STUDY OF Cu-DOPED ZnO FILMS DEPOSITED ON DIFFERENT SUBSTRATES USING MAGNETRON SPUTTERING

AHMAD SAUFFI BIN YUSOF

UNIVERSITI SAINS MALAYSIA

2019

STUDY OF Cu-DOPED ZnO FILMS DEPOSITED ON DIFFERENT SUBSTRATES USING MAGNETRON SPUTTERING

by

AHMAD SAUFFI BIN YUSOF

Thesis submitted in fulfilment of the requirements
for the degree of
Master of Science

February 2019

ACKNOWLEDGEMENT

Alhamdulillah, praises to Allah for the health and blessing in completing this thesis. The path toward this road has been long and challenging. Without the help and support of many people, this journey would not come to end. The list are too many to be written here, however immeasurable appreciation and deepest gratitude for the help and support are extended to the following person who in one way or another have contributed the most in making this study possible.

Above all, I would like to extend my heartfelt appreciation to my supervisor, Prof. Dr. Zainuriah Hassan for her invaluable guidance, immerse knowledge and her tremendous effort to offer in every possible help to finish this thesis. She consistently allowed this thesis to be my own work, but steered me in the right direction whenever she thought I needed it. It was a great honour to finish the work under her supervision. I owe my deepest gratitude for the financial support that has been given as her Graduate Research Assistant. It has been a greatly enriching experience to me to work under her authoritative guidance. I also want to thank my co-supervisor, Assoc. Prof. Dr. Norzaini Zainal.

I also want to express my deep sincere thanks to all staff members of Nano-Optoelectronics Research and Technology Laboratory (NOR Lab) for their cooperation and generous attitude in helping me to complete the requirement for my MSc degree. I am thankful to all my colleague who has been always helping and encourage me throughout the years.

Most of all, I wish to express my profound appreciation and sincere gratitude to my beloved parents who has provided me with their prayers, encouragements and support throughout my MSc study.

TABLE OF CONTENTS

ACKNOWLEDGEMENT	ii
TABLE OF CONTENTS	iii
LIST OF TABLES	vi
LIST OF FIGURES	vii
LIST OF SYMBOLS	x
LIST OF ABBREVIATIONS	xii
ABSTRAK	xiii
ABSTRACT	xv
CHAPTER 1 - INTRODUCTION	**1**
1.1 Introduction	1
1.2 Problem statement	3
1.3 Research objective	4
1.4 Originality of the research work	5
1.5 Thesis structure	5
CHAPTER 2 - THEORY AND LITERATURE REVIEW	**7**
2.1 Introduction	7
2.2 Fundamental properties of copper	8
2.3 Fundamental properties of ZnO	8
2.3.1 Crystal structure	9
2.3.2 Electrical properties	10
2.3.3 Optical properties	12
2.4 Deposition technique of CZO films	13
2.4.1 Sputtering (introduction)	15
2.4.2 DC and RF sputtering	17
2.4.3 Magnetron sputtering	19
2.4.4 Co-sputtering	20
2.5 Effects of sputtering parameters on the properties of deposited CZO films	21
2.5.1 Base pressure	21

2.5.2 Substrates temperature 22
2.5.3 Post annealing treatment 23
2.6 Characterization theory 23
2.6.1 X-ray diffraction (XRD) 24
2.6.2 Field emission scanning electron microscope (FE-SEM) and energy dispersive X-ray (EDX) 26
2.6.3Ultraviolet visible near-infrared (UV-Vis-NIR) spectrophotometry 27
2.6.4 Atomic force microscopic (AFM) 30
2.6.5 Hall effect measurement 32

CHAPTER 3 - METHODOLOGY AND CHARACTERIZATION METHOD **35**

3.1 Introduction 35
3.2 Deposition techniques 35
3.2.1 Co-sputtering technique 36
3.2.1(a) Substrate preparation 37
3.2.1(b) Sputtering set-up 38
3.2.1(c) Annealing 40
3.2.2 RF sputtering 41
3.2.2(a) Substrate preparation 41
3.2.2(b) Sputtering set-up 42
3.3 Characterization Tools 44
3.3.1 X-ray diffraction (XRD) 44
3.3.2 Field emission scanning electron microscope (FE-SEM) and energy dispersive X-ray (EDX) 45
3.3.3 Ultraviolet visible near-infrared (UV-Vis-NIR) spectrophotometry 47
3.3.4 Atomic force microscopic (AFM) 47
3.3.5 Hall effect measurement 49

CHAPTER 4 - RESULTS AND DISCUSSION **50**

4.1 Introduction 50

4.2 Analysis of co-sputtering (different Cu %) on glass substrate 50
4.2.1 Surface morphology analysis 51
4.2.2 X-ray diffraction analysis 54
4.2.3 Optical analysis 59
4.2.4 Hall effect measurement analysis 63
4.3 Analysis of RF sputtering of ZnO (10wt% Cu doped) target on p-GaN/Al_2O_3 and n-GaN/Al_2O_3 substrates at different thickness. 64
4.3.1 Surface morphology analysis 64
4.3.2 X-ray diffraction analysis 65
4.4 Analysis of RF sputtering of ZnO (10wt% Cu doped) target on glass, p-GaN/Al_2O_3 and n-GaN/Al_2O_3 substrates at 200 °C substrates temperature 70
4.4.1 Surface morphology analysis 70
4.4.2 X-ray diffraction analysis 74
4.4.3 Optical analysis 76
4.4.4 Hall effect measurement analysis 78
4.5 Summary 81

CHAPTER 5 - CONCLUSION AND FUTURE WORK 83
5.1 Conclusion 83
5.2 Future work 84

REFERENCES 86

LIST OF TABLES

		Page
Table 2.1	(002) peak parameter of some Cu-doped ZnO films.	10
Table 2.2	Electrical properties of some Cu-doped ZnO films.	11
Table 2.3	Optical properties of some Cu-doped ZnO films.	13
Table 2.4	History of processes for making Cu doped ZnO film	14
Table 3.1	Co-sputtering parameters.	39
Table 3.2	Annealing parameters.	40
Table 3.3	RF sputtering parameters.	43
Table 3.4	X-ray diffraction system specifications.	45
Table 3.5	FE-SEM system specifications.	46
Table 3.6	AFM system specifications.	48
Table 4.1	Parameter of (0002) diffraction peaks of CZO films deposited at different DC power.	56
Table 4.2	Parameter of (0002) diffraction peaks of CZO films deposited at different DC power annealed at 400 °C.	58
Table 4.3	Electrical properties of Cu-doped ZnO deposited at different DC power after annealing at 400 °C.	62
Table 4.4	Optical band gap of CZO films as a function of sputtering power of Cu.	64
Table 4.5	Summary of RMS value and grain size estimated from AFM	69
Table 4.6	Effect of the deposition thickness on the parameters of the CZO films (0002) diffraction peaks.	69
Table 4.7	Summary of RMS roughness value estimated from AFM.	74
Table 4.8	Parameters of ZnO and CZO films diffraction peaks.	76
Table 4.9	Electrical properties of ZnO and CZO thin films deposited on different substrates.	80

