



**SYNTHESIS AND CHARACTERIZATION OF  
 $\text{Cu}_2\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4$  QUINTERNARY ALLOY  
NANOSTRUCTURES USING SOL-GEL  
ELECTROSPINNING TECHNIQUE**

by

**AUTHMAN SALIM IBRAHEAM  
(1341911104)**

A thesis submitted in fulfillment of the requirements for the degree of  
Doctor of Philosophy in Nanomaterial Engineering

**Institute of Nano Electronic Engineering  
UNIVERSITI MALAYSIA PERLIS (UniMAP)**

2016

## DECLARATION OF THESIS

Author's full name AuthmanSalimIbraheam

Date of birth 15 \ 02 \ 81

Title: SynthesisandCharacterizationof  $Cu_2Zn_{1-x}Cd_xSnS_4$ QuinternaryAlloy  
NanostructuresUsing Sol- Gel Electrospinning Technique

Academic Session2015/ 2016

Hereby declare that the thesis becomes the property of Universiti Malaysia Perlis  
(UniMAP) and to be placed at the library of UniMAP. This thesis is classified as:

- CONFIDENTIAL** (Contains confidential information under the Official  
Secret Act 1972)\*
- RESTRICTED** (Contains restricted information as specified by the  
organizationwhere research was done)\*
- OPEN ACCESS** I agree that my thesis is to be made immediately  
available as hard copy or on-line open access (full  
text)

I, the author, give permission to the UniMAP to reproduce this thesis in whole or  
in part for the purpose of research or academic exchange only (except during a  
period of years, if so requested above).

Certified by:

\_\_\_\_\_  
**SIGNATURE**

**A9996408**  
(NEW IC NO. / PASSPORT No.)

Date:

\_\_\_\_\_  
**SIGNATURE OF SUPERVISOR**

**Assoc.Prof.Dr. Yarub. Al-Douri**  
**NAME OF SUPERVISOR**

Date:

## ACKNOWLEDGEMENT

"All praises and thanks to almighty ALLAH"

In the name of Allah, Most Gracious, Most Merciful, First and foremost, I thank the Almighty Allah for giving me inspiration, patience and health to complete this doctoral study

I am deeply indebted to Prof. Dr. Yarub. Al-Douri, my supervisor who guided me and motivated me throughout the stages of doing this study. He has been instrumental in turning my dream into reality through his valuable guidance and constructive comments. I would also like to thank my co-supervisor, Prof. Uda. Hashim for his kindness and help. My appreciation also goes to the staff in the Nanomaterial engineering and Technology Laboratory for their cooperation, technical assistance and valuable contribution to my work. In addition, I would like to thank Prof. Evan T Salem from University of Technology, Baghdad, Iraq for his help me and good discussion. Special thanks are due to all my colleagues for their feedback and encouragement. I am what I am, because of my family: my father , mother ,my brothers , Sattar, Eyad, Omer, Mustafa and my sisters. Last, and most important, I extend special thanks to my wife who accompany me during this important time in our lives. Without their endless love, patience and support, I could not have a chance to complete this study. My thanks also go to University Malaysia Perlis (UniMAP) for providing me the suitable environment to make this thesis better.

AuthmanSalimIbraheam

Perlis, Malaysia. January 2016

## TABLE OF CONTENTS

	PAGE
<b>THESIS DECLARATION</b>	<b>i</b>
<b>ACKNOWLEDGMENT</b>	<b>ii</b>
<b>TABLE OF CONTENTS</b>	<b>iii</b>
<b>LIST OF TABLES</b>	<b>vii</b>
<b>LIST OF FIGURES</b>	<b>viii</b>
<b>LIST OF SYMBOLS</b>	<b>ix</b>
<b>LIST OF ABBREVIATIONS</b>	<b>xi</b>
<b>ABSTRAK</b>	<b>xii</b>
<b>ABSTRACT</b>	<b>xiv</b>
<b>CHAPTER 1 INTRODUCTION</b>	<b>1</b>
1.1 Overview	1
1.2 Problem Statement	2
1.3 Research Objectives	4
1.4 Scope of Research	5
1.5 1.5. Novelty of research	7
1.6 Thesis Outline	7
<b>CHAPTER 2 LITERATURE REVIEW AND THEORETICAL BACKGROUND</b>	<b>9</b>
2.1 Physical Properties of CZTS	9
2.2 Current-Voltage ( <i>I-V</i> ) Characteristics	14
2.3 Defect Physics/Chemistry of CZTS	17
2.4 CZTS Solar Cell Structure and Band Alignment	18
2.5 Evolution of Cu <sub>2</sub> ZnSn <sub>4</sub> thin film solar cell efficiency	22

