DEPOSITION AND CHARACTERISATION OF SOLUTION PROCESSED INDIUM GALLIUM ZINC OXIDE THIN FILM ON SILICON SUBSTRATE

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by

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TABLE OF CONTENTS

ACKNOWLEDGEMENT... ii

TABLE OF CONTENTS.. iii

LIST OF TABLES vi

LIST OF FIGURES.. vii

LIST OF SYMBOLS... xi

LIST OF ABBREVIATIONS... xii

ABSTRAK.. xiii

ABSTRACT... xv

CHAPTER 1 INTRODUCTION

1.1 Introduction.. 1

1.2 Problem statement.. 2

1.3 Research objectives... 4

1.4 Originality of research work.. 4

1.5 Thesis structure... 4

CHAPTER 2 LITERATURE REVIEW

2.1 Introduction.. 7

2.2 History of IGZO.. 7

2.3 Fundamental properties of IGZO... 10

2.3.1 Amorphous IGZO.. 11

2.3.2 Crystalline IGZO……………………………………..………… 13

2.4 Deposition techniques of IGZO film…………………………………..... 17

2.5 Important experimental parameters………………..…...…………………... 17

2.5.1 Annealing temperature…………………………………………... 20

2.5.2 Annealing time…………………………………………………... 21

2.5.3 Annealing ambient……………………………………………… 23

2.5.4 Effects of molar ratio on IGZO films characteristics……….......... 25

2.6 Summary……………………………………………………………… 27

CHAPTER 3 MATERIALS AND METHODS

3.1 Introduction………………………………….……………………... 29

3.2 IGZO film preparation..…………………………………………………… 31

3.2.1 Synthesis of IGZO precursor solution……………………………... 31

3.2.2 Si substrate preparation………………………………………….. 32

3.3 Spin coating procedures…………………………………………………… 33

3.4 Post deposition annealing process……………..……………………... 34

3.5 Film characterisation…………………………………………………….. 35

3.5.1 Morphological Characterisation – Field Emission Scanning Electron Microscopy with Energy Dispersive X-ray…………….... 35

3.5.2 Topographical Characterisation – Atomic Force Microscopy…..…. 36

3.5.3 Structural Characterisations – X-Ray Diffraction………………….. 36

3.5.4 Optical Characterisations – Ultraviolet-Visible Spectroscopy…….. 38

3.5.5 Functional Group Characterisations – Fourier Transform Infrared Spectroscopy………………..…………………………………..… 38

3.5.6 Optical characterisations – Photoluminescence……………………. 39

3.5.7 Thickness and refractive index characterisations………………….. 39

3.5.8 Electrical characterisations – Current density-gate voltage (J-V_g) and Hall effect measurement…………………………………..... 40

CHAPTER 4 RESULTS AND DISCUSSIONS

4.1 Introduction……………………………………………..……..………… 42

4.2 Effect of annealing temperatures on IGZO film properties………………... 42

4.3 Effect of annealing time on IGZO film properties…………………….…... 62

4.4 Effect of annealing ambient on IGZO film properties…………………….... 78

4.5 Effect of In:G:Zn molar ratio on IGZO film properties……………………. 92

4.6 Evaluation of the optimised film for device application………………….. 111

4.7 Summary……………………………………………………………….. 112

CHAPTER 5 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusion of the study……………………………………………...… 113

5.2 Recommendations for future work……………………………………….. 116

REFERENCES…………………………………………………………….... 118

LIST OF PUBLICATIONS

LIST OF TABLES

Page

Table 3.1 The calculated volume of precursor solutions represented molar ratio of In:Ga:Zn………………………………............................... 32

Table 3.2 Annealing conditions for the study of variation of annealing parameter…………………………………………………………... 35

Table 4.1 Atomic percentage of O, Zn, Ga and In on IGZO films annealed in air, oxygen, nitrogen, and argon ambient and gas density of oxygen, nitrogen and argon……………………………………..…. 81

Table 4.2 In, Ga, Zn and O atomic percentage of IGZO films prepared by different molar ratios; In:Ga:Zn = 1:1:1, 1:1:2, 1:2:1 and 2:1:1…… 94

Table 4.3 Effective ionic radius of In, Ga, and Zn cations…………………...…. 94

Table 4.4 Reported value of energy gap of individual ZnO , Ga_2O_3, In_2O_3, and IGZO materials……………..……………………………..…. 101

Table 4.5 Hall effect result of optimised IGZO film prepared with 1:1:1 (In:Ga:Zn) ratio annealed at 500°C for 30 min in air ambient…….112

LIST OF FIGURES

		Page
Figure 2.1	(a) $InGaO_3(ZnO)$ depicted as a space-filling model along the (001) axis (b) Models of cation coordination……………………...	14
Figure 3.1	Flowchart of fabrication and characterisations process of IGZO film……………………………………………………….....	30
Figure 3.2	The primary process of spin coating IGZO solution onto Si substrate…………………………………………………..….....	34
Figure 3.3	IGZO film on Si substrate with coated Al contacts…………….....	39
Figure 4.1	High resolution X-ray diffraction (HRXRD) patterns of IGZO films as annealed at different temperatures (300, 500, 700 and 900°C)……………………………………………..…….	45
Figure 4.2	Lattice parameter, c of IGZO films as annealed at different annealing temperature (300, 500, 700, 900°C)……………………	46
Figure 4.3	Crystallite size (D) and strain (ε) determined for IGZO films annealed at different temperatures (500 – 900°C) using Scherrer's formula…………………………………………………	47
Figure 4.4	3D surface topographies of IGZO film annealed at different temperatures (a) 300°C, (b) 500°C, (c) 700°C and (d) 900°C…..…………………………………………………	48
Figure 4.5	Surface morphologies at 100kX magnification of IGZO film annealed at different temperatures (a) 300°C, (b) 500°C, (c) 700°C and (d) 900°C………………………………………..	49
Figure 4.6	Schematic energy band diagrams showing direct and indirect transitions of IGZO films obtained at different annealing temperatures (a) 300, (b) 500, (c) 700 and (d) 900°C….	51
Figure 4.7	FESEM cross-sectional images for IGZO film annealed at different temperatures (a) 300, (b) 500, (c) 700 and (d) 900°C…...	55
Figure 4.8	Comparison between film thickness as measured by FESEM cross-sectional (t_{ox}), Filmetrics (t_{fox}) and refractive index of IGZO films regarding annealing temperatures (300, 500, 700 and 900°C)……………………………………………………....	57
Figure 4.9	Photoluminescence (PL) spectra of IGZO sample as annealed at different temperatures (300, 500, 700 and 900°C)……………..	58

Figure 4.10 FTIR absorbance spectra of IGZO sample as annealed at different temperatures (300, 500, 700 and 900°C)……………….. 60

Figure 4.11 Current density vs gate voltage (J-V_g) characteristics of IGZO film annealed at different temperatures (300, 500, 700 and 900°C……………………………………………………………… 62

Figure 4.12 Grazing incidence X-ray diffraction (GIXRD) patterns of IGZO films as annealed at different time (5, 15, 30 and 60 min)……..… 63

Figure 4.13 Crystallite size (D) and microstrain (ε) of IGZO films annealed at different time (5, 15, 30 and 60 min) determined by Williamson-Hall plot……………………..…………………….. 64

Figure 4.14 3D surface topographies of IGZO films annealed at different time (a) 5, (b) 15, (c) 30 and (d) 60 min………………………...…… 66