LIST OF FIGURES

		Page
Figure 2.1	Interaction of ions with surfaces during the sputtering process	16
Figure 2.2	Eroded zone observed on the surface of the target.	20
Figure 2.3	Diffraction of X-rays by the crystal.	25
Figure 2.4	Schematic representation of a UV-Vis-NIR spectrophotometer	29
Figure 2.5	Schematic of an AFM system.	31
Figure 2.6	The schematic of the tip convolution model.	32
Figure 2.7	Schematic of the Hall effect in long thin bar semiconductor.	32
Figure 2.8	Schematic of the Van der Pauw configuration.	34
Figure 3.1	Overview of HHV Auto 500 sputtering system.	36
Figure 3.2	Flow chart of CZO fabrication process.	37
Figure 3.3	Glass cleaning procedure.	38
Figure 3.4	Schematics of the sputtering system.	39
Figure 3.5	Thermolyne 21100 tube furnace system.	40
Figure 3.6	Flow chart of CZO fabrication process.	41
Figure 3.7	Schematic of the p-GaN/Al_2O_3 and n-GaN/Al_2O_3 substrates.	42
Figure 3.8	p-GaN/Al_2O_3 and n-GaN/Al_2O_3 substrates cleaning procedure.	42
Figure 3.9	Substrates pasted on the substrate holder.	43
Figure 3.10	PANalytical X'Pert Pro X-ray diffraction system.	45
Figure 3.11	FEI Nova NanoSEM 450 field emission scanning electron microscope (FE-SEM) coupled with energy dispersive X-ray (EDX) system.	46
Figure 3.12	Agilent Technology Carry Series ultraviolet visible near-infrared (UV-Vis-NIR) spectroscopy system.	47
Figure 3.13	Dimension Edge Bruker atomic force microscope (AFM) system.	48
Figure 3.14	Indium contact on the surface of the sample	49
Figure 3.15	Hall effect measurement system.	49

Figure 4.1	FE-SEM images and EDX measurement of Cu-doped ZnO films deposited on glass at different DC power. (a) ZnO, (b) 8 W, (c) 10W, (d) 12.	52
Figure 4.2	FE-SEM images and EDX measurement of Cu-doped ZnO deposited on at different DC power after annealing at 400 °C. (a) ZnO, (b) 8 W, (c) 10 W, (d) 12.	53
Figure 4.3	XRD pattern of un-doped and Cu doped ZnO deposited at different DC power; inset shows the details of the ZnO and CZO films deposited at 8 W DC power.	56
Figure 4.4	XRD pattern of ZnO and CZO films deposited at different DC power (8 W, 10 W, 12 W) annealed at 400 °C.	58
Figure 4.5	(a) Transmittance spectra of un-doped and Cu doped ZnO films deposited at different DC power, (b) Tauc plot and the optical band gap of the films.	61
Figure 4.6	(a) Transmittance spectra of un-doped and Cu-doped ZnO films annealed at 400 °C, (b) Tauc plot and the optical band gap of the films.	62
Figure 4.7	FE-SEM images and EDX measurements of CZO deposited on p-GaN/Al_2O_3 with different thicknesses; (a) 100 nm (b) 200 nm (c) 300 nm.	66
Figure 4.8	FE-SEM images and EDX measurements of CZO deposited on n-GaN/Al_2O_3 with different thicknesses; (a) 100 nm (b) 200 nm (c) 300 nm.	67
Figure 4.9	AFM images of CZO films (5μm x 5μm) deposited on p-GaN/Al_2O_3 at different thicknesses; (a) 100 nm (b) 200 nm (c) 300 nm.	68
Figure 4.10	AFM images of CZO films (5μm x 5μm) deposited on n-GaN/Al2O3 at different thicknesses; (a) 100 nm (b) 200 nm (c) 300 nm.	68
Figure 4.11	XRD pattern of CZO films deposited on (a) p-GaN/Al_2O_3 and (b) n-GaN/Al_2O_3 substrate at different thickness	69
Figure 4.12	FE-SEM images and EDX measurements of ZnO films deposited on; (a) glass, (b) n-GaN/Al_2O_3, (c) p-GaN/Al_2O_3 substrates.	71
Figure 4.13	FE-SEM images and EDX measurements of CZO films deposited on; (a) glass, (b) n-GaN/Al_2O_3, (c) p-GaN/Al_2O_3 substrates.	72

Figure 4.14 AFM images of ZnO films (5µm x 5µm) deposited on different substrates; (a) glass, (b) n-GaN/Al_2O_3, (c) p-GaN/Al_2O_3. 73

Figure 4.15 AFM images of CZO films (5µm x 5µm) deposited on different substrates; (a) glass, (b) n-GaN/Al_2O_3, (c) p-GaN/Al_2O_3. 73

Figure 4.16 XRD pattern of ZnO and CZO deposited on glass substrates. 75

Figure 4.17 XRD pattern of ZnO and CZO films deposited on p-GaN/Al_2O_3 and n-GaN/Al_2O_3 substrates. 75

Figure 4.18 (a) Transmission spectra of ZnO and CZO films deposited on glass substrates, (b) Tauc plot and the optical band gap of the films 77

LIST OF SYMBOLS

A	Lattice constant
A	Area
B	Magnetic field strength
C	Lattice constant
D	Distance
D	Interplanar spacing of the crystal plane
D	Average crystal size
e	Charge of electron
E_C	Conduction band
E_F	Fermi level of semiconductor
E_g	Semiconductor band gap
E_V	Valence band
F	Force
h	Planck's constant
$(hkil)$	Miller-Bravais indices
I	Current
I_o	Saturation current
k	Boltzmann's constant
m_o	Electron mass
m_p	Hole mass
m^*	Effective mass
n	Refractive index
n	Bulk density
n	Free electron concentration
N_D	Donor concentration
N_A	Acceptor concentration
q	Electron charge
R_H	Hall coefficient
R_s	Sheet resistance

S	Sensitivity
T	Absolute temperature
V	Voltage
V_H	Hall voltage
w	Width
α	Thermal expansion coefficient
α	Absorption coefficient
ε_o	Absolute dielectric constant
μ	Carrier mobility
θ	Incident/Diffraction angle
λ	Wavelength

LIST OF ABBREVIATIONS

a.u.	Arbitrary unit
AFM	Atomic force microscope
Cu	Copper
CZO	Copper doped zinc oxide
DAP	Donor-acceptor pair
DC	Direct current
EDX	Energy dispersive X-ray
eV	Electron volt
FE-SEM	Field emission scanning electron microscope
FET	Field effect transistor
FWHM	Full width at half maximum
HCP	Hexagonal closed packing
IR	Infrared
I-V	Current-voltage
LED	Light emitting diode
ML	Monolayer
MBE	Molecular beam epitaxy
MOCVD	Metal organic chemical vapour deposition
PL	Photoluminescence
RF	Radio frequency
RT	Room temperature
rms	Root mean square
sccm	Standard cubic centimetre per minute
SEM	Scanning electron microscope
TCO	Transparent conductive oxide
UHV	Ultra high vacuum
UV	Ultra violet
Vis	Visible
XRD	X-ray diffraction
ZnO	Zinc oxide