2.6	Deoxyribonucleic acid (DNA)	24
2.7	Dengue	25
2.8	Detection of Dengue	27
2.9	The Previous Studies	29
<b>CHAPTER 3 PUBLISHED PAPER</b>		45
A.S.	Ibraheam, Y. Al-Douri, U. Hashim , M.R. Ghezzar , A.AddouWaleed, K. Ahmed.Cadmium effect on optical properties of $Cu_2Zn_{1-x}Cd_xSnS_4$ quinternaryalloys nanostructures.Solar Energy 114,39–50	45
3.1	Paper Synopsis	45
3.1.1	Cadmium effect on optical properties of $Cu_2Zn_{1-x}Cd_xSnS_4$ quinternaryalloys nanostructures	48
A. S.	Ibraheam, Y. Al-Douri, Abubaker S. Mohammed, Deo Prakash4 , U. Hashim, K.D.VermaElectrical, Optical and Structural Properties of $Cu_2Zn_{0.8}Cd_{0.2}SnS_4$ Quinternary Alloy Nanostructures Synthesized by spin Coating Technique.Int. J. Electrochem. Sci., 10 ,9863 – 9876	49
3.2	Paper Synopsis	49
3.2.1	Electrical, Optical and Structural Properties of $Cu_2Zn_{0.8}Cd_{0.2}SnS_4$ Quinternary Alloy Nanostructures Synthesized by spin Coating Technique	52
A. S.	Ibraheam, Y. Al-Douri, J. M. S. Al-Fhdawi, Hamid S. AL-Jumaili, K. D. Verma, U. Hashim1 • R. M. Ayub, A. Rahim Ruslinda1 • M. K. M Arshad A. H. Reshak, S. B. Abd Hamid. Structural, optical and electrical properties of $Cu_2Zn_{1-x}Cd_xSnS_4$ quinternary alloys nanostructures deposited on porous silicon.Microsyst Techno,pp1-8	53
3.3	Paper Synopsis	53
3.3.1	Structural, optical and electrical properties of $Cu_2Zn_{1-x}Cd_xSnS_4$ quinternary alloys nanostructures deposited on porous silicon	57

A. S. Ibraheam, Y. Al-Douri, Nabeel Z. Al-Hazeem, U. Hashim, DeoPrakash, and K. D. Verma	58
Effect of Cadmium Concentration on Structural, Optical, and Electrical Properties of $\text{Cu}_2\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4$ Quinternary Alloy Nanofibres, ynthesized by Electrospinning Technique. Journal of Nanomaterials. 2016, 1-11	
3.4 Paper Synopsis	58
3.4.1 Effect of Cadmium Concentration on Structural, Optical, and Electrical Properties of $\text{Cu}_2\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4$ Quinternary Alloy Nanofibres, ynthesized by Electrospinning Technique	61
A. S. Ibraheam <sup>1</sup> , Y. Al-Douri <sup>1</sup> , U. Hashim <sup>1</sup> , Deo Prakash <sup>3</sup> , K. D. Verma, and M. Ameri <sup>5</sup> (2016) Fabrication, analysis and characterization of $\text{Cu}_2\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4$ quinternary alloy nanostructures deposited on GaN	62
3.5 Paper Synopsis	62
3.5.1 Fabrication, analysis and characterization of $\text{Cu}_2\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4$ quinternary alloy nanostructures deposited on GaN	65
Authman S. Ibraheam, Yarub Al-Douri, Subash C.B. Gopinath, Uda Hashim. A Novel Quinternary Alloy ( $\text{Cu}_2\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4$ ) Nanostructured Sensor for Biomedical Diagnosis. Scientific Reports, under review in March (2016)	66
3.6 Paper synopsis	66
3.6.1 A Novel Quinternary Alloy ( $\text{Cu}_2\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4$ ) Nanostructured Sensor for Biomedical Diagnosis	69
<b>CHAPTER 4 CONCLUSIONS AND FUTURE WORKS</b>	69
5.1 Conclusion	69
5.2. Future works	72
<b>REFERENCES</b>	74
<b>APPENDIX A: PATENT PENDING</b>	85

<b>APPENDIX B: LIST OF PUBLICATIONS INCLUDED IN THE THESIS</b>	86
<b>APPENDIX C: LIST OF PUBLICATIONS NOT INCLUDED IN THE THESIS</b>	88
<b>APPENDIX D: PRODUCT EXHIBITED FROM THESE WORK</b>	90
<b>APPENDIX E: TABLES FOR UNPUBLISHED PAPERES AND PUBLISHED PAPERES</b>	92
<b>APPENDIX F: FIGURES FOR UNPUBLISHED PAPERS AND PUBLISHED PAPERS</b>	94

