been invented and explored for about 40 years. Among different deposition methods such as electron beam, CVD and sol-gel, magnetron sputtering emerged as robust method with many advantages such as low substrate temperatures, i.e. at room temperature, good adhesion of films on substrates, superior thickness uniformity and high film density, relatively inexpensive deposition method and scalability to large areas [110]. However, the sputtering method also has disadvantages such as the unwanted bombardment on the growing films. RF magnetron sputtering could reduce this negative effect due to its smaller effective power on deposited atoms and reactive gas ions [111]. Therefore, RF sputtering was adopted in this work. On the other hand, as AZO thin film development provides greater contribution to the application of OPV in replacement of ITO, many research works have been done to improve both electrical and optical performance. However, the mechanism of conduction in AZO has not been clearly reported. Understanding on physics of electrical conduction and optical transparency of AZO thin films are desired for a more complete explanation to the performance. In this thesis, research work would be focused on the conduction mechanism of AZO thin films, the influence of sputtering parameters on AZO thin films and the optimization of AZO thin films by sputtering. Stability of AZO thin films would be studied in terms of
their degradation. Finally, AZO thin films would be applied in OLEDs after film refinement.
CHAPTER 2 THEORY

In this chapter, a number of theories and issues related to this work are presented. A brief introduction to the thin film deposition process is given. The working principle of sputter deposition is discussed, followed by the main issues in details in governing the thin film performance in terms of electrical and optical properties, crystal structure and physical structure of thin films. Then, measurement techniques in this research are introduced. Lastly, working principle, characterization and optical coupling of organic light emitting device are mentioned as well.

2.1 Sputter Deposition

Sputter deposition is a physical vapor deposition (PVD) method. In sputter deposition, thin film is deposited by sputtering which is a process that atoms or molecules are ejected from a solid source material, called “target”, due to the collisions of energetic ions. Then, the ejected atoms or molecules are deposited onto a Si wafer or glass surface, called “substrate”.

Sputter deposition is widespread technique for the production of extremely thin films of the order ranging from tens of nanometers to several microns. It is extensively used in semiconductor industry to deposit thin film of various materials for integrated circuit processing, TCO coating, anti-reflective coating on glass, contact metal coating inside thin-film transistor and most familiarly low-e coating on glass. Moreover, it is also used as the process to deposit metal layers such as Al during the fabrication of CDs and DVDs.
2.1.1 The Working Principle of Sputter Deposition

The following is the operating mechanism of sputter deposition. It is driven by momentum exchange of ions and material atoms due to collisions [39-41].

Diode Sputter Deposition

Fig. 2.1 – Fig. 2.4 depicts the working principle of diode sputter deposition [41-42]. First of all, pump down the vacuum chamber to reach a specific level. Then, introduce a gas, often an inert gas typically Argon (Ar), into a pre-pumped vacuum chamber that can move around freely as shown in Fig. 2.1. Other than Ar, inert gas like Neon (Ne) is preferable for sputtering light elements while Krypton (Kr) and Xenon (Xe) are used for heavy elements.
When the power supply is on, it introduces a live electrode into this low pressure gas environment. Some electrons escape from the cathode due to kinetic energy gained. These free electrons are immediately accelerated away from the cathode.

These accelerated electrons may collide with the neutral Ar atoms in their path. During electron-Ar atom collisions, accelerated electrons collide with outer shell electrons of Ar atoms and knock them off the Ar atoms giving out positively charged Ar ions and electrons as shown in Fig. 2.2.

![Diode sputter deposition process](image)

**Fig. 2.2 Diode sputter deposition process 2 [41]**

Then, positive charged Ar ions accelerate towards the cathode striking the surface of the target material. When the Ar ions carry energy that are above surface binding energy of the target material, atoms of target material and additional free electrons are given out by energy transfer as shown in Fig. 2.3.
Atoms of target material are deposited onto the surface of the substrate as thin film after a successful series of deposition processes, i.e. adsorption, surface diffusion, nucleation and development of film structure. Meanwhile, those additional free electrons move in their own path travelling around inside the vacuum chamber. Fig. 2.4 shows some atoms of target material are deposited on the substrate.

The additional free electrons feed the formation of Ar ions and the continuation of the plasma. Free electrons eventually collide with Ar ions and find way back into the outer electron shells of the Ar ions. During the electron-Ar ions collisions, they combine together to form neutral Ar gas atoms and release energy in the form of photon. This explains why the plasma appears to be glowing.
However, diode sputtering has two major problems. They are slow deposition rate and over-extensive bombardment of substrate causing overheating and structural damage of target. Improvement in science and technology brought about the appearance of magnetron sputter deposition [41-42].

**Magnetron Sputter Deposition**

The development of magnetron sputtering solves the problems caused by diode sputtering. By placing some magnets of alternative poles behind the cathode, free electrons are trapped in a magnetic field directly above the target surface due to Hall Effect [43]. These electrons move in an extensive and circuitous path when they are trapped in the magnetic field. Thus, free electrons cannot bombard with the substrate.
as they do in diode sputtering [44]. Thus, the bombardment of substrate is not too extensive. In addition, this increases the probability of ionization of gas atoms because mean free path of electrons is shorten. As a result, the increase in available ions appreciably enhances the sputter yield. Fig. 2.5 is a schematic setup of a deposition chamber with magnetron sputtering [45].

![Diagram of deposition chamber with magnetron sputtering]

Fig. 2.5 Schematic setup of a deposition chamber with magnetron sputtering [45]

### 2.1.2 Characteristics of Sputter Deposition

In fact, there are various deposition methods other than sputter deposition. For example, thermal evaporation, spin coating, electron beam deposition, pulse laser deposition, chemical vapor deposition, etc. Therefore, there are some pros and, on the contrary, some cons of sputtering as a deposition method.
An important advantage of sputter deposition is that it can deposit materials with very high melting point. In addition, the films deposited have a composition close to that of the source material and the difference between films and the source material is constant. Generally, sputtered films have better adhesion. Sputtering can perform either top-down or bottom-up while evaporation can only perform the latter one.

The average number of atoms ejected from the target per incident ion is called the sputter yield \( S \). It is the removal rate of surface atoms of target due to ion bombardment and is defined as [43]

\[
S = \frac{N_e}{N_i}
\] (2.1)

where \( N_e \) is the number of atoms ejected from the target and \( N_i \) is the number of incident ions. Sputter yield depends on several factors such as 1) incident angle, energy and mass of ion and 2) mass and surface binding energy of target atom.

### 2.1.3 Power Supply

There are two types of power supplies for sputter deposition. They are direct current (DC) and radio frequency (RF).
**DC Power Supply**

Fig. 2.6 below shows a DC power supply sputtering [43]. Under DC power supply, the sputtering target is the cathode for discharge while the substrate is the anode. The plasma is created and sustained by the DC via mechanisms that pertain to the abnormal glow regime – secondary electron emission at the cathode and impact ionization of the neutral gas atoms [43]. However, DC sputtering can only apply to conducting targets because positive charges on the surface of the target can built up blocking further attraction of positive ions when it deals with insulating targets. The voltage needed is of the order $10^{12}$ volts, which is impossible for targets to withstand such a high value due to arching, harm and maybe brought about cracking.

![Diagram of DC power supply sputtering](image)

**Fig. 2.6 DC power supply sputtering [43]**
**RF Power Supply**

For insulating target material, the sputtering glow discharge cannot be sustained in DC sputtering due to the immediate build-up, for about $10^{-7}$ second, of a surface charge of positive ions on the front side of the target [42, 46]. This situation was improved by Wehner in 1955 [47]. The development of RF power supply allows sputter deposition having the ability to work with both conducting and insulating target materials. RF sputtering has an impedance matching network which is for forming a resonant circuit and acting like a transformer [46]. Fig. 2.7 shows a typical RF sputtering system [46]. The radio-frequency generator is used to generate electromagnetic power in the MHz region, typically 13.56 MHz [48].

![Fig. 2.7 RF power supply sputtering [46]](image-url)
Fig. 2.8 shows the time-behavior of RF cathode voltage [48]. When the target is negatively charged, sputter deposition occurs similar to the case of DC power supply. When the target is positively charged, the target picks up electrons which then nullify the buildup of positive charge. Meanwhile, since substrate and chamber act as a very large electrode and these periods of time are short enough, sputtering of substrate is not likely to happen.

![Diagram of RF cathode voltage time-behavior](Image)

**Fig. 2.8 Time-behavior of RF cathode voltage [48]**

RF power supply is easier to keep plasma going under these conditions [49]. There are fewer gas collisions instead more lines of sight deposition [49]. It can operate at a lower working gas pressure [49]. Now, it works better because there is no need of magnetic confinement and optimum coating uniformity can be obtained at a slower deposition rate [48]. The matching network and components are very well designed such that there is no arching and more stable during sputtering and the target is very flat without racetrack and poisoning after the process [48].
2.2 Conduction Mechanism in AZO Thin Films

Individually, ZnO is an n-type semiconductor. Electrical conductivity of ZnO is mainly due to a Zn excess at interstitial sites [50]. Modification can be made to its electrical properties by thermal treatment with hydrogen [51]. It can be improved by cationic doping with a trivalent atom such as Al, which is also known as charge compensation phenomenon. Shallow donor states are introduced in ZnO.

AZO thin films are highly conducting and behave like typical degenerate semiconductor. They are non-stoichiometric oxides easily having crystallographic point defects during deposition process. These defects include interstitial atoms and vacancies. Electrical conductivity ($\sigma$) can be defined as [52]

$$\sigma = n\mu e$$

(2.2)

where $n$ is the carrier concentration of thin films, $\mu$ is the carrier mobility of thin films and $e$ is the charges of an electron.

2.2.1 Carrier Concentration of Thin Films

Carrier concentration of TCO thin films depends critically on the nature and quantity of impurities incorporated in the films and oxidation state of the metal component. In other words, carrier concentration is provided by native donors and/or impurity donors depending whether there is any dopant ions substituting into the metal oxide.
**ZnO Thin Films**

ZnO is insulating as a bulk material but is conducting as thin films. There is no any impurity donor for ZnO thin films. Carriers are provided by native donors, that is oxygen vacancies, inside ZnO thin films. Weaker oxidizing atmosphere is needed for high electrical conduction because Zn is chemically active in oxidation state during deposition [53]. The oxygen-vacancy formation under reducing conditions can be described by the following reaction

\[ O_o^X \rightarrow \frac{1}{2}O_2(g) + V_o + 2e^- \]  

(2.3)

where each oxygen vacancy gives out two electrons. There is oxygen outgassing from the material in this reducing process. Extra free electrons associate with metal defect states near the bottom of the conduction band [54].

**AZO Thin Films**

Several defect reactions can be observed when AZO thin films are grown by sputter deposition. These reactions can be expressed by the following [55].

\[ Al_2O_3 \rightarrow 2O_o + 2Al_{Zn}^+ + \frac{1}{2}O_2(g) + 2e^- \]  

(2.4)

\[ Al_2O_3 \rightarrow 2O_o + 2Al_{Zn}^+ + O_i^{2-} \]  

(2.5)

\[ Al_2O_3 \rightarrow 3O_o + 2Al_{Zn}^+ + V_{zn}^{2-} \]  

(2.6)

\[ 2Al_{Zn}^+ + 2O_o + \frac{1}{2}O_2(g) + 2e^- \rightarrow Al_2O_3 \]  

(2.7)
Eqn. (2.4) explains why there is an increase in carrier concentration in AZO films during sputtering. Eqn. (2.5) and eqn. (2.6) accounts for the defect formation for charge compensation to carrier concentration while eqn. (2.7) describes the deposition of Al$_2$O$_3$ when the Al ions concentration is over the solubility limit. Eqn. (2.4) is thought to be under relatively low oxygen partial pressure and eqn. (2.5) and eqn. (2.6) are closer to relatively high oxygen activity.

By taking non-equilibrium defects and energetic favorability to zinc vacancies than oxygen interstitials, for AZO thin films, carriers are provided by not only native donors, i.e. oxygen vacancies, but also impurity donors, i.e. Al$_2$O$_3$. Therefore, n of AZO thin films is affected by both dopant concentration and oxidizing condition. Chemical reactions affecting carrier concentrations of AZO films become:

\[
O_o^x \rightarrow \frac{1}{2} O_2(g) + V_o + 2e^- \quad (2.3)
\]
\[
Al_2O_3 \rightarrow 2O_o + 2Al_{Zn}^+ + \frac{1}{2} O_2(g) + 2e^- \quad (2.4)
\]
\[
2Al_{Zn}^+ + 2O_o + \frac{1}{2} O_2(g) + 2e^- \rightarrow Al_2O_3 \quad (2.7)
\]

where each oxygen vacancy gives out two free electrons. In addition, two free electrons are given out during the removal of oxygen interstitials of Al$_2$O$_3$ dopant. Oxygen gas is generated in above two processes. Trivalent Al cations substitute Zn ions in ZnO. High defect concentration associates with lowering of conduction band to a minimum. However, when carrier concentration becomes too large, there will be a reduction in carrier mobility due to the scattering of free electrons in the conduction
band [54]. When the amount of Al ions exceeds the solubility limit, Al ions will interact with each other and Al-Al intragrain clusters may be formed as a result.

2.2.2 Carrier Mobility of Thin Films

For complete degeneracy inside AZO thin films, carrier concentration and mobility have an inversely proportional relationship which is governed by the relationship \( \mu \propto n^{-2/3} \). Mobility is defined by eqn. (2.8)

\[
\mu = \frac{e \tau}{m^*}
\]  

(2.8)

where \( m^* \) is the effective mass of electrons in the conduction band, \( \tau \) is the average time between collisions and \( e \) is electron charge. Carrier mobility depends critically on the types of scattering dominating inside films and is improved by decreasing the number of scattering centers. There are several scattering sources and the carrier mobility can be expressed as follows for polycrystalline AZO films [56]

\[
\frac{1}{\mu} = \frac{1}{\mu_i} + \frac{1}{\mu_n} + \frac{1}{\mu_g} + \frac{1}{\mu_c} + \frac{1}{\mu_l}
\]  

(2.9)

where \( \mu_i \), \( \mu_n \), \( \mu_g \), \( \mu_c \) and \( \mu_l \) are the mobilities due to ionized impurity scattering, neutral impurity scattering, grain boundary scattering, intragrain cluster scattering and lattice vibration scattering respectively.
*Ionized Impurity Scattering* ($\mu_i$)

For mobility dominated by ionized impurity scattering, Brooks-Herring Model is used to calculate the theoretical value. Within this model, scattering potential is given by $V(r) = \frac{Ze^2}{4\pi\epsilon r} \exp(-\beta r)$ [57]. When optical transition or carrier transport of AZO films occurs in a band positioned far from the conduction band bottom or the valance band top, nonparabolic effects should be taken into consideration [58]. With nonparabolicity in the conduction band for the energy ($E$)-momentum ($\hbar k$) taken into account as reported by Pisarkiewicz et. al. [59], the modified Brooks-Herring-Dingle (B-H-D) theory became

$$\frac{\hbar^2 k^2}{2m_c^*} = E + cE^2$$  \hspace{1cm} (2.10)

where $m_c^*$ is electron effective mass in the conduction band and $c$ is the nonparabolic coefficient. Then, Pisarkiewicz incorporated $m_c^*$ as a function of energy and represented by

$$m_c^* = \hbar^2 k (dE/dk)^{-1} = m_{co}^*(1 + 2cE)$$  \hspace{1cm} (2.11)

where $m_{co}^*$ is the electron effective mass at the bottom of the conduction band. According to T. Minami’s paper done in 2001 [60], the value of $m_{co}^* = 0.28 \, m_0$ was derived for AZO thin films. Put this value back into eqn. (2.8), the mobility due to ionized impurity scattering.
\[ \mu_i = e\tau/0.28m_o(1 + 2cE) \quad (2.12) \]

**Neutral Impurity Scattering (\mu_n)**

In the case of neutral impurity scattering, hydrogen-like neutral impurities are considered as the scattering sources. Approximation of elastic scattering of electrons by neutral hydrogen is adapted in neutral impurity scattering. By scaling the Bohr radius \( a_o \) and the ground state binding energy \( E_o \), effective Bohr radius \( a_e \) and binding energy \( E_e \) can be obtained by the following equations [61] where \( \kappa \) is the dielectric constant, \( m^* \) is the effective mass of the semiconductor and \( m_e \) is the free-electron mass.

\[ a_e = a_o(\kappa m_e/m^*) \quad (2.13) \]
\[ E_e = E_o(m^*/m_e\kappa^2) \quad (2.14) \]

Erginsoy fitted the approximated results and gave the mobility due to neutral impurity scattering, which was independent of temperature [62],

\[ \mu_n = 8\pi\kappa\epsilon_o E_e/20N_i\hbar e \quad (2.15) \]

where \( N_i \) is the density of neutral impurities.