KAJIAN FILEM ZnO YANG DIDOP DENGAN Cu ATAS SUBSTRAT BERLAINAN MENGGUNAKAN PERCIKAN MAGNETRON

ABSTRAK

Filem nipis zink oksida (ZnO) telah berkembang menjadi satu topik penyelidikan yang menarik kerana ciri-cirinya yang serba guna. Kebelakangan ini, banyak perhatian telah diberikan kepada filem ZnO yang didopkan dengan kuprum (Cu) kerana potensinya dalam peranti semikonductor. Fokus kajian ini adalah berkaitan dengan filem nipis ZnO yang tidak didop dan didop dengan kuprum (CZO) yang disediakan menggunakan percikan magnetron reaktif. Pelbagai faktor percikan diperkenalkan untuk menambah baik ciri-ciri filem tersebut terutama dengan cara mengubah kandungan Cu dan jenis substrat. Struktur kristal, ciri optik, morfologi permukaan dan ciri elektrikal yg terdapat pada filem telah dikaji menggunakan belauan sinar-x (XRD), spektrofotometer ultraungu–cahaya nampak (UV-VIS), mikroskopi imbasan elektron pancaran medan (FE-SEM), mikroskopi daya atomik (AFM) dan pengukuran kesan Hall dengan konfigurasi Van der Pauw empat titik. Filem ZnO dan CZO telah dimendapkan atas substrat kaca, p-GaN/Al_2O_3 dan n-GaN/Al_2O_3 dengan menggunakan percikan magnetron frekuensi radio sasaran ZnO (pendopan Cu 10wt %) pada suhu 200° C. Keputusan XRD menunjukkan filem ZnO dan CZO yang telah difabrikasikan mempunyai struktur heksagon wurtzit yang kecenderungan orientasinya lebih kuat pada paksi-c. Transmisi bagi semua filem yang dimendapkan di atas substrat kaca adalah lebih daripada 85% di kawasan cahaya nampak. Pengurangan jalur jurang tenaga optikal diperolehi apabila Cu dimasukkan ke dalam ZnO. Filem CZO yang telah dimendapkan menunjukkan permukaan yang lebih licin jika dibandingkan dengan filem ZnO. Keputusan pengukuran Hall menunjukkan filem

CZO yang dimendapkan atas n-GaN/Al_2O_3 substrat mempunyai mobiliti dan kekonduksian (2.21 x 10^2 cm^2/Vs, 3.63 x 10^3 1/Ω cm) yang lebih tinggi dibandingkan dengan filem ZnO yang tidak didop (6.95 cm^2/Vs, 54.21 1/Ω cm).

STUDY OF Cu-DOPED ZnO FILMS DEPOSITED ON DIFFERENT SUBSTRATES USING MAGNETRON SPUTTERING

ABSTRACT

Zinc oxide (ZnO) thin films have emerged as an interesting research area owing to its useful properties. Recently, lots of attention have been given to doped ZnO films with copper (Cu) atom, due to its favourable potential in semiconductor devices. This work was focused on the un-doped and Cu-doped ZnO (CZO) thin films prepared by reactive magnetron sputtering. Different sputtering parameters were introduced to improve the properties of the films mainly by manipulating the Cu content and the type of substrate. The crystal structure, optical properties, surface morphology and electrical properties were investigated by using X-ray diffraction (XRD), ultraviolet-visible (UV-VIS) spectrophotometer, field emission scanning electron microscopy (FE-SEM), atomic force microscopy (AFM) and Hall effect measurement with a four-point Van der Pauw configuration. ZnO and CZO films were deposited on the glass, p-GaN/Al_2O_3 and n-GaN/Al_2O_3 substrates using radio frequency magnetron sputtering of ZnO (10wt% Cu doped) target at 200° C. XRD results indicated that ZnO and CZO films with preferential orientation along c-axis that belongs to a hexagonal wurtzite structure were fabricated. The transmittance of all ZnO and CZO films deposited on the glass substrate were more than 85% in the visible region. Optical band gap reduction was observed when Cu introduced into ZnO structure. Deposited CZO films showed a smoother surface as compared to ZnO films. Hall measurement results revealed that CZO film deposited on n-GaN/Al_2O_3 substrates has higher mobility and conductivity (2.21×10^2 cm^2/Vs, 3.63×10^3 1/Ω cm) than un-doped ZnO films (6.95 cm^2/Vs, 54.21 1/Ω cm)

CHAPTER 1

INTRODUCTION

1.1 Introduction

As scientific exploration expanded, nanoscience and nanotechnology have become an emerging field of science involving understanding and controlling of matter at the nano scale with the dimension typically ranging from one nanometer to several hundred nanometers. These rapid expanded research areas are contributed by different modern multidisciplinary of science involving field of physics, engineering, chemistry and biology. The pronounced interest in semiconductor materials is driven by the combination of several benefits in comparison to its bulk material.

On the nanometer scale, materials or structure may exhibit new and unique physical properties compared to its bulk state such as the band gap of semiconductor materials and its crystal quality can be tuned by varying the materials dimensions. For the past few years, wide band gap semiconductor such as ZnO has become the major attraction in the research communities driven by the prospect of potential to develop into light emitting devices and transparent conductive oxides (TCOs) [1]. Due to this promising potential, a strong motivational for a comprehensive understanding and development of ZnO based material has been done.

ZnO has a long history dated back to the Bronze Age where ZnO is a by-product of copper ore smelting which is called cadmia that is deposited on chimney wall which later was used as an ointment to heal wound. The application in medicine and pharmaceutical continue up to now such as sunscreen. Then in the Middle Age period, the main application of ZnO is used as a main material in the production of brass (Cu-Zn alloy) before it’s been replaced with metallic Zn.

In semiconductor realms, the main idea behind the development of ZnO is to become the substrate for GaN which is seen as a promising wide band gap material for short wavelength photonic devices. With further understanding of ZnO achieved, it shows that ZnO itself is a valuable wide band gap material. In 1912, the first scientific paper of ZnO has been published by A.A Somerville [2]. The paper explains the effect of temperature on the electrical properties of ZnO cylindrical rod. This mark the beginning of scientific research period. This paper lead to first electronic application of ZnO as a thin film in surface acoustic wave devices.

Zinc oxide (ZnO) is a direct wide band gap (3.37 eV) II-VI semiconductor compound which consist of metal from group 2 (Zn) and chalcogen from group 16 (O) [3]. ZnO also is an inorganic compound that exhibits as a white powder that is insoluble in water with high melting point at 1975 °C. In many features, ZnO is considered to become an alternative device material to GaN due to its relatively low production cost and vast availability for bulk single crystal. The significant interest in ZnO based material systems is due to several combination of benefits in comparison to its relatively close sibling GaN. Among those are high stability and large free-exciton binding energy (60 meV) at room temperature compare to GaN (21-25 meV) [4]. This could make ZnO based devices to operate at or even higher than room temperature and in hostile environment.

