FABRICATION AND CHARACTERIZATION OF METAL OXIDE THIN FILMS BY SPUTTERING METHOD FOR PN JUNCTION APPLICATIONS

AZMIZAM BIN MANIE @ MANI

THESIS SUBMITTED IN FULFILLMENT FOR THE DEGREE OF MASTER OF SCIENCE

FACULTY OF SCIENCE AND NATURAL RESOURCES
UNIVERSITY MALAYSIA SABAH
2017

UNIVERSITI MALAYSIA SABAH

BORANG PENGESAHAN STATUS TESIS

JUDUL: **FABRICATION AND CHARACTERIZATION OF METAL OXIDE THIN FILMS BY SPUTTERING METHOD FOR PN JUNCTION APPLICATIONS**

IJAZAH: **MASTER OF SCIENCE (PHYSICS WITH ELECTRONICS)**

Saya **AZMIZAM BIN MANIE @ MANIE**, Sesi Pengajian **2011-2016**, mengaku membenarkan tesis Sarjana ini disimpan di Perpustakaan Universiti Malaysia Sabah dengan syarat-syarat kegunaan seperti berikut:-

1. Tesis ini adalah hak milik Universiti Malaysia Sabah.
2. Perpustakaan Universiti Malaysia Sabah dibenarkan membuat salinan untuk tujuan pengajian sahaja.
3. Perpustakaan dibenarkan membuat salinan tesis ini sebagai bahan pertukaran antara institusi pengajian tinggi.
4. Sila tandakan (/)

[ ]	SULIT	(Mengandungi maklumat yang berdarjah keselamatan atau kepentingan Malaysia seperti yang termaktub di dalam AKTA RAHSIA 1972)
[ ]	TERHAD	(Mengandungi maklumat TERHAD yang telah ditentukan oleh organisasi/badan di mana penyelidikan dijalankan)
[/]	TIDAK TERHAD	

Disahkan oleh,

AZMIZAM BIN MANIE @ MANI

(Tandatangan Pustakawan)

Tarikh: 20 JUN 2017

(Assco. Prof. Dr. Saafie Salleh)

DECLARATION

I hereby declare that the work in this thesis is my own except for quotation, equations, summaries and references which have been acknowledged.

29 MARCH 2016

Azmizam Bin Manie @ Mani
PS20118154

CERTIFICATION

NAME : **AZMIZAM BIN MANIE @ MANI**

MATRIC NO. : **PS20118154**

TITLE : **FABRICATION AND CHARACTERIZATION OF METAL OXIDE THIN FILMS BY SPUTTERING METHOD FOR PN JUNCTION APPLICATIONS**

DEGREE : **MASTER OF SCIENCE (PHYSICS WITH ELECTRONICS)**

VIVA DATE : **29 MARCH 2017**

CERTIFIED BY;

1. **SUPERVISOR**

Assoc. Prof. Dr. Saafie Salleh

Signature

ACKNOWLEDGEMENT

First and foremost, my deepest gratitude to Almighty Allah (S.T) for grants me the strength and enthusiasm to finish this master thesis. Hopefully this research will give benefit to the community and become the starting point for me to pursue higher education level in the future.

A special gratitude to my supervisor, Assoc. Prof. Dr. Saafie Salleh, whose helped and guided me all the time and Madam Saturi Baco for the suggestion and support during the period of this research. Their guidance, idea and constructive comments helped me to coordinate my research and finally complete the thesis.

I also would like to express my appreciation to my beloved family especially to my parents, Manie @ Manie Bin Sulai @ Sullai and Abania Binti Ladis for their endless moral, support, love and understanding which become my source of motivation to finish this thesis. To my sister and her husband, my siblings and the rest of family, thanks for being such supportive and always be with me through thick and thin. And to you, finally i had completed our dream to get my master degree, even though you are not here with me anymore.