For thin films that are grown by targets with dopants, the amount of neutral impurity scattering centers is far less than that of ionized impurity [63]. Mobility due
to neutral impurity scattering under those circumstance can be neglected because of the significant difference between neutral and ionized impurities.

*Grain Boundary Scattering ($\mu_g$)*

When considering the mobility of AZO thin films dominated by grain boundary scattering, Seto proposed the first comprehensive model [64]. Poisson’s equation was solved by the abrupt depletion-layer approximation. Then, the model was modified by taking into account of concentration of the ionized traps in solving Poisson’s equation by Baccarani et al. [65]. Fig. 2.9 shows a boundary model of semi-infinite crystallite depicting rectangular grains with grain size ($L_G$), separated by identical grain boundaries, parallel to each other. The traps at the grain boundary were assumed to be constant. Intergranular potential barrier height, $E_b$, depending on carrier concentration, trap density ($Q_t$) and depletion layer width ($d$) could be calculated. According to T. Minami, the potential barrier height at the grain boundary of AZO thin films was obtained by fitting $Q_t=10^{-13}$ cm$^{-2}$ and $d=2$ nm [60].

![Fig. 2.9 Boundary model of semi-infinite crystallite [65]](image-url)
Using the above model, the mobility due to grain boundary scattering, $\mu_g$, can be represented by the following equation by Seto. [64]

$$\mu_g = L_G q (8\pi m^*_c kT)^{-1/2} \exp(-E_b/kT)$$  \hspace{1cm} (2.16)

where $L_G$ is the grain size, $q$ is the charge of a trap, $T$ is the temperature and $E_b$ is the potential barrier, which depends on trap density ($Q_t$) and depletion layer width ($d$).

**Intragrain Cluster Scattering ($\mu_c$)**

The mobility due to intragrain cluster scattering inside thin films considers the difference between ionized impurities and charged clusters. When ionized impurities react with each other and form clusters, the impurity concentration has to be replaced by the cluster concentration in order to account for the change in mobility. This change should scale as $\mu_c^{-1} \propto n_i q_i^* z^2$ where $n_i$ is the concentration and adsorbate and $q_i^*$ is the effective charge [66].

The intragrain cluster scattering mobility was derived as the form of eqn. (2.17) [67]

$$\mu_c = e \sum_k \left(\frac{\hbar k}{m^*}\right)^2 \tau_c(k) \frac{\partial f(E_k)}{\partial E_k} \left[\sum_k f(E_k)\right]^{-1}$$  \hspace{1cm} (2.17)

where $f(E_k)$ is the distribution of electrons in the quantum wire and $\tau_c$ is the momentum relaxation time.
The heavy incorporation of Al ions leads to the intragrain accumulation forming various clusters such as Al-Al and Al-O. Intragrain cluster scattering has crucial role in term of the size of clusters.

*Lattice Vibration Scattering* (*µ_l*)

The lattice vibration scattering mobility depends on temperature having the relationship, $\mu_l \propto \frac{1}{T}$. It can be expressed as [56]

$$\mu_l = \left( \frac{\Pi}{3} \right)^{1/3} \frac{e\hbar C_l}{m^*E_d^2K_B^2n_e^{1/3}}$$ (2.18)

where $E_d$ is the deformation potential constant and $C_l$ is the elasticity modulus. It is more dominant in range of high temperature. The contribution of lattice vibration scattering can be neglected at room temperature.

Therefore, the effective mobility was the summation of the effects due to ionized impurity scattering, grain boundary scattering and intragrain cluster scattering when AZO thin films are sputtered at room temperature.

### 2.3 Optical Properties of AZO Thin Films

Electromagnetic radiation propagates differently in materials than in free space. When light travels in different media, there is a change in the phase velocity and the
intensity of the radiation. Therefore, it can be described by the complex index of refraction.

\[ N = n - ik \]  

(2.19)

The quantity \( n \) is the real index of refraction and \( k \) is the absorption index. The spatially dependent portion of the electric field of a wave propagating in the \( x \)-direction is then expressed by eqn. (2.20) where \( \lambda \) is the wavelength in free space. The real function represents an exponential attenuation of the wave due to absorption within the material. The imaginary portion reflects propagation without absorption. In the highly absorbing metals, \( n \) is usually small compared with \( k \). On the other hand, the dielectric films used for optical purposes are highly non-absorbing and \( k \) is vanishingly small compared with \( n \).

\[ E = E_0 \exp \left( -\frac{i2\pi Nx}{\lambda} \right) = E_0 \exp \left( -\frac{2\pi kx}{\lambda} \right) \exp \left( -\frac{i2\pi Nx}{\lambda} \right) \]  

(2.20)

Of the total radiation energy incident on an object, a fraction of \( R \) is reflected from the top surface and a fraction \( T \) is transmitted through the object. The remaining fraction is lost through electronic absorption \( (A) \) processes and by scattering \( (S) \) at the surface and volume imperfections. Adding the various contribution gives

\[ R + T + A + S = 1 \]  

(2.21)
For light passing through a medium of refractive index $n_0$, impinging normally on a transparent film of refractive index $n_1$ and absorption constant $k_1$, $R$ can be represented as

$$ R = \frac{(n_0-n_1)^2+k_1^2}{(n_0+n_1)^2+k_1^2} $$(2.22)

AZO thin films are interesting class of materials somewhat between metals and dielectrics known as transparent conductors. According to electromagnetic theory, high conductivity and optical transparency are mutually exclusive properties in AZO thin films since photons are strongly absorbed by the density of charge carriers. Their absorptions in relevant portion of the spectrum are low. The excellent transmission is terminated at short wavelengths with the onset of the ultraviolet absorption edge. At long wavelength, the high optical transmission is limited again by absorption due to lattice vibration [68].

There is an interesting phenomenon occurs in this regime where values of $n$ and $k$ are generally not independent of each other but are connected by electromagnetic theory through so-called dispersion relations in eqn. (2.23) and eqn. (2.24) where $\varepsilon_1$ and $\varepsilon_0$ are the permittivities of the solid and the free space respectively, $\gamma$ is the reciprocal of the carrier relaxation time which is inversely related to the electrical conductivity. When $n=k$, the optical properties totally change. The critical value of $\omega$ where this situation occurs is called the plasma frequency $\omega_p$ and $\lambda_p$ is the corresponding plasma wavelength. At the optical transition, the conductivity is high and $\gamma^2$ becomes negligible. $\lambda_p$ can be formulated as eqn. (2.25).
\[ n^2 - k^2 = \varepsilon_1 - \frac{n_c q^2}{m^* \varepsilon_0 (\omega^2 + \gamma^2)} \]  
(2.23)

\[ 2nk = \frac{m_c q^2}{m^* \varepsilon_0 \omega (\omega^2 + \gamma^2)} \]  
(2.24)

\[ \lambda_p = \frac{2\pi c}{q} \left( \frac{\varepsilon_0 \varepsilon_1 m^*}{n_c} \right)^{1/2} \]  
(2.25)

From eqn. (2.25), the plasma wavelength depends in the carrier concentration \( n_c \). This means that films can be prepared to possess the desired admixture of optical reflectivity and electrical resistivity. For electromagnetic wave propagates into different films, the films exhibit metal-like reflection when \( \lambda > \lambda_p \). If \( \lambda < \lambda_p \), the high transmittance of a dielectric occurs.

AZO films generally have high plasma wavelengths. Wavelength of almost the entire visible light spectrum is smaller than plasma wavelength of AZO. When visible light incidents into AZO films, most of the light is transited through the films and AZO films are transparent. The oscillatory nature of the reflected light intensity, caused by interference effects, has a periodicity related to the film thickness and index of refraction. For given wavelengths, maxima and minima in the reflected intensity occur at specific film thicknesses.

### 2.4 Crystal Structure

There are three general types of solids, i.e. amorphous, polycrystalline and single crystal. They are characterized by the size of ordered regions, which is the spatial volume where atoms or molecules have a regular geometric arrangement or
periodicity, within the material. The sizes of ordered regions of amorphous materials are of the order within a few atomic or molecular dimensions. Polycrystalline materials have a number of regions with order over many atomic or molecular dimensions. Those ordered regions are called grains, which are separated from one another by grain boundaries. Single crystal materials have a high degree of order or regular geometric periodicity throughout the entire volume of the material [69].

![Fig. 2.10 Model of materials with different crystallinity [69]](image)

A representative unit or group of atoms in single crystal materials is repeated at regular intervals in each of the three dimensions. The periodic arrangement of the unit or group in the crystal is called the lattice. Each unit or group can be represented by a lattice point. Single crystal lattices have translational symmetries that can be characterized by three non-coplanar directions and those translation directions may not be perpendicular to each other. There are 7 crystal classes with some of them may have more than one arrangement, i.e. simple, base-centered, body-centered and face-centered, contributing to 14 Bravais lattices. The 7 crystal systems are triclinic, monoclinic, orthorhombic, rhombohedral, tetragonal, hexagonal and cubic, ascending in order from least to most symmetric [69].
2.4.1 Crystallinity of AZO Films

AZO crystallizes in two main forms, hexagonal wurtzite and cubic zincblende. The wurtzite structure is the most stable at ambient conditions and thus the most common form of structure for AZO films. The wurtzite structure is non-centrosymmetric. It has properties such as piezoelectricity and pyroelectricity. The zincblende form can be stabilized by growing AZO on substrates with cubic lattice structure. The important feature of zincblende structure is that each atom has four nearest neighbor atoms. In both cases, aluminum, zinc and oxide centers are tetrahedral [70].

![Models of wurtzite (left) and zincblende (right) structures](image)

Fig. 2.11 Models of wurtzite (left) and zincblende (right) structures [70]

2.4.2 X-Ray Diffraction

Crystal structure of thin films can be found by the technique of X-ray diffraction (XRD), which analyzes both reflection of X-ray and observation of X-ray wave
interference. It measures the average spacing between layers or rows of atoms, determines the orientation of a single crystal or polycrystalline grain, finds the crystal structure of an unknown material and measures the size, shape and internal stress of small crystalline regions [71]. Every crystalline material gives a unique diffraction pattern, which is the same for same material, and in a mixture of two or more substances each produces its pattern independently from the others [72].

The working principle of XRD makes use of Bragg’s Law, which is based on the scattering of X-ray by atoms [73]. The phenomenon can be considered as Fig. 2.12 that X-rays are partially scattered by atoms when they strike the surface of a crystal. The part of the X-ray that is not scattered passes through to the next layer of atoms, where again part of the X-ray is scattered and part passes through to the next layer. This causes an overall diffraction pattern, similar to how a grating diffracts a beam of light. In order for an X-ray to diffract the sample must be crystalline and the spacing between atom layers must be close to the radiation wavelength. If beams diffracted by two different layers are in phase, constructive interference occurs and the diffraction pattern shows a peak. However, if they are out of phase, destructive interference occurs and there is no peak. Diffraction peaks only occur for, by Bragg’s Law, \( \sin \theta = \frac{n \lambda}{2d} \) [74], where \( \theta \) is the angle of incidence of the X-ray, \( n \) is an integer, \( \lambda \) is the wavelength of incident X-ray which is similar to the atomic layer spacing and \( d \) is the spacing between atom layers.
For the instrumentation of XRD, it consists of an X-ray source which is usually an X-ray tube, a sample stage, a detector and a way to vary angle $\theta$. Fig. 2.13 shows the operation of XRD [74]. The X-ray is directed to the sample at some angle $\theta$ and, meanwhile, the detector reads the intensity of reflected X-ray on the opposite side of the source at $2\theta$ away from the source path. The incident angle is then increased over time while the detector keeps at an angle $2\theta$ from the source path.
Results are acquired in the form of peak intensity against $2\theta$. Crystalline samples will diffract since they possess highly regular structure while amorphous one will not show diffraction pattern. Therefore, peaks will up across values of $2\theta$ for crystalline materials. If there is no peak shown, the sample material does not have crystal structure but is in amorphous state. There are several important significances of the peak shape implied from the result of XRD. They are peak position, peak width and peak intensity. An unknown crystalline material can be identified by the peak position. From Scherrer equation, eqn. (2.26), the crystalline grain size of the sample can be found where $D$ is the mean diameter of the grains under a certain ordered domains, $\lambda$ is the wavelength of X-ray, $\beta$ is the line broadening in radian at half the maximum peak intensity (FWHM) and $\theta$ is the Bragg angle \[75\].

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (2.26)$$

Peak intensity reveals the crystallinity of the sample that is the number of ordered grains under at the respective orientation. After classifying the type of materials being examined, d-spacing can be calculated from the peak positions and Bragg’s Law together. Lattice constants can, furthermore, be derived from eqn. (2.27), which is the relationship between d-spacing, Miller indices and lattice constants for hexagonal AZO crystal system \[76\].

$$\frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2} \quad (2.27)$$
2.5 Physical Structures of Thin Films

The physical structures such as film thickness and surface composition of thin films can be analyzed to study the characteristics of thin films. Furthermore, they would determine the film applications. Physical structures thus provide a bridge of understanding between the deposition step and the film characteristics.

2.5.1 Thickness

A thin film is a layer of material ranging from a few nanometers or fractions of monolayer of atoms to several micrometers in thickness. If a shadow mask or vacuum tape is employed during the deposition to define an edge to the film, thickness can be determined directly with a stylus profiler. This technique is called surface profilometer technique. The instrument drags a stylus across the film while measuring stylus vertical deflection to about 1 nm. The edge of the mask or vacuum tape must be sharp enough so that the substrate height variation across the shadow region is significantly less than the film thickness. Fig. 2.14 below illustrates a microscopic view of substrate and mask.

Fig. 2.14 Illustration of shadow effect
2.5.2 Surface Composition

The surface composition of thin films can be examined by X-ray photoelectron spectroscopy (XPS) which is a surface-sensitive quantitative spectroscopic technique that measures the elemental composition at the parts per thousand range, chemical state and electronic state of the elements that exist within the thin film. XPS spectra are obtained by irradiating a material with a beam of X-ray while simultaneously measuring the kinetic energy and number of electrons that escape from the top 0 to 10 nm of the sample being analyzed [77]. The separation between two peaks is known as spin orbital splitting. The values of spin orbital splitting of a core level of an element in different compounds are nearly the same. Spin orbital splitting and peak area ratios assist in element identifications.

Chemical shift in XPS is a change in binding energy of a core electron of an element due to a change in the chemical bonding of that element. In qualitative view, core binding energies are determined by electrostatic interaction between it and the nucleus reduced by the electrostatic shielding of the nuclear charge from all other electrons in the atom, including valence electrons. Removal or addition of electronic charge as a result of changes in bonding alters the shielding [78]. Therefore, an increase in binding energy of an element in XPS pattern indicates its oxidation and vice versa.

2.6 Thin Film Characterizations and Respective Techniques

There are different measurement techniques to study the thin film properties. After the analysis and characterization of those properties, we can explore the physics
of the film mechanisms from the bottom up. Some basic thin film properties include sheet resistance ($R_s$), optical transmittance ($T$), carrier concentration ($n$) and carrier mobility ($\mu$).

### 2.6.1 Sheet Resistance

From Fig. 2.15, a thin conducting film with current passing through surfaces 1 and 2 has a length and a cross sectional area ($A$), consisting of width ($w$) and thickness ($t$). The average resistance can be expressed as,

$$R = \frac{V}{I} = \frac{\rho \text{(length)}}{t \times w} \quad [79],$$

where $\rho$ is the resistivity of the thin film. A useful concept is to visualize the special case of the resistance of one square, i.e. length=$w$, of the thin film. Eqn. (2.28) shows the result of resistance of one square of conducting material, which is also regarded as sheet resistance ($R_s$).

$$R_s = \frac{\rho}{t} \quad (2.28)$$

Fig. 2.15 Diagram of a thin conducting film [79]
$R_s$ of thin films can be found by the use of four-point probe technique. The technique, which is four in line probes of constant spacing contacting the surface of sample material, is one of the oldest technologies available. Electrical current is passed between the two outer probes while an established voltage between the other inner probes is measured as Fig. 2.16 [80]. The obtained values of current and voltage determine $R_s$ of the sample by eqn. (2.29) [81]. The voltage is measured with a pair of probes same as the pair used for current flow in order to eliminate the potential difference between the wires. The contact diameter of the probes must be much smaller than $s$ and the distance from the edge of the probe array to the edge of the film should be much larger than $s$ from Fig. 2.16 [82]. Thus, point contacts are employed in four-point probe technique. There are several correction factors such as geometry should be inputted to get a much accurate and precise value of $R_s$.

$$R_s = \frac{\pi}{\ln 2} \frac{V}{l} = 4.53 \frac{V}{l}$$  \hspace{1cm} (2.29)

Fig. 2.16 Schematic diagram of four-point probe technique [80]
2.6.2 Carrier Concentration and Mobility

Carrier concentration \((n)\) and carrier mobility \((\mu)\) are the transport properties of thin films. They can be measured by Hall Effect technique. When a current carrying thin film sample is placed inside a magnetic field, there will be induced Lorentz force acting on the charge carriers. Carriers are deflected and accumulated at one side of the films according to the direction of Lorentz force. Afterwards, charges inflowing through the thin films experience both induced Lorentz force and repulsive electrostatic force from the accumulated carriers. At the instant when induced Lorentz force balance with the electrostatic force, no further accumulation of carriers occurs. The voltage formed across the thin film is called Hall Voltage. Fig. 2.17 shows the schematic diagram of Hall Effect [9].