Due to pronounce interest in the properties of ZnO, various thin film deposition techniques have been documented such as sputtering, pulse laser deposition, molecular beam epitaxy (MBE) and metal organic chemical vapour deposition (MOCVD). The highest quality of ZnO thin film that has been reported was fabricated on Al_2O_3 substrate using MBE and MOCVD techniques [5], [6]. Among those, magnetron

sputtering offer high deposition rate, uniform coating, compatible with variety type of substrates and easy to control deposition thickness.

Even though with all promising features, the major problem in the development and commercialization of ZnO based devices is producing stable p-type doping with high mobility and hole concentration. This is due to ZnO having a doping asymmetry limitation problem [7]. N-type conductivity can be easily produced by doping group 13 element such as aluminium (Al) into lattice size of ZnO but to dope p-type, it proofs to be challenging. Nevertheless, the p-type ZnO has been reported to be achievable with group V doping such as N, P, As and Sb [8]. This causes the major step back in mid 90s.

However, with the advancement in more sensitive characterization tools and highly controllable deposition approaches, ZnO has make its way into various promising fields especially in optoelectronic devices such as flat panel display and transparent conductive oxide (TCO). The subsequent part is a detailed account of the objective and contents of this thesis.

1.2 Problem statement

Currently, commercialized TCOs are dominated by indium tin oxide (ITO) films. TCOs is an electrical conductive material with high optical transmittance within the visible region of spectrum. Its resistivity should be around 10^{-4} Ω cm and the optical transmittance should be above 80% in the visible region with its band gap higher than 3 eV [9]. Typically, TCOs which is widely used in optoelectronic devices for example flat panel display and solar cell are fabricated using thin films deposition method such as magnetron sputtering and pulse laser deposition.

More than 80% of current TCOs used widely were consisting of ITO glasses. With the recent world-wide scarcity of indium reserves which is the main ingredient for ITO scientific communities have initiated some initiatives to find suitable substitute materials [10]. Among the candidates, doped and un-doped ZnO thin film are the great potential materials due to their wide band gap, massive availability, non-toxicity, bio compatibility with organic system and high transparency in visible light region.

The interesting properties of ZnO as a wide band gap material seems to be stimulating the exploration in fabrication and characterization of ZnO based transparent electrode. However the electrical resistivity of ZnO was high compared to most TCO electrode at average 10^{-3} Ω cm [11] with limiting resistivity at 2×10^{-4} Ω cm [3]. This remarkable combination of conductivity and transparency is usually impossible in intrinsic stoichiometric oxides. However, it can be achieved by producing them with a non-stoichiometric composition or by introducing appropriate dopants.

Thus, for the design and realization of ZnO-based transparent electrode devices, one of the most significant issues was doping. The opto-electrical properties of ZnO can be engineered to achieve desirable value by introducing doping element impurities into ZnO lattice site such as titanium (Ti) [12], aluminium (Al) [13], silver (Ag), copper (Cu) [14], tin (Sn) [15] and gold (Au) [16]. Among these, Cu is a naturally abundant and non-toxic element which makes Cu a high potential dopant. Cu has same radius and electronic shell with Zn, thus making doping easier.

1.3 Research objective

The objective of this work can be summarised as follows:

1. To study the influence of Cu doping on the crystallinity, optical transmittance and resistivity of the CZO thin films deposited on glass substrate by using magnetron co-sputtering technique of ceramic ZnO and Cu metal target with RF and DC source respectively.
2. To study the effect of the substrates (n-GaN/Al_2O_3 and p-GaN/Al_2O_3) on the resistivity of the deposited CZO films by using RF magnetron sputtering of ZnO (10wt% Cu doped) target.

1.4 Originality of the research work

Cu-doped ZnO films deposited on various substrate such as silicon, glass and sapphire have been reported previously [17]–[19]. With all the complex deposition system and different type of substrates, the resistivity of the deposited CZO films are still considerably high and rather unstable. In this study, un-doped and Cu-doped ZnO films deposited on glass, n-GaN/Al_2O_3 and p-GaN/Al_2O_3 substrates by using RF magnetron sputtering of ZnO (10wt% Cu doped) target were investigated. Low resistance with high optical transmittance in the visible region of CZO films has been successfully attained [20]. It shows that the capability in producing good quality CZO films can be achieved through a simple magnetron sputtering with appropriate selection of substrates.

1.5 Thesis structure

The following work consist of detailed study of crystal structure, surface morphology and optical properties of sputtered CZO thin film. A brief explanation on introduction and objective of this project are written in this chapter which is chapter 1.

Following the introduction, chapter 2 discuss the literature review. This chapter gives the fundamental concept and basic theory about the properties of ZnO thin films alongside with works that have been done in previous literature. The knowledge about crystal structure, lattice parameters, optical properties, and electrical properties are also described in chapter 2.

All the experimental techniques that have been carried out in this project are summarized in chapter 3. This includes but not limited to substrate preparation, sputtering theory and parameters and annealing furnace. Chapter 3 also discuss about the characterization method and technique that has been implemented in this project to determine the properties of sputtered CZO thin films. Further discussion in this chapter include the kind of method that are involved, basic theory and overview on how the machine operates and how to use and handle the machines correctly that can lead to the production of favourable results.

Results that has been obtained throughout this project are displayed and discussed in chapter 4. Finally, chapter 5 summarizes the work and provides a brief conclusion to the thesis.

CHAPTER 2

THEORY AND LITERATURE REVIEW

2.1 Introduction

ZnO has become a major backbone for today's modern technology. The applications of ZnO are not limited to electronic devices, it also has been utilized globally in the industry such as in rubber and ceramic production, where ZnO as white paint is used as an activator in the vulcanization process [21] and used to manufacture glass and porcelain enamels [22]. ZnO also has been used in painting and paper coating, where ZnO is applied as a coating material to reduce the degrading effect of sunlight or ultraviolet rays as well as to improve the overall finish and give opacity since ZnO has strong optical UV absorption and high transparency to visible light [23].

ZnO also has been widely used in cosmetic industry as a sunscreen. In the scientific realms, ZnO has been recognized widely and become the main subject in many scientific research predated back as early as 1912 [2]. The reason behind the interest of this material is due to its several advantages in the semiconductor properties such as wide direct band gap (3.37 eV) that makes it suitable to become short wavelength optoelectronics devices and its large exciton binding energy (60 meV) which enables device to operate at high efficiency excitonic emission in room temperature [24] together with its other unique material properties such as high transmittance in visible and ultraviolet region, piezoelectricity, non-toxic and naturally abundant [25].

These advantages make ZnO a good candidate for solid state lighting devices [26] and TCOs application [27]. With the recent advancement in the growing technology, the vast availability of high quality large bulk single crystal can be achieved and it can

be grown with relatively low production cost, making ZnO more favourable than GaN. Following the basic introduction, the fundamental properties of ZnO which include crystal structure, electrical properties, optical properties and defects will be further discussed later in this chapter.