©This item is protected by original copyright

## LIST OF TABLES

NO.		PAGE
2.3	Determined band offsets and constants related with CdS and CZTS	21

©This item is protected by original copyright



## LIST OF FIGURES

NO.		PAGE
2.1	Crystal structures of CIGS and CZTS	10
2.2	(a) Electrical equivalent circuit of a solar cell. (b) Typical $I$ - $V$ characteristics of a solar cell	15
2.3	CZTS solar cell structure	19
2.4	Band diagram for CdS	20
2.5	Band diagram for CZTS	20
2.6	Band bending prediction with a) a spike in the conduction band and a cliff on the valence band and b) a cliff in both bands	22

©This item is protected by original copyright

## LIST OF SYMBOLS

$T$	Thickness
a, b, c	Lattice Parameters
hkl	Miller Indices
$d_{hkl}$	Inter Planar Spacing
$\Lambda$	The Wavelength
$\beta$	The Full Width at Half Maximum
$\theta$	Bragg Angle
$\delta$	The dislocation density
E	Micro Strain
K	Boltzmann's Constant
T	Temperature
A	the absorption
A	Absorption Coefficient
$E_t$	the tail width
$P_{max}$	maximum power point
$E_g$	Energy Band gap
D	The crystallite size
T	Transmission of Light
$h\nu$	Photo Energy
$E_{phonon}$	The Phonon Energy
P	Density
$B_0$	the observation
I	Current

$A$	Area of Contact
$Q$	Electron Charge
$\rho$	Resistivity
$I_{ph}$	The Photocurrent
$I_{dark}$	Current in dark
$\Delta m$	difference of substrate weight
$C$	Velocity of light
$H$	Efficiency
$\Delta$	the dislocation density
$I-V$	Current–Voltage
$R$	Responsivity
$S$	The Photoconductor Sensitivity
$T$	Time
$J_m$	current density
$V_m$	Voltage
$H$	Efficiency
$FF$	fill factor
$J_{SC}$	current density
$P$	power density
$V_{OC}$	open circuit voltage
$J_{SC}$	Short circuit current
$R_{sh}$	shunt resistance
$P_{in}$	incident light power density

## LIST OF ABBREVIATIONS

2-D	Two Dimensional
3-D	Three Dimensional
a. u.	Arbitrary Unit
AFM	Atomic Force Microscope
<i>CZCTS</i>	$\text{Cu}_2\text{ZnCdSnS}_4$
CZTS	$\text{Cu}_2\text{ZnSnS}_4$
EDX	Energy dispersive X-ray
F-SEM	Field Emission-Scanning Electron Microscope
FWHM	Full Width at Half Maximum
M	Molarity
$M_s$	number of moles
$M_{wt}$	molecular weight
PD	Photodetector
PL	Photoluminescence
PS	porous silicon
$R_{ec}$	Decay Time of Photoconductive Device
$R_{es}$	Rise Time of Photoconductive Device
RMS	Root Mean Square
UV-Vis	Ultraviolet-Visible
V	liquid size
W	weight
XRD	X-ray Diffraction

# Sintesis, Analisis Dan Pencirilan Struktur Nano Alloi Kuinterari Quinteranry Menggunakan Kaedah Sol- Gel elektrospinning teknik

