UNIVERSITI PUTRA MALAYSIA

SYNTHESIS AND CONDUCTIVITY OF COPPER ZINC TIN SELENIDE QUATERNARY CHALCOGENIDE SEMICONDUCTOR

LEONG YONG JIAN

FS 2016 32

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MASTER OF SCIENCE

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2016

There are several absorber layer have been developed for solar cell application such as CdTe, CIGS and CIGSe. However, due to its toxicity and low absorption issue, Zinc and Tin have been introduced to substitute the Indium and Galium to form a new absorber material which is CZTSe. Conductivity of the material is playing an important role in determining the transporting electron properties. Several methods such as pulsed laser ablation, magnetron sputtering and co-evaporation method have been chosen to synthesize CZTSe. In this study, Solvothermal method has been chosen to synthesize Copper Zinc Tin Selenide ($Cu_2ZnSnSe_4$ or CZTSe) due to few benefits such as able to produce crystalline phase, easily manipulate the size, simple equipment and affordable cost. The concentrations of $CuCl_2.2H_2O$, $Zn(CH_3COO)_2{\cdot}(H_2O)_2$ and $SnCl_4{\cdot}5H_2O$ were varied separately in three experiments to observe the effect of the precursors towards the formation of CZTSe. X-ray diffraction (XRD), X-ray fluorescence (XRF), Raman spectroscopy, Field emission scanning electron microscopy (FESEM) and Resistivity measurements with Van der Pauw configurations have been used to characterize the material properties. The CZTSe is attributed to tetragonal crystal structure based on XRD ICSD database. Raman spectroscopy has been further investigated to verify the formation of CZTSe phase which shows the wavenumber at about $172cm^{-1}$, $195cm^{-1}$ and $233cm^{-1}$. The $CuCl_2.2H_2O$ precursors showed the irregular grain size morphology. The $Zn(CH_3COO)_2{\cdot}(H_2O)_2$ precursors showed the irregular grain size and rod-like structure morphology. The $SnCl_4{\cdot}5H_2O$ precursors showed the irregular grain size and small particles grow on the surface material. The stoichiometry of CZTSe was slowly changing and deviate from the ideal ratio which is 2:1:1:4 by substituting the atom position in the crystal structure. The $CuCl_2.2H_2O$ precursors and $Zn(CH_3COO)_2{\cdot}(H_2O)_2$ precursors showed the increasing conductivity trend whereas the $SnCl_4{\cdot}5H_2O$ showed the decreasing conductivity trend due to the formation of SnO_2.

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By

LEONG YONG JIAN

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfillment of the Requirements for the Degree of Master of Science

April 2016

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Master of Science

SYNTHESIS AND CONDUCTIVTY OF COPPER ZINC TIN SELENIDE QUATERNARY CHALCOGENIDE SEMICONDUCTOR

By

LEONG YONG JIAN

April 2016

Chairman : Josephine Liew Ying Chyi, PhD
Faculty : Science

There are several absorber layer have been developed for solar cell application such as CdTe, CIGS and CIGSe. However, due to its toxicity and low absorption issue, Zinc and Tin have been introduced to substitute the Indium and Galium to form a new absorber material which is CZTSe. Conductivity of the material is playing an important role in determining the transporting electron properties. Several methods such as pulsed laser ablation, magnetron sputtering and co-evaporation method have been chosen to synthesize CZTSe. In this study, Solvothermal method has been chosen to synthesize Copper Zinc Tin Selenide ($Cu_2ZnSnSe_4$ or CZTSe) due to few benefits such as able to produce crystalline phase, easily manipulate the size, simple equipment and affordable cost. Ethylenediamine (En) behaves as a good complexing agent in creating a step by step stage for the binary and ternary compounds to react and form quaternary compounds. The formation of CZTSe will favor in alkaline condition which is caused by En. The concentrations of $CuCl_2.2H_2O$, $Zn(CH_3COO)_2{\cdot}(H_2O)_2$ and $SnCl_4{\cdot}5H_2O$ were varied separately in three experiments to observe the effect of the precursors towards the formation of CZTSe. X-ray diffraction (XRD) has been used to determine the phases and structure. X-ray fluorescence (XRF) has been used to identify the chemical composition. Raman spectroscopy has been used to confirm the formation of CZTSe phase. Field emission scanning electron microscopy (FESEM) has been used to study the morphology of the samples. Resistivity measurements with Van der Pauw configurations have been used to observe the electrical properties. The CZTSe peaks have been confirmed by XRD peak at $2\theta = 27.2^o$, 45.1^o, 53.3^o, 65.5^o and 72.3^o and it is attributed to tetragonal crystal structure based on XRD ICSD database. Raman spectroscopy has been further investigated to verify the formation of CZTSe phase which shows the wavenumber at about $172cm^{-1}$, $195cm^{-1}$ and $233cm^{-1}$. The results obtained showed that the precursors' concentrations play an important role in the samples morphology. The $CuCl_2.2H_2O$ precursors showed the irregular grain size morphology. The $Zn(CH_3COO)_2{\cdot}(H_2O)_2$ precursors showed the irregular grain size and rod-like structure morphology. The $SnCl_4{\cdot}5H_2O$ precursors showed the irregular grain size and small particles grow on the surface material. The stoichiometry of CZTSe was slowly changing and deviate from the ideal ratio which is 2:1:1:4 by substituting the atom position in the crystal structure. The $CuCl_2.2H_2O$ precursors and