My sincere thanks also go to lecturers, lab assistance in Physics department for all their favour and also all staff in Faculty of Science and Natural Resources whose being there to help me. Special thanks for Madam Hasiah Salleh and Dr Nik Aziz Nik Ali (UMT) and Dr. Mohd Adib Ibrahim (SERI, UKM) for helping in sample characterize and giving some guidance in my research.

Last but not least, I would like to thank my fellow lab mates (Makmal Sains Bahan) for the ideas, the encouragement and assistance to go through all obstacles and challenge during the period of my research.

Azmizam Bin Manie @ Mani

12 March 2016

ABSTRACT

Metal oxides are the most common minerals on the earth due to their compositions, chemical and physical properties and widely used in many fields such as transparent electronics, piezoelectric transducers, sensors and electro-optical devices. Cu_2O and ZnO one of the well-known metal oxide material among the researcher and both materials receive positive review from lots of researchers. ZnO is a natural n-type semiconductor and Cu_2O is a p-type semiconductor. Therefore, this research describes about the fabrication of Cu_2O and ZnO thin films and discusses the characteristic of thin films deposited by RF magnetron sputtering technique. The substrate used to deposit thin films will be cut, cleaned and heated. Favorable deposition parameter such as nominal thickness from 100 nm to 500 nm and substrate temperature from 50 °C to 250 °C is chosen in order to analyze the characteristic of thin films. ZnO thin films show preferential orientation of (0 0 2) at 34° and the crystallite grain size increase as the increment of thin films thickness. ZnO thin films also shows same preferential orientation of (0 0 2) at 34° and the crystallite grain size also increase as the increment of thin films substrate temperature. The ZnO estimated optical band gap was 3.20- 3.24 eV for different thin film thickness while 3.26 eV for different thin film substrate temperature. The surface roughness of ZnO thin films was found increased as the thickness increased, while the surface roughness was found decreased as the substrate temperature increased. Cu_2O thin films show major preferential orientation of (1 1 1) at 36° and minor preferential orientation of (1 1 0) and (1 1 3) at 31° and 64°, the crystallite grain size increase as the increment of thin films thickness. Cu_2O thin films also shows same preferential orientation of (1 1 1) at 36° and the crystallite grain size also increase as the increment of thin films substrate temperature. The Cu_2O estimated optical band gap was in range of 1.95 -2.05 eV for different thin film thickness while for different substrate temperature was about 2.0 – 2.1 eV. The surface roughness results of Cu_2O thin films was found increased as the thickness increased, while the surface roughness was found decreased as the substrate temperature increased. The closest ideality factor obtain for Cu_2O/ZnO to the ideal ideality factor was 12.5, found to be at thickness Cu_2O of 200nm paired with the ZnO at thickness of 500nm.