## ABSTRAK

Tujuan utama kerja penyelidikan yang dibentangkan dalam tesis ini adalah mensintesis struktur nano  $\text{Cu}_2\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4$  dengan kepekatan Cd ( $x=0$  to 1) di atas gelas, silikon berliang (PS), silikon teroksida ( $\text{SiO}_2$ ) and substrat GaN menggunakan kaedah berbeza penyalutan spin dan teknik elektrospinning bagi heterosimpang, sel solar dan aplikasi pengesanan DNA Denggi jenis-2. Dalam kerja ini, kami telah mengkaji kesan kepekatan (0.3, 0.5, 0.7 dan 0.9 mol/L) tembaga (Cu) yang berbeza ke atas sifat struktur, morfologi, optikal dan elektrik struktur nano aloi kuinterari  $\text{Cu}_2\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4$  yang disediakan menggunakan kaedah penyalutan spin. Luang jalur terus struktur nano aloi kuinterari  $\text{Cu}_2\text{Zn}_{0.8}\text{Cd}_{0.2}\text{SnS}_4$  menurun apabila kepekatan Cu meningkat daripada 1.81 eV pada 0.3 M kepada 1.60e V pada 0.9 M. Nilai penghantaran dalam julat 63-49% juga bergantung kepada kepekatan Cu. Indeks refraktif dan pemalar dielektrik optikal dikira dan selaras dengan hasil eksperimen dan teori. Sifat elektrik dikaji oleh ukuran kesan Hall menunjukkan kenkonduksian jenis-p dengan pembawa kepekatan antara  $7.819 \times 10^{12} \text{ cm}^{-3}$  dan  $3.76 \times 10^{14} \text{ cm}^{-3}$ . Ia mencerap penurunan linear dalam luang jalur  $\text{Cu}_2\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4$  / struktur struktur nano aloi kuinterari gelas seperti peningkatan kepekatan Cd. Nilai penghantaran adalah 73% pada  $x = 0$  and 39% pada  $x = 1$ . Ukuran Kesan Hall menyarankan supaya semua struktur nano matang mempunyai konduksi jenis-p. Keputusan XRD menunjukkan struktur nano aloi kuinterari  $\text{Cu}_2\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4$  mempunyai polihabluran pelbagai fasa dengan orientasi utama bersama arah (112) dan (312) dengan struktur kesterit pada  $x=0$  dan struktur stannit pada  $x=1$ . Struktur nano aloi kuinterari  $\text{Cu}_2\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4$  atas PS (63.93%) dan si substrat dengan kepekatan Cd berbeza dimasukkan melalui penyalutan spin yang berjaya diuji bagi heterosimpang. Arus ke voltan (I-V) heterosimpang Ag/n-PS/ $\text{Cu}_2\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4$ /Ag  $x= 0, 0.6, 1$  dicirikan. Photosensitiviti meningkat apabila kepekatan Cd meningkat kepada (3401.36) bagi  $x=0.6$  berbanding (282.40) bagi  $x=0$  dan (567.68) bagi  $x=1$ . Kaedah berbeza bagi teknik elektronikspinning digunakan bagi pensintesis nano optik aloi kuinterari  $\text{Cu}_2\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4$ . Sifat optikal yang dikendalikan melalui UV-Vis menunjukkan bahawa luang jalur menurun daripada 1.75 eV kepada 1.61 eV apabila kepekatan Cd meningkat. ZnO:Al/CdS/ $\text{Cu}_2\text{Zn}_{0.4}\text{Cd}_{0.6}\text{SnS}_4$ /Al/gelas dipilih bagi menfabrikasikan sel solar di bawah AM 1.5 G pencahayaan solar yang disimulasi dengan keamatan 100  $\text{mW/cm}^2$  kecekapan penukaran tertinggi 3%. struktur nano aloi kuinterari  $\text{Cu}_2\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4$  dengan kandungan Cd  $x=0, 0.6, 1$  yang berbeza disediakan menggunakan teknik penyalutan spin ke atas substrat GaN. Pencirilan elektrik diod Ag/n-GaN / $\text{Cu}_2\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4$ /Ag melalui arus kepada pencirilan voltan (I-V) menunjukkan respon-foto tertinggi komposisi  $\text{Cu}_2\text{Zn}_{0.4}\text{Cd}_{0.6}\text{SnS}_4$ . Akhir sekali, struktur nano aloi kuinterari ( $\text{Cu}_2\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4$ ) dengan kepekatan Cd yang berbeza melalui teknik penyalutan spin ke atas substrat  $\text{SiO}_2$  disintesis. Saiz biasa bijian struktur nano aloi kuinterari ( $\text{Cu}_2\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4$ ) adalah diantara 27.06 nm bagi  $\text{Cu}_2\text{ZnSnS}_4$  dan 43.12 nm for  $\text{Cu}_2\text{CdSnS}_4$ . Anjakan luang jalur PL daripada 1.79 eV ( $x=0$ ) kepada 1.69 eV ( $x=1$ ) diperhatikan. Tambahan lagi, struktur novel yang dihasilkan dikenal pasti lebih sesuai bagi biopengesanan, seperti yang dibuktikan oleh pengesanan DNA jenis-2 Denggi dengan ketentuan/spesifisiti tinggi. Biopenderia menunjukkan struktur nano aloi kuinterari boleh memperoleh sensitiviti sehingga 100fM dan boleh membeza layan DNA tertentu daripada denggi untuk melawan satu atau tiga salah padanan.

©This item is protected by original copyright

# Synthesis and Characterization of $\text{Cu}_2\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4$ Quinternary Alloy Nanostructures Using Sol- Gel Electrospinning Technique