Figure 4.15 Comparison between film thickness as measured by FESEM cross-sectional (t_{ox}), Filmetrics (t_{fox}) and RMS surface roughness of IGZO films annealed at different time (5, 15, 30 and 60 min)…………………………………………………….. 66

Figure 4.16 Surface morphologies at 100 kX magnification of IGZO film annealed at different time (a) 5, (b) 15, (c) 30 and (d) 60 min……. 67

Figure 4.17 Schematic energy band diagrams showing direct and indirect transitions of IGZO films obtained at different annealing time (a) 5, (b) 15, (c) 30 and (d) 60 min……………………..... 69

Figure 4.18 IGZO film's cross-sectional view as measured by FESEM (a) 5, (b) 15, (c) 30 and (d) 60 min ....…………………………….. 71

Figure 4.19 Energy dispersive X-ray (EDX) analysis on films oxide/Si interface……………………………………………………….….. 71

Figure 4.20 Photoluminescence (PL) spectra of IGZO film annealed at different time (a) 5, (b) 15, (c) 30 and (d) 60 min……………..…. 73

Figure 4.21 Refractive index of IGZO films annealed at different time (a) 5, (b) 15, (c) 30 and (d) 60 min……………………………..… 74

Figure 4.22 FTIR absorbance spectra of IGZO sample as annealed at different time (5, 15, 30, 60 min)……………………………..…... 76

Figure 4.23 Current density vs gate voltage (J-V_g) characteristics of IGZO film annealed at different time (5, 15, 30 and 60 min)…..… 77

Figure 4.24 Grazing incidence X-ray diffraction (GIXRD) patterns of IGZO films as annealed in air, oxygen, nitrogen, and argon

ambient…………………………………………………………..….. 80

Figure 4.25 FTIR spectra of IGZO films as annealed in air, oxygen, nitrogen, and argon ambient……………………………..…….. 83

Figure 4.26 Photoluminescence spectra of IGZO films annealed in different ambient; air, oxygen, nitrogen and argon………..……... 84

Figure 4.27 Schematic energy band diagram of IGZO films as annealed in (a) air, (b) oxygen, (c) nitrogen, and (d) argon ambient……….. 87

Figure 4.28 AFM 3D topographies of IGZO films as annealed in air, oxygen, nitrogen, and argon ambient…………………...……… 87

Figure 4.29 RMS surface roughness and thickness of IGZO films annealed in air, oxygen, nitrogen and argon ambient……………………….. 88

Figure 4.30 Cross sectional image of IGZO films annealed in (a) air, (b) oxygen, (c) nitrogen, and (d) argon ambient…………….…… 89

Figure 4.31 Refractive index of IGZO films as annealed in air, oxygen, nitrogen, and argon ambient…………………………….... 90

Figure 4.32 Current density vs gate voltage (J-V_g) characteristics of IGZO films as annealed in air, oxygen, nitrogen, and argon ambient…… 92

Figure 4.33 Surface morphologies of IGZO films prepared with different In:Ga:Zn molar ratio solution (a) 1:1:1, (b) 1:1:2, (c) 1:2:1 and (d) 2:1:1……………………………………………...….. 96

Figure 4.34 X-ray diffraction patterns of IGZO films prepared by molar ratio of In:Ga:Zn = 1:1:1, 1:1:2, 1:2:1 and 2:1:1……………….…. 97

Figure 4.35 AFM 3D topographies of IGZO films prepared by molar ratio of In:Ga:Zn. (a) 1:1:1, (b) 1:1:2, (c) 1:2:1 and (d) 2:1:1…..... 99

Figure 4.36 RMS surface roughness of IGZO films prepared by molar ratio of In:Ga:Zn = 1:1:1, 1:1:2, 1:2:1 and 2:1:1………………… 100

Figure 4.37 Schematic energy band diagram of IGZO films prepared by molar ratio of In:Ga:Zn. (a) 1:1:1, (b) 1:1:2, (c) 1:2:1 and (d) 2:1:1……………………………………………...… 102

Figure 4.38 Photoluminescence spectra of IGZO films prepared by molar ratio of In:Ga:Zn = 1:1:1, 1:1:2, 1:2:1 and 2:1:1………...…… 104

Figure 4.39 FTIR absorbance spectra of IGZO films prepared by molar ratio of In:Ga:Zn = 1:1:1, 1:1:2, 1:2:1 and 2:1:1………………… 105

Figure 4.40 FESEM cross sectional views of IGZO films showing film

thickness (t_{ox}) prepared by molar ratio of In:Ga:Zn. (a) 1:1:1, (b) 1:1:2, (c) 1:2:1 and (d) 2:1:1 107

Figure 4.41 Film thickness (t_{fox}) and refractive index of IGZO films prepared by molar ratio of In:Ga:Zn = 1:1:1, 1:1:2, 1:2:1 and 2:1:1 108

Figure 4.42 Current density vs gate voltage (J-V_g) of IGZO films prepared by molar ratio of In:Ga:Zn = 1:1:1, 1:1:2, 1:2:1 and 2:1:1 110

LIST OF SYMBOLS

D	crystallite size
d	path difference
I	Current
J	Current density
K	Crystallite-shape numerical factor
k	Dielectric constants
m	Numerical factor
n	Order of diffraction
n	Wavelength number
R	Percentage of reflected light
t	Thickness
V_g	Gate voltage
α	Absorption coefficient
ε	Strain
θ	Bragg diffraction angle
λ	Wavelength
β	FWHM in radian

LIST OF ABBREVIATIONS

E_g^d	Direct energy gap
E_g^{id}	Indirect energy gap
3D	Three dimensional
AFM	Atomic force microscopy
CAAC	c-axis aligned crystal
EDX	Energy dispersive X-ray
E_g	Energy gap
FESEM	Field emission scanning electron microscopy
FTIR	Fourier Transform Infrared
FWHM	Full width half maximum
GIXRD	Grazing incidence X-ray diffraction
HRXRD	High resolution X-ray diffraction
IGZO	Indium gallium zinc oxide
PL	Photoluminescence
RMS	Root-mean-square
RPM	Revolutions per minute
SiO_2	Silicon dioxide
TEM	Transmission electron microscopy
TFT	Thin film transistor
TCO	Transparent conducting oxide
TOS	Transparent oxide semiconductor
UV	Ultraviolet
XPS	X-ray photoelectron spectroscopy