ABSTRAK

PEMBUATAN DAN PENCIRIAN FILEM NIPIS OKSIDA LOGAM DARI KAEDAH UNTUK APLIKASI SIMPANG PN

Oksida logam adalah mineral biasa di bumi disebabkan komposisinya , sifat kimia dan fizikal dan digunakan secara meluas dalam pelbagai bidang seperti elektronik telus cahaya, transduser piezoelektrik, sensor dan peranti elektro-optik. Cu_2O dan ZnO salah satu dari bahan oksida logam yang terkenal di kalangan penyelidik dan kedua-dua bahan menerima ulasan positif dari ramai penyelidik. ZnO adalah semikonduktor semulajadi jenis n dan Cu_2O adalah semikonduktor jenis p. Oleh itu, kajian ini menerangkan tentang pembuatan filem nipis Cu_2O dan ZnO dan membincangkan ciri-ciri filem nipis yang dimendapkan oleh teknik memercit magnetron RF. Substrat digunakan untuk mendapan filem nipis akan dipotong, dibersihkan dan dipanaskan. Parameter pemendapan yang sesuai seperti ketebalan nominal dari 100 nm hingga 500 nm dan suhu substrat dari 50 °C hingga 250 °C dipilih untuk menganalisis ciri-ciri filem nipis. Filem nipis ZnO menunjukkan orientasi utama (0 0 2) pada 34° dan peningkatan saiz butiran kristalit sama seperti peningkatan ketebalan filem nipis. Filem nipis ZnO juga menunjukkan orientasi utama yang sama (0 0 2) pada 34° dan saiz butiran kristalit juga meningkat kerana kenaikan suhu substrat filem nipis. Jurang jalur optik ZnO dianggarkan 3.20 - 3.24 eV bagi ketebalan filem nipis yang berbeza manakala dianggarkan 3.26 eV untuk filem nipis bagi suhu substrat yang berbeza. Kekasaran permukaan filem nipis ZnO didapati meningkat ketika ketebalan meningkat, manakala kekasaran permukaan didapati menurun ketika suhu substrat meningkat. Filem nipis Cu_2O menunjukkan orientasi utama (1 1 1) pada 36° dan orientasi lain (1 1 0) dan (1 1 3) pada 31° dan 64° dan peningkatan saiz butiran kristalit sama seperti kenaikan ketebalan filem nipis. Filem nipis Cu_2O juga menunjukkan orientasi utama sama (1 1 1) pada 36° dan saiz butiran kristalit juga meningkat kerana kenaikan suhu substrat filem nipis. Jurang jalur optic Cu_2O dianggarkan dalam lingkungan 1. 95- 2.05 eV untuk ketebalan filem nipis yang berbeza manakala untuk suhu substrat yang berbeza adalah pada 2.0 - 2.1 eV. Keputusan kekasaran permukaan filem nipis Cu_2O didapati meningkat ketika ketebalan meningkat, manakala kekasaran permukaan didapati menurun ketika suhu substrat meningkat. Faktor terunggul terdekat untuk mendapatkan untuk Cu_2O / ZnO faktor idealistis yang sesuai adalah 12.5, didapati pada ketebalan Cu_2O daripada 200nm dipasangkan dengan ZnO pada ketebalan 500nm.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATION AND SYMBOLS

Ev	-	Electron Volt
RF	-	Radio frequency
nm	-	nanometer
Å	-	Angstrom
μm	-	Micrometer
DC	-	Direct current
C	-	Celsius
Pa	-	Pascal
V_T	-	Turn on voltage
ϕ_b	-	Barrier height
sccm	-	Standard cubic centimetre per minute
FWHM	-	Full width half maximum

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

This thesis will discuss the properties of ZnO and Cu_2O thin films. An RF powered Magnetron Sputtering system was used to fabricate the thin films at various thicknesses and substrate temperatures. The thin films also be studied in the form of p-n heterojunction.

1.1 The Overview of the Study.

The technology of thin film is rising every day, as the number of application from thin film also increases. A thin film is a layer of material ranging from fractions of a nanometer to several micrometers in thickness (Chopra and Maini, 2010). The earliest documented inorganic thin films were gold layers, produced chemi-mechanically by Egyptians approximately 5000 years ago. The earliest published electroplating experiments were ~1800 AD, immediately after the invention of the DC electrochemical battery by Volta. Chemical vapor deposition (CVD) of metal films was reported in 1649, atmospheric arc deposition of oxides in the mid-1760s, and atmospheric plasmas in 1857. Sols were produced in the mid-1850s and sol-gel films synthesized in 1885. Vapor phase film growth including sputter deposition, vacuum arc deposition, plasma-enhanced CVD and evaporation (Greene, 2014). Thin films have interesting properties which are different from those of the bulk materials which they are made of and are applied in many fields. Thin films are used for protective coatings on tools, photo detector in optoelectronic applications, solar cell in energy applications, resistor in electronic applications and so on (Höglund, 2008).