## ABSTRACT

The principal aim of the research work presented in this thesis is to synthesise nanostructured  $\text{Cu}_2\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4$  with different Cd concentrations ( $x=0$  to 1) on glass, porous silicon (PS), oxidized silicon ( $\text{SiO}_2$ ) and GaN substrates using different methods of spin coating and electrospinning techniques for heterojunction, solar cell and Dengue type-2 DNA detector applications. In this work, we have studied the different effect copper (Cu) concentrations (0.3, 0.5, 0.7 and 0.9 mol/L) on the structural, morphological, optical and electrical properties of  $\text{Cu}_2\text{Zn}_{0.8}\text{Cd}_{0.2}\text{SnS}_4$  quinternary alloy nanostructures prepared by spin coating technique. The direct band gap of  $\text{Cu}_2\text{Zn}_{0.8}\text{Cd}_{0.2}\text{SnS}_4$  quinternary alloy nanostructures decreases as Cu concentration increases from 1.81 eV at 0.3M to 1.60 eV at 0.9M. The transmittance value in the range 63-49% was also dependent on Cu concentration. The refractive index and optical dielectric constant are calculated and gave good agreement with experimental and theoretical results. Electrical properties studied by Hall Effect measurement, showed p-type conductivity, with a carrier concentration between  $7.819 \times 10^{12} \text{ cm}^{-3}$  and  $3.76 \times 10^{14} \text{ cm}^{-3}$ . It was observed a linear decreasing in the band gap of  $\text{Cu}_2\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4$ /glass quinternary alloy nanostructures as Cd concentration increases. The transmittance value was 73% at  $x=0$  and 39% at  $x=1$ . Hall Effect measurements suggest that all the grown nanostructures have p-type conduction. XRD results showed that  $\text{Cu}_2\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4$  quinternary alloy nanostructures has multiphase polycrystalline with preferential orientation along (112) and (312) directions with kesterite structure at  $x=0$  and stannite structure at  $x=1$ . The  $\text{Cu}_2\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4$  quinternary alloy nanostructures on PS (63.93%) substrate with different Cd concentration deposited via spin coating technique were successfully examined for heterojunction. The current-to-voltage (I-V) of Ag/n-PS/ $\text{Cu}_2\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4$ /Ag heterojunction at  $x=0, 0.6, 1$  was characterized. The photosensitivity increases as Cd concentration increases to of (3401.36) for  $x=0.6$  compared with (282.40) for  $x=0$  and (567.68) for  $x=1$  respectively. Different method electrospinning technique is used to synthesise of  $\text{Cu}_2\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4$  quinternary alloy nanofibres. Energy gap was decreased from 1.75 eV to 1.61 eV as Cd concentration increases. ZnO:Al/CdS/ $\text{Cu}_2\text{Zn}_{0.4}\text{Cd}_{0.6}\text{SnS}_4$ /Al/glass were selected to fabricate solar cells under simulated AM 1.5 G solar illumination with intensity of  $100 \text{ mW/cm}^2$  the highest conversion efficiency of 3%. Also  $\text{Cu}_2\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4$  quinternary alloy nanostructures with different Cd contents  $x=0, 0.6, 1$  were prepared using spin coating technique on GaN substrate. The electrical characterization of the Ag/n-GaN/ $\text{Cu}_2\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4$ /Ag diode through current to voltage (I-V) characterization showed the highest photo-response of  $\text{Cu}_2\text{Zn}_{0.4}\text{Cd}_{0.6}\text{SnS}_4$  composition. Finally, The quinternary alloy ( $\text{Cu}_2\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4$ ) nanostructure with different Cd concentrations via spin coating technique on  $\text{SiO}_2$  substrate was synthesised. The average grain size of  $\text{Cu}_2\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4$  quinternary alloy nanostructure was between 27.06 nm for  $\text{Cu}_2\text{ZnSnS}_4$  and 43.12 nm for  $\text{Cu}_2\text{CdSnS}_4$  nanostructures. A shift of PL band gap from 1.79 eV ( $x=0$ ) to 1.69 eV ( $x=1$ ) was observed. Furthermore, the generated novel structure was found to be more suitable for biorecognition, as evidenced by Dengue type-2 DNA detection with higher specificity. The biosensor shown with quinternary alloy nanostructure could attain the sensitivity to

100 fM and able to discriminate specific DNA from dengue against single and triple mismatches.

©This item is protected by original copyright



# CHAPTER 1

## INTRODUCTION

### 1.1. Overview

The need for sustainable energy sources is always current and solar cells can be one of the main solutions. Especially thin film solar cells have a high potential since only a small amount of active material is needed for every solar cell. Cu(In,Ga)Se<sub>2</sub>(CIGS) is one of the most highperforming, commercial alternatives but due to the high price and limited availability of the metal indium it has been increasingly interesting to search for replacements for this material. One of the most promising alternatives is Cu<sub>2</sub>ZnSnS<sub>4</sub>(CZTS) and Cu<sub>2</sub>CdSnS<sub>4</sub> (CCTS) (Katagiri et al. 2001; Kamoun et al. 2007; Levenco et al. 2012).