![Schematic diagram of Hall Effect technique](image-url)

Fig. 2.17 Schematic diagram of Hall Effect technique [9]
Carrier concentration \((n)\) and mobility \((\mu)\) can be extracted by using eqn. \((2.30)\) and eqn. \((2.31)\) \([9]\), where \(B\) is the magnetic field strength, \(I\) is the current, \(t\) is the thickness of the thin film, \(V_H\) is the Hall Voltage and \(\rho\) is the resistivity of the sample.

\[
n = \frac{-BI}{tV_He} \quad \text{(2.30)}
\]

\[
\mu = \frac{|V_Ht|}{Bl\rho} \quad \text{(2.31)}
\]

### 2.6.3 Optical Transmittance

Transmittance \((T)\) of thin films can be acquired by the use of spectrophotometry technique. A spectrophotometer is employed to measure the amount of light that a sample absorbs. The instrument operates by producing light of any selected wavelength by spectrometer and measuring the intensity of light in the form of number of photons per second reaching a detector called photometer after passing a beam of light through the sample. The photometer delivers a voltage signal to a display \([83]\).

First, the intensity of light \((I_o)\) passing through a blank is measured. Then, the intensity of light \((I)\) passing through the thin film sample is measured. The transmittance \((T)\) is simply the fraction of light in the original beam that passes through the sample and reaches photometer as eqn. \((2.32)\) while absorbance \((A)\) is the remainder of light as eqn. \((2.33)\).

\[
T = \frac{I}{I_o} \quad \text{(2.32)}
\]

\[
A = -\log_{10} T \quad \text{(2.33)}
\]
2.7 Principle of OLED

Organic electroluminescence (EL) was discovered in 1960s [84], which a light emission from non-crystalline organic materials was obtained. Not much attention has been drawn due to the high applied voltage and low luminance at that time. A doubled layer organic light emitting diode (OLED) based on small molecules by thermal vacuum deposition achieving high luminance with low operating voltage was reported in 1987. In 1990, Cambridge first reported polymer light emitting devices base on conjugated polymer [85].

![Basic structure of OLED](image)

Fig. 2.18 Basic structure of OLED [86]

For the basic configuration of OLED [86], there are two electrodes, an anode and a cathode, and a hole injection layer (HIL), an emissive layer (EML) and electron transporting layer (ETL) in between of them. The functions of HTL, ETL and EML
are injection and transportation of holes, injection and transportation of electrons and formation of excitons respectively. Hole blocking layer (HBL) and electron blocking layer (EBL) can be added inside the sandwich for a more complex OLED. They confine the carriers at EML and enhance the efficiency of OLED. The role of TCOs such as ITO and AZO acts as an anode in OLED to inject carriers and transmit light.

Fig. 2.19 Working principle of OLED

Electrons and holes are injected from cathode and anode respectively when a voltage is applied across an OLED, which is depicted as Fig. 2.19. Holes move towards to the EML through HTL at highest occupied molecular orbital (HOMO) while electrons pass through ETL to reach EML at lowest unoccupied molecular orbital (LUMO). Electrons and holes pair up to form excitons at EML and light is given out when there is the radiatively decay of excitons.
2.8 Characterizations of OLED

In this research work, the performances of OLED can be characterized by driving voltage, current efficiency, hole-electron balance, power efficiency and quantum efficiency.

2.8.1 Current Density-Voltage Characteristics

Current density-voltage (J-V) characteristic shows the current per unit area with respect to the relative applied voltage of an OLED. Overall resistance and carrier injection density of the device are shown. Increasing bias voltage injects more carriers to the electrodes. In other words, the slope of J-V curve indicates the efficiency of injection. If the resistance of the electrodes is larger, larger threshold voltage and tardy increase of J-V curve can be observed.

2.8.2 Yield

Yield measures the luminous intensity per ampere of the device in unit of cd/A and the plot of it against current density imply the balance of hole and electron carriers. A horizontal line can be observed from the above relationship when charges are balanced. In general speaking, mobility of most hole materials is faster than that of electron materials by one or two order of magnitude. The imbalance of charge carriers results in shifting of the recombination zone of excitons which affect the luminous intensity and emission peak wavelength due to microcavity.
2.8.3 Quantum Efficiency

Quantum efficiency $\eta(q)$ is defined as the ratio of the number of emitted light quanta per unit time to the number of carriers flowing across unit area per unit time, which is influenced by the factor of formation of excitons, relaxation and extraction from the device [87].

Internal quantum efficiency (IQE) is expressed as eqn. (2.34) where $\gamma$ is the number of excitons formed per unit volume per unit time divided by the carriers flowing across unit area, $\eta_1$ is the luminance efficiency of the excitons and $\eta_2$ is the ratio of radiative transition from singlet excitons. $\gamma$ depends on the minority carriers which limits the amount of excitons formed. There are two kinds of excitons, i.e. singlets and triplets. Singlet exciton is the only one source undergoing radiative relaxation and generating light. $\eta_1$ is the probability of creating one singlet exciton during every electrical excitation which is 25%. $\eta_2$ is the success rate of radiative decay instead of thermal deactivation of excitons.

$$\eta_{int} = \gamma \times \eta_1 \times \eta_2$$

$$\eta_{ext} = \eta_{int} \times \eta_{coupling}$$

External quantum efficiency (EQE), eqn. (2.35), takes all factors of loss in device into account. $\eta_{coupling}$ is the fraction of light emitted at the surface to the light produced in the bulk, which is around 20%, due to the trapping of light. It is determined by the device structure and the refractive indices of the composed layers.
2.9 Optical Coupling of OLED

A large portion of light is trapped inside the device of OLED due to the mismatch of the refractive indices of different layers. Fig. 2.20 demonstrates the reflections and transmissions of light rays inside an OLED [88]. There is only 18.9% of light emerging into air (ray I) while 34.2% and 46.9% of light are trapped inside substrate (ray II) and TCO (ray III) by total internal reflection between substrate/air interface and TCO/substrate interface respectively [89]. The trapped light undergoes edge emission or dissipation. Therefore, an appropriate structure of OLED which matches the optical properties of TCO can maximize the light coupling factor $\eta_{\text{coupling}}$ and enhance the performance of OLED with the use of microcavity effect.

![Fig. 2.20 Reflections and transmissions of light rays inside an OLED](image)

2.9.1 Microcavity Effect

Microcavity has been used as enhancing light out-coupling of OLED and studied by several groups [90-94]. By tuning the cavity resonance to wavelengths near the peak of EL wavelength, the emission of light can be spatially and spectrally redistributed and increase the amount of out-coupling of light from the device [95].
The optical cavity of OLED has two reflectors, i.e. cathode and anode, separated by the organic layers and forms a Fabry-Pèrot resonator as shown in Fig. 2.21.

![Diagram of Fabry-Pèrot resonator](image)

**Fig. 2.21 Diagram of Fabry-Pèrot resonator**

The resonance condition of the system is satisfied when the dimension of the spacer layer is in the order of the wavelength of the emitting dipoles [96]. The resonance condition along the axis of cavity is given by eqn. (2.36) and eqn. (2.37) for ideal reflectors [97] where \( L \) is the cavity length between two reflectors, \( m \) is the cavity mode number, \( \lambda_{res} \) is the resonance wavelength, \( n_i \) is the refractive index, \( d_i \) is the thickness of the \( i \)th layer and \( \theta_{int} \) is the internal angle of observation with respect to the cavity axis while external observation angle can be calculated by Snell’s Law. Eqn. (2.37) becomes eqn. (2.38) when penetration of light into reflectors is taken into consideration in real cases where \( \phi_1 \) and \( \phi_2 \) are the phase shift of two reflectors [97].

\[
2L \cos \theta_{int} = \phi m \lambda_{res} \quad (2.36)
\]
\[
L = \sum_i n_i d_i \quad (2.37)
\]
\[
L = \sum_i n_i d_i + \frac{\lambda_{res}}{4\pi} (\phi_1 + \phi_2) \quad (2.38)
\]
Besides cavity length of the device, another factor having an impact on microcavity effect is the position of emitter. For an ideal cavity, the intensity of emission can be raised by placing the emissive dipoles at antinode of a standing wave in the cavity. On the contrary, emissive dipoles located at nodes of a standing wave minimize the emission intensity. In Fig. 2.22(a), some various modes of cavity standing wave patterns are depicted. Three different situations for the emitting dipoles in an ideal cavity are displayed, left one is the emissive layer is fully extended between the reflectors while middle and right one is located at exactly at antinode and node respectively, with mirror spacing \( d=1 \) in Fig. 2.22(b) [97].

Fig. 2.22 Cavity standing wave patterns for different modes
CHAPTER 3 EXPERIMENTAL DETAILS

This chapter mentioned about the experimental instruments used in this work in detail. First of all, substrates preparation process is presented. After that, thin film deposition system used to obtain the samples is thoroughly described. Setups of experiments and analytical work examining the examples to investigate the thin film performance of AZO will be given. Sputtered AZO thin films are applied to act as a transparent anode in OLED device. Finally, details of OLED fabrication and measurement set-up for OLED devices will be introduced.

3.1 Substrate Preparation

There were two types of substrates used in this work. They were plain glass and Si wafer substrates. These substrates were treated and prepared by some cleaning process in order to remove any adsorption of atmospheric moisture and oil.

3.1.1 Plain Glass Substrate

The plain glass substrate was the same as those used for super-twisted nematic (STN) liquid crystal display (LCD) glass and was produced from Nippon Electric Glass Co., Ltd. It was cut into the size of 25 mm × 25 mm. The glass substrate must be cleaned before it was sputtered to have a surface for good adhesion between the substrate and the sputtered targets. The cleaning procedures were systemically consisting of a sequence of ultrasonic baths by the ultrasonic cleaner, modeled Bransonic® Ultrasonic Cleaner Model, soaked in diluted detergent solution, called TFD4, and de-ionized (DI) water separately. The process was in the order as follows,
i.e. detergent, DI water and, finally, DI water again. Each step lasted for 30 mins. The detergent solution was used to remove grease and dust on the surface. DI water has far fewer minerals than regular tap water and is often used in science labs [98]. It was used to remove residues of contaminants [98]. After these cleaning procedures, substrate was put in an oven, model Binder, Universal drying and heating ovens Model ED23-UL, at 110°C overnight to dry off any water left on the surface and to minimize the adsorption of moisture.

3.1.2 Si Wafer Substrate

The Si (100) wafer was purchased commercially from Wafer World, Inc. of size with diameter of 4 inches. It was p-type with one-side polished. Large piece of Si wafer was cut into small pieces of Si wafer substrates of the size of 15 mm × 15 mm. They were soaked in acetone, ethanol and DI water orderly and had ultrasonic baths. Acetone is a very good solvent that is a very polar substance and dissolve almost all organic compounds [99]. Ethanol has been rendered into denatured alcohol when acetone is added to it [100]. Denatured alcohol can be used as a liquid sander or a stain remover [100]. Therefore, ethanol soaking got rid of grease stains on Si wafer substrates. The role of DI water in Si wafer substrate cleaning is the same as that in plain glass substrate cleaning. After the above cleaning procedures, Si wafer substrates had hydrophobic effect which was the tendency of nonpolar substances to aggregate in aqueous solution and exclude water molecules [101-102]. Finally, they were stored the oven overnight.
3.2 Magnetron Sputter Deposition System

The magnetron sputtering system used in this work was MGS-500, Multi-Gun Sputter System from JunSun Tech. It was used to sputter AZO thin films. The sputtering system equipped with a turbomolecular pump and an oil rotatory mechanical pump had a two-stage pumping system. The chamber pressure could be pumped down to around $10^{-7}$ mbar. It had three separate mass flow controller and channels controlling different sputtering gases entered the chamber under the sputtering process. The choices of sputtering gases feeding the chamber were 1) pure 99.9% argon (Ar), 2) 10% oxygen in argon (10% O$_2$/Ar) and 3) 5% hydrogen in argon (5% H$_2$/Ar). The content of sputtering gases introduced was controlled by a separate mass flow control (MFC) by which MFC 1 controlled the amount of Ar, MFC 2 controlled the amount of (10% O$_2$/Ar) and MFC 3 controlled the amount of (5% H$_2$/Ar). The smallest tunable gas unit by the MFCs was 0.1 Standard Cubic Centimeter per Minute (sccm). Therefore, different composition of sputtering gases inside the chamber could be obtained by controlling the mass flow rates of different sputtering gases.

Inside the vacuum chamber, there is a circular substrate holder connected to a rotational motor and thereby substrates could be rotated under sputter deposition. Above the substrate holder, there was a heater. Substrates could be heated up to 500$^\circ$C during sputtering and whether high temperature sputtering or room temperature sputtering. Below the substrate, there were three independent sputter guns of which each had a shutter to control whether the gun was covered or open and thus the sputter deposition. Different targets could be placed on top of the guns as the
same as Fig. 2.5. The target-to-substrate distance kept constant at 13 cm. Sputter guns were connected to either an external DC or RF power supply. The confocal design of the sputtering system allowed preparation of consecutive thin films of three materials without breaking the vacuum inside the chamber. This could reduce the chance of thin films undergoing oxidation while different types of thin films were deposited and ensure thin films obtained were merely under the factors of sputtering. Fig. 3.1 illustrates the design of a confocal sputtering system [41]. Since there were three independent sputter guns and separately one RF and one DC power supplies, co-sputtering of different target materials could be possibly carried out. Water coolant flew around the sputter guns and also the turbomolecular pump to prevent overheating of turbomolecular pump and targets during sputtering and vacuum pumping.

Fig. 3.1 Confocal sputtering system design [41]

The target used in this work was circular ceramic AZO target purchased from Kintec Company with the dimension of 2 inches diameter × 0.2 inches thick. The
purity of the target was 99.99% and had a composition ratio of 98:2 in ZnO to Al\textsubscript{2}O\textsubscript{3} (98 ZnO: 2 Al\textsubscript{2}O\textsubscript{3}).

The followings were the tunable parameters of this magnetron sputtering system: type and power output of power supplies, substrate temperature, gas composition and thus the working pressure during sputtering, sputtering time and substrate rotational speed.

3.3 Measurements for Characterizations of AZO

To investigate AZO thin films performance and the physics theory underlying the performance, different measurement techniques are used. In this section, software and hardware involved in the measurement setup to characterize AZO thin films are briefly introduced.

3.3.1 Surface Profilometer

The thickness of sputtered thin film was measured by the Veeco Dektak 150 Surface Profilometer. It determined film thickness by measuring the step heights of the film edges relative to the substrate. The film edges were made by covering a small region of the substrate with a piece of vacuum tape. An average of several measurements was taken in order to obtain a more objective result. There was an error about ±2 nm, which was a very small, in the result due to the shadow effect made by the thickness of vacuum tape. Therefore, the result was reliable. It was further used to calculate the sputter yield under a specific condition by dividing the result by sputtering time.
3.3.2 Four-Point Probe

The sheet resistance of sputtered AZO thin films was measured by four-point probe system which is from KeithLink Technology Co. Ltd. Then, the measured values of sheet resistance together with the values of thickness of AZO thin films obtained in section 3.3.1 were used to calculate the resistivity.

3.3.3 Spectrophotometer

The optical transmittance of sputtered thin film was measured by the HP UV-VIS Spectrophotometer Model 8453. The measurement wavelength ranged from 190 nm to 1200 nm and the measurement unit was down to the scale of nm. Plain glass substrate was measured as a background spectrum. Results acquired by thin film samples had to subtract this background spectrum to obtain the exact transmission spectrum regarding to the thin films themselves.