PEMENDAPAN DAN PENCIRIAN FILEM NIPIS INDIUM GALIUM ZINK OKSIDA MENGGUNAKAN PEMPROSESAN LARUTAN ATAS SUBSTRAT SILIKON

ABSTRAK

Penyelidikan ini dijalankan untuk memendapkan filem nipis polikristal indium gallium zink oksida (IGZO) ke atas substrat silikon menggunakan kaedah pemprosesan larutan. Secara khusus, kaedah sol-gel telah dipilih untuk menyediakan larutan bahan IGZO dan kaedah salutan putaran digunakan untuk memendap filem. Filem IGZO polikristal yang optimum ditentukan daripada mengkaji parameter eksperimen iaitu suhu penyepuhlindapan, masa penyepuhlindapan, ambien penyepuhlindapan dan nisbah molar In:Ga:Zn. Daripada kajian ini, didapati bahawa suhu penyepuhlindapan melebihi 500°C telah mendorong pembentukan filem $In_2Ga_2ZnO_7$ polikristal dengan kekasaran punca min kuasa dua (RMS) terendah (3.50 nm), menghilangkan kecacatan liang yang wujud pada permukaan filem, menunjukkan sifat fotoluminesen yang tidak terjejas oleh kecacatan pada filem dan pengendalian arus yang stabil daripada analisis ketumpatan arus (J) lawan voltan get (V_G). Selain itu, penyepuhlindapan filem IGZO pada 900°C telah terbukti mendorong lapisan antara muka (IL) antara oksida/Si. Kemudian, didapati penyepuhlindapan selama 30 minit pada suhu 500°C dalam ambien udara menghasilkan filem IGZO polikristal dengan jurang tenaga 3.26 eV yang mampu menjana ketumpatan arus tinggi tanpa sebarang kerosakan sehingga voltan get 10 V. Daripada kajian ambien penyepuhlindapan, didapati bahawa ambien udara telah membentuk filem IGZO dengan RMS rendah (8.65 nm), indeks biasan rendah, dan kekonduksian arus yang lebih tinggi sebagai

tindak balas kepada peningkatan voltan get. Akhir sekali, IGZO 1:1:1 yang disepuhlindapkan pada 500°C selama 30 minit dalam ambien udara memaparkan ciri-ciri permukaan keseluruhan yang baik, jurang jalur tenaga yang luas (3.26 eV) dan pengaliran arus yang sangat baik. Analisis kesan Hall yang dijalankan pada filem IGZO polikristal yang dioptimumkan telah mendedahkan kepekatan cas pembawa ialah 10^{16} cm^{-3} dan mobiliti Hall ialah 15.2 cm^2/Vs.

DEPOSITION AND CHARACTERISATION OF SOLUTION PROCESSED INDIUM GALLIUM ZINC OXIDE THIN FILM ON SILICON SUBSTRATE

ABSTRACT

This research was conducted with an objective to deposit optimum polycrystalline indium gallium zinc oxide (IGZO) on silicon (Si) substrate by using solution processed method. Specifically, sol-gel method was selected to prepare IGZO precursor solution and spin coating method was used to deposit the film. The optimised polycrystalline IGZO film was determined from studying the experimental parameters which were annealing temperature, annealing time, annealing ambient and In:Ga:Zn molar ratio. From this study, it was obtained that annealing temperature above 500°C has induced the formation of polycrystalline $In_2Ga_2ZnO_7$ film with lowest root-mean-square (RMS) roughness (3.50 nm), vanished the void defects existed on the film's surface, displayed undegraded photoluminescence property due to films' defects and stable current conductivity from current density (J) vs gate voltage (V_G) analysis. Besides, annealing the IGZO film at 900°C has proven to induce interfacial layer (IL) between oxide/Si. Later, it was found that 30 min annealing at 500°C temperature in air ambient produced polycrystalline IGZO film with 3.26 eV energy gap which is able to generate high current density without any breakdown up to 10 V gate voltage. From the study of annealing ambient, it was found that air ambient has established IGZO film with low RMS (8.65 nm), low refractive index, and higher current conductivity in response to increasing gate voltage. Finally, IGZO 1:1:1 annealed at 500°C for 30 min in air ambient displayed the overall acceptable surface characteristics, wide energy band gap (3.26 eV) and excellent current conduction. Hall effect analysis conducted on

optimised polycrystalline IGZO film has revealed the carrier concentration of 10^{16} cm^{-3} and Hall mobility of 15.2 cm^2/Vs.

CHAPTER 1

INTRODUCTION

1.1. Introduction

The interest in semiconductor technology was undeniably growing since it was discovered as far back as 1821 [1]. Semiconductor materials has been used in numerous different applications such as laser diodes [2], solar cells [3], integrated circuits [4], and others. With the grow of scientific exploration, semiconductor technology has become an important field of science which the interest is drawn towards material understanding and control of the material properties before it could be implemented into electrical and electronic devices.

Transparent oxide semiconductors (TOSs) are a class of inorganic oxides based on multi-component combinations of post-transition metal cations with $(n\text{-}1)d^{10}ns^{0}$ electronic configuration ($n \geqslant 5$) [5]. TOSs are usually transparent from the infrared to the visible spectrum due to a large bandgap (>3.2 eV) [6]. In addition to transparency, TOSs have high electrons mobilities even in their amorphous phases due to the special electron structures [6]. This makes them very promising for transparent thin-film transistor (TTFTs) applications. Indium gallium zinc oxide (IGZO) is a TOS that was known as a compound semiconductor material, consisting of indium (In), gallium (Ga), zinc (Zn) and oxygen (O) that typically used in thin film transistor (TFTs) technology [7–9]. IGZO has the advantages of high electron mobility [10] and high transparency due to its wide bandgap (~3.5 eV) [11].

In comparison to amorphous silicon (a-Si) and organic semiconductors, IGZO based TFTs owns several advantages such as the magnitude of electron mobility is at

least one or two orders higher even in the amorphous state (a-IGZO) (>10 cm^2/Vs), low process temperatures for the amorphous phase including room temperature deposition makes it possible to deposit the film on flexible substrates, good transparency to visible light makes it more suitable in display applications and transparent circuits, non-toxic and costly effective to fabricate [12]. These advantages make IGZO as transparent oxide semiconductor a futuristic candidate for the next generation large screen flat panel displays and flexible electronics.

1.2. Problem statement

Abundant studies on the amorphous IGZO (a-IGZO) had been reported due to its preferable low deposition temperature of markedly below 300°C [10]. In general, low temperature process would cut costs and simplify the film growth process but nonetheless came with drawbacks. One of the challenges of low-temperature deposition is a-IGZO could suffer from defects namely hydroxyl group impurities, surface defects such as voids that would eventually act as charge trap [13]. The identified problems in the synthesis of IGZO films were mostly related to the presence of native and induced defects, both within the volume of the material such as oxygen vacancy, interstitial atoms and at the surface that would interact with other layers such as interfacial layer. Thus, to improve a functional IGZO-based device performance, it was highly necessary for IGZO film deposited at low temperature to undergo additional steps to improve film characteristics. Heat treatment is one of the steps that is carried out post film deposition with aims to modify properties in terms of morphology, topography, structural, optical and electrical [14, 15].

While solution processed suits the requirement of low temperature deposition for amorphous IGZO, systematic study on the polycrystalline IGZO films has never been reported. Polycrystalline IGZO could be realised by annealing treatment at specific

range of temperature in between the temperature that produced amorphous structure and single crystal structure [16]. As, the formation of a-IGZO usually required low temperature below 300°C [10] while single crystal could be formed at higher temperature, in some cases it varied from 700°C to 900°C [17–19], thus, varying the annealing temperature from 300°C to 900°C would be useful to get polycrystalline IGZO structure. It is understood that the outcome of the heat treatment process is also influenced by parameters such as annealing time and annealing ambient. For instance, annealing treatment up to 60 min at 300°C would likely form strong M-O bonds in the compound semiconductor and reduce the formation of deep trap that could cause charge scattering and lower charge mobility [20]. On the other hand, various ambient such as air, oxygen rich (oxygen), oxygen deficient (nitrogen) and noble gas (argon) would bring significant effects towards polycrystalline IGZO film in determining the defect sites formed inside the material and, hence, have a significant influence on the carrier concentration and carrier mobility [21]. In addition, for a multicomponent oxide semiconductor like IGZO, each metal cation is known to contribute to film carrier concentration and carrier mobility. For example, In^{3+} would favour to higher carrier mobility due to the overlap of the 5s orbital [22] while Ga^{3+} is responsible to control the free carriers by the formation of strong bond with oxygen [23]. Therefore, varying the molar ratio as 1:1:1, 1:1:2, 1:2:1 and 2:1:1 would be relevantly useful in this study.