$\text{Cu}_2\text{B}^{\text{II}}\text{B}^{\text{IV}}(\text{S}; \text{Se})_4$  ( $\text{B}^{\text{II}} = \text{Mn, Fe, Co, Ni, Zn, Cd, Fe}$  and  $\text{Hg}$ ;  $\text{B}^{\text{IV}} = \text{Si, Ge, and Sn}$ ), is a quaternary semiconducting material which has been generating interest over the last decade for applications in photovoltaics. Cu<sub>2</sub>ZnSnS<sub>4</sub> offers favorable optical and electronic properties that are useful for thin film applications, and is composed of abundant in the crust of the earth and non-toxic elements. Furthermore, CZTS film has high absorption coefficients ( $>10^4 \text{ cm}^{-1}$ ), an optimal direct band gap (Ito & Nakazawa, 1988; Katagiri et al., 2001; López-Vergara et al 2013). Kesterite Cu<sub>2</sub>ZnSnS<sub>4</sub>, (CZTS), is a quaternary semiconducting material which has been generating interest over the past decade for applications in thin film photovoltaics. CZTS offers favorable optical and electronic properties that are advantageous for thin film applications, and is composed

of abundant, non-toxic elements. The current record for CZTS photovoltaic efficiency is 6.7% (Todorov et al 2010), although higher efficiencies are necessary for the commercialization of CZTS. Current processing methods for CZTS are either expensive or detrimental to the environment, requiring harsh organic solvents and/or energy-intensive procedures. Nanocomposite techniques present a unique alternative to explore crystal growth in complex chalcogenide alloys, and could allow for the large-scale deployment of CZTS-based thin film photovoltaics for energy generation. The use of stable, solid phase precursors and environmentally benign processing methods may allow for successful scalability of CZTS (Shiet al., 2013; Kabalah et al., 2013; Michael et al., 2013; Malerba et al., 2014;).

## 1.2. Problem Statement

At present, facing the increasingly serious global energy crisis, it is of pressing importance for material research to explore environment-friendly, effective-cost, and high-efficiency solar cells (Beek, Wienk et al. 2004, Su, Ke et al. 2012, Kosten, Atwater et al. 2013). Among various kinds of solar cells, the  $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$  (CIGS) thin-film solar cell has been paid much attention due to its high power conversion efficiency and stability (Ramanathan, et al. 2005, Schmidt, Ras et al. 2012). However, the high costs of gallium and indium obstruct further development in the field of thin-film solar cell (Wadia, Alivisatos et al. 2009). In recent years, some efforts have been made to find lower cost materials with earth-abundant elements.  $\text{Cu}_2\text{ZnSnS}_4$  (CZTS), as a potential material to substitute CIGS, has attracted great interest due to its direct band gap ( $E_g = 1.5$  eV) with high absorption coefficient and earth-abundant elements by replacing In

with Zn, Ga with Sn and Se with S (Todorov and Mitzi 2010, Rath, et al. 2012, Tablero 2012, Li, Li et al. 2013, Shin, Gunawan et al. 2013).

Furthermore, to improve CZTS-based solar cells, and a good choice to fabricate multi-junction solar cells of different energy band gaps with various junctions can hopefully span the whole wavelength range in the solar spectrum via  $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ ,  $\text{In}_x\text{Ga}_{1-x}\text{P}$  and  $\text{In}_x\text{Ga}_{1-x}\text{As}$  quaternary, alloys that have been used to fabricate multi-junction solar cells due to their tunable band gap by controlling In concentration. Therefore, it is important to find a band gap-tunable material based on  $\text{Cu}_2\text{ZnSnS}_4$  (CZTS),  $\text{Cu}_2\text{CdSnS}_4$  (CCTS) for realizing the future of effective-cost tandem solar cells with earth-abundant elements. Recently, copper-based quaternary semiconductors, such as  $\text{Cu}_2\text{ZnSnS}_4$  (CZTS) and  $\text{Cu}_2\text{CdSnS}_4$  (CCTS) have attracted high interest due to their potential applications in thin film solar cells (Guan, Shi et al. 2014, Li, Cao et al. 2015). In addition, the band offset at interface is one of the most fundamentally physical parameters, which is often used to assess some important interface effects, i.e., quantum confinement and carrier transport, in particular, for the design of solar cells and other optoelectronic devices.

Thin CdS buffer layer is invariably made use in the solar cells fabrication. Indeed, CdS remains the best-suited buffer material for using in chalcopyrite-based thin film solar cells. Rusu et al. (Rusu et al. 2009) have used elastic recoil detection analysis to show that the Cd and S diffuse into the absorber layer in CdS/CuGaSe<sub>2</sub> chalcopyrite solar cells. Cadmium and sulfur concentrations are found to be more than 0.1% even deep inside the absorber layer. Similar diffusion of Cd and S into the absorber layer in CdS/Cu<sub>2</sub>ZnSnS<sub>4</sub> solar cells can lead to the formation of a mixed  $\text{Cu}_2\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4$  solid solution at the interface. Thus, it is important to study the band gap variations,