2.2 Fundamental properties of Copper

Copper with its distinctive reddish-orange colour is a chemical element with the symbol Cu and atomic number 29. Cu come from group IB or group 11 element same as silver and gold. The electronic configuration is $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $3d^{10}$ $4s^1$. The valence electron of Cu can be assume to be either +1 or +2 depending on electronic configuration.

At unionized state, Cu atom has $3d^{10}$ $4s^1$ configuration in its outer cell electronic configuration. However for Cu^{2+} with $3d^{10}$ outer shell configuration, one un-pair electron will give a rise to a spin angular momentum of ½ that can cause on net magnetic moment. Cu^{+} (0.06 nm) and Cu^{2+} (0.054 nm) has quite similar ionic radii with Zn^{2+} (0.06 nm).

2.3 Fundamental properties of ZnO

ZnO is one of the most important II-VI binary compound semiconductors which consist of an anion (O^{2-}) and cation (Zn^{2+}). ZnO is an inorganic compound in which its chemical bond is a mixture of ionic and covalent bond. However its properties tend to lean toward ionic bond. ZnO has low solubility in water (0.0004% at 17.8 °C) and will decompose at 1975 °C.

2.3.1 Crystal structure

Similar to another II-VI binary compound, ZnO can physically exist over a range of different crystalline phases from wurtzite to rock-salt and zinc-blende [28]. Commonly under ambient condition, doped and un-doped ZnO will crystallize in the form of the thermodynamically stable wurtzite structure where each zinc atom is bounded with four oxygen atoms by sp^3 covalent bond, the vertices of the tetrahedron.

When relatively high external hydrostatic pressure (~10 GPa) is exerted onto ZnO structure, wurtzite ZnO can be transformed into the rarely observed rock-salt NaCl-type structure. The zinc-blende is a metastable structure and can only be stabilized by growing ZnO on cubic orientation substrates.

The wurtzite crystal structure comes from the hexagonal crystal system with space group $P6_3mc$ in the Hermann-Mauguin notation or C_{6v}^4 in the Schoenflies notation and the structure is fourfold coordinated where each atom is surrounded by four nearest neighbour atom [29]. Each hexagonal closest packed (hcp) sub-lattices are occupied by two atom species that displace against each other along the threefold c-axis coordinate.

The lattice parameter of ZnO wurtzite structure has been previously determined by a different kind of method where the commonly accepted constant value for a-parameter (basal plane lattice) is 0.3253 nm and for c-parameter (axial lattice) is 0.5215 nm with the density of 5.63 g cm^{-3} [30]. The values slightly deviate from the ideal wurtzite structure due to several factors that have been reported such as the concentration of defect (e.g., zinc antisites, oxygen vacancies) and foreign atoms, external strains (e.g., caused by the substrate) and temperature. Table 2.1 shows the (002) peak parameters of some Cu-doped ZnO films.

Since the tetrahedral coordination exist in the wurtzite structure, it will produce a non-inversion symmetric structure where the reflection of the crystal cannot transform into itself relatively at any given point. The result of this lattice symmetry is the possession of piezoelectricity and pyro-electricity properties in ZnO [31].

Table 2. 1: (002) peak parameter of some Cu-doped ZnO films.

Deposition method	Substrate	Cu (at. %)	2θ (°)	FHWM	C (nm)	σ (GPa)	Ref.
RF sputtering (Zn), Cu foil	Glass	0.7	34.09	0.39	0.5257	-2.34	[32]
RF sputtering (Zn), Cu foil	p-Si (100)	1.8	~34.25	0.35	0.5260	-2.45	[33]
RF sputtering (Zn), Cu foil	Si	-	34.04	0.77	0.5263	-2.38	[34]
Co-sputtering, ZnO (RF)/Cu (DC)	glass	16.4	34.75	0.43	0.5159	2.06	[35]
Co-sputtering, ZnO (RF)/Cu (DC)	glass	16.4	34.78	0.44	0.5156	2.19	[36]
RF sputtering, alloy target ($Zn_{1-x}Cu_xO$)	glass	5.0	34.30	0.43	0.5202	0.13	[37]
RF sputtering doped target	n-GaN	~5	34.590	0.126	0.5182	0.967	*

* Values obtained from this experiment in Chapter 4.

2.3.2 Electrical properties

ZnO is recognized due to its wide direct band gap of ~3.37 eV at room temperature which has a high potential for short wavelength optoelectronic devices [38]. The band gap of ZnO can further be engineered to meet the requirements for a given application. This is achieved by a process called doping where a small percentage of chosen impurities atoms in a measured quantity is introduced into the crystal lattice site of a semiconductor which usually creates impurities level within the energy band gap. Through doping, the position of the Fermi level in the materials can be changed either shifted towards the conduction band in the n-type semiconductor or shifted towards

the valence band in the p-type semiconductor by controlling the carrier concentration of the particular polarity (electrons and holes) in the system.

In the n-type semiconductor, the impurities are ionized in the form of donors which donate an additional free electron to the conduction band whereas in the p-type semiconductor, the impurities are ionized in the form of acceptors providing free holes to the valence band. The carrier concentration in intrinsic ZnO is still considered low (roughly 10^6 cm^{-3} at room temperature) for practical application such as TCO [39]. The electrical properties of some Cu-doped ZnO films are given in Table 2.2.

Table 2. 2: Electrical properties of some Cu-doped ZnO films.

Deposition method	Cu (at. %)	Substrate	Carrier type	Resistivity (Ω-cm)	Ref.
DC sputtering (Zn), Cu foil	9.9	n-Si (100)	n	~9 x 10^3	[40]
Co-sputtering, ZnO (RF)/Cu (DC)	9.0	Glass	n	2.85	[41]
Co-sputtering, ZnO (RF)/Cu (DC)	-	Glass	n	~25.0	[42]
RF sputtering (Zn), Cu vapour vacuum arc	-	Si (100)	n	2 x 10^{11}	[43]
Multilayer sputtering, , ZnO (RF)/Cu (DC)	-	Flexible PEN	n	3.87 x 10^{-5}	[44]
MBE	-	Al_2O_3 (0001)	n	0.37	[17]
			p	0.44	
PLD	-	Al_2O_3 (0001)	n	2.5 x 10^{-1}	[45]
			p	~10^5	
Spray pyrolysis	1.5	Glass	n	3.6 x 10^{-1}	[46]
Spray pyrolysis	5	Glass	n	2.63	[47]
			p	1.63	
RF sputtering doped target	~5	n-GaN/Al_2O_3	n	2.76 x 10^{-4}	*
		p-GaN/Al_2O_3	p	3.50 x 10^6	

* Values obtained from this experiment in Chapter 4.