Semiconductors are materials that have electrical conductivity intermediate between the electrical conductivity of good conductors (such as aluminium and copper) and good insulators (some glasses and plastics). There is several materials that exhibit semiconducting behaviour but only a very few of them are of much interest in electronics. Silicon is one of the most important semiconductor materials and is the active material in almost all electronic devices. A few other semiconductors for example, gallium arsenide is essential because they can be used to make optoelectronic devices. Materials are semiconductors in part because of their chemistry (the electronic structure of the constituent atoms) and in part because of their structure (the way in which atoms are organized to make the solid material). Semiconductor materials are particularly useful for electronics due to electrical conductivity of the pure material can be greatly changed by the introduction of a small number of impurities. In addition, semiconductors are strongly influenced by applied fields (including electric, magnetic and electromagnetic fields) (Greve, 2012).

Devices such as emitters, detectors, amplifiers and repeaters use semiconductor devices. New semiconductor materials such as gallium nitride (GaN) and silicon carbide (SiC) are emerging that are far more tolerant of high temperatures and operate at higher current densities and frequencies than existing devices. Devices made from these materials are highly attractive for high power, high frequency and high temperature operation.

The distinction among three categories of conductor, semiconductor and insulator is based on the energy band in material. For insulator, it has the highest occupied band, called the valence band, is filled and the other energy band is conduction band where completely empty. The energy separation between these two bands is called energy gap. The energy gap for insulator is very high such that carriers cannot be promoted from valence band to conduction band, so there is no current can flow in that material.

Metal is highly conductive material because the conduction band consists of many electrons and empty states. The large current can be supported because most of the electrons within the conduction band can contribute to current conduction due to the existence of many vacancies where electrons can move under action of driving field.

Semiconductor is something like insulator, but with relatively small energy gap separating conduction band and valence band. At absolute zero temperature, the conduction band is completely empty and valence band is completely filled. As the temperature is raised to room temperature, the energy gap is sufficiently small that some measurable of conduction band occur. Therefore, semiconductor will conduct a current at room temperature but with higher resistance than metal (Brennan, 2005).

Based on the energy band model as shown in Figure 1.1, it is easier to understand the differences among metal, insulator and semiconductor. Semiconductor has nearly filled valence band and nearly empty conduction band separated by a band gap as shown in Figure 1.1(a). As for insulator, the band gap is larger compare to semiconductor, with totally filled valence band and totally empty conduction band as shown in Figure 1.1(b). Figure 1.1(c) shows the band diagram for conductor, where the conduction band partially filled and holds the conduction electrons (Hu, 2010).

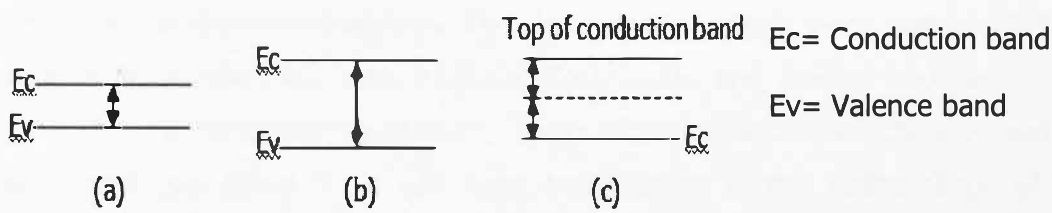

Figure 1.1 : Energy band diagrams for (a) Semiconductor (b) Insulator and (c) Conductor

Source : Chenming Calvin Hu (2010)

Semiconductor has two types, intrinsic and extrinsic semiconductor. Intrinsic semiconductor has no intentionally added impurities where extrinsic semiconductor has intentionally added impurities called dopants. For intrinsic semiconductor, the promoting electrons from valence band produce carriers within conduction band.

The vacancy named as hole is produced when electron is promoted from valence band to conduction band is called hole. As a result, the conduction band is no longer empty and can conduct current, like valence band is no longer completely filled and can conduct current too.

As for extrinsic semiconductor, the dopant has two types. These are n-type dopants called donors and p-type dopants called acceptors. When a semiconductor is doped with donors, the equilibrium electron concentration becomes larger than the equilibrium hole concentration and therefore the semiconductor is called n-type. While a semiconductor is doped with acceptor, the equilibrium hole concentration becomes larger than the equilibrium electron concentration and therefore the semiconductor is called p-type (Brennan, 2005).