Due to the importance of heat treatment and varying the molar ratio of In:Ga:Zn towards regulating the carrier concentration and carrier mobility of polycrystalline IGZO film that has been mentioned, this research work is conducted to study and systematically report the properties of polycrystalline IGZO film on the changes made in annealing parameters and evaluate the optimised IGZO film for its carrier concentration and carrier mobility.

1.3. Research objectives

This research aimed to address the following objectives:

I. To deposit polycrystalline IGZO film via solution processed method which adopts ultrasonic bath process in the solution preparation.

II. To determine the parameters in optimising polycrystalline IGZO film from changing the annealing temperature, annealing time, annealing ambient and In:Ga:Zn molar ratios.

III. To evaluate the use of optimised polycrystalline IGZO film as transparent oxide semiconductor (TOS) in terms of mobility and carrier concentration.

1.4. Originality of research work

Deposition and characterizations of amorphous IGZO film had been continuously reported especially for active channel layer use in thin film transistor due to its low processing temperature. Research gap in the study of solution processed polycrystalline IGZO film on silicon substrate which systematically reported the effect of changing pre and post deposition parameter towards the films' properties is noticed. Furthermore, the adoption of ultrasonic bath in the preparation of homogenous IGZO precursor solution has never been reported for IGZO elsewhere but have been reported numerously for TiO_2 [24] and ZnO [25]. Therefore, in this study, preparation of polycrystalline IGZO solution will be assisted by ultrasonic bath and the characteristics of polycrystalline IGZO film will be investigated as annealing temperature, annealing time, annealing ambient and In:Ga:Zn molar ratio change.

1.5. Thesis structure

This thesis comprises of five main chapters that are mainly split into research backgrounds and experimental section.

Chapter 2 provides and introduction and the literature review of the topic. The flow of the literature starts with the history of IGZO material followed by the properties of IGZO material that had been reported by far. The scarcity in the study of polycrystalline IGZO could be noticed as reports were mostly about amorphous and single crystal IGZO. It discussed the comparisons of amorphous and crystal IGZO films and reveal the importance of studying polycrystalline IGZO film via solution process. Additionally, the uses of IGZO in various applications were elaborated.

Chapter 3 presents all the materials and apparatus involved in this study and the method chosen to carry out the research work including the theory and working principles of the selected method. It describes the preparation steps of the precursor solution and substrate, deposition technique of IGZO films, post-deposition treatment process and the potential advantages of the selected approach. It also describes the flow of the experiment from varying the annealing temperature, annealing time, annealing ambient and finally the molar ratio of In:Ga:Zn.

Chapter 4 presents the enriched discussion of the results obtained from the experiments. Outcomes from each characterization technique were analysed and examined. Polycrystalline IGZO film characteristics due to the change of the experimental parameter were sought through its morphological, topographical, structural, optical, and electrical analysis. The optimum parameters were identified from the overall film's behaviour and the evaluation of the film for transparent oxide semiconductor is elaborated.

Chapter 5 concludes the study with an overview of the research achievement and a discussion of research highlights that contributed to optimum carrier concentration and carrier mobility. Finally, few suggestions regarding this topic are listed out for any improvement in future research related to polycrystalline IGZO materials.

CHAPTER 2

LITERATURE REVIEW

2.1. Overview

This chapter will present the literature review and the determined research gap that has led to this research being conducted. To begin, basic understanding of metal oxides will be introduced and some of the applications in electronics will be described in this chapter. Next, the progress of semiconductor material development from the conventional SiO_2 to InGaZnO (IGZO) will be clarified. The three categories of material namely conductor, semiconductor and insulator will be elaborated. Then, the fundamental characteristics of IGZO semiconductor material will be discussed. The established methods for polycrystalline IGZO film deposition will be listed and the review on solution processed method to synthesise various metal oxide semiconductor is also highlighted. Afterwards, an in-depth discussion of how annealing parameters including annealing temperature, annealing time, and annealing ambient with a particular focus on IGZO-based device including other material, that were generally obtained from the literature review will be presented. Finally, the influence of molar ratio as an important component in solution process is mentioned.

2.2. History of IGZO

Metal oxides had wide variety of applications in electronics in three major categories. It has been known to serve as both dielectric or conductive materials in transparent and flexible applications. Apart from that, metal oxide was also very promising in semiconducting applications. As the size of silicon transistor had evolved to a reduced thickness of approximately less than 1 nm to meet commercial pressure

in producing ever higher functionality at lower costs, gate leakage current has surfaced as a limiting factor [26]. Thus, to solve the problem, materials with higher dielectric constants (k), was introduced to replace the conventional SiO_2. High-k dielectrics would cancel the aforementioned issue by the ability to allow equivalent capacitance density in a physically thicker oxide [27].

Metal oxides with high-k dielectrics were available many forms, most commonly in binary metal oxides such as Ta_2O_3 [28], Al_2O_3 [29], and ternary metal oxides such as La-doped ZrO_2 [30], $GdScO_3$ [29]. To date, the research on optimising metal oxide as dielectric layer was ongoing whereby recently, the work has brought to creation of multi-layered dielectrics incorporating different high-k metal oxides stacked together for even better device performance [31].

The second major use of metal oxide was as conductive component usually formed into electrodes on display applications [32]. In other words, transparent metal oxides that were channelled into conductive used was termed as transparent conductive oxides (TCOs). The first few TCOs reported in history was back in 1907 where the conductive properties of CdO, Cu_2O, and PbO were proposed. But only in the 20s century after the vacuum technology has been established, more metal oxide was developed and became significantly useful in electronics devices and other field which include as anti-static coatings, glass coatings, heat reflecting and window heating elements [33, 34].

The most renowned TCOs during that time was indium tin oxide (ITO) due to its film conductivity tunability via the control of Sn incorporation. Then the use of metal oxide as TCO_S progressed from front electrode in rectifying photocells to the gate electrode in flat panel displays. Later, ITO was used as both the gate electrode and source/drain electrodes in the fabrication of fully transparent thin film transistor (TFT).

The impact of rapid technological change has put on a higher demand on TCOs material as the field of thin-film electronics moved towards flexible applications [11].

The realisation of a metal oxide being used as semiconductor in TFT was introduced by Klasen and Koelmans (1964) after developing a new back-side exposure process for photolithography of transparent semiconducting oxide (TSO), SnO_2 to create a self-aligned TFT structure back in the 60s [35]. The discovery had urged the efforts in unfolding more metal oxide-based films such as SnO_2 carried out by Aoki and Sasakura in 1970 and Boesen and Jocobs in 1968 with lithium doped zinc oxide (ZnO:Li). Work continued sporadically on metal oxide transistor devices with reports such as Sb doped SnO_2 (SnO_2:Sb), In_2O_3 and ZnO until finally in 2003, the work of Hoffman et al. on ZnO recorded a satisfying electrical performance for a metal oxide based TFT.