3.3.4 X-Ray Diffraction

Crystalline structure of thin film was examined by Bruker AXS D8 Advance XRD. The X-ray source used in this measurement was non-monochromated CuKα where the wavelength was 0.15406 nm. The measurement scanning range was carried out from 20° to 80° with each step-up division of 0.02° taking place every 0.2 seconds. Results obtained could be compared with the stored database as a reference.
3.3.5 Hall Effect

Carrier concentration and mobility of AZO thin films were measured by Hall Effect measurement which carried out at HKUST. Samples were fabricated to a hall bar pattern by employing a shadow mask. In Fig. 3.2, picture on the left showed the dimensions of the pattern of deposited AZO thin film for Hall measurement while there was the shadow mask on the right. It was a symmetric six-contact Hall bar geometry with contacts located to the end of AZO. Contact pairs were placed symmetrically about the midpoint of the samples long axis. This allowed two equivalent measurement sets to check for sample homogeneity in Hall coefficient. The vertical ends were lengthened to avoid the shorting out of Hall voltage at the end contacts.

Fig. 3.2 Patterned AZO for Hall Effect measurement
The setup of Hall measurement was illustrated as Fig. 3.3. Electric wires were connected to patterned AZO films with the use of silver paint and copper tape at contact points. An electromagnet was placed to provide a magnetic field to the films, whose strength was managed by a power supply. A current reversal switch was used to control the direction of the magnetic field. The magnetic field was calibrated by a Teslameter. Source Measure Unit (SMU) (Agilent B2900A) was used to give a constant current source and measure the Hall Voltage.
3.3.6 X-ray Photoelectron Spectroscopy

XPS measurements were performed using a VG Multilab ESCA 2000 system with a monochromatic Al Kα X-ray source with energy about 200-2000 eV. C 1s line of adventitious hydrocarbon on the specimen surface which had a binding energy of 284.8 eV was used as charge reference for calibrating AZO samples.

3.4 OLED Fabrication

OLED devices were fabricated as an application of AZO, which played the role of a transparent electrode. In this section, the details of OLED fabrication procedure will be described.
3.4.1 Preparation of OLED Substrate

OLED devices were fabricated using commercial ITO and in-house AZO. They were patterned as the left side of Fig. 3.4 while the relative shadow mask used was on the right. Already-patterned commercial ITO glasses of dimension 45 mm x 45 mm from Tinwell Technology Ltd. underwent the cleaning procedures mentioned in section 3.1.1. For in-house AZO, shadow mask was placed on top of the cleaned plain glass substrate to prepare AZO thin films with pattern. No cleaning were done to as-deposited in-house AZO after sputtering due to the possibility in changes of AZO properties during the process. They were stored in vacuum chamber or glove box filled with nitrogen before further fabrication to minimize the potential of contamination.

![Patterned AZO for OLED fabrication](image)

Fig. 3.4 Patterned AZO for OLED fabrication

3.4.2 Materials Used in OLED Device

The materials used in OLED in this work and their chemical structures are listed in Table 3.1.
### Table 3.1 Materials used in OLED

<table>
<thead>
<tr>
<th>Material Abbreviation</th>
<th>IUPAC Name</th>
<th>Chemical Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>NPB</td>
<td>N,N'-Di(naphthalene-1-yl)-N,N'-diphenylbenzidine</td>
<td><img src="image" alt="Chemical Structure" /></td>
</tr>
<tr>
<td>Alq&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Tris(8-hydroxyquinoline) aluminumIII</td>
<td><img src="image" alt="Chemical Structure" /></td>
</tr>
<tr>
<td>LiF</td>
<td>Lithium Fluoride</td>
<td></td>
</tr>
</tbody>
</table>

3.4.3 Device Structures of OLED

Structures of OLED devices adopted in this work were the basic one and summarized in Table 3.2 with the thickness of each layer given in the brackets. In experiment, the total thickness of device would be varied to tune the microcavity effect. The details of thickness of OLED structure would be discussed in chapter five.
### Table 3.2 Device structures of OLED

<table>
<thead>
<tr>
<th>OLED</th>
<th>Device Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Green OLED</td>
<td>Anode/NPB(70)/Alq₃(60)/LiF(1)/Al(80)</td>
</tr>
</tbody>
</table>

#### 3.4.4 Pre-treatment on OLED Substrates

As an application of AZO to act as an anode in OLED, the work function of AZO, which is around 4.4 eV, had to be considered. The highest occupied molecular orbital (HOMO) of most hole transport materials have a value higher than 5 eV below vacuum. For matching with the HIL, the work function of AZO needed to be raised in order to achieve a more efficient hole injection into the HOMO of hole transport materials. There is a energy barrier for hole injection causing an increase in driving voltage of the device. Surface treatments were done to in-house AZO films and commercial ITO glass to improve hole injection. They were exposed to oxygen plasma for 25 seconds at 100W RF to remove hydrocarbon contaminants and enhance their work functions due to a change in ratio of surface elements [103] after the preparation work described in section 3.4.1. Then, they were subjected to CFₓ plasma for 7 seconds at 100W RF power to form an ultrathin plasma polymerized fluorocarbon film which improves hole injection and durability against atmospheric moisture [104].

#### 3.4.5 Fabrication of OLED by Thermal Evaporation

All the organic materials and metal of OLED in this research were evaporated by a ten-source evaporation system (JunSun Tech., Model OM-2000R). Each
evaporation source had an individual shutter and was isolated by partitions to control the coating thickness of each layer and prevent cross contamination respectively. Every source was composed of a pair of electrodes and a resistive metal basket made of tungsten or a crucible and separate power supply so that each one could be independently operated.

Above the evaporation sources, substrate mount and mask holder were used to place up to ten pieces of OLED substrates and shadow masks of desirable patterns respectively. Each mask had an individual shutter to control the material depositing on the substrate with desirable patterns. The pattern of organic mask and metal mask were depicted as Fig. 3.5 on the left and right respectively. To fabricate the OLED devices without breaking vacuum, five pairs of organic and metal masks were used.

Fig. 3.5 Shadow masks for OLED fabrication

Fig. 3.6 was the schematic diagram of the patterned AZO substrate with organic films and metal cathode. Each OLED device contains four active areas of 0.1 cm³ for this pattern configuration. Fabrication started when the pressure of the chamber was below 5 x 10⁻⁶ Torr to minimize the contamination and reaction between evaporation
materials and residual gas such as moisture and oxygen because most of the organic materials were sensitive to moisture. The deposition rate was monitored in real time by quartz crystal microbalance during fabrication. The coating rates for organic materials and metals were 1 Ås\(^{-1}\) and 8 Ås\(^{-1}\) respectively.

![Fig. 3.6 Schematic diagram of OLED device (Red square: active area)
(Blue: AZO anode; Yellow: organic layers; Gray: Metal cathode)](image)

**3.4.6 Encapsulation of OLED Device**

Performance of OLED device degraded quickly once exposing to air because organic materials and metal cathode were sensitive to oxygen and moisture. Therefore, encapsulation was necessary to slow down the rate of degradation and extend the life time of the device. All the devices in this research were encapsulated in a dry nitrogen-filled glove box which was interconnected to the thermal evaporator. UV curing epoxy (ThreeBond Co., LTd. UV Curing Resin 3055B) was applied to the edges of a square cover glass (22 cm x 22 cm) with a piece of desiccant for absorbing the moisture. Using the cover glass covered up the area which was deposited organic
films and metal electrode. Devices were encapsulated by exposing the epoxy to UV lamp for four minutes.

3.4.7 Characterizations of OLED Device

The performance of OLED device was characterized by the measurement set-up in Fig. 3.7. The OLED device was driven by the source measure unit (SMU) (Keithley, Model 236) and programmable spectra colorimeter (Spectra scan, Model PR650) captured the light emitted by the device. Voltage-current-luminance (V-I-L) characteristics, electroluminescence (EL) spectrum, commission International de l’Eclairage (CIE) coordinates, power efficiency and current yield could be measured.

Fig. 3.7 Measurement set-up for OLED device
CHAPTER 4 CHARACTERIZATIONS OF AZO THIN FILMS WITH RF SPUTTERING

In this chapter, various in-house AZO thin films were sputtered under many different sputtering conditions. They were tested and characterized according to different tunable sputtering parameters such as gas composition and sputtering working pressure. Their electrical and optical properties were measured in order to have a thorough understanding of the physics of conduction mechanism and optical performance of AZO films. The impacts of sputtering parameter on the behavior of AZO were studied. In addition, a comparison of sensitivity of deposition of AZO and ZnO to sputter environment had been made to study their distinction. Finally, degradation of AZO thin films was examined.

4.1 Influences of Oxygen Content on AZO Thin Films

In this section, the factor of oxygen content in sputtering environment for AZO thin films would be discussed. It was done by tuning the MFC to vary the amount of oxygen feeding into the vacuum chamber of the magnetron sputter deposition system. Details of the sputtering conditions would be given in section 4.1.2. AZO thin films were measured in electrical and optical properties to understand the mechanism of AZO films sputtered under different oxygen content. The composition inside AZO films was also studied.
4.1.1 Review and Motivation

From section 2.2, the conduction mechanism in AZO thin films was theoretically mentioned. Eqn. (2.3), eqn. (2.4) and eqn. (2.7) gave the formulas contributing the carrier concentration of AZO thin films in section 2.2.1 while eqn. (2.9) considering the carrier mobility of AZO thin films dominated by different scatterings, i.e. ionized impurity scattering, neutral impurity scattering, grain boundary scattering, intragrain cluster scattering and lattice vibration scattering, was discussed in details in section 2.2.2.

\[
O_o^x \rightarrow \frac{1}{2}O_2(g) + V_o + 2e^- \quad (2.3)
\]

\[
Al_2O_3 \rightarrow 2O_o + 2Al_{Zn}^+ + \frac{1}{2}O_2(g) + 2e^- \quad (2.4)
\]

\[
2Al_{Zn}^+ + 2O_o + \frac{1}{2}O_2(g) + 2e^- \rightarrow Al_2O_3 \quad (2.7)
\]

\[
\frac{1}{\mu} = \frac{1}{\mu_i} + \frac{1}{\mu_n} + \frac{1}{\mu_g} + \frac{1}{\mu_c} + \frac{1}{\mu_l} \quad (2.9)
\]

From above equations, each oxygen vacancy gives out two free electrons and two free electrons are given out during the removal of oxygen interstitials of Al$_2$O$_3$ dopant. Thus, film effective carrier mobility is also affected. Therefore, oxygen content inside the environment of vacuum chamber during sputter deposition plays an important role to the mechanisms of AZO thin films and critically affects the properties of films. From section 2.3, plasma wavelength of thin films is expressed by eqn. (2.25). From section 2.4.2, crystalline grain size is given by eqn. (2.26),
\[ D = \frac{0.9\lambda}{\beta \cos \theta}, \]  From section 2.6.1, resistivity of thin film equals to sheet resistance multiplies film thickness given by eqn. (2.28).

### 4.1.2 Sputtering Conditions

To explore the effects on AZO thin films to oxygen environment inside vacuum chamber, the flow rate of gas (10% O\textsubscript{2}/Ar) feeding into the chamber was tuned by MFC 2 of the sputter system while other sputtering parameters, such as the base Ar gas flow from MFC 1, type and power value of power supply, substrate temperature, sputtering time, base pressure and substrate rotational speed, were kept constant. Table 4.1 shows the fixed values of the specific sputtering parameters in the experiment sets. Table 4.2 and Table 4.3 show the different flow rate of (10% O\textsubscript{2}/Ar) in the experiment set 1 and set 2 respectively.

<table>
<thead>
<tr>
<th>Fixed Sputtering Parameters</th>
<th>Parameter Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base Ar Gas Flow</td>
<td>50 sccm</td>
</tr>
<tr>
<td>Power Supply</td>
<td>RF 80W</td>
</tr>
<tr>
<td>Substrate Temperature</td>
<td>room temperature</td>
</tr>
<tr>
<td>Sputtering Time</td>
<td>20 minutes</td>
</tr>
<tr>
<td>Substrate Rotational Speed</td>
<td>10 revolutions/minute</td>
</tr>
<tr>
<td>Base Pressure</td>
<td>(&lt; 3.0 \times 10^{-6} ) ) mbar</td>
</tr>
<tr>
<td>Working Pressure</td>
<td>(6.0-6.1 \times 10^{-4} ) mbar</td>
</tr>
</tbody>
</table>

Table 4.1 Fixed sputtering parameters in examining the effect of oxygen content
4.1.3 Mechanism of AZO Films

Table 4.4 and Table 4.5 below show the physical properties, i.e. thickness, and electrical properties such as sheet resistance and resistivity of AZO samples from set 1 and set 2 respectively.

In set 1, the flow rate of (10% O₂/Ar) was increased from 0 sccm to 4 sccm with every 0.5 sccm as an interval. Sheet resistance of AZO samples increased significantly while thickness had gradual decline under the increase in flow rate. Meanwhile, resistivity was raised dramatically with that increment. In set 2, the flow rate of (10% O₂/Ar) was increased every 0.5 sccm from 0 sccm to 1.5 sccm while of (5% H₂/Ar) was increased every 1 sccm from 1 sccm to 3 sccm. The properties of AZO samples showed similar change in thickness, sheet resistance and resistivity as set 1.
<table>
<thead>
<tr>
<th>Flow Rate of (10% O₂/Ar) in sccm</th>
<th>Sheet Resistance (Ω/sq.)</th>
<th>Thickness (nm)</th>
<th>Resistivity (mΩ·cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4982</td>
<td>73</td>
<td>36.37</td>
</tr>
<tr>
<td>0.5</td>
<td>6588</td>
<td>70</td>
<td>46.11</td>
</tr>
<tr>
<td>1</td>
<td>9969</td>
<td>68</td>
<td>67.79</td>
</tr>
<tr>
<td>1.5</td>
<td>21098</td>
<td>65</td>
<td>137.14</td>
</tr>
<tr>
<td>2</td>
<td>35727</td>
<td>64</td>
<td>228.65</td>
</tr>
<tr>
<td>2.5</td>
<td>52526</td>
<td>61</td>
<td>320.41</td>
</tr>
<tr>
<td>3</td>
<td>69627</td>
<td>63</td>
<td>432.56</td>
</tr>
<tr>
<td>3.5</td>
<td>85202</td>
<td>64</td>
<td>545.29</td>
</tr>
<tr>
<td>4</td>
<td>1099711</td>
<td>60</td>
<td>658.27</td>
</tr>
</tbody>
</table>

Table 4.4 Resistivity of AZO samples in examining the effect of oxygen content set 1

<table>
<thead>
<tr>
<th>Gas Flow Rate in sccm</th>
<th>Sheet Resistance (Ω/sq.)</th>
<th>Thickness (nm)</th>
<th>Resistivity (mΩ·cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10% O₂/Ar: 0 5% H₂/Ar: 0</td>
<td>4982</td>
<td>73</td>
<td>36.37</td>
</tr>
<tr>
<td>10% O₂/Ar: 0.5 5% H₂/Ar: 1</td>
<td>5826</td>
<td>68</td>
<td>39.62</td>
</tr>
<tr>
<td>10% O₂/Ar: 1 5% H₂/Ar: 2</td>
<td>7297</td>
<td>64</td>
<td>43.78</td>
</tr>
<tr>
<td>10% O₂/Ar: 1.5 5% H₂/Ar: 3</td>
<td>8497</td>
<td>60</td>
<td>50.98</td>
</tr>
</tbody>
</table>

Table 4.5 Resistivity of AZO samples in examining the effect of oxygen content set 2
Fig. 4.1 Resistivity against oxygen flow rate under the effect of oxygen set 1

Fig. 4.2 Resistivity against oxygen flow rate under the effect of oxygen set 2
Fig. 4.1 depicts the change of resistivity of the samples with the increase in oxygen flow in set 1 while Fig. 4.2 shows the resistivity change with the increase in both oxygen and hydrogen flow in set 2. From the two figures, resistivity of AZO samples increased with the increase in oxygen content and the change formed an exponential shape. The resistivity of the AZO film deposited in only an Ar gas atmosphere (oxygen flow ratio = 0%) was about $3.6 \times 10^{-2} \ \Omega \cdot \text{cm}$, but the resistivity of the AZO film deposited at 4 sccm flow rate of (10% O$_2$/Ar) was $6.6 \times 10^1 \ \Omega \cdot \text{cm}$ in set 1 while that deposited at 1.5 sccm flow rate of (10% O$_2$/Ar) and 3 sccm flow rate of (5% H$_2$/Ar) was $5.1 \times 10^{-2} \ \Omega \cdot \text{cm}$ in set 2.