Metal oxide gains attraction from researcher due to Metal Oxide favorable characteristics which are low temperature fabrication, high carrier mobility, large frequency operation, extreme mechanical bend ability, together with transparency, conformability, stretch ability, and water dissolubility that is suitable for the fabrication of electronics devices. The first reported metal oxide semiconductors were binary compounds, such as SnO_2, ZnO, In_2O_3, and Ga_2O_3, in either a pure composition or with impurity dopants. These binary materials are characterized by wide band gap above 3 eV and large transmission in the visible range above 80%.The resulting films are n-type semiconducting, yielding a high carrier concentration (N) in the order of 10^{16} cm^{-3} – 10^{21} cm^{-3} which is attributed to native donors, such as oxygen (O_2) vacancies. Metal oxide also exists as p-type materials. In general, p-type metal oxide semiconductors are characterized by a band gap E_g ranging from 1.3 eV to 2.7 eV, high transmittance in the visible range (>85%), and carrier density (N) from 10^{8} cm^{-3} (for NWs) 259 to 10^{15} cm^{-3} for high-quality single crystals.

In this research, the main materials that used in fabrication of thin films are Zinc Oxide (ZnO) and Cuprous Oxide (Cu_2O). Both materials receive positive review from lots of researchers. Cu_2O/ZnO is an attractive all-oxide candidate for low-cost photovoltaic applications. The materials are abundant, non-toxic and relatively stable. ZnO is a natural n-type semiconductor with an energy gap of around 3.37 eV (Chen et al., 1995).

ZnO has been used to fabricate many crucial devices such as solar cell (Chen et al., 2010), light emitting devices (Nakahara et al., 2010), and photo detectors (Wang and Lin, 2010). ZnO has been drawing the attention of researchers, because of its unique properties such as high electrochemical stability, resistivity control, and transparency in the visible range with a wide band gap, absence of toxicity and abundance in nature (Ismail et al., 2001). ZnO based thin films also have attracted a great interest nowadays in semiconductor materials field because of its inexpensive and environmental friendly in term of non-toxic properties compared to Indium Tin Oxide (ITO).

Cu_2O is a semiconductor with a band gap of 2.0 eV (Olsen et al., 1982). Although not optimal (1.5 eV), its band gap nearly ideal when used as a top cell or absorber layer in hetero junction solar cell. It is suitable material for solar cell because of its direct band gap and optical absorption coefficients. Cu_2O is also used as cathode material for micro batteries (Souza et al., 2006), random access memories (Yang et al., 2008), high temperature superconductors (Li et al., 1991) and gas sensor (Samarasekara et al., 2006).

Several techniques have been proposed for fabrication of thin films such as sol gel method, spray pyrolisis, metal-organic chemical vapour deposition (MOCVD), pulsed laser deposition (PLD), dip-coating hydrothermal method and magnetron sputter. Among all these techniques, magnetron sputtering is applied because of the ability to produce high quality thin film with a high density and high adhesion, and can be performed at low substrate temperature with good uniformity of the film thickness in a large area. This study will establish the characteristic of films fabricated using RF magnetron sputtering.

Sputtering, also known as sputter etching, is used for patterning semiconductor wafers, cleaning surfaces, micromachining, depth profiling, and several applications which require careful, microscopic erosion of a surface. Sputter deposition is used for film deposition on semiconductor wafers, on magnetic media and head surfaces, for coating tools and cutting surfaces for wear resistance (this includes, by the way, such tools as shaving razors), for reflective coatings on window glass, for coating the insides of plastic bags and the surfaces of automobile parts, and several other wide-ranging applications (Rossnagel, 1995).