The important work of Hoffman et al., along with work from Carcia et al. and Masuda et al. was the kick-off to a new era of research in metal oxide semiconductors in electronic applications and ever since, numerous remarkable improvements in material performance and variations in deposition methods were reported, not only on ZnO but also on other binary material like SnO_2 and In_2O_3 films. However, TFTs based on these binary oxides (ZnO, SnO_2, In_2O_3) withal comes with shortcomings particularly with the control of the threshold voltage (V_{th}), device stability, and surface uniformity. These limitations originated from the high concentration of residual free electrons due to native defects, such as zinc interstitials and oxygen vacancies was presented in the material, leading to large number of free electrons. Another issue with ZnO was the creation of grain-boundary free film was very challenging where most studies would ultimately result in polycrystalline ZnO devices with disparities in device performance [36].

Therefore, in 2003, as an effort to fix the problems, Nomura et al., established a more complex multicomponent oxide of InGaZnO (IGZO) for TFT application. Implementation of single crystal IGZO had successfully gotten rid of the grain boundaries issues and eventually improved the density of defects and normally off TFTs at 0 V gate bias was achieved. Furthermore, crystalline IGZO-based TFTs managed to demonstrate other accountable excellent characteristics of TFTs such as high mobility of 80 cm^2/Vs, threshold voltage (V_{th}) = -3 V, and an on-off current ratio of 10^6.

In the following year, the same group led by Nomura et al. discovered amorphous IGZO (a-IGZO) whereby its utilization as channel layer in TFT has proven to show comparably satisfying results as crystalline IGZO TFTs [37]. The work employed a room temperature deposition to obtain a-IGZO which exhibited Hall effect mobilities larger than 10 cm^2/Vs, which had a significantly larger magnitude than the conventional a-Si:H. The flexible and transparent TFTs device was showing good electrical characteristics and stable during repetitive bending test [37]. The abovementioned work had been a turning point in semiconductor technology which later attracted vast interest of research on this leading material with majority of the studies were inclined towards a-IGZO due to its low processing temperature.

2.3. Fundamental properties of IGZO

InGaZnO which is simply known with acronym IGZO is a compound with the combination of indium (In), gallium (Ga), zinc (Zn) and oxygen (O). IGZO was originally founded by Kimizuka et al. for the first time in 1985 [38]. In his work, Noboru Kimizuka had pioneered the idea of crystalline IGZO ceramics using thermal annealing at 1400°C for 30 min. IGZO compound is defined by the general formula $(InGaO_3)_x(ZnO)_y$ where x and y are natural number [39].

IGZO is constantly being researched because its reproducibility through simple fabrication process yet still possesses good stability, and shows the most commercial potential among other materials [40]. IGZO has wide bandgap (~3.5 eV), high transparency in visible region [17] which was superior for transparent electronic, high electron mobility and suitable for large-area deposition [41].

Historically, every element included in the IGZO structure for its own unique contributions, which led to Ga incorporation in the well-known binary oxides, InZnO (IZO) TFTs [42]. Since GaZnO (GZO) has a lower mobility than that of IZO and Ga would bond stronger to oxygen than either Zn or In ions. Thus, Ga^{3+} would help in suppressing the oxygen vacancies defects in IGZO thin film and thus further controlling the carrier concentration in IGZO. In^{3+} cations contribute to a high mobility due to an overlap of its 5s orbitals and Zn^{2+} offers stabilization and an enhancement of electrical properties [42].

In IGZO, the valence band is formed primarily by O 2p and Zn 3d-orbitals, while the conduction band is formed by the s and p orbitals of the three metals with some influence by the O 2p-orbitals [43]. The electronic configurations of In^{3+}, Ga^{3+} and Zn^{2+} are $4d^{10}5s^0$, $3d^{10}4s^0$ and $3d^{10}4s^0$, respectively. IGZO structures are divided into two main categories, either amorphous or crystalline. While most of reported studies were inclined towards amorphous IGZO due to its low processing temperature, crystalline IGZO is nevertheless importantly studied.

2.3.1. Amorphous IGZO

Amorphous IGZO (a-IGZO) represented a revolutionary idea that comes in a package of low temperature deposition process but results in ultrasmooth surfaces that suppress interface traps and avoid scattering efficiently [23]. The special feature of a-IGZO not having grain boundaries would obviates the primary limitation of mobility

exists in other polycrystalline semiconductors, which is a huge advantage for process integration [23]. a-IGZO can be prepared at room temperature and reported as stable up to 500°C while maintaining its great properties as comparable to the crystalline IGZO. The reason that a-IGZO would retain in amorphous state at higher temperature (<500°C) was due to the pure Ga_2O_3 that naturally prone to exist in the amorphous phase. Furthermore, Ga_2O_3 inclusion disrupts the crystalline process of ZnO and/or In_2O_3 because of difference in oxygen coordination numbers [43].

In the case of TFTs, a-IGZO film has been the crowd favourite to use as a channel layer because its Hall mobility was greater than 10 cm^2/Vs [44] and its low toxicity makes it more advantageous over other amorphous oxide materials [45]. Furthermore, IGZO was less sensitive to the disorders regardless of its state [46]. The conduction band of a-IGZO is defined by the In 5s orbital hybridised with oxygen 2p states that forms the transport path for carrier electrons. The orbitals overlap among the neighbouring metal ns orbitals is regardless of the distorted metal-oxygen-metal scattered in the IGZO amorphous structure [47]. Therefore, it exhibit very high electron mobilities even in the amorphous phase, comparable to the mobilities of crystalline IGZO [48].

The issue that has been regarded to low deposition temperature is the incomplete dihydroxylation process. In that case, a-IGZO is believed to consist high amount of the organic O-H complexes that would results in charge trap due to its polar nature. Besides, it also associates with different types of defects and further increases the concentration of free carriers. So, the depositing temperature must be carefully adjusted to avoid those organic residuals [49]. a-IGZO fabricated at room temperature is vulnerable in some manufacturing processes, such as etching and sputtering. Furthermore, reliability of a-IGZO TFTs such as degradation under bias temperature

stress remain unresolved. From an industrial point of view, device reliability is one of the most crucial aspects. Thus, a-IGZO use in TFTs for commercial products is highly concerned [13].

2.3.2. Crystalline IGZO

Kimizuka et al. was the first to study the structure of IGZO compounds in 1985 by synthesising single crystal $InGaO_3(ZnO)_y$ powder compounds from constituent In_2O_3, Ga_2O_3, and ZnO powders. IGZO compound is categorised as homologous oxides with the formula $RMO_3(ZnO)_y$ (R = Sc, In; M = Al, Ga, Fe) with a structure composed of y ± (M/Zn)-O blocks sandwiched between alternating RO_2 layers [50]. Kimizuka et al. found that $InGaO_3(ZnO)_y$ adopt R3m symmetry when y is odd and $P6_3/mmc$ when y is even [51, 52]. An example structure for $InGaO_3(ZnO)_y$ for y = 1 composition is shown in Figure 2.1 where In cation planes are marked by the purple lines while mixed Ga/Zn cation planes are labelled by the mixed green and gray lines.