Thus introducing dopants is important to increase the carrier concentration but a limit must be set. The mobility of the carrier which influences the conductivity of the ZnO is strongly affected by doping concentration and temperature [48]. Heavily doped material will result in low carrier mobility primarily due to impurities scattering and low transparency in the visible region. While in high temperature, the reduction in the carrier mobility is mainly caused by lattice scattering (phonon colliding with ionized carrier) since the density of the phonons in the solid materials increases with temperature. Even though the mobility is decreased, the conductivity still increases with temperature due to carrier concentration that increases exponentially with temperature.

2.3.3 Optical properties

Optical properties of a semiconductor is a by-product of interplay between intrinsic and extrinsic effect [49]–[51]. Intrinsic optical transition is associated with electrons and holes which occupied the conduction and valence band. Extrinsic optical transition is associated with discrete electronic states in the band gap of the material created by dopants or centers, and therefore influence both optical absorption and emission processes [52].

Due to this pronounce interest, the optical properties of ZnO have been studied by various experimental procedure such as transmittance, absorbance, reflectance and photoluminescence. Table 2.3 shows optical properties of some Cu-doped ZnO films. The analysis of the optical spectra of the material is one of the beneficial tools in determining the optical band gap and the impurity state of the material. The optical absorption spectra usually exhibit a rise at a certain value of the incident photon energy, which can be ascribed to the excitation of electrons from the valance band to

conduction band. Thus from that, the optical band gap of the material can be calculated.

Table 2. 3: Optical properties of some Cu-doped ZnO films.

Deposition method	Substrate	Cu (at. %)	Transmittance	Band gap (eV)	Ref.
RF sputtering (Zn), Cu foil	FTO	10	-	3.05	[53]
DC sputtering (Zn), Cu foil	Glass	-	-	3.21	[14]
Co-sputtering, ZnO (RF)/Cu (DC)	Glass	16.4	-	~2.83	[35]
Co-sputtering, ZnO (RF)/Cu (DC)	Glass	9	< 65%	1.89	[41]
Co-sputtering, ZnO (RF)/Cu (DC)	Glass	16.4	-	2.88	[36]
RF sputtering, alloy target ($Zn_{1-x}Cu_xO$)	Glass	2	> 85%	~3.15	[54]
RF sputtering, alloy target ($Zn_{1-x}Cu_xO$)	Glass	5	> 85%	~3.16	[37]
PLD	Fused silica	15	> 75%	2.70	[55]
Spray pyrolysis	Glass	4	> 40%	3.11	[47]
Spin coating	Quartz	3.89	-	2.64	[56]
RF sputtering doped target	glass	~5	~90%	3.30	*

* Values obtained from this experiment in Chapter 4.

2.4 Deposition techniques of CZO films

The properties of the thin films are significantly dependant on its deposition techniques. To satisfy the demand in various commercial applications of modern technology which requires specific properties in the thin films, series of the development on the deposition techniques has been reported to deposit CZO thin films including, but not limited to spin-coating [57], spray pyrolysis [46], co-precipitation [58] and sputtering deposition [14]. By understanding various deposition methods, the

thin films deposition process can be precisely controlled at the atomic level with the desired thickness to meet the requirement of the particular functionality. Table 2.4 shows some of the processes for making Cu-doped ZnO films.

The selection of the deposition techniques is defined by different aspects such as cost, reproducibility, films quality and the complexity of the equipment. Among those the most documented technique to deposit CZO films are by using magnetron sputtering system due to its conceptual simplicity and easy scalability.

Over the years, different sputtering target configuration has been archived to incorporate Cu into ZnO films on the desirable substrate such as by using magnetron co-sputtering of ZnO ceramic target and Cu metal target with RF and DC source respectively and DC or RF reactive magnetron sputtering of Cu chips/foils embedded Zn metal target [20-21]. The amount of deposited Cu percentage can be controlled simply by changing the sputtering power or varying the area of Cu chip embedded on the target.

Table 2. 4: History of processes for making Cu doped ZnO film.

Deposition method	Reference
RF sputtering of Zn target with Cu foil/chips	[59]
DC sputtering of Zn target with Cu foil/chips	[60]
Co-sputtering of ZnO (RF) and Cu target (DC)	[61]
RF Sputtering of compound target	[62]
Multilayer Sputtering ZnO (RF) and Cu target (DC)	[44]
Sequential DC Sputtering of Zn and Cu target	[63]
Co-precipitation	[64][65]
PA-MBE	[17]
PLD	[66]
Spray pyrolysis	[67]
Spin coating	[68]
DFT	[69][70]

2.4.1 Sputtering (introduction)

Sputtering is one of the most broadly used and well established method to deposit not only binary compound material such as metal-oxides and metal-nitrides thin films but also it has been used to deposit composite, alloy or mixture compound thin films that depend on the composition of the target materials [22-24].

Sputtering is a type of physical vapour deposition technique in which the surface of the target is bombarded with high energy positive ions (process gas ions) within the plasma causing an atom to be liberated from the surface of the target by means of momentum transfer process between the process gas ions and the target atom.

Prior to deposition, the substrate to be coated is placed inside the vacuum chamber. To achieve high-quality coating, clean environment with only chosen materials is needed. Thus, the pressure of the chamber is evacuated to high vacuum level to remove any residual gases from the chamber to minimize potential contaminants. Once the desired base pressure (usually $\sim 10^{-5}$ Pa) is achieved, a process gas is introduced into the system and deliberately controlled by using mass flow controller.

Typically, the process gas is chosen from gas that has high molecular weight such as xenon and argon [74]. This is because these type of gases can effectively facilitate high-energy collision, causing an increase in deposition rate. If reactive sputtering is needed, gases such as O_2 to form oxide and N_2 to form nitrides can be added to the chamber during the process.

The sputtering process is initiated by generating the plasma. This is accomplished by supplying high voltage between the cathode (target) and anode (substrate). Through this process, electron in the processing gas will accelerate away from the cathode and gain very high kinetic energy. The electron then will collide with the outer electronic

shell of the nearby processing gas molecules causing an electrostatic repulsion and ionize them. The positive ions now will be attracted and accelerate toward the cathode at high velocity, leading to the high-energy collision with the target surface.

Each successful collision can cause the energy of the ions to be transformed into heat and other particles or may be buried inside the target, which is called ion implantation. Then one or all of the following types of particles will be emitted which are neutral atom where the ions maybe reflected and neutralized during the process, phonon, secondary electron and sputtering atoms as shown in Fig. 2.1.

Once the particles on the target surface get enough energy from the momentum of the collision, sputtering atom will be ejected onto the vacuum environment inside the chamber. With high kinetic energy, the sputtering atom will reach to the surface of the substrate and condense on the substrates as thin film [75]. The secondary electron plays an important role in maintaining the electron and sustaining the plasma by reaccelerating back the electron away from the target to ionize more processing gas atom that will be used to sputter the target. The steps are repeated throughout the process.