Oxygen is regarded as oxidizing gas having high oxidation effect while hydrogen is regarded as reducing gas with a low oxidation number. They were introduced during sputtering to tune the electrical properties of thin films. As the analysis for the results, AZO thin film was non-stoichiometric oxide that had crystallographic point defects such as interstitial atoms and vacancies during deposition process. Oxygen vacancy is one of the sources contributing carriers in AZO thin film. From set 1, when oxygen content in the AZO film was increased, the vacancy concentration decreased. From set 2, the oxidation effect of oxygen gas outran the reduction effect of hydrogen gas even they were of the same gas flow ratio and this led to a gradual decrease in number of oxygen vacancies in AZO film.

Fig. 4.3 gives the transmittance of AZO samples deposited under different sputtering ambient oxygen flow rate. The samples were sputtered under 0, 1 and 2 sccm of (10% O$_2$/Ar) from set 1, 0.5 sccm of (10% O$_2$/Ar) + 1 sccm of (5% H$_2$/Ar) and 1 sccm of (10% O$_2$/Ar) + 2 sccm of (5% H$_2$/Ar) from set 2.
The optical transmittance spectra showed wavelength range of 200 to 1100 nm of AZO thin films at different oxygen flow ratio. Sharp fundamental absorption edges
were observed in all the spectra at around 300 nm. No significant shifts were found in the spectra. These films had high transmittance of above 80% in visible light range and high absorption in UV regions. Meanwhile, they all depicted high transmittance in the near-infrared regions. There was a relationship observed from Fig. 4.3 that the transmittance of samples slightly increased with the increasing amount of oxygen flow ratio fed into the sputtering ambient. The average transmittance of the samples increased from about 81% to 83%. AZO sample sputtered under 2 sccm of (10% $\text{O}_2$/Ar) showed the highest transmittance in visible region while that under 0 sccm of (10% $\text{O}_2$/Ar) was the lowest one. With more oxygen flow ratio existed in the vacuum chamber, it diffused into the samples and filled up the holes. The number of oxygen vacancies reduced. Therefore, scattering of light was less likely to occur contributing a higher transmittance. Moreover, the optical properties of AZO thin films, again, proved the oxidation effect of oxygen gas dominated the reduction effect of hydrogen gas even when the flow ratio of oxygen and hydrogen was balanced because higher transmittance was found for a higher flow rate of gas.

The crystal structures of AZO samples, sputtered under 0, 1, 2 and 3 sccm of (10% $\text{O}_2$/Ar), chosen from set 1 were investigated by XRD with CuKα radiation source ($\lambda = 0.15406$ nm). It examined the influence of oxygen on crystal growth of AZO thin films. This particular XRD profiles were displayed as Fig. 4.4. For all the selected samples, only one peak corresponding to the (002) plane appeared and no other diffraction pattern was observed. It suggested that these films were of a high c-axis preferential orientation. The AZO films were crystalline and proved of a single-phase hexagonal wurtzite structure.
Fig. 4.4 XRD patterns for AZO films deposited with various oxygen flow rates

The diffraction peaks of the AZO samples located at the 2θ dominant peak from 34.38° to 34.32° from the growing condition from 0 to 3 sccm (10% O2/Ar) flow rate, which were close to that of the standard ZnO crystal. The little peak shift implied that the crystal c-axis of the films were prolonged. This effect was due to oxygen atoms situated in Zn-O bond center causing the lattice constant of films increase. On the other hand, as the oxygen flow ratio was increased, the peak intensity had a mild increase and the peak became sharper moderately. Table 4.6 gives the detailed information on peak intensity, FWHM of XRD (002) peak and grain size of all the AZO samples. The grain size was calculated by Scherrer equation from eqn. (2.26). Fig. 4.5 graphically shows the FWHM and grain size of respective AZO films deposited under different oxygen flow ratios.
<table>
<thead>
<tr>
<th>Flow Rate of (10% O₂/Ar) in sccm</th>
<th>Peak Intensity</th>
<th>FWHM (degree)</th>
<th>Grain Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2123</td>
<td>0.56</td>
<td>14.8</td>
</tr>
<tr>
<td>1</td>
<td>2314</td>
<td>0.52</td>
<td>16</td>
</tr>
<tr>
<td>2</td>
<td>2441</td>
<td>0.46</td>
<td>18.1</td>
</tr>
<tr>
<td>3</td>
<td>2505</td>
<td>0.44</td>
<td>18.9</td>
</tr>
</tbody>
</table>

Table 4.6 Grain size, peak intensity and FWHM of XRD (002) peak for AZO films deposited with various oxygen flow rates

Fig. 4.5 FWHM of XRD (002) peaks and the grain sizes for AZO films deposited with various oxygen flow rates
According to eqn. (2.26), grain size is inversely proportional to FWHM. As oxygen flow ratio was increased, FWHM of XRD (002) peak decreased while grain size of the AZO samples grew larger. FWHM decreased from 0.56° to 0.44° and grain size increased from about 15 to 19 nm when flow rate of (10% O₂/Ar) increased from 0 to 3 sccm. The crystallinity of the films improved. Therefore, oxygen gas could be regarded as a resource for crystallization of AZO thin films during sputter deposition.

Surface and atomic composition analysis by XPS was performed to find the elements in the AZO thin films under different oxygen ratio feeding. Fig. 4.6 shows the XPS spectra of the AZO samples grown at 0 and 2 sccm (10% O₂/Ar) flow rates. Peaks were depicted at binding energies of 1021.9 eV, 530.9 eV, 73.8 eV and 284.8 eV from Zn 2p, O 1s, Al 2p and C 1s respectively in the wide scan XPS spectra. Other peaks might come from other elements in air, like hydrogen and nitrogen, from the duration before achieving ultra high vacuum in the equipment and in the chamber during sputtering, like argon. They were out of interest in the investigation and could be neglected since the processing time for the samples was the same.

The position of the Al 2p peak at 73.8 eV was smaller than that at 74.4 eV corresponding to the Al 2p peak in the Al₂O₃. Al atoms were incorporated into the ZnO lattice as the difference in binding energy was due to the energy transfer between the matrix ions and the dopants.
Fig. 4.6 XPS wide scan spectra for AZO sputtered at various oxygen flow rates

Fig. 4.7 Intensity spectra with baseline correction against binding energy for AZO sputtered at various oxygen flow rates
The XPS wide scan spectra for intensity against binding energy with baseline correction of AZO samples obtained under 0 and 2 sccm of (10% O$_2$/Ar) flow rates is shown as Fig. 4.7. The intensity levels of Zn 2p and O 1s of sample sputtered under 2 sccm (10% O$_2$/Ar) flow rate were higher than that under 0 sccm flow rate while the situations did not appear in C 1s and Al 2p. Table 4.7 analyzes the elemental compositions percentage on the surfaces of the samples. A phenomenon could be observed that the compositions of Zn 2p and O 1s rose up, by a percentage of 1.5% and 1.7% respectively from 0 to 2 sccm flow rate of (10% O$_2$/Ar), when there was an increase in sputtering oxygen flow ratios. The O 1s peak was directly related to O$^{2-}$ ions in the oxygen-deficient region of the ZnO$_{1-x}$ matrix and also in the oxygen of the hexagonal wurtzite structure. The increase in the amount of O 1s implied a decrease in the number of oxygen vacancies in the AZO films. Meanwhile, there was a decrease in elemental composition of Al 2p revealing a drop in the incorporation of Al atoms into ZnO lattice when the oxygen flow ratio increased. The amount of C 1s had negligible change under the increase of oxygen flow ratio.

<table>
<thead>
<tr>
<th>Flow Rate of (10% O$_2$/Ar) in sccm</th>
<th>Elemental Percentage</th>
<th>in %</th>
<th>Zn 2p</th>
<th>O 1s</th>
<th>C 1s</th>
<th>Al 2p</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td></td>
<td></td>
<td>70.6</td>
<td>10.4</td>
<td>5.5</td>
<td>13.5</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
<td>72.1</td>
<td>12.1</td>
<td>5.1</td>
<td>10.7</td>
</tr>
</tbody>
</table>

Table 4.7 Elemental compositions on the surfaces of AZO samples sputtered at various oxygen flow rates
Fig. 4.8 XPS narrow scan spectra for Zn 2p peaks for AZO samples sputtered at various oxygen flow rates.

Fig. 4.8 depicts the XPS narrow scan spectra for Zn 2p peaks for AZO films deposited at 0 and 2 sccm flow rate of (10% O₂/Ar). For AZO sputtered at 0 sccm flow rate of (10% O₂/Ar), two peaks were found, i.e. Zn 2p₃/2 = 1021.9 eV and Zn 2p₁/₂ = 1044.9 eV. Peaks of 2p₃/2 and 2p₁/₂ were located at 1023.1 eV and 1046.3 eV respectively for the one sputtered at 2 sccm flow rate of (10% O₂/Ar). The spin-orbit splitting energies of both AZO samples, in which of 23 eV and 23.2 eV respectively at 0 and 2 sccm flow rate of (10% O₂/Ar), for the Zn 2p were in reasonable agreement with that reported in the literature [105]. Obvious peak shifts towards higher binding energy could be seen when oxygen flow ratios increased indicating Zn existed in a more oxidized state.
4.1.4 Summary

In this experiment, AZO thin films were deposited at different oxygen flow rates. When oxygen flow ratio was increased, electrical properties of AZO thin film became poorer in the way that its resistivity raised dramatically and, meanwhile, optical performance was slightly improved. AZO thin films were crystallized without additional oxygen flow, but their crystallinity had a direct proportional relation with oxygen flow ratios. XPS spectra evidently proved the reduction of oxygen vacancies and the oxidation state of Zn when there was an increase in oxygen flow ratio.

For the conduction mechanism of AZO samples, the number of carriers given out during the removal of oxygen interstitials of Al$_2$O$_3$ dopant as shown in eqn. (2.4) did not have significant change when there was an increase in oxygen feeding during sputter deposition because samples were sputtered from the same ceramic AZO target which the purity and composition of the target remained the same. However, the number of carriers contributed by oxygen vacancies as shown in eqn. (2.3) was drastically suppressed as the oxygen flow ratio was increased. The situation of Al$_2$O$_3$ deposition when the Al ions concentration was over the limit of solubility shown in eqn. (2.7) was not likely to differ with the increment of oxygen flow ratio.

Effective carrier mobility expressed as eqn. (2.9) involved mobilities due to ionized impurity scattering, neutral impurity scattering, grain boundary scattering, intragrain cluster scattering and lattice vibration scattering. For neutral impurity scattering, the amount of neutral impurity scattering centers was much less than that of the ionized impurity and, thus, it could be negligible. Clusters were unlikely to form with the introduction of oxygen flow since the sputter yield and surface
nucleation of film deposition did not varied much. Mobility due to intragrain cluster scattering could be negligible. The lattice vibration scattering was dominant in the high temperature range. Its contribution could be negligible at room temperature. When oxygen flow ratio was increased during sputtering, the amount of ionized impurity fell and led to a rise in mobility due to ionized impurity scattering. Grain size of the films enlarged and contributed an expansion in mobility due to grain boundary scattering. Therefore, effective carrier mobility was increased.

The influence of oxygen on optical properties of AZO films was the slight enhancement of average transmittance. Higher plasma wavelength was a result of the decline in number of carrier concentration in films. Therefore, when electromagnetic wave propagated into the films, more visible light was transmitted through them.

4.2 Influences of Sputtering Working Pressure on AZO Thin Films

In this section, the factor of working pressure in sputtering environment for AZO thin films would be discussed. It was done by tuning the MFC to vary the amount of pure argon feeding into the vacuum chamber of the magnetron sputter deposition system. Details of the sputtering conditions would be given in section 4.2.1. AZO thin films were measured in electrical and optical properties to understand the mechanism of AZO films sputtered under these changes.
4.2.1 Sputtering Conditions

To explore the effects on AZO thin films to working pressure inside vacuum chamber during sputtering, the flow rate of pure 99.9% argon gas (Ar) feeding into the chamber was tuned by MFC 1 of the sputter system while other sputtering parameters, such as type and magnitude of power supply, substrate temperature, sputtering time, base pressure and substrate rotational speed, were kept constant. Table 4.8 shows the fixed values of the specific sputtering parameters in the experiment set. Table 4.9 shows the different flow rate of Ar and the respective working pressure.

<table>
<thead>
<tr>
<th>Fixed Sputtering Parameters</th>
<th>Parameter Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power Supply</td>
<td>RF 80W</td>
</tr>
<tr>
<td>Substrate Temperature</td>
<td>room temperature</td>
</tr>
<tr>
<td>Sputtering Time</td>
<td>20 minutes</td>
</tr>
<tr>
<td>Substrate Rotational Speed</td>
<td>10 revolutions/minute</td>
</tr>
<tr>
<td>Base Pressure</td>
<td>&lt; 3.0 × 10⁻⁶ mbar</td>
</tr>
</tbody>
</table>

Table 4.8 Fixed sputtering parameters in examining the effect of working pressure

<table>
<thead>
<tr>
<th>Varied Sputtering Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar Flow Rate (sccm)</td>
</tr>
<tr>
<td>50</td>
</tr>
<tr>
<td>30</td>
</tr>
<tr>
<td>20</td>
</tr>
<tr>
<td>15</td>
</tr>
<tr>
<td>Working Pressure (10⁻³ mbar)</td>
</tr>
<tr>
<td>6</td>
</tr>
<tr>
<td>3.6</td>
</tr>
<tr>
<td>2.6</td>
</tr>
<tr>
<td>2.1</td>
</tr>
</tbody>
</table>

Table 4.9 Argon flow rate and respective working pressure in examining the effect of sputtering working pressure
4.2.2 Mechanism of AZO Films

Table 4.10 below shows AZO samples deposited at different Ar flow rates, its respective working pressure, thickness and sputter yield. AZO samples were sputtered at Ar flow rates of 50, 30, 20 and 15 sccm and the working pressures were 6x10^{-3}, 3.6x10^{-3}, 2.6x10^{-3} and 2.1x10^{-3} mbar respectively. The higher the Ar flow rate, the higher was the working pressure. Thickness and sputter yield were inversely proportional to the flow rate of Ar and working pressure. Therefore, the lower the sputtering working pressure, the higher were the thickness of film and sputter yield.

<table>
<thead>
<tr>
<th>Flow Rate of Ar in sccm</th>
<th>Working Pressure (10^{-3} mbar)</th>
<th>Thickness (nm)</th>
<th>Sputter Yield (nm/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>6</td>
<td>73</td>
<td>3.7</td>
</tr>
<tr>
<td>30</td>
<td>3.6</td>
<td>88</td>
<td>4.4</td>
</tr>
<tr>
<td>20</td>
<td>2.6</td>
<td>92</td>
<td>4.6</td>
</tr>
<tr>
<td>15</td>
<td>2.1</td>
<td>97</td>
<td>4.9</td>
</tr>
</tbody>
</table>

Table 4.10 Sputter yield of AZO samples in examining the effect of sputtering working pressure
Table 4.11 below shows the physical properties, electrical properties and the respective working pressure of AZO samples deposited at different Ar flow rates. Sheet resistance of the samples fell to a minimum when sputtering working pressure decreased. Then, it rose back with further decrease in working pressure. This phenomenon also occurred in film resistivity which took thickness into account as a parameter.

<table>
<thead>
<tr>
<th>Flow Rate of Ar in sccm</th>
<th>Working Pressure $(10^{-3}$ mbar)</th>
<th>Sheet Resistance $(\Omega$/sq.$)$</th>
<th>Thickness (nm)</th>
<th>Resistivity $(\text{m}\Omega\cdot\text{cm})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>6</td>
<td>4982</td>
<td>73</td>
<td>36.37</td>
</tr>
<tr>
<td>30</td>
<td>3.6</td>
<td>2337</td>
<td>88</td>
<td>20.57</td>
</tr>
<tr>
<td>20</td>
<td>2.6</td>
<td>1380</td>
<td>92</td>
<td>12.7</td>
</tr>
<tr>
<td>15</td>
<td>2.1</td>
<td>1665</td>
<td>97</td>
<td>16.15</td>
</tr>
</tbody>
</table>

Table 4.11 Resistivity of AZO samples in examining the effect of sputtering working pressure
Fig. 4.9 Sputter yield of samples sputtered at different working pressure

Fig. 4.9 shows the sputter yield of samples deposited at different working pressure. The sputter yield had a decreasing trend as the working pressure rose. It could achieve up to 6 nm/min at 0.5 x 10\(^{-3}\) mbar and declined at higher sputtering working pressure. When the flow rate of Ar was increased, more Ar gas atoms were introduced into the vacuum chamber and led to a rise in sputtering working pressure. The deposited AZO materials underwent more collisions between Ar atoms inside the chamber in their path from the target to the substrate during sputtering. As a result, sputter yield was slow down for longer travelling time due to higher frequency of collisions at higher working pressure.
Resistivity of AZO samples sputtered at different Ar flow rate and thus different working pressure were demonstrated in Fig. 4.10. A general phenomenon was observed that resistivity decreased with a drop in working pressure during sputtering. However, it declined to a minimum to about 12 mΩ·cm when the working pressure was around 2.6 x10^{-3} mbar. Then, it rose up and deteriorated with further reduction in working pressure. Taking all in all, the trend of resistivity against sputtering working pressure formed a parabolic shape with a minimum point. The above results could be understood by the microscopic view of film deposition of sputtering.
Surface diffusion occurs after the weakly adsorbed state known as physical adsorption, whereas a deposited molecule experiences an attraction due to interaction with the surface molecules of substrate upon arriving within a few atomic distances and is trapped due to momentum dissipation into substrate surface during this interaction [81]. It is one of the most important determinations of film structures because it allows the adsorption species to find each other, find the most active sites, or find epitaxial sites for further nucleation in deposition. During the process of surface diffusion, it takes time to implement before carrying out nucleation. When the sputtering working pressure was high, sputter yield was slow down as explained in Fig. 4.9. The low sputter yield lengthened the time to execute surface diffusion of deposited AZO materials and gave time to traces of oxygen content inside the vacuum chamber to fill up the vacancies in film deposition. Thus, resistivity of AZO samples was deteriorated due to fewer oxygen vacancies. Therefore, the lower the working pressure, there more oxygen vacancies and lower resistivity of AZO samples respectively.