Unlike a-IGZO, crystalline IGZO is less preferrable due to higher temperature requirement (>500°C) that limits the choice of substrate [53]. However, there are still number of studies that work on crystalline IGZO films. It is interesting to recall that the first IGZO compound semiconductor reported by Kimizuka and Mohri was in crystalline phase [38]. Fundamentally, crystal state of IGZO is differentiated into two other groups; the first group requires lower processing temperature is called crystalline IGZO which includes c-axis aligned crystal (CAAC) IGZO and nanocrystalline IGZO. The second group requires specific processing temperature is called crystal IGZO which includes single crystal IGZO and polycrystal IGZO.

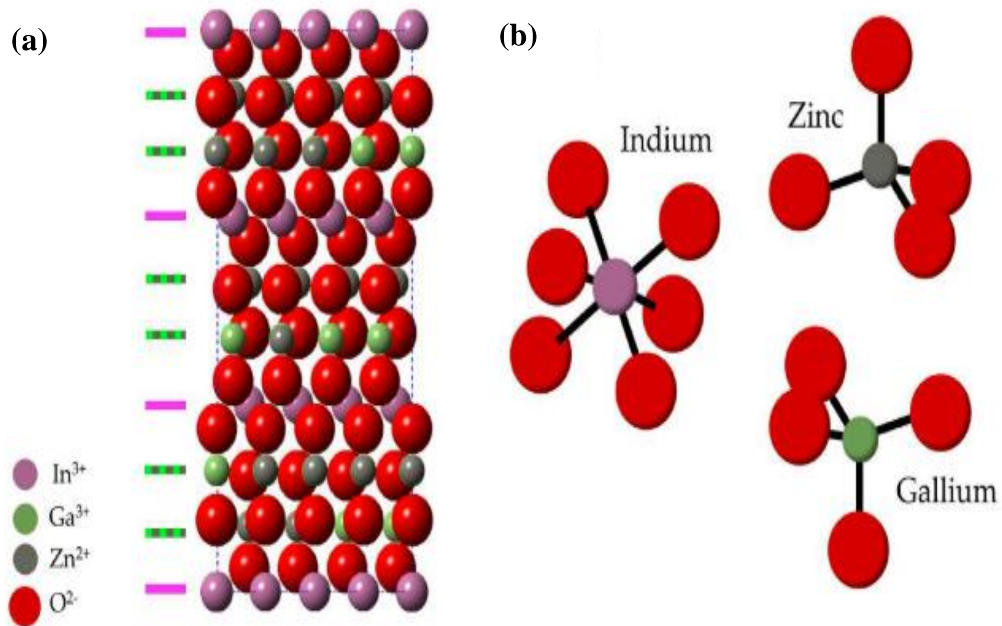


Figure 2.1 (a) $InGaO_3(ZnO)$ depicted as a space-filling model along the (001) axis (b) Models of cation coordination [54].

CAAC-IGZO could be defined as the intermediate crystalline phase that has a structure in between an amorphous structure and a crystal structure. In a report, Yamazaki demonstrated a nano crystallised IGZO film showing strong crystallographic texture, referred to as CAAC-IGZO. In the study, IGZO layer was sputtered onto substrate heated to 300°C to form CAAC-IGZO and further annealed at 450°C to improve film uniformity and an increase the quality of c-axis-aligned crystalline regions. The study focused on the morphology of the film and its behaviour as TFTs wholly [55] and stated that CAAC material has excellent uniformity and stability as the amorphous phase and exhibits remarkably low leakage currents (10-24 A/µm). Nevertheless, the field-effect mobility value was below 10 cm^2/Vs. In one hand, it showed that a low-temperature crystallization technique managed to yield good mobility of IGZO for TFTs application while on the other hand, the grain boundaries in polycrystalline IGZO might form energy barriers that impede the charge carrier

conduction, sometimes resulting in degradation of electron mobility to values lower than that of a-IGZO [56].

Variations in crystallisations temperature is noticed in the literatures. For example, Kumar et al. reported that a-IGZO started to be polycrystalline above 500°C [57]. In contrast, Yang at al. produced polycrystalline IGZO at much lower temperature of 95°C using polycrystalline IGZO nanoparticle gel obtained at 180°C prior to film deposition [48].

It is certain that formation of single crystal IGZO would involve higher processing temperature to catalyst nucleation and bring the atoms together. Kimizuka used elevated temperature of 1400°C in the attempt to establish IGZO compound for the first time [38]. In one of many available reports on single crystal IGZO, Kim et al. addresses that the employment of epi-grown ZnO thin film as a seed layer has successfully promoted crystallization of the multicomponent oxides and produces single-phase IGZO at 900°C [18] and similarly, ZnO buffer layer assisted growth of single crystal IGZO at 900°C [19]. In a different study, Jo et al. reported that single crystal IGZO could be formed with the minimum temperature of 850°C and confirmed through transmission electron microscopy analysis (TEM) that the transformation of IGZO structure from amorphous to crystal phase occurs at 700°C [17]. By reviewing these aforementioned studies, it is justified that varying the annealing temperature would result in different IGZO structure.

Crystalline IGZO films exhibit some advantages over the a-IGZO films such as better acid corrosion resistance by 74% higher, indicating that crystalline IGZO film can provide more stable performance in applications [13]. However, application of high temperature could undermine IGZO properties. Suko et al. stressed in term of

TFTs performance that crystallisation at higher temperature (600-800°C) has deteriorated the field effect mobility owing to the effect of grain boundary scattering.

From few reports mentioned above, we noticed that crystallization temperature may differ depending on the deposition method, ambient ratio, and film thickness [13, 58]. However, it is noticed that regulating the experimental parameters such as annealing temperature would not only affect the crystallisations but the overall film properties. Furthermore, in order to expand the use of a material, the understanding about material behaviour towards various experimental parameters is very important. For instance, for a metal to carry a capacitive role, polycrystalline films may be preferable to amorphous films since it probably has higher density and higher dielectric constant [59]. The development and improvement of IGZO is of particular interest because it has high potential for future applications such as gas sensors [60], biosensor, and others [49]. Today, the utilization of IGZO material was not limited only for display devices but has expanded into different types of applications. For example, memristive devices based on IGZO film for neuromorphic applications was reported recently by Azevedo Martins et al. The IGZO-based memristor successfully operated at a low voltage, shows good endurance, and retention up to 10^5 s under air conditions [61, 62]. Besides, IGZO material was also recently used in IGZO-based Schottky diode [40] and IGZO-based CBRAM devices [63].

Since IGZO has bright futures in wide applications, it is motivational to study IGZO films properties thoroughly before implementing it to any devices. Studies on unitary and binary metal oxides thin film such as ZnO [64–70], AlZnO [71–73], InZnO [74] properties has been reported abundantly. However, for IGZO, a systematic discussion about the influence of changing an experimental parameter towards the alteration in morphological, structural, optical, and electrical properties of IGZO films

and how does each behaviour relate to other properties was barely reported, especially for crystalline IGZO.

2.4. Deposition techniques of IGZO film

It is acknowledged that various experimental parameters, including the film formation methodology are prominent to determine IGZO films properties. From a simple setup to a high vacuum process, various techniques have been established to deposit a uniform IGZO films, which includes sputtering [76–78], pulse laser deposition (PLD) [46,79-80], solution-process [81–85] and metal-organic chemical vapor deposition (MOCVD) [85, 86].