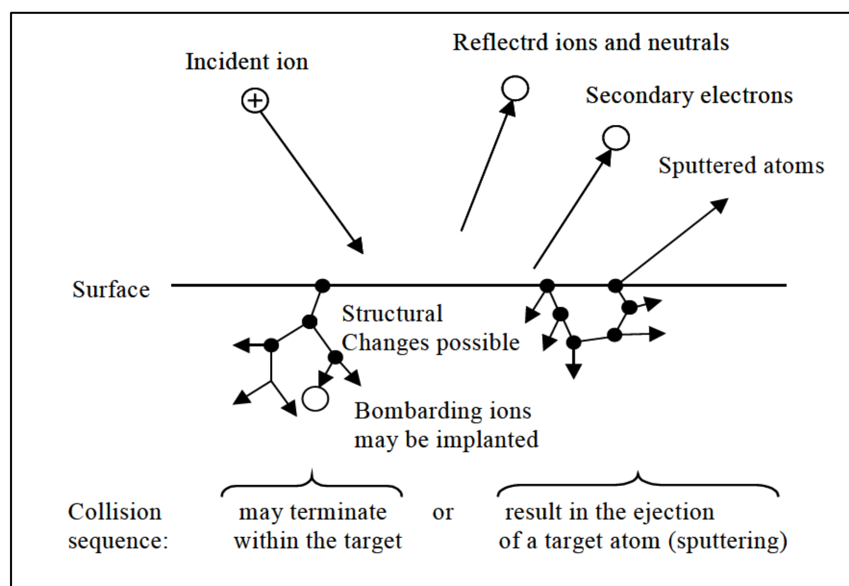

Fig 2. 1: Interaction of ions with surfaces during the sputtering process (adopted from Chapman, 1980).

The magnetron sputtering system uses planar magnetron target [76]. This is where the word ‘magnetron’ come from. The system uses very strong magnet to confine the plasma near the target surface, leading to a higher density of ions in the plasma. This will increase the efficiency of collision between the electron and gas molecule, resulting in an improvement of deposition rate. For the conductive materials, it can be deposited by using direct current (DC) power supply and insulator can be deposited by using radio frequency (RF) power supply.

The main advantages of sputtering are, high deposition rate, ability to sputter any metal, alloy or compound, high coating uniformity on larger surface area substrates, high purity films and high films adhesion [77]. Sputtering offer higher deposition coverage area compared to other deposition techniques due to the whole target surface become the main source compared to evaporation process in which the source is from the point where the electron beam hits the surface.

Since the sputtering atom carries high kinetic energy from the bombardment process, it results in an improvement in adhesion to the substrate surface. Thus, indicate that sputtering is a very powerful technique that can be utilized in different kind of applications.

2.4.2 DC and RF sputtering

The effectiveness of the sputtering deposition process depends on the correct selection of the target power delivery system. Depending on the type of the power supply used, sputtering can be divided into two modes which are DC and RF biasing. DC sputtering is an effective method to deposit conductive materials such as metals. However, DC sputtering cannot be used to sputter insulating or dielectric materials.

To maintain the generation of plasma, electrically conductive electrodes are required. If one of those electrodes are non-conductive such as using insulating cathode (target), it would cause the charge to remain localized when ions collide with the target surface. The positive charge will accumulate on the surface of the target, making the bombardment process harder. Thus, resulting in the termination of the glow discharge and consequently stopping the deposition process.

Therefore to solve the problem, the deposition of non-conductive materials can be accomplished via alternative current (AC) power supply so that the sputtered target can be bombarded with ions and electron alternately. The positive charge build-up during a one-half cycle can be naturalized by the electron bombardment in the next cycle.

Since the electron has higher mobility and lower mass compared to ions, the electron will have higher velocity and can travel further during each half cycle. Thus, more electron will reach the surface of the target in the positive half cycle compared to positive ions in the negative cycle. This will induce the target to be self-biased negatively leading to the acceleration of ions towards the negative charge surface. Thus, the glow discharge can be maintained subsequently prompting a successful sputtering process.

The frequency of the oscillating voltage is in radio frequency (RF) range in which most of the RF sputtering system is fixed which is at 13.56 MHz [78]. The RF potential causes an electron to perform an oscillating motion in the alternating field producing an ionizing collision. Thus resulting in the generation of the glow discharge. To make sure sufficient power can be delivered into the sputtering chamber, RF system requires an impedance matching network to modulate and matches the RF power transfer

between the sputtering chamber and RF generator to 50 Ω impedance which is favourable in the generation of the plasma [79].

2.4.3 Magnetron sputtering

In the magnetron sputtering system [80], an additional strong magnetic field is applied on the surface of the cathode by mounting electromagnets or permanent magnet on the back of the target. The reasons behind this technique are to confine the primary and secondary electron in the localized region in the vicinity of the cathode. When the magnetic field is applied on the surface of the target, the electron corresponds by traveling in spiral motion along the magnetic field line near the target. In the region where the magnetic field and electric field are perpendicular to one another, the path of the electron will be altered subjected to the Lorentz force which can be written as;

$$\vec{F} = -q(\vec{E} + \vec{v} \times \vec{B}) \tag{2.1}$$

where $\vec{E}$ is the electric field, $\vec{v}$ is the electron velocity, $\vec{B}$ is the magnetic field, q is the particle charge and $\vec{F}$ is the force experienced by the electron.

When electron reaches the surface of the target, it will be repelled by the negative potential of the cathode. The superposition between the electric field forces $\vec{F} = q\vec{E}$ and Lorentz force $\overrightarrow{F_L} = -q\vec{v} \times \vec{B}$ cause the electron to drift in a hopping cycloidal motion along the $E \times B$ drift path [81]. The combination of both motions increase the mean free path length of the electron and produce a higher chance for electron to undergo a successful ionizing collision with the process gas atom before reaching the anode. Consequently, improving the efficiency of the sputtering process.

The motion of the ions and the sputtered atoms are not restricted by the field due to its higher mass compared to an electron. Since the generated secondary electrons are trapped in the cycloidal orbit, it prevents the electrons from accelerating and making direct collision with the anode that can cause self-heating of the substrate or damage on the films to be coated.

This confinement of electron motion occurs around the region called “racetrack”. This phenomenon can be clearly observed on the target where its surface will erode preferentially along the “racetrack” region and will progress deepen over time. This is due to the plasma is most intense in this region, leading to greater ionization and bombardment on this particular surface area of the target. Thus producing the erosion zone as can be seen in Fig. 2.2.