The main advantages of sputtering over other PVD methods are its ability to sputter large-size targets, simplifying the deposition of thins with uniform thickness over large wafer, film thickness is easily controlled by fixing the operating parameters and adjusting the deposition time, control of the alloy composition, as well as other film properties such as step coverage and grain structure, is more easily accomplished. Sputter-cleaning of the substrate in vacuum prior to film deposition will be carried out and device damage induced by X-rays generated by electron beam evaporation must also be avoided (Doolittle, t:th).

1.2 Research Problem

Thin films deposition is crucial because it is important to deposit uncontaminated thin film. From the preparation of deposition to environment during the preparation and deposition methods affect how good the deposited thin films. Also, to fully optimize the film properties, the selection of preferable deposition parameter also included. The type of materials used in this research has major role in thin film deposition because the materials should have wide range of application in daily life.

The guidelines from past researcher had been analyzed to investigate appropriate preparation condition to obtain preferable quality of selected materials of thin films to determine factors (deposition parameters) that influence thin film conditions and then identify the optimum fabrication condition to fabricate p-n junction.

1.3 Research Motivation

This research is carried out to fabricate the p-n heterojunction thin film consists of ZnO and Cu_2O layer of thin films. Thin films of ZnO and Cu_2O will be deposited by varied the thickness and substrate temperature parameters. The nominal thickness parameter varied from 100nm to 500nm with interval of 100nm thickness.

The substrate temperature parameter varied from 50°C to 250°C with interval of 50°C. The thin films will be characterized using UV-Visible, X-ray diffractometer, Profilometer and I/V measurement. Thin films of ZnO and Cu_2O with various thickness and substrate temperature were fabricated and characterized to investigate the optical, structural, surface roughness and electrical properties.

1.4 Research Objective

The research objectives are outlined as follows

1.4.1 To fabricate the ZnO and Cu_2O thin films using RF powered magnetron sputtering.

1.4.2 To obtain the optical properties, structural properties and electrical characteristics of fabricated ZnO and Cu_2O thin films.

1.4.3 To analyze and evaluate the p-n characteristics of fabricated ZnO and Cu_2O thin films.

1.5 Research Limitation

This research had some limitation, due to minimize the scope of this research and provide accurate and sufficient information of the results. The deposition parameters such thin film thickness had been limited from 100 nm to 500 nm and substrate temperature had been limited from 50°C to 250°C.

1.6 Research Contribution

The findings of this research give benefit to the growth of thin films technology, especially in optoelectronic devices. As the thin film technology continuously evolving, the demand for a good control on material structure is therefore crucial. The new characteristics and parameter established for this research will greatly assist in the development of small circuitry using thin film technology. For example, this research will contribute more specifically to the technology of solar cell fabrication. Generally, solar cell fabrication consists of p-n junction and hopefully the findings of thin film p-n junctions from this research could help the technology more advance in the future.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Metal oxides have become one of the most important inorganic materials in device applications such as light emitting diodes, field effect transistors and solar cells (Hofstetter and Morkoc, 2010). Metal oxides demonstrate a wide range of properties depending on their crystal structure and bonding between the metal cation and oxygen (Nkhaili et al., 2015). Metal oxide nanostructures are the focus of current research efforts in nanotechnology since they are the most common minerals on the earth due to their special shapes, compositions, chemical and physical properties. They have now been widely used in many areas, such as transparent electronics, piezoelectric transducers, ceramics, catalysis, sensors, electro-optical and electro-chromic devices (Wang and Song, 2006). Among the metal oxides materials, ZnO and Cu_2O are more attractive because these materials are abundant in nature, inexpensive and nontoxic. Thin film hetero junction between p-type Cu_2O and n-type ZnO has received attention because of the successful demonstration of ZnO and Cu_2O thin film deposition by various methods such as molecular beam epitaxy (MBE) (Morkoç and Özgür, 2009), magnetron sputtering (Ellmer, 2001), chemical vapor deposition (CVD) (Stavale, 2013) and electrochemical deposition (Ievskaya, 2014). The performance of thin film hetero junction depends on the electrical and optical properties of each layer which comprises the device and the quality of the interface between the films that form the junction.