structural, morphological, optical and electrical properties of  $\text{Cu}_2\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4$  layers with various Cd contents in order to optimize the solar cell efficiency. All the constituents of The  $\text{Cu}_2\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4$  alloy quaternary compound are abundant in the earth's crust reducing concerns of materials costs. CZCTS is derived from compound chalcopyrite  $\text{CuInS}_2$  by replacing indium element (In) which belongs to the third group (III) elements by cadmium (Cd) and zinc (Zn) in the second group (II) and the element of tin (Sn) in the fourth group (IV) by ratio of 50:50. The  $\text{Cu}_2\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4$  alloy quaternary has a direct band gap, a high absorption coefficient at the visible solar spectrum wavelengths and a p-type conductivity as well as non-toxicity. Because of that considerable work is being carried on the quaternary compound semiconductor  $\text{Cu}_2\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4$  so as to optimize its opto-electronic properties for using as absorber layer of thin film solar cells.

### 1.3. Research Objective

The objective is as the followings:

- 1- To study of various Cd concentration on the structural, morphological, optical and electrical properties of the  $\text{Cu}_2\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4$  quaternary alloy nanostructures using spin coating and electrospinning technique grew on glass substrate
- 2- To research the of copper (Cu) concentration on the structural, morphological and optical properties of  $\text{Cu}_2\text{Zn}_{0.8}\text{Cd}_{0.2}\text{SnS}_4$  quaternary alloy nanostructures grew on glass substrate.

- 3- To elaborate the effect of etching times porous silicon (PS) as substrate prepared by electrochemical etching method followed by deposited  $\text{Cu}_2\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4$  for characterization, analysis, optical properties and electrical properties of current–voltage (I–V) characteristics and UV photoresponse of the Ag/n-PS / $\text{Cu}_2\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4$ /Agheterojunction when  $x= 0, 0.6, 1$ .
- 4- To investigate the effect of various Cd concentration on the structural, morphological and optical properties of  $\text{Cu}_2\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4$  quinary alloy nanostructures using spin coating technique prepared on oxidized silicon ( $\text{SiO}_2$ ) substrate and their application in the detection of DNA sequence from Dengue type-2
- 5- To study the effect of various Cd concentration on the structural, morphological, optical and electrical properties of the  $\text{Cu}_2\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4$  quinary alloy nanostructures using spin coating technique grew on GaN substrate .

#### 1.4. Scope of research

The significance of this study includes **firstly**, the preparation of  $\text{Cu}_2\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4$  quinary alloy nanostructures for photovoltaic (PV) absorber layers using a sol-gel spin coating and electrospinning technique without sulfurization was investigated. The obtained  $\text{Cu}_2\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4$  quinary alloy nanostructures were analyzed, characterized and simulated on glass substrate, and the optimum Cd content (x) for PVs applications was determined. **Secondly**, prepared  $\text{Cu}_2\text{Zn}_{0.8}\text{Cd}_{0.2}\text{SnS}_4$

quinternary alloy nanostructures with different copper (Cu) concentration (0.3, 0.5, 0.7 and 0.9 mol/L) also were analyzed, characterized and simulated on glass substrate. **Thirdly**, the formation of porous silicon prepared by electrochemical on n-type Si (100) substrate. The process of etching time is 30, 60 and 120 min and the current density is 5 mA/cm<sup>2</sup> DC. The selected optimal etching parameters to control the shape, size, and surface morphology were using as substrate to study the structural properties and optical properties of Cu<sub>2</sub>Zn<sub>1-x</sub>Cd<sub>x</sub>SnS<sub>4</sub> quaternary alloy nanostructures. In addition to investigate the electrical properties of Ag/n-PS/Cu<sub>2</sub>Zn<sub>1-x</sub>Cd<sub>x</sub>SnS<sub>4</sub>/Ag heterojunction at x = 0, 0.6, 1. **Fourthly**, the sol-gel method was used for the preparation of a novel Cu<sub>2</sub>Zn<sub>1-x</sub>Cd<sub>x</sub>SnS<sub>4</sub> quinternary alloy nanostructure with different Cd concentrations (x = 0, 0.2, 0.4, 0.6, 0.8, 1) on oxidized silicon substrate. Further, we characterized Cu<sub>2</sub>Zn<sub>1-x</sub>Cd<sub>x</sub>SnS<sub>4</sub> quinternary alloy nanostructures and investigated how the stacking order of the precursor films affected the structural, morphological, and optical properties of the resultant CZTS nanostructures. The novelty of this Cu<sub>2</sub>Zn<sub>1-x</sub>Cd<sub>x</sub>SnS<sub>4</sub> quinternary alloy nanostructure was evidenced by demonstrating with the detection of DNA sequence for Dengue serotype-2, the obtained results displayed high-performance of Cu<sub>2</sub>Zn<sub>1-x</sub>Cd<sub>x</sub>SnS<sub>4</sub> quinternary alloy nanostructure to be used as a biosensor. **Lastly**, study, high quality Cu<sub>2</sub>Zn<sub>1-x</sub>Cd<sub>x</sub>SnS<sub>4</sub> quinternary alloys nanostructures were deposited on GaN substrates with Cd concentration (x=0, 0.6, 1) and study the structural properties given by X-ray diffraction (XRD) and field emission-scanning electron microscope (FE-SEM), and optical properties of Cu<sub>2</sub>Zn<sub>1-x</sub>Cd<sub>x</sub>SnS<sub>4</sub> quaternary alloy nanostructures by PL, in addition to investigate the electrical properties of Ag/n-GaN/Cu<sub>2</sub>Zn<sub>1-x</sub>Cd<sub>x</sub>SnS<sub>4</sub>/Ag heterojunction at x = 0, 0.6, 1.