$Zn(CH_3COO)_2{\cdot}(H_2O)_2$ precursors showed the increasing conductivity trend whereas the $SnCl_4{\cdot}5H_2O$ showed the decreasing conductivity trend due to the formation of SnO_2.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia Sebagai memenuhi keperluan untuk ijazah Sarjana Sains

SINTESIS DAN KEKONDUKSIAN TENTANG KUPRUM ZINK TIMAH SELENIDA KUARTENARI CHALCOGENIDE SEMIKONDUKTOR

Oleh

LEONG YONG JIAN

April 2016

Pengerusi : Josephine Liew Ying Chyi, PhD
Fakulti : Sains

Banyak penyelidikan telah dijalankan oleh para penyelidik mengenai bidang solar sel dengan menggunakan bahan CdTe, CIGS dan GIGSe. Disebabkan oleh ketosikan and penyerapan yang rendah, zink dan timah telah diperkenalkan untuk menggantikan Indium dan Galium bagi menghasilkan bahan yang baru iaitu Kuprum Zink Timah Selenida (CZTSe). Kekonduksian merupakan salah satu sifat yang penting bagi menentukan pengangkutan electron. Banyak cara seperti “pulsed laser ablation”, “magnetron sputtering” and “Co-evaporation” telah diperkenalkan untuk menghasilkan CZTSe. Bagi penyelidikan ini, solvothermal teknik diperkenalkan oleh sebab-sebab berikutnya: menghasilkan kristal, memanipulasikan zarah saiz, peralatan yang senang digunakan dan kos yang murah. Kuprum Zink Timah Selenida ($Cu_2ZnSnSe_4$ or CZTSe) telah berjaya disintesis melalui teknik solvothermal. Ethylenediamine (En) dipilih sebagai agen pengkompleks atas sebab ia dapat menyediakan CZTSe secare berperingkat dari binary compound, pertigaan compound sampai kuartenari compound. Pembentukan CZTSe lebih mengutamakan dalam keadaan alkali yang disebabkan oleh En. Kepekatan $CuCl_2.2H_2O$, $Zn(CH_3COO)_2{\cdot}(H_2O)_2$ and $SnCl_4{\cdot}5H_2O$ telah diubahkan secara berasingan dalam tiga experiment untuk memerhatikan kesan kepekatan dalam membentukan CZTSe. Sifat- sifat struktur, komposisi, morfologi, elektrik telah dilaksanakan oleh analisis pembelauan sinar-X (XRD), analisis pendafluor sinar-X (XRF), mikroskopi Raman, mikroskopi medan pancaran pengimbasan electron (FESEM) dan analisis kerintangan dengan konfigurasi Van der Pauw. CZTSe telah berjaya disintesis pada sudu $2\theta = 27.2^o$, 45.1^o, 53.3^o, 65.5^o and 72.3^o. Sudu-sudu tersebut disahkan dengan ICSD 98-006-7242. Kristal Struktur bagi CZTSe ialah tetragonal. Mikroskopi Raman digunakan dengan tujuan mengesahkan lagi pembentukan CZTSe. Nombor gelombang pada $172cm^{-1}$, $195cm^{-1}$ and $233cm^{-1}$ telah menunjukan pembentukan CZTSe. Keputusan menunjukan kesan kepekatan memainkan peranan yang penting dalam morfologi sampel-sampel. Siri $CuCl_2.2H_2O$ menunjukan bentuk zarah yang tidak teratur. Siri $Zn(CH_3COO)_2{\cdot}(H_2O)_2$ menunjukan bentuk zarah yang tidak teratur dan rod struktur morfologi. Siri $SnCl_4{\cdot}5H_2O$ menunjukan bentuk zarah yang tidak teratur dan zarah yang kecil mengembang atas permukaan sampel. CZTSe Stoikiometri berubah secara lambat dan menyimpang dari ideal nisbah 2:1:1:4 dengan menggantikan kedudukan atom dengan atom lain dalam krystal struktur. Pelopor yang berbeza akan menpunyai sifat electrik yang berbeza. Siri

$CuCl_2.2H_2O$ dan Siri $Zn(CH_3COO)_2{\cdot}(H_2O)_2$ menunjukan peningkatan dalam sifat kekonduksian. Siri $SnCl_4{\cdot}5H_2O$ menunjukan penurunan dalam sifat kekonduksian disebabkan oleh kewujudan SnO_2.

ACKNOWLEDGEMENTS

It's been a challenge and tough life during my Master study. Firstly, I would like to express my gratitude to my project supervisors, Dr. Josephine Liew Ying Chyi for her passion, patience and professionalism in guiding me. During my master study, my supervisor is the one who motivate me and encourage me.