When the working pressure was below a saturation point, i.e. 2.6 x 10^{-3} mbar in this experiment, resistivity established an inversely proportional relation with the working pressure. At low working pressure, sputter yield was fast due to fewer collisions between deposited molecules and inflow gas atoms. The energetic deposited AZO materials might destroy the molecules preference in surface diffusion and affect the nucleation of film deposition due to the bombardment when arriving to the substrate. As a result, beyond a saturation point, the lower the working pressure, the higher was the resistivity of the AZO samples.
Fig. 4.11 Transmittance of AZO samples with different working pressure

Working Pressure:
- $T_1 = 6 \times 10^{-3}$ mbar
- $T_2 = 3.6 \times 10^{-3}$ mbar
- $T_3 = 2.6 \times 10^{-3}$ mbar
- $T_4 = 2.1 \times 10^{-3}$ mbar

Transmittance (%)

Wavelength (nm)

visible light range    UV region    NIR region

$T_1: 74.7\%$

$T_3: 85.6\%$

$T_3: 79.3\%$

$T_1: 82.3\%$
Fig. 4.11 is the optical transmittance spectra from 200 nm to 1100 nm wavelength of AZO samples deposited at different sputtering working pressure. In general, all samples sputtered at different working pressure showed sharp fundamental absorption edges at around 300 nm. No significant shifts were found in the spectra. The average transmittance in visible light range for these samples was about 80%. They gave high transmittance in near-infrared regions. In particular, for the AZO samples sputtered below $3.6 \times 10^{-3}$ mbar working pressure, there was a slight peak in the interface between violet and ultraviolet regions at around 400 nm. They dropped down and became almost flat all over the rest of the spectra. For the AZO samples sputtered at $6 \times 10^{-3}$ mbar working pressure, there was no peak found at around 400 nm but a moderate increase beyond wavelength of 400 nm. It was observable higher than the others in red and near-infrared regions. When comparing the samples with each other, several trends could be concluded. The higher the sputtering working pressure, the higher was the optical transmittance in red and near-infrared regions. The lower the sputtering working pressure, the higher was the transmittance peak at around 400 nm except below $2.6 \times 10^{-3}$ mbar due to the difference in nucleation by high energy bombardment of deposited materials. Overall, AZO sample sputtered at $2.6 \times 10^{-3}$ mbar working pressure possessed the best transmittance spectrum.
4.2.3 Summary

In this experiment, AZO thin films were deposited at different sputtering working pressures. The sputter yield had a decreasing trend as the working pressure rose. When working pressure was increased, electrical properties of AZO thin film became better and then poorer after a saturation point. When working pressure was decreased, optical properties of AZO thin film became better and then poorer after a saturation point in visible light range.

For the conduction mechanism of AZO samples, sputter yield was lower due to higher frequency of collisions between target materials and inflow gas atoms at higher working pressure. Resistivity of AZO samples decreased with decreasing working pressure because less oxygen atoms filled up the vacancies during surface diffusion. After a minimum point, resistivity of AZO samples increased with decreasing working pressure because energetic deposited materials collided strongly to the substrate and affect film nucleation. Transmittance of AZO samples increased and decreased with decreasing working pressure in violet region and red region respectively except below a saturated pressure.

In a nutshell, AZO thin film sputtered at 2.6 x 10^{-3} mbar working pressure had the best performance in both electrical and optical properties in this experiment set.
4.3 Influences of Hydrogen Gas Variation on AZO Thin Films

In this section, the factor of hydrogen content in sputtering environment for AZO thin films would be discussed. Details of the sputtering conditions would be given in section 4.3.2. AZO thin films were measured in electrical and optical properties to understand the mechanism of AZO films sputtered under different hydrogen ratios.

4.3.1 Review

From section 2.2, the conduction mechanism in AZO thin films was theoretically mentioned. Eqn. (2.3), eqn. (2.4) and eqn. (2.7) gave the formulas contributing the carrier concentration of AZO thin films in section 2.2.1. From section 2.3, plasma wavelength of thin films is expressed by eqn. (2.25). From section 2.6.1, resistivity of thin film equals to sheet resistance multiplies film thickness given by eqn. (2.28).

\[
O_o^{\chi} \rightarrow \frac{1}{2} O_2(g) + V_o + 2e^- \quad (2.3)
\]

\[
Al_2O_3 \rightarrow 2O_o + 2Al_{zn}^+ + \frac{1}{2} O_2(g) + 2e^- \quad (2.4)
\]

\[
2Al_{zn}^+ + 2O_o + \frac{1}{2} O_2(g) + 2e^- \rightarrow Al_2O_3 \quad (2.7)
\]

From section 4.1, introduction of oxygen content during sputtering deteriorated the electrical properties of AZO thin films while slightly improved the optical properties. The vacuum chamber shall be oxygen free since the effects on electrical performance outweighed optical one. From section 4.2, sputtering working pressure of \(2.6 \times 10^{-3}\) mbar obtained AZO thin films with better electrical and optical
performance. Therefore, 20 sccm Ar gas flow but no oxygen gas mixture added would be adopted as the base gas flow in this experiment set.

4.3.2 Sputtering Conditions

To explore the effects on AZO thin films to hydrogen environment inside vacuum chamber, the flow rate of gas (5% H₂/Ar) feeding into the chamber was tuned by MFC 3 of the sputter system while other sputtering parameters, such as the base Ar gas flow from MFC 1, type and power value of power supply, substrate temperature, sputtering time, base pressure and substrate rotational speed, were kept constant. Table 4.12 shows the fixed values of the specific sputtering parameters in this experiment set while Table 4.13 shows the varying sputtering parameters, which is the different flow rate of (5% H₂/Ar).

<table>
<thead>
<tr>
<th>Fixed Sputtering Parameters</th>
<th>Parameter Value</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Base Ar Gas Flow</strong></td>
<td>20 sccm</td>
</tr>
<tr>
<td><strong>Power Supply</strong></td>
<td>RF 80W</td>
</tr>
<tr>
<td><strong>Substrate Temperature</strong></td>
<td>room temperature</td>
</tr>
<tr>
<td><strong>Sputtering Time</strong></td>
<td>20 minutes</td>
</tr>
<tr>
<td><strong>Substrate Rotational Speed</strong></td>
<td>10 revolutions/minute</td>
</tr>
<tr>
<td><strong>Base Pressure</strong></td>
<td>&lt; 3.0 × 10⁻⁶ mbar</td>
</tr>
<tr>
<td><strong>Working Pressure</strong></td>
<td>2.6-3.6 ×10⁻³ mbar</td>
</tr>
</tbody>
</table>

Table 4.12 Fixed sputtering parameters in examining the effect of hydrogen ratio
Additional Flow Rate of (5% H\textsubscript{2}/Ar) in sccm

<table>
<thead>
<tr>
<th>Flow Rate (sccm)</th>
<th>Working Pressure (10\textsuperscript{-3} mbar)</th>
<th>Sheet Resistance (Ω/sq.)</th>
<th>Resistivity (mΩ·cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.6</td>
<td>1380</td>
<td>12.7</td>
</tr>
<tr>
<td>2</td>
<td>2.7</td>
<td>1278</td>
<td>9.59</td>
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<tr>
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<td>2.9</td>
<td>986</td>
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</tr>
<tr>
<td>6</td>
<td>3.0</td>
<td>847</td>
<td>6.78</td>
</tr>
<tr>
<td>8</td>
<td>3.2</td>
<td>653</td>
<td>5.49</td>
</tr>
<tr>
<td>10</td>
<td>3.4</td>
<td>477</td>
<td>4.2</td>
</tr>
<tr>
<td>12</td>
<td>3.6</td>
<td>559</td>
<td>4.81</td>
</tr>
</tbody>
</table>

Table 4.13 Hydrogen flow rate in examining the effect of hydrogen content

### 4.3.3 Mechanism of AZO Films

Table 4.14 shows the electrical properties such as sheet resistance and resistivity of AZO samples. The flow rate of (5% H\textsubscript{2}/Ar) was increased from 0 sccm to 12 sccm with every 2 sccm as an interval. Working pressure increased from 2.6 x 10\textsuperscript{-3} mbar to 3.6 x 10\textsuperscript{-3} mbar when (5% H\textsubscript{2}/Ar) was increased from 0 sccm to 12 sccm. Sheet resistance and resistivity of AZO samples decreased significantly to a minimum and became saturated under the increase in flow rate. With further increase in hydrogen flow rate, Sheet resistance and resistivity of AZO samples rose up.

Table 4.14 Resistivity of AZO samples in examining the effect of hydrogen content
Fig. 4.12 depicts the change of resistivity of the samples with the increase in hydrogen flow rate. A parabolic curve with a minimum point could be observed by the relation established between resistivity of AZO samples and hydrogen content. Most of the samples got the resistivity of several mΩ·cm, which was quite conductive, under hydrogen sputtering ambient. The minimum point located at 10 sccm (5% H₂/Ar) flow rate with resistivity of about 4 mΩ·cm. This behavior can be understood by two competing processes. They were the increase in carrier concentration contributed by oxygen vacancies as native donors improving the stoichiometry of the AZO samples and the development Al-Al intragrain clusters worsening the transportation of carriers.
Since hydrogen gas was a reducing gas, it could increase the number oxygen vacancies for thin film deposition during sputtering. It contributed carriers as given by eqn. (2.3). Eqn. (2.4) was given by impurity donors mainly from the target. When hydrogen flow ratio was increased, carrier concentration was increased in sputtered AZO samples and film conductivity was enhanced. When the amount of Al ions exceeded the solubility limit, Al ions interacted with each other and Al-Al intragrain clusters may be formed as a result. Eqn. (2.7) might take place more frequently reducing the number of carriers and, on the other hand, cluster formation affected mobility due to intragrain cluster scattering and thus effective carrier mobility. Therefore, resistivity of the samples increased with further increment in hydrogen flow ratio after obtaining a minimum resistivity.

Fig. 4.13 reveals the optical transmittance spectra from 200 nm wavelength to 1100 nm wavelength of AZO samples deposited at different hydrogen flow ratio, i.e. 6, 8, 10 and 12 sccm of (5% H₂/Ar). In general, all samples sputtered at different working pressure showed sharp fundamental absorption edges at around 300 nm. No significant shifts were found in the spectra. The average transmittance in visible light range for these samples was above 80%. They gave high transmittance in near-infrared regions. All the samples shared the same waveform outline that the optical mechanism for was almost the same. They all showed a slight peak in the interface between violet and ultraviolet regions at around 400 nm and had a very mild increase to the near-infrared region. When the ratio of hydrogen gas increased, there was a very slight drop in the average transmittance from visible light range to near-infrared region.
Fig. 4.13 Transmittance of AZO samples with different hydrogen flow ratio
4.3.4 Summary

In this experiment, AZO thin films were deposited at different hydrogen flow ratio. When hydrogen flow rate was increased, electrical properties of AZO thin film became better with higher conductivity and then were deteriorated with a drop down in conductivity after a saturated amount of hydrogen flow ratio. When flow rate of hydrogen was increased, optical properties of AZO thin film had slightly been degenerated in the average transmittance of the visible light range with similar waveform shape in optical transmittance.

For the conduction mechanism of AZO samples, resistivity of AZO samples, at first, had a dramatic decrease as the flow rate of hydrogen mixture increased because the gas increased the number of vacancies for deposited thin films during sputtering. When the amount of Al ions exceeded the solubility limit, Al ions interacted with each other and Al-Al intragrain clusters may be formed as a result. When hydrogen flow ratio continued to increase, above formation occurred more frequently with negative effects in both carrier concentration and carrier mobility in the aspects of reduction of oxygen vacancies and slowdown of intragrain cluster scattering mobility respectively. Resistivity of AZO samples began to become worse with further increase in hydrogen flow rate after a most suitable amount was introduced due to the domination of oxygen vacancies generation by clusters formation.

To be concluded, the improvement of electrical performance greatly outweighed the room of little drop in optical performance of AZO thin films when hydrogen flow ratio increased. 10 sccm (5% H₂/Ar) flow rate was the most suitable amount to obtain best performance in both electrical and optical properties in this experiment set.
4.4 Deposition Sensitivities of AZO and ZnO to Sputtering Environment

In this section, the factor of deposition sensitivities of both AZO and ZnO thin films to sputtering environment would be discussed. Details of the sputtering conditions would be given in section 4.4.2. XRD were performed to investigate the crystal structure of AZO and ZnO thin films grown at different conditions. The lattice parameters of the c-axis of the films were compared to show the difference of AZO and ZnO in sensitivity to sputtering environment.

4.4.1 Review and Motivation

XRD showed the preferred crystallographic orientation of thin films. Lattice parameter variation from XRD for changes in sputtering parameters reflected the sensitivity to the growth environment. It was an indicator to reveal the formation of defects and presence of impurity elements.

Thin ZnO and AZO films, generally, exhibited the hexagonal wurtzite structure as mentioned in section 2.4.1. They showed a preferred orientation of grains having the crystallographic c-axis oriented, which was equivalent to Miller indices (002) most commonly, parallel to the substrate normal. From section 2.4.2, the theoretical lattice parameter of AZO and ZnO was given by eqn. (2.27) with unit cell length $a=325.0$ pm and $c/a=1.602$ [105]. By Bragg’s Law, $n\lambda = \frac{2d}{\sin\theta}$, lattice parameter could be found by the diffraction peaks in XRD [76].

$$\frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2 +hk+k^2}{a^2} \right) + \frac{l^2}{c^2}$$

(2.27)
4.4.2 Sputtering Conditions

To investigate the deposition sensitivity to sputtering environment, two same experiment sets were done on AZO and ZnO separately. Table 4.15 shows the fixed values of the specific sputtering parameters in this experiment set while Table 4.16 shows the varying sputtering parameters, which is the different flow rate of (5% H₂/Ar) for both thin AZO and ZnO films.

<table>
<thead>
<tr>
<th>Fixed Sputtering Parameters</th>
<th>Parameter Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base Ar Gas Flow</td>
<td>20 sccm</td>
</tr>
<tr>
<td>Power Supply</td>
<td>RF 80W</td>
</tr>
<tr>
<td>Substrate Temperature</td>
<td>room temperature</td>
</tr>
<tr>
<td>Sputtering Time</td>
<td>20 minutes</td>
</tr>
<tr>
<td>Substrate Rotational Speed</td>
<td>10 revolutions/minute</td>
</tr>
<tr>
<td>Base Pressure</td>
<td>&lt; 3.0 × 10⁻⁶ mbar</td>
</tr>
<tr>
<td>Working Pressure</td>
<td>2.6-3.4 ×10⁻³ mbar</td>
</tr>
</tbody>
</table>

Table 4.15 Fixed sputtering parameters in examining deposition sensitivities of AZO and ZnO

<table>
<thead>
<tr>
<th>Additional Flow Rate of (5% H₂/Ar) in sccm</th>
</tr>
</thead>
<tbody>
<tr>
<td>AZO</td>
</tr>
<tr>
<td>0</td>
</tr>
<tr>
<td>5</td>
</tr>
<tr>
<td>10</td>
</tr>
</tbody>
</table>

Table 4.16 Hydrogen flow rate in examining deposition sensitivities of AZO and ZnO
4.4.3  Lattice Parameter Variations of AZO and ZnO Thin Films to Changes in Sputtering Environment

The crystal structures of AZO and ZnO samples, sputtered under 0, 5 and 10 sccm of (5% H₂/Ar), were investigated by XRD with CuKα radiation source (λ = 0.15406 nm). XRD profiles of the samples showed only one peak corresponding to the (002) plane appeared and no other diffraction pattern was observed. Enlarged XRD patterns displaying the c-axis (002) diffraction peaks of AZO and ZnO samples were depicted as Fig. 4.14 and Fig. 4.15 respectively.