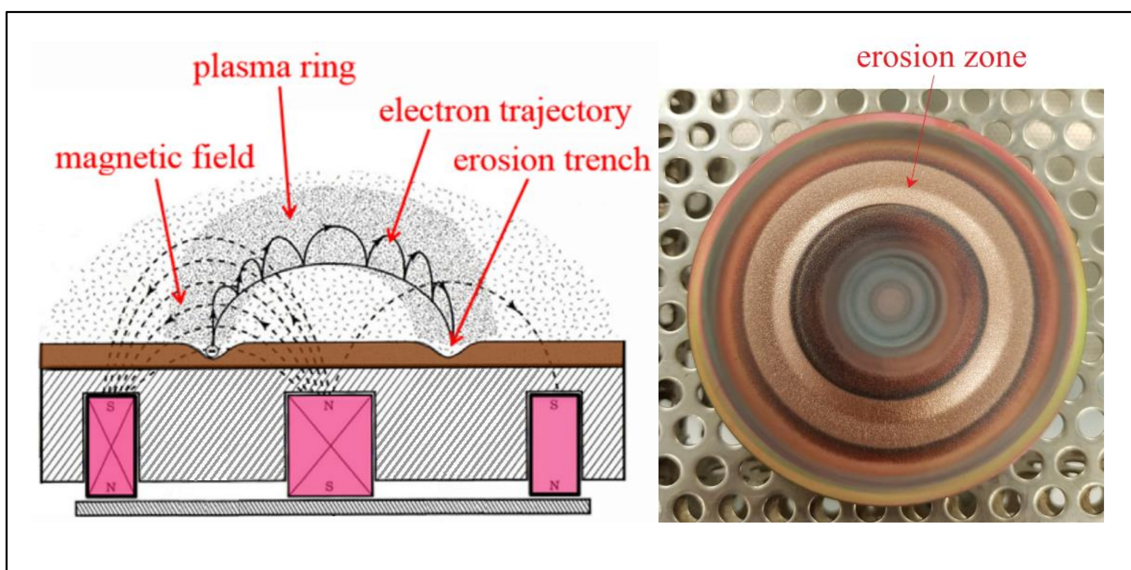

Fig 2. 2: Eroded zone observed on the surface of the target.

2.4.4 Co-sputtering

Co-sputtering is a technique where 2 or more targets are used simultaneously or alternately to deposit thin film on the surface of the substrate. Doped, alloy or composite films can be formed when 2 or more targets are sputtered simultaneously.

If the target is sputtered alternately, artificial periodic multilayer films can be designed. By varying the output power density of each target individually, the stoichiometry of deposited films can be controlled.

2.5 Effects of sputtering parameters on the properties of deposited CZO films

Sputtering is a complex process which involves a lot of different parameters that can affect the deposition process such as base pressure, substrate temperature, sputtering power, target structure and substrate structure. The properties and the quality of the deposited CZO films which include surface morphology, microstructure, optical properties and electrical properties are the product of the interplay of those parameters. Thus allowing the sputtering process to have huge control over the deposition process. Several details about the different deposition parameters are briefly discussed below.

2.5.1 Base pressure

Base pressure is one of the most important process parameter in the sputtering technique in which it can influence the rate of the contaminant and impurities that exist in the sputtering chamber. The impurities may come from the substrate and the target itself but mostly it originated from the trace gas that exhibits in the surrounding atmosphere. Thus, it is important to evacuate the sputtering chamber to a high pressure (usually ~10^{-5} Pa) before the sputtering process begin. The trace gas may affect the quality and the purity of the deposited films by reacting with it or simply include in the films as unwanted impurities.

2.5.2 Substrate temperature

In the deposition of the CZO thin films, the substrate temperature is one of the major parameters that can influence the outcome (microstructure properties) of the deposited CZO films. It involves the effect of the adatoms mobility with its respective energy which is located on the surface of the substrate. Ma *et al*. (2011) in his study reveal that the intensity of the ZnO (002) orientation will be enhanced by increasing the substrate temperature up to 350 °C [32].

This is because by increasing the value of the substrate temperature, it will provide the sputtered atoms with an additional surface mobility attribute in the improvement of the surface diffusion of the adsorbed species on the substrate's surface. However, if the substrate temperature is further increased above 350 °C, the reduction in the intensity of ZnO (002) orientation will be observed. This phenomena also has been observed in another study by Lee *et al*. (2010) that suggested the crystal planes which are perpendicular and parallel to the substrate surface will coalesce together at an excessive temperature resulting in the retardation of ZnO (002) orientation [61].

Yu *et al*. (2015) also stated that the lattice constant c of deposited CZO films decreases with increasing substrate temperature [35]. This is associated with the residual stress coming from the particular difference in the thermal expansion between the substrate and the deposited films. As the temperature of the substrate is increased, the energy of the deposited particles also will increase.

Thus, enhancing the migration of adatoms on the surface of the substrate. The films can be deposited with less defect and releases the internal stress of the films. It will lower the free energy of the crystal so that the atom can be arranged more compact. Leading to the increase in the packing density of the films and subsequently reduce the lattice constant c of deposited CZO films.

2.5.3 Post annealing treatment

Post annealing is one of the most common practice in a device fabrication process as it can influence the stability and reproducibility of the device as well as chemically activate the doped materials. According to Ma *et al*. (2011) there are two possible scenario that can happen after post annealing process which is the crystal quality of the films will be improved and the oxygen vacancies and Zn interstitials will be increased [32].

However if the samples are further annealed at excessive high temperature, it will results in the formation of high concentration of oxygen vacancies. Thus it will promote the formation of Cu_xO phase since the Zn-O bond energy is relatively quite low at about 159 kJ/mol [82]. Ahn *et al*. (2007) carried out a post annealing procedure of CZO films at 500 °C. It showed that the films has better transmittance in the infrared region compare to as deposited films[53].

This is due to when the deposition is carried out at room temperature, the CZO films are may not fully crystallized. It is plausible that Cu atom are not oxidizing completely, leaving behind the Cu metallic feature in the films which is responsible for the absorption in infrared region.

2.6 Characterization theory

In this work, five major characterization methods have been used to characterize the properties of the deposited films. The x-ray diffraction was used to determine the crystallization and structural changes of films. The surface morphology and its elemental composition was analysed by using Field emission scanning electron microscope and energy dispersive X-ray.

The optical transmittance was measured using Ultraviolet-Visible-Near Infrared spectroscopy. The surface structure and its roughness were measured using atomic force microscope and the electrical properties of the samples were measured using Hall effect measurement with a four-point Van der Pauw configuration. The working principle of these devices will be concisely discussed accordingly.

2.6.1 X-ray diffraction (XRD)

X-ray is generated in a vacuum cathode ray tube. This is achieved by supplying current within the tube, causing the inside filament to heat up. Throughout this process, the electron will be emitted from the filament. The higher the current, the greater the number of the electrons emitted. Then, the electron will be accelerated towards the anode target by supplying high voltage (typically 15-60 kV) within the tube. When the electron acquires high kinetic energy, the collision of electron and the target will occur. Eventually, the electron will get sufficient energy from the bombardment process and knock off inner shell electron of the target materials, producing characteristic x-ray spectra of that target. The anode target is commonly made of copper with long wavelength of Cu-Kα_1 (λ = 1.540598 Å) and Cu-Kα_2 (λ = 1.544426 Å), which give good resolution for registering the pattern.

These x-ray spectra are filtered by using foils or monochromator to produce monochromatic x-rays, which is required in the diffraction process. The generated x-ray are collimated and directed onto the sample at angle θ. The interaction of incident monochromatic x-ray beam with the sample plane will cause those x-ray beams to be scattered and can interfere constructively and destructively which depends on the existence of the certain phases within the samples.