Solution process is a great approach to deposit IGZO film especially at the research level. Basically, solution process begin with preparation of substrate and precursor solution, followed by film deposition step like spin coating [87]. Comparing the solution process to the physical high vacuum method, spin coating method has many advantages for depositing multicomponent oxide semiconductors, such as simple operation, easy control over the solution composition ratio and film thickness and costly efficient [88, 89]. In a more general manner, solution processed oxide semiconductor is likely promising for future low-cost applications [90]. Sol-gel method was among the famous route in preparing metal oxide thin film such as ZnO [3], and TiO_2 [24] using acetate and nitrate precursors. The solution was continuously stirred at temperature around 70°C for 30-60 min in environments such as nitrogen and air, followed by film deposition by dip or spin coating [87].

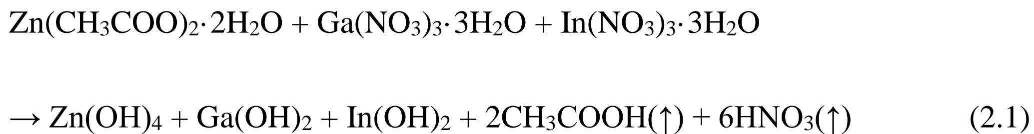
2.5. Important experimental parameters

Spin coating method generally comes along with few steps so the desired film characteristics could be obtained. Chemical conversion of the precursor material into

stable oxide film requires specific amount of thermal energy which is supplied through an annealing process. Commonly, solution process IGZO used zinc acetate dihydrate [$Zn(CH_3COO)_2{\cdot}2H_2O$], gallium nitrate hydrate [$Ga(NO_3)_3{\cdot}xH_2O$] and indium nitrate hydrate [$In(NO_3)_3{\cdot}xH_2O$] as the main source of In, Ga and Zn.

There are three basic stages that occur at three different temperature levels. From thermogravimetric analysis (TGA) of IGZO precursor solution, the three levels could be presented as first, the low temperature (60-130°C) where large weight is lost due to decomposition followed by hydrolysation of solution to M–OH. The second part is when temperature is slightly elevated to 190-210°C, dehydroxylation and alloying took place where film loses the hydroxyl component and the combination of InGaZnO develop. The final stage occurs at higher temperature which is in range of 305-420°C is crystallisation stage where atoms in IGZO alloy started to get organised [89]. An example of formation of IGZO metal oxide film from precursor solution as a function of temperature could be understood as below:

1. Decomposition and hydrolysis (60-130°C)



$$Zn(CH_3COO)_2{\cdot}2H_2O + Ga(NO_3)_3{\cdot}3H_2O + In(NO_3)_3{\cdot}3H_2O$$
$$\rightarrow Zn(OH)_4 + Ga(OH)_2 + In(OH)_2 + 2CH_3COOH(\uparrow) + 6HNO_3(\uparrow) \qquad (2.1)$$

2. Dihydroxylation and alloy (190-210°C)

$$Zn(OH)_2 + Ga(OH)_3 + In(OH)_3 \rightarrow InGaZnO_4 + 4H_2O(\uparrow) \qquad (2.2)$$

3. Crystallization (305-420°C)

$$\text{amorphous } InGaZnO_4 \rightarrow \text{polycrystalline } InGaZnO_4 \qquad (2.3)$$

The annealing process has two stages which is called pre-annealing and post-annealing. Pre-annealing is carried out briefly at lower temperature in between coating

in order to dry up the solvent and form a solid layer. On the other hand, post-annealing is usually realised for a longer period at higher temperature. For instance, high-quality solution-processed metal oxides film requires annealing temperature exceeds 300°C [86]. Other purpose of post-annealing the film includes but not limited to remove impurities, promote metal-oxide bond formation and crystallisation, and decrease the concentration of defect states [91]. Many available studies agree that annealing treatment is necessary in solution process method of growing film. For example, Street at al. claimed that by annealing at a relatively high temperature of 300-500°C, IGZO films coated on glass substrates are densified [92]. In different studies, Sundraresan et al. stated that post-annealing has created well-defined and uniform grains on ZnO films [93] and Yadav et al. stressed that annealing treatment is one of the main factors that affect morphology and optical properties of sol-gel ZnO films [94].

In addition, Lee at al. explained in a study of post-annealed IGZO TFTs with high-k Al_2O_3 gate dielectric that annealing step can improve or degrade the electrical characteristics of the TFT as it change the chemical and physical properties of the whole TFT and highly recommended a thorough study about the influence of the post-annealing on film properties [95]. Similarly, Pham et al. discusses the importance of detailed analysis on IGZO film properties as it could induce point defects which would result in modification in the thermoelectric properties [96]. Hwang et al. in a study of solution-processed IGZO emphasised the importance of annealing to complete material decomposition and oxidation and implied that the study of film properties must be presented in detailed [97].

Annealing of IGZO film is performed at a specific temperature for an appropriate period in a controlled ambient to obtain its desired characteristics. Many previous

works have inspected various parameters subjected to different annealing temperature, time and ambient in the studies of IGZO films and IGZO-based applications.

2.5.1. Annealing temperature

Previous works on metal oxides has acknowledged the importance of varying annealing temperature in their works but there are inconvenient number of studies that systematically report on the effect of the variation on material properties. Commonly, the discussions were limited to the performance of TFTs in terms of transfer and output characteristics. For example, Wang and Furuta observed the changes in TFTs performance after annealed the entire TFTs at 300, 350, and 400°C in nitrogen atmosphere for 1 h [98]. Similarly, Street et al. applied different annealing temperature in the range 350−500°C to IGZO TFTs and presented the effects in the scope of TFTs performance [92]. Exceptionally, Park et al. annealed samples before depositing electrodes to eliminate interaction between the separate layers during annealing, using a tube furnace at temperatures of 300, 600, 800, and 1000°C in air ambient for 1 h yet all results were in the scope of TFTs performance [99]. A comparison study between rapid thermal annealing (RTA) at 600°C and conventional thermal annealing (CTA) at 500°C was also discussed in terms of operation characteristics of IGZO-based TFTs [100].

Occasionally, it is notable that some studies discussed the effect of annealing in terms of film's physical, optical, and electrical properties from field emission scanning electron microscopy (FESEM) [96], transmission electron microscopy (TEM) [97], X-ray diffraction (XRD) [97, 96] analysis, film transmittance [97] and Hall effect measurement [96]. Few studies also included photoluminescence (PL), Fourier transform infrared (FTIR) analysis, and X-ray photoelectron spectroscopy (XPS) [96]. For example, Shin et al. [101] addressed the occurrence of an initial crystallization of

IGZO structure detected using XRD analysis when annealed at 700°C. In another study, Pham et al. [96] emphasised that IGZO crystallinity was dependent on annealing temperature and it also influence photoluminescence behaviour from emergence of PL peaks and changes in peaks intensities. Jeon et al. studied co-sputtered IGZO deposited on glass substrates using In_2O_3 and GZO targets that were annealed at 100, 200 and 300°C for 30 min. From AFM analysis, a lower root mean square (RMS) surface roughness (1.09 nm) was observed and significantly a low electrical resistivity (3.2×10^{-4} Ω·cm) were obtained through Hall effect measurement using the highest annealing temperature (300°C) [102]. Kumar et al. established a-IGZO films by magnetron sputtering, annealed the films in a tubular furnace for 1h at 400 and 500°C in a mix ambience of nitrogen and oxygen gas at a flow rate of 3 sccm and results were observed through XRD, XPS and capacitance-voltage (C-V) data [57].