![Enlarged XRD patterns of (002) diffraction peaks for AZO thin films deposited at various hydrogen flow rates](image)

Fig. 4.14 Enlarged XRD patterns of (002) diffraction peaks for AZO thin films deposited at various hydrogen flow rates
From Fig. 4.14 and Fig. 4.15, the (002) XRD peaks were observed at $2\theta = 34.38^\circ$ and $2\theta = 34.40^\circ$ for AZO and ZnO samples respectively grown without any hydrogen gas flow, which were close to the standard ZnO crystal of $2\theta = 34.42^\circ$ shown in vertical dotted lines in both figures. Both of them showed peak shift to a higher diffraction angle when the hydrogen flow ratio was increased, but with different shift amplitude. The peak position of AZO samples shifted to $2\theta = 34.56^\circ$ at 5 sccm and $2\theta = 34.68^\circ$ at 10 sccm (5% H$_2$/Ar) flow rate while to $2\theta = 34.44^\circ$ at 5 sccm and $2\theta = 34.46^\circ$ at 10 sccm for that of ZnO samples. The peak shifts were due to the fact that oxygen to be bound to hydrogen atoms and be extracted from the AZO and ZnO films during sputtering, resulting in the shrinkage of AZO and ZnO with increasing amount of hydrogen.
Fig. 4.16 shows the relation between lattice parameter of the c-axis of AZO and ZnO samples and hydrogen flow ratio. The lattice parameter of ZnO thin films was much closer to the value of bulk ZnO when there was an increase in hydrogen flow rate while that of AZO thin films tended to be shorter upon the changes in gas compositions. In addition, the degree of change of c-axis length in AZO was much greater than ZnO under the same amount of increase in hydrogen ratio. It could be deduced that AZO films were more sensitive to the growth environment than ZnO films since lattice parameter variation, in general, was an indication of the formation of defects or presence of impurity elements.
4.5 Electrical Properties of As-deposited AZO Thin Film At Low Temperature

In this section, the electrical properties of as-deposited AZO thin film described in section 4.3.2, sputtered under the gas flow rate of 20 sccm Ar and 10 sccm (5\% H\textsubscript{2}/Ar), 80W RF power supply and 20 min sputtering time, was measured at low temperature. Electronic transport properties were explored by the measurement of low temperature resistance against temperature done in cryostat ranged from 20K up to 330 K.

Resistance of the AZO sample was recorded at 20, 40, 60, 80, 100, 150, 200, 250 273, 300 and 330K. With the use of a constant voltage source applying from -5V to 5V to the sample, relative current passing through the sample was measured at different temperature. Electrical properties of the AZO sample could be understood in the point of view of energy level shifting.

Fig. 4.17 shows the graph of current against voltage of the AZO sample at different temperature. From the figure, y-intercepts of the selected sample varied with different temperatures. They increased with lower temperature. When the applied voltage was zero, the current was zero at T=330K. Current increased to about 0.1 mA at T=20K when applied voltage remained at zero. There was no observable change in the slope of the sample at different temperature. However, the slope of the sample had a general increase when temperature was decreased analytically.
Fig. 4.17 I-V curves of the selected AZO sample at low temperatures

Fig. 4.18 Resistivity of the selected AZO sample at low temperatures
From the energy level point of view, the metallic behavior of AZO thin films was due to Al donor electrons filling up the lower levels in the conduction band. In degenerate semiconductors, the overlapping of the impurity band of the Al donor with the ZnO conduction band was called the Burstein-Moss effect. Fig. 4.18 shows the variation of resistivity at low temperatures of the selected sample. It revealed that resistivity of the sample decreased with decreasing temperature at first from T=330K to T=150K, and then increased with decreasing temperature from T=150K to 20K. It could be seen that the regions were apparently split at T=125K. The AZO sample showed a metal to semiconductor transition. The decrease in resistivity with decreasing temperature was due to the reduction in thermal energy lowering the number of electrons vibrating with the energy needed to scatter the conducting electron. The resistivity increased with further decreasing temperature due to the recombination of Al donors and electrons. The Fermi energy level shifted further above the conduction band increasing the energy required by the electrons to be promoted from impurity donor to the conduction band.

CHAPTER 5 OPTIMIZATION AND APPLICATION OF AZO FILMS IN OLED DEVICE

In this chapter, a relationship of AZO properties as a function of sputtering time was built. An optimum condition for and degradation of AZO were established after contributing factors of sputtering parameters on AZO were considered. Application of AZO films in OLED was presented with refinement of film properties as anodes in the device and simulation of modifying the device structure.
5.1 Properties of AZO Films As A Function of Sputtering Time

In this section, the factor of sputtering time on the properties of AZO thin films would be discussed. Details of the sputtering conditions would be given in section 5.1.2. AZO thin films were measured in electrical and optical properties to understand the mechanism of AZO films sputtered under different sputtering time. Electronic properties of the samples would be studied from Hall Effect technique to have a clear picture on their conduction and scattering characteristics. The crystalline integrity of the films was also analyzed.

5.1.1 Review and Motivation

From section 4.1 to section 4.3, the influences of the sputtering parameters of oxygen flow ratio, working pressure and hydrogen flow ratio had been explored already. The most suitable value of each parameter on the electrical and optical properties of AZO thin films was discussed. Preliminarily, to obtain AZO thin film with better performance both electrically and optically, there shall not be any introduction of oxygen flow ratio and the flow rate of Ar and (5% H₂/Ar) shall be 20 sccm and 10 sccm respectively.

The only factor left that had a decisive and relatively big effects comparing to the other unconsidered parameters on the properties of AZO films was the sputtering time. After this work was done, optimization of AZO films sputtered with RF power supply at room temperature was aimed to be completed. In addition, they were readily used for applications with different thickness and different electrical and optical properties according to the needs of device designers.
5.1.2 Sputtering Conditions

To investigate the effects of sputtering time on properties of AZO films, the flow rate of pure 99.9% argon (Ar) and (5% H\textsubscript{2}/Ar) feeding into the chamber were kept constant at 20 sccm by MFC 1 and 10 sccm by MFC 3 respectively. The only varying parameter was the deposition duration. Table 5.1 shows the fixed values of the specific sputtering parameters in the experiment set. Table 5.2 shows the different sputtering time for deposition of AZO films.

<table>
<thead>
<tr>
<th>Fixed Sputtering Parameters</th>
<th>Parameter Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base Ar Gas Flow</td>
<td>20 sccm</td>
</tr>
<tr>
<td>Base (5% H\textsubscript{2}/Ar) Flow Rate</td>
<td>10 sccm</td>
</tr>
<tr>
<td>Power Supply</td>
<td>RF 80W</td>
</tr>
<tr>
<td>Substrate Temperature</td>
<td>room temperature</td>
</tr>
<tr>
<td>Substrate Rotational Speed</td>
<td>10 revolutions/minute</td>
</tr>
<tr>
<td>Base Pressure</td>
<td>&lt; 3.0 \times 10^{-6} mbar</td>
</tr>
<tr>
<td>Working Pressure</td>
<td>3.4 \times 10^{-3} mbar</td>
</tr>
</tbody>
</table>

Table 5.1 Fixed sputtering parameters in examining the effect of sputtering time

<table>
<thead>
<tr>
<th>Sputtering Time in min</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
</tr>
</tbody>
</table>

Table 5.2 Different deposition duration in examining the effect of sputtering time
5.1.3  Crystalline Integrity of AZO Films As A Function of Sputtering Time

The crystalline integrity of AZO samples, sputtered at 20, 60, 100 and 140 mins, were investigated by XRD with CuKα radiation source (λ = 0.15406 nm). It examined the influence of sputtering time on crystal growth of AZO thin films. This particular XRD profiles were displayed as Fig. 5.1. For all the selected samples, two peaks corresponding to the (002) plane and (103) plane appeared. It suggested that these films were of c-axis preferential orientation and the other higher degree orientation. When sputtering time increased, the intensity of (002) peak first increased and then decreased after reaching maximum at 100 mins while that of (103) peak increased all the way up with the sputtering time. Initially, (002) was the dominant peak. (103) orientation became dominant eventually when the sputtering time was beyond 100 mins.

Fig. 5.1 XRD patterns for AZO films deposited at various sputtering time
Table 5.3 gives the detailed information on FWHM and grain size of XRD (002) and (103) peaks of the selected AZO samples. The grain size was calculated by Scherrer equation from eqn. (2.26). Fig. 5.2 graphically shows the FWHM and grain size of respective AZO films deposited at different sputtering time.

<table>
<thead>
<tr>
<th>Sputtering Time in sccm</th>
<th>FWHM of (002) (degree)</th>
<th>FWHM of (103) (degree)</th>
<th>Grain Size of (002) (nm)</th>
<th>Grain Size of (103) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.51</td>
<td>0.97</td>
<td>16.4</td>
<td>9.6</td>
</tr>
<tr>
<td>60</td>
<td>0.38</td>
<td>0.71</td>
<td>21.6</td>
<td>13.1</td>
</tr>
<tr>
<td>100</td>
<td>0.35</td>
<td>0.65</td>
<td>23.7</td>
<td>14.3</td>
</tr>
<tr>
<td>140</td>
<td>0.34</td>
<td>0.63</td>
<td>24.2</td>
<td>14.6</td>
</tr>
</tbody>
</table>

Table 5.3 Grain size and FWHM of XRD (002) and (103) peaks deposited at various sputtering time

Fig. 5.2 FWHM and the grain size of XRD (002) (solid lines) and (103) (dash lines) peaks for AZO films deposited at various sputtering time
According to the formula, grain size is inversely proportional to FWHM. As sputtering time was increased, FWHM of XRD (002) and (103) peaks decreased while grain size of the AZO samples grew larger. Grain size increased from about 16 to 24 nm for (002) peaks and nearly doubled in size of that for (103) peaks, from 9 to 14 nm, when the time increased from 20 to 140 mins. The crystallinity of the films improved largely with sputtering time and film thickness.

Enlarged XRD patterns displaying the c-axis (002) diffraction peak and (103) diffraction peak of selected AZO samples were depicted as Fig. 5.3 and Fig. 5.4 respectively. The unstressed (002) preferential orientation located at 2θ = 34.42° and the unstressed (103) preferential orientation located at 2θ = 62.85° were shown accordingly in the figures.
The diffraction peaks shifted to higher diffraction angle from 34.5° to 34.6° from Fig. 5.3 and 62.85° to 63.05° from Fig. 5.4 for (002) and (103) peaks respectively when sputtering time was increased from 20 to 120 mins. Thin films could be stressed even without the application of external loading. Film stress tended to increase with thickness. The residual stress resulted from the lattice mismatch between the film and substrate. Here, in the samples, tensile stress existed due to the use of vacuum tape on substrate during sputter deposition. The higher degree of shifting in diffraction angle implied that there was higher tensile stress in the AZO samples when sputtering time was increased. When the thickness reached a limit that tensile stress was too high for the preferred orientation, defects came in the film and add-atoms had difficulties in arranging their sites. It explained why (103) orientation dominated (002) orientation when sputtering time exceeded 100 mins.
5.1.4 Electrical Properties of AZO Films As A Function of Sputtering Time

Table 5.4 below shows the thickness, sheet resistance and also resistivity of AZO samples from the different sputtering time. The sputtering time was increased from 20 mins to 180 mins with every 20 mins as an interval except for the last interval replaced by 40 mins instead. The sputter yield for this experiment set was about 4.4 nm/ min as shown in Fig. 5.5 with thickness increased from 88 to 786 nm. Sheet resistance and resistivity of the AZO samples had significant shrinkages from 477 Ω/sq. to 9.65 Ω/sq. and from about 4 x 10^{-3} Ω·cm to about 7 x 10^{-4} Ω·cm respectively. To establish relations between them, resistivity of AZO samples decreased when sheet resistance decreased with the increasing sputtering time as thickness was increased.

<table>
<thead>
<tr>
<th>Sputtering Time in min</th>
<th>Thickness (nm)</th>
<th>Sheet Resistance (Ω/sq.)</th>
<th>Resistivity (mΩ·cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>88</td>
<td>477</td>
<td>4.2</td>
</tr>
<tr>
<td>40</td>
<td>196</td>
<td>183</td>
<td>3.59</td>
</tr>
<tr>
<td>60</td>
<td>260</td>
<td>77.5</td>
<td>2</td>
</tr>
<tr>
<td>80</td>
<td>370</td>
<td>45.1</td>
<td>1.66</td>
</tr>
<tr>
<td>100</td>
<td>476</td>
<td>27.9</td>
<td>1.33</td>
</tr>
<tr>
<td>120</td>
<td>579</td>
<td>20.8</td>
<td>1.2</td>
</tr>
<tr>
<td>140</td>
<td>610</td>
<td>11.8</td>
<td>0.72</td>
</tr>
<tr>
<td>180</td>
<td>786</td>
<td>9.65</td>
<td>0.76</td>
</tr>
</tbody>
</table>

Table 5.4 Resistivity of AZO samples in examining the effect of sputtering time
Fig. 5.5 Sputter yield of samples sputtered at different sputtering time

Fig. 5.6 Sheet resistance against film thickness of samples of different time
Fig. 5.6 shows the sheet resistance against thickness of AZO samples of different sputtering time. Sheet resistance dropped very steeply from thickness of 100 to 300 nm, declined gradually from 300 to 600 nm and, finally, became saturated staying nearly constant beyond that range. Sheet resistance formed an exponential decay shape with film thickness. From the figure, sheet resistance of AZO samples followed two main mechanisms with equations $y=674.60 - 2.365x$ for dramatic decrease and $y=34.307 - 0.032x$ for stable saturation. It was proved that sheet resistance of AZO films had a large dependence on film thickness. It could be due to the formation of electron traps by stress induced defects when the film was below 300 nm and the trapping of free carriers by surface states for above 300 nm.

Fig. 5.7 Resistivity of AZO films as a function of sputtering time
Fig. 5.7 illustrates the resistivity as a function of sputtering time of the AZO samples. Resistivity, which was the slope of sheet resistance against thickness graph, was closely correlated to Fig. 5.6. It demonstrated a significant decrease with increasing sputtering time initially, followed by a slight increase after reaching the minimum resistivity of about $7 \times 10^{-4} \ \Omega \cdot \text{cm}$ at sputtering time $t = 140$ mins. The increase in conductivity with increasing film thickness might be contributed by the increase in carrier concentration and carrier mobility. To further explore the change in conductivity, electronic properties of the AZO samples were done by Hall Effect.

Fig. 5.8 shows the carrier concentration and carrier mobility of AZO samples deposited at different sputtering time. $n$ and $\mu$ ranged from around $2.3$ to $4.8 \times 10^{20} \ \text{cm}^{-3}$ and around $7$ to $16.5 \ \text{cm}^2/\text{Vs}$ respectively from 20 to 180 mins sputtering time.