## 1.5. Novelty of research

Deposited  $\text{Cu}_2\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4$  quaternary alloys nanostructures onto n-type porous silicon (PS) and GaN substrates, and to investigate the electrical properties of Ag/n-PS/ $\text{Cu}_2\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4$ /Ag, and Ag/GaN/ $\text{Cu}_2\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4$ /Ag heterojunction at  $x= 0, 0.6, 1$  for heterojunction applications through (I–V) characterization. It is indicated that  $\text{Cu}_2\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4$  quaternary alloy nanostructure was evidenced by demonstrating with the detection of DNA sequence from Dengue type-2, the obtained results displayed high-performance of  $\text{Cu}_2\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4$  quaternary alloy nanostructure to be used as a biosensor.

## 1.6. Outline of the Thesis

The thesis is organized into five chapters. The first chapter describes the overview of  $\text{Cu}_2\text{ZnSnS}_4$ , problem statement, objectives, and scope of research. It briefly highlights study importance and associated problems to solve the current limitation, significances of overall structure of the thesis.

Chapter two present two physical properties of  $\text{Cu}_2\text{ZnSnS}_4$  and reviews the literatures on the properties and application of  $\text{Cu}_2\text{ZnSnS}_4$  in solar cell.

The third chapter depicts the deposited  $\text{Cu}_2\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4$  quaternary alloy nanostructures on glass substrate using by spin coating technique with different Cd concentration ( $x=0-1$ ), the  $\text{Cu}_2\text{Zn}_{0.8}\text{Cd}_{0.2}\text{SnS}_4$  quaternary alloy nanostructures with different Cu concentrations 0.3, 0.5, 0.7 and 0.9 Mol/L on glass substrate. The results

obtained from the research are analyzed and characterized by techniques are X-ray diffraction (XRD), scanning electron microscopy (FE-SEM), EDX, atomic force microscopy (AFM), UV-Vis spectroscopy, PL and Hall measurement performed at room temperature. Also the deposited  $\text{Cu}_2\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4$  quaternary alloy nanostructures onto n-type porous silicon (PS) substrate, oxidized silicon. The results obtained from the research are analyzed and discussed. The current to voltage (I-V) and current to time (I-t) characterises under illuminating were 490 nm and 3mW on/off for Ag/n-PS/ $\text{Cu}_2\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4$ /Ag heterojunction at  $x= 0, 0.6, 1$ . Displays electrospinning technique alternative synthesis route for preparation of  $\text{Cu}_2\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4$  quaternary alloy nanofibres for photovoltaic (PV) absorber layers without sulfurization and all samples annealed at 300 °C under  $\text{N}_2$  atmosphere for 40 min, focuses on the properties and preparation of nanostructured  $\text{Cu}_2\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4$  quaternary alloy on oxidized silicon under different Cd concentration, and its applications to  $\text{Cu}_2\text{Zn}_{0.2}\text{Cd}_{0.6}\text{SnS}_4$  quaternary alloy nanostructures in the detection of DNA sequence from Dengue type-2. The current to voltage (I-V) and current to time (I-t) characterized under illuminating were 490 nm and 3mW on/off for Ag/n-Si/ $\text{Cu}_2\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4$ /Ag heterojunction at  $x= 0, 0.6, 1$ . Also used sol-gel method for preparation  $\text{Cu}_2\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4$  quaternary alloy nanostructures with different Cd contents ( $x = 0, 0.6, 1$ ) on GaN substrates. Analysis and characterization techniques, are (XRD), FE-SEM and AFM. In addition to investigate the electrical properties of Ag/GaN / $\text{Cu}_2\text{Zn}_{1-x}\text{Cd}_x\text{SnS}_4$ /Ag diode at  $x= 0, 0.6, 1$  for heterojunction applications through (I-V) characterization and current to time (I-t) characterization illuminating were 490 nm and 3 mW on/off.

Finally, the conclusion of the overall works and suggestions for the future works that could be summarized in chapter four