2.5.2. Annealing time

The importance of annealing dwell time parameter is undebatable in growing a good quality metal oxide film. Correct annealing would ensure complete process of decomposition and oxidation and prevent film from generating defects and which would further result in changes of the film properties [67]. Defects of metal oxide films are classified into few categories which include but not limited to morphological defects, surface detects [103], grain boundaries, crystal defects [104], dislocations and point defects such as zinc interstitials, oxygen vacancies [97] and zinc vacancies [105].

Thus, apart from establishing a suitable annealing temperature, controlling the annealing dwell time is believed to allow more rigorous manipulation of film characteristics and the effect could be clearly observed based on the previous studies. For example, Troughton et al. has deposited a-IGZO film by pulsed direct current (DC) magnetron sputtering and annealed at low temperature annealing (<300°C). Result has

confirmed a reduction in the film density when annealing time exceeded 3h due to oxygen absorption [106]. Chowdhury et al. investigated the effect of annealing time towards bias stress and light-induced instabilities of a-IGZO TFT. XPS data showed increment in binding energy with respect to annealing time which suggested the occurrence of a more ordered amorphous IGZO network, a lower concentration of native defects, and a less possibility of defect generation during device operation [107]. Some studies suggested a long annealing time to gain better characteristics. For examples, Jeon et al. implemented a 10 h annealing at 250°C for a-IGZO TFT in order to bring about stronger M-O bonds and less O-H bonds that consequently moved threshold voltage (V_{th}) into positive gate direction and improved positive bias stability [108]. In a similar manner, Li et al. observed V_{th} and device stability subjected to 200°C annealing for 0, 1, 2, 3 and 4 h durations and confirmed that a-IGZO TFT annealed for 4 h exhibited a better V_{th} and was more stable under gate bias stress [109].

More studies regarding the effects of annealing time were conducted previously on ZnO thin films. Data has shown changes in oxygen interstitial and zinc interstitial portrayed through changes in photoluminescence peak shifting and changes in luminescence intensity of deep level emission area with the adjustment of annealing time for ZnO film [65, 110, 111]. Besides, Kumar et al. and Shu-wen reported [112, 113] increment in ZnO film conductivities as annealing time was increased. Considering majority of the previous studies have reported about the effect of annealing time on the properties of a-IGZO at device capacity, it is convinced that there is a gap in the systematic study of annealing dwell time effects towards IGZO films in obtaining high charge mobility and controlled carrier concentration for optimum transparent oxide semiconductor.

2.5.3. Annealing ambient

Annealing ambient take as much role as the temperature and dwell time in determining the properties of IGZO film, regardless of the deposition parameter [114]. Different ambient like nitrogen and oxygen could change the chemical composition of a film, effectively alter the content of oxygen ions and oxygen vacancies and modify the electrical characteristics of film [46], transform the morphology of the film and disturb the interface between layers [115] and in the case of forming gas ambient, hydrogen passivates the interface traps on the films [116].

Electrical characteristics of IGZO-based oxide TFTs especially the instability of TFTs under bias stress has a strong function with the annealing ambient. To limit the existence of water or oxygen molecules on the interface of channel and dielectric layers, the principal mechanism of ambient leading the change of properties is necessary to study [117]. Number of studies had published results of annealing IGZO in various ambient conditions. Park et al. convinced that proper annealing ambient was crucial since it contributed to modifications in the IGZO internal structure and led to an enhancement in the oxidation state of the metal that subsequently eliminated oxygen vacancies defects. In the study, oxygen was decided as an effective ambient for controlling the carrier concentration of the active layer, decreasing electron traps, and enhancing TFT performance [115]. Huang et al. addressed the improvement and reliability of IGZO TFT when annealed in oxygen ambient compared to nitrogen ambient. It was highlighted that the modification was due to oxygen vacancies and oxygen ions of IGZO annealed in oxygen ambient were relatively reduced after the treatment [46]. The literature study has demonstrated that oxygen content in IGZO film is highly impactful and Chen at al. agreed that it strongly influences the conductivity of the IGZO film [118].

Nonetheless, effects of annealing ambient on ZnO and GaZnO (GZO) were also reported. As reported by Du Ahn et al., annealing in hydrogen ambient caused oxygen vacancies in the GZO films to increase [119]. In different study, annealing of ZnO in oxygen gas led to a reduction in carrier concentration and mobility, presumably due to the incorporation of oxygen into the grains and the grain boundaries. On the other hand, annealing in nitrogen gas led to a slight change in carrier concentration and a significant reduction in mobility, due to nitrogen enhancing further defect creation [120]. It was learned that annealing the ZnO films in an oxygen ambient caused oxygen incorporation into the films, which then settled for the vacancies. Differently, annealing in a hydrogen gas resulted in the removal of oxygen in the system and hence created additional oxygen vacancies that act as donor centres in the ZnO film [121, 122]. In general, it was found in previous studies that oxygen, nitrogen, hydrogen, and forming gas ambient had affected oxygen vacancy concentration in ZnO films [120–123].

On device point of view, many studies have reported about the effect of annealing ambient on the properties of IGZO TFTs. For example, Lin et al. annealed fabricated TFTs in vacuum, oxygen, and forming gas ambience for 1 h to observe the change in TFT performance [116]. The outcome showed better threshold voltage (V_{th}) and sub-threshold swing (SS) showed by TFTs annealed in oxygen and forming gas [116]. Tiwari et al. explained the beneficial effect of argon, nitrogen, and oxygen annealing ambient through photoluminescence analysis and TFTs performance characteristics. From the PL analysis, the defect chemistry in the films such as zinc vacancy (V_{Zn}), zinc interstitial (Zn_i), and oxygen vacancy (V_O), were remarkably enhanced in argon, while suppressed in nitrogen and oxygen ambient. The fabricated IGZO TFTs showed field-effect mobility of 16.10 cm^2/Vs, the threshold voltage (V_{th}) of 1.50 V, the

subthreshold swing of 0.21 V/decade, and the negative bias illumination stress shifting of -2.75 V in nitrogen ambient [124].

However, it was noticed that there was no available study that reports on the properties of IGZO film in a detailed study on the influence of annealing ambient. Besides, no available study has included argon ambient as a parameter. Therefore, to find a more adequate condition in preparing a highly reliable IGZO film, the effect of annealing ambient on the properties of IGZO films was reported in this study.

2.5.4. Effects of molar ratio on IGZO films characteristics

One of the important parameters when dealing with film formation of multicomponent oxide semiconductor using solution process method is choosing the accurate molar ratio to prepare the precursor solution. Molar ratio is a conversion factor that depends on the ratio between individual amounts of two or more entities to render stoichiometry involved in the reaction kinetics [125]. The control of molar ratio is usually represented by solution volume ratio or solution weight ratio of individual element while the molar concentration of the individual precursor is maintained throughout the process [81, 126, 127].

As known, multicomponent materials often have special properties that a single material does not have due to unique contributions of every element involved. As mentioned, Ga offers stronger chemical bonds with oxygen, compares to In and Zn, thus more Ga incorporation will suppress the concentration of free carriers [45]. In a study, Xie et al. agreed that with the help of Ga, lower concentration of free carriers resulted in V_{th} swung toward positive and higher on-off ratio of IGZO TFT [81].

On the other hands, In corporation is highly beneficial for transparent and flexible device as it allow the advantage of very low or even room-temperature processing for semiconductor [23]. It is known that in IGZO system, In^{3+} is in charge of increasing