![Fig. 5.8 Carrier concentration and mobility of AZO at different sputtering time](image_url)
Carrier concentration increased significantly from 20 to 120 mins and had a moderate decrease after \( t = 120 \) mins. The initial increase in \( n \) was due to the increase of oxygen vacancy contribution by native donors which was given by eqn. (2.3). The gradual decrease in \( n \) was as a result of the formation of Al-Al intragrain clusters by the interaction of Al ions each other when the limit of solubility was exceeded which was given by eqn. (2.7). It also coincided with the crystal defect revealed in section 5.1.3 that the shifting of dominant peak from (002) to (103) occurred when the tensile stress exceeded the limit in the preferential (002) orientation when sputtering time reached \( t = 140 \) mins. Carrier mobility increased steadily from 20 to 120 mins and had more dramatic increase after \( t = 120 \) mins. Effective carrier mobility was influenced by ionized impurity scattering, neutral impurity scattering, grain boundary scattering, intragrain cluster scattering and lattice vibration scattering. For neutral impurity scattering, the amount of neutral impurity scattering centers was much less than that of the ionized impurity and, thus, it could be negligible. The lattice vibration scattering was dominant in the high temperature range. Its contribution could be negligible at room temperature. Mobility due to intragrain cluster scattering came into effect and became slower after \( t = 120 \) mins. The amount of ionized impurity increased and led to a drop in mobility due to ionized impurity scattering when sputtering time increased. Grain size of the films enlarged with respect to sputtering time and contributed an enhancement in mobility due to grain boundary scattering. From the result of mobility in Fig. 5.8, the mobility due to grain boundary scattering dominated that due to ionized impurity scattering and intragrain cluster scattering.
5.1.5 Optical Properties of AZO Films As A Function of Sputtering Time

Fig. 5.9 illustrates the optical transmittance spectra from 200 nm wavelength to 1100 nm wavelength of AZO samples deposited at different selected sputtering time, i.e. 20, 60, 100 and 140 mins. All samples sputtered at different time showed sharp fundamental absorption edges but there tended to be a red shift towards longer wavelength with longer sputtering time. The average transmittance in visible light range for these samples was all above 80% and it increased from 83% to 92% for the sputtering from 20 mins to 140 mins. They gave high transmittance in near-infrared regions. Oscillatory nature of spectra with maxima and minima was found when sputtering time reached 60 mins. It was the interference effect caused by reflected light intensity relating periodically to film thickness and index of refraction. Higher frequency and blue shift of oscillatory nature occurred for increasing sputtering time. In addition, the incident light path inside the AZO samples also increased with increasing sputtering time and thus thickness. On the other hand, the increase in average transmittance in visible light range for longer sputtering time was due to the enhanced crystallinity and growth of larger grains. Less grain boundary scattering executed for those films while more intragrain cluster scattering and ionized impurity scattering took place. By comparing the impacts, better average transmittance in visible light range was a result of that grain boundary scattering outweighed the other two scattering as a function of sputtering time on AZO thin films, which was in good agreement with the previous result discussed in section 5.1.4.
Fig. 5.9 Transmittance of AZO samples sputtered at different sputtering time
5.1.6 Summary

In this experiment, AZO thin films were deposited at different sputtering time. When sputtering time was increased, crystallinity of AZO thin films became better as grain sizes inside the films grew larger. In addition, it was found that defects came into the films when sputtering time was over 100 mins as the tensile stress of the films exceeded shifting the dominant diffraction peak from (002) orientation angle to (103).

Conductivity had a significant increase with increasing sputtering time initially and then had a slight decrease after reaching the minimum resistivity of about $7 \times 10^{-4}$ Ω·cm at sputtering time $t = 140$ mins. The increase in conductivity was due to the enhancement of carrier concentration and mobility. Better carrier mobility was demonstrated with the significant increase in mobility due to grain boundary scattering, which dominated mobilities due to intragrain cluster scattering and also ionized impurity scattering, as the crystal structure improved when the sputtering time increased. Higher carrier concentration was revealed due to the more contribution of oxygen vacancies by native donor with the increase in sputtering time, but it had a moderate drop down when the sputtering time was higher than 120 mins because the formation of Al-Al intragrain clusters came to effect.

The average transmittance in visible light range for AZO thin films was increased from 83% to 92% for the sputtering from 20 mins to 140 mins. Higher frequency and blue shift of oscillatory nature occurred for increasing sputtering time. Better average transmittance in visible light range was a result of that less grain boundary scattering, which outweighed the other intragrain cluster scattering and ionized impurity
scattering scattering as a function of sputtering time on AZO thin films, occurred inside the films.

In conclusion, taking all factors into consideration, AZO thin films sputtered at 20 sccm Ar and 10 sccm (5% H₂/Ar) for a sputtering time of 140 mins had the best performance in account of both electrical and optical properties.

5.2 Degradation of AZO Films at Atmospheric Pressure

In this section, the characteristics of degradation of AZO films would be discussed. The as-deposited AZO films, which had different sputtering time as described in section 5.1.2 except for the one at 180 mins and its thickness was mentioned in Table 5.4, were stored inside the desiccators at room temperature and atmospheric pressure. Their electrical and optical properties were measured half-yearly after deposition and compare them with the data acquired immediately after being sputtered.

Table 5.5 below shows the thickness, resistivity immediately after being sputtered, resistivity after half year and resistivity after one year of AZO samples for the different sputtering time. The sputtering time was increased from 20 mins to 140 mins with every 20 mins as an interval. The thickness of the samples increased from 88 to 610 nm. In general, the films were degraded with respect to the storage time that resistivity was increased as the storage time increased. However, samples with different thickness had different extent of degradation. In other words, degradation of AZO films was thickness dependent.
### Table 5.5 Half-yearly resistivity of AZO samples with different sputtering time

<table>
<thead>
<tr>
<th>Sputtering Time in min</th>
<th>Thickness (nm)</th>
<th>Resistivity After Sputtering (mΩ·cm)</th>
<th>Resistivity After Half Year (mΩ·cm)</th>
<th>Resistivity After One Year (mΩ·cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>88</td>
<td>4.2</td>
<td>5.09</td>
<td>5.9</td>
</tr>
<tr>
<td>40</td>
<td>196</td>
<td>3.59</td>
<td>3.84</td>
<td>4.1</td>
</tr>
<tr>
<td>60</td>
<td>260</td>
<td>2</td>
<td>2.12</td>
<td>2.24</td>
</tr>
<tr>
<td>80</td>
<td>370</td>
<td>1.66</td>
<td>1.72</td>
<td>1.78</td>
</tr>
<tr>
<td>100</td>
<td>476</td>
<td>1.33</td>
<td>1.38</td>
<td>1.43</td>
</tr>
<tr>
<td>120</td>
<td>579</td>
<td>1.2</td>
<td>1.24</td>
<td>1.28</td>
</tr>
<tr>
<td>140</td>
<td>610</td>
<td>0.72</td>
<td>0.73</td>
<td>0.74</td>
</tr>
</tbody>
</table>

Table 5.5 Half-yearly resistivity of AZO samples with different sputtering time.

![Fig. 5.10 Resistivity as a function of storage time for different AZO thickness](image)
Fig. 5.10 and Fig. 5.11 show the resistivity as a function of storage time and resistivity percentage change respectively for different AZO thickness. The AZO samples degraded significantly for thin films below 200 nm and the percentage change in resistivity was about 10-17%. The degradation became much gentler when the thickness was higher than 200 nm and the percentage change in resistivity was less than 8%. The thicker the AZO film, the more stable was the film resistivity. The degradation was due to the diffusion of oxygen molecules in air into the film surface. Moreover, the degradation took place slightly higher in rate in the first half year than in the second half year, but the films behaved more or less the same on the relationship between resistivity change and thickness.
Fig. 5.12 Transmittance change of AZO films at 20 and 140 mins sputtering time

Fig. 5.12 graphically shows the transmittance difference between measurements taken immediately after sputtering and taken after half-year storage in desiccators of AZO samples deposited at sputtering time of 20 and 140 mins. Observable degradations in transmittance were found after storage of half year for both samples. Peak transmittance for them was significantly lower than that before storage. In general, peak transmittance had red shift after storage. The thicker the film, the higher degree was the peak shifting. Average transmittance of the samples dropped about 1% after the storage.

In conclusion, AZO films were relatively air stable, which was important in its application, in comparison with other TCO films.
5.3 Fabrication of OLED Device with the Use of AZO Film As Anode

In this section, AZO films were applied in OLEDs as anodes. The devices were fabricated to demonstrate the performance of AZO in its application of OLED. Conventional bottom-emission OLEDs had been selected to fabricate in order to have easy comparisons in device characteristics with the reference device prepared using commercial ITO.

There were two different pre-treatments done on as-deposited AZO films before OLED fabrication to examine the effect of matches of work function of AZO films with that of other organic material layers. They were optimum plasma treatment for in-house AZO, i.e. 60 second oxygen plasma + 30 second CF<sub>x</sub> plasma, (called treatment 1 later on) and standard plasma treatment for commercial ITO, i.e. 25 second oxygen plasma + 7 second CF<sub>x</sub> plasma, (called treatment 2). The work functions of AZO films after treatment 1 and treatment 2 were 5.43 eV and 4.96 eV respectively while that of commercial ITO after treatment 2 was 5.2eV.

Basic green emission OLEDs using NPB and Alq<sub>3</sub> were adopted in this experiment set. Table 5.6 shows the structures and details of the OLED devices.

<table>
<thead>
<tr>
<th>Green OLED</th>
<th>Details and Structures</th>
</tr>
</thead>
<tbody>
<tr>
<td>Structure (nm)</td>
<td>Anode/NPB(70)/Alq&lt;sub&gt;3&lt;/sub&gt;(60)/LiF(1)/Al(80)</td>
</tr>
<tr>
<td>Anode (nm)</td>
<td>AZO (610) and commercial ITO (80)</td>
</tr>
<tr>
<td>Pre-treatment 1</td>
<td>60 second oxygen plasma + 30 second CF&lt;sub&gt;x&lt;/sub&gt; plasma</td>
</tr>
<tr>
<td>Pre-treatment 2</td>
<td>25 second oxygen plasma + 7 second CF&lt;sub&gt;x&lt;/sub&gt; plasma</td>
</tr>
</tbody>
</table>

Table 5.6 Details and structures of OLED fabrication for AZO application
Fig. 5.13 J-V curves of OLED devices with different anodes

Fig. 5.14 Yield against current density of OLED devices with different anodes
Fig. 5.15 Power efficiency against current density of OLED devices

Fig. 5.16 Emission spectra of OLED devices at 20mA current density
Fig. 5.17 Normalized emission spectra of OLED devices at 20mA current density

The performance of the selected OLED devices were characterized and shown from Fig. 5.13 to Fig. 5.17 above. Fig. 5.13 depicted the J-V characteristics of the OLED devices while Fig. 5.14 and Fig. 5.15 demonstrated respectively yield against current density and power efficiency against current density of the OLED devices. Fig. 5.16 and Fig. 5.17 respectively gave the emission spectra and normalized emission spectra of OLED devices when the current density was 20mA.

From J-V curves, all devices exhibited good diode-like behavior. Under a constant current, the voltages in AZO device were competitive to those for ITO devices. In particular, AZO with pre-treatment 1 had better J-V characteristics and lower turn-on voltage because of the lower resistance and higher work function leading more matched carrier injection. Holes and electrons were not perfectly
balanced for AZO devices due to the imbalance of carrier mobility and not optimized design of the OLED structure. Power efficiency of AZO device with treatment 1 was very close to the performance of ITO device as shown in Fig. 5.15.

From Fig. 5.16 and Fig. 5.17, the luminescence intensity of AZO devices were much lower than that of ITO device and there exhibited emission shifting for AZO devices because microcavity effect of the AZO devices seriously trapped the light inside the OLED device. The excited photons could not be effectively outcoupled. This problem could be solved by changing the microcavity properties inside the AZO devices. It could be done by designing a new device structure with various thicknesses of the organic layers in order to tune the cavity length of OLED device.

5.4 ETFOS Simulation for Application of AZO in OLED Device

In this section, ETFOS was used to simulate the emission spectra and transmittance of OLED devices with the use of AZO as anodes. OLED structures with different NPB thickness were simulated in order to tune the cavity length of device and adjust the outcoupling effect of OLED. This simulation was regarded as a solution to the microcavity effect and outcoupling problem associated with AZO application in OLED devices discussed in section 5.3.

First of all, a simulation correlated to the emission spectra of AZO device revealed in Fig. 5.16 was done to compare the experimental and simulated results. This simulation was shown in Fig. 5.18 of which the black line displayed the experimental ITO device and the red and the pink one demonstrated the experimental and simulated AZO device. Table 5.7 gave the simulation details of the AZO device.
Green OLED | Simulation Details
-----|------------------
**Structure (nm)** | Anode/NPB(70)/Alq\textsubscript{3}(60)/LiF(1)/Al(80)
**Anode (nm)** | AZO (610)
**Recombination Zone** | Fixed at the interface between NPB and Alq\textsubscript{3}

Table 5.7 Simulation details of AZO device with NPB thickness of 70 nm

![Graph](image.png)

Fig. 5.18 Emission spectra of experimental and simulated AZO device (NPB=70)

From Fig. 5.18, the simulated and experimental results were pretty much close to each other in terms of emission intensity. There existed a slight peak shift towards smaller wavelength and a line broadening in experimental emission to simulated emission but the simulation was good enough to be regarded as a reference to examine the emission behavior of AZO device.
Fig. 5.19 simulated the transmission spectra of OLED device with thickness of NPB = 70 nm using ITO and AZO as anodes. For AZO device, more blue light, wavelength of 400 – 480 nm, could be coupled out but suppressed at other wavelength in visible light range when comparing with ITO device. This explained the dramatic drop in emission intensity of AZO device since the emission wavelength of Alq₃ was about 532 nm which located within the suppression range of the cavity of this structure.

![Simulated transmission spectra of OLED with varied anodes (NPB=70)](image)

Fig. 5.19 Simulated transmission spectra of OLED with varied anodes (NPB=70)

Simulation of AZO device structure was varied in term of thickness of NPB in order to tune the cavity length. Table 5.8 shows the simulation details of AZO device structure with changing NPB thickness. NPB thickness increased from 70 to 190 nm with every 30 nm as an increment interval.
<table>
<thead>
<tr>
<th>Green OLED</th>
<th>Simulation Details</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Structure (nm)</strong></td>
<td>Anode/NPB(X)/Alq$_3$(60)/LiF(1)/Al(80)</td>
</tr>
<tr>
<td><strong>Anode (nm)</strong></td>
<td>AZO (610)</td>
</tr>
<tr>
<td><strong>NPB Thickness (nm)</strong></td>
<td>70, 100, 130, 160 and 190 nm</td>
</tr>
<tr>
<td><strong>Recombination Zone</strong></td>
<td>Fixed at the interface between NPB and Alq$_3$</td>
</tr>
</tbody>
</table>

Table 5.8 Simulation details of AZO device with different NPB thicknesses

![Simulation Details of AZO Device with Different NPB Thicknesses](image)

**Fig. 5.20** Simulated transmission spectra of AZO device with different NPB thickness

From **Fig. 5.20**, the cavity of the device was changed when cavity length was increased. Relative transmittance of structure of 160 nm NPB thickness was among the highest and had the greatest outcoupling level at wavelength of 532 nm corresponding to the emission wavelength of Alq$_3$.  

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Fig. 5.21 shows the simulated emission intensity of the AZO device with different NPB thickness. Structure with NPB thickness of 160 nm contributed the highest emission intensity due to more outcoupling light and the highest transmittance under the microcavity effect.

With the use of ETFOS software simulation, the microcavity effect of OLED device could be solved by manipulating the cavity length of the structure. Therefore, the performance of application of AZO in OLED device could be enhanced.
CHAPTER 6 CONCLUSION

To conclude, when oxygen flow ratio was increased, electrical conductivity of AZO thin film became poorer as its resistivity increased dramatically meanwhile optical performance has slightly improved. Without additional oxygen flow, AZO thin films have polycrystalline structure and their crystallinity had a direct proportional relation with oxygen flow ratios. XPS spectra evidently proved the reduction of oxygen vacancies and the oxidation state of Zn when there was an increase in oxygen flow ratio.

The sputter yield has a decreasing trend as the working pressure rose. When working pressure was increased, electrical properties of AZO thin film became better and then degraded after reaching a saturation point. When working pressure was decreased, optical properties of AZO thin film became better and then poorer after a saturation point in visible light range.

When hydrogen flow rate was increased, electrical properties of AZO thin film became better with higher conductivity and then were deteriorated with a drop down in conductivity after a saturated amount of hydrogen flow ratio. When flow rate of hydrogen was increased, optical properties of AZO thin film has slightly been degraded in the average transmittance of the visible light range.

AZO films were more sensitive to the growth environment than ZnO films since AZO had larger lattice parameter variation to changing sputtering condition indicating the easy formation of defects or presence of impurity elements. Moreover, AZO films showed a metal to semiconductor transition in electrical behavior when they were at low temperature.
When sputtering time was increased, crystallinity of AZO thin films became better as grain sizes inside the films grew larger. In addition, it was found that defects came into the films when sputtering time was over 100 mins as the tensile stress of the films exceeded shifting the dominant diffraction peak from (002) orientation angle to (103). Conductivity had a significant increase with increasing sputtering time initially and then had a slight decrease after reaching the minimum resistivity of about $7 \times 10^{-4} \, \Omega \cdot \text{cm}$ at sputtering time $t = 140$ mins. The increase in conductivity was due to the enhancement of carrier concentration and mobility. The average transmittance in visible light range for AZO thin films was increased from 83% to 92% for the sputtering from 20 mins to 140 mins. Higher frequency and blue shift of oscillatory nature occurred for increasing sputtering time.

AZO films are relatively stable in air which is important in application. They could be applied in OLED devices as anodes after optimum sputtering condition was established. In its application, they had to be pre-treated with plasma treatment before the fabrication of OLED. In the performance of AZO devices, it was found that they were very competitive in terms of power efficiency, yield and J-V curve behavior. However, much light was trapped inside them. It could be solved by ETFOS simulation to vary the cavity length of the structure and improve light outcoupling effect.
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