Other than that, I would like express my appreciation to my co-supervisors, Prof. Dr. Zainal Abidin Talib, and Prof. Dr. W.Mahmood Mat Yunus and Dr. Nizam Tamchek for their guidance, advices and suggestions throughout the year. I am so grateful that I have been given an opportunity to expose and carry on the project under their supervision.

Besides, I would like to extend my gratitude to my fellow lab mates who are Fakhrurrazi Ashari, Lee Han Kee, Ibrahim, Manahil, Batool and my friends in Department of Physics and Chemistry for their willingness to share their knowledge with me throughout the year. The way to analyze and solve the problems is always the skills that I have learned from them throughout the project. I am truly grateful.

Special thanks are dedicated to the others who are once helping me during my Master study for their assistance and teaching me all the way. I feel supportive from my family especially my beloved, Yunie Yeap Soon Yu for supporting me no matter what are the problems. They are p[my core in my life for supporting me all the time. In addition, I would like to thank to Pn Norhaslinda for running the X-ray Diffractometry, Pn Noriza for running the X-ray Fluorescence, Pn Roslina for running Raman spectroscopy and Hi-Tech instruments operators for running FESEM. With their professionalism assistance, I'm sure that I'm able to complete my Master study with excellent results.

I certify that a Thesis Examination Committee has met on 19 April 2016 to conduct the final examination of Leong Yong Jian on his thesis entitled "Synthesis and Conductivity of Copper Zinc Tin Selenide Quaternary Chalcogenide Semiconductor" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Master of Science.

Members of the Thesis Examination Committee were as follows:

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the Supervisory Committee were as follows:

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CZTSe	Copper Zinc Tin Selenide, $Cu_2ZnSnSe_4$
CTSe	Copper Tin Selenide, Cu_2SnSe_3
ZnSe	Zinc Selenide
Cu_2Se	Copper Selenide
PV	Photovoltaic
GaAs	Galium Arsenide
InP	Indium Phosphide
CdTe	Cadmiun Telluride
CIS	Copper Indium Sulfide
CIGSe	Copper Indium Galium Selenide
En	Ethylenediamine
CIGS	Copper Indium Galium Sulfide
CCTSe	Copper Cadmium Tin Selenide
CZTS	Copper Zinc Tin Sulfide
XRD	X-Ray Diffraction
FESEM	Field Emission Scanning Electron Microscopy
EDX	Energy Dispersive X-ray
EG	Ethylene Glycol
FWHM	Full Width at Half Maximum
$ZnCl_2$	Zinc Chloride
SEM	Scanning Electron Microscopy
CTAB	Cetyltrimethylammonium Bromide
XRF	X-Ray Fluorescence
k	Shape factor

λ	Wavelength of the X-ray
β	Line broadening at the full width half maximum (FWHM)
θ	Bragg angle from the diffraction process
D	Crystallite size
P_A	Resistivities in ohm-cm
P_B	Resistivities in ohm-cm
t_s	Sample thickness in cm
I	Current through the sample in amperes
f_A	Geometrical factors based on sample symmetry
f_B	Geometrical factors based on sample symmetry
ρ	Resistivity of the material
σ	Conductivity of the materials
R	Resistance of the materials, Ω
V	Potential difference across the conductor, V
d	The spacing between atomic planes in the crystalline phase

CHAPTER 1

INTRODUCTION

1.1 General Introduction

Solar cells, also known as photovoltaic cells (PV), have been applied as alternative electrical power source in many applications such as landing obstruction lights for airports, power sources for residential areas and trading building, perimeter alarm transmitters, electronic border fences, radio relay station, navigation aid sensors and other applications (A.R. Jha, 2010). The presence of solar energy since 1954 has proved its importance as one of the renewable and green sources of energy after wind and hydro energy. The development of renewable energy sources is due to the increasing of environmental pollution problems from coal, wood, oil and gas (i.e. emission of carbon dioxide causing the depletion of ozone layer, and global greenhouse effect). For an example, nuclear energy based electric power station capable to produce huge amounts of electrical power, however, the radioactive nuclear material will worsen our health. As one of the renewable resources of energy, solar energy provides clean, pollution–free and self-sufficient all the time (A.R. Jha, 2010). Due to these advantages, electric power station utilizing solar cells are helpful in many developed country.

Generation of electrical power by solar cell employed energy conservation of an electromagnetic wave and quantum mechanics concept. By absorbing sunlight energy, solar cells generate electricity through photoelectric effect. When sunlight strikes the materials, electrons absorb sunlight energy, also known as photon energy, and possess sufficient kinetic energy to escape. Holes have been created when electrons escape. When the electrons are captured, it generates electric current. In order to increase the electrical power generation, solar cells have been transformed into solar modules and then solar array and arranged in array (Gil Knier, 2002). This is a general idea how the solar cells have been implemented in solar array system application. However, synthesizing solar material is the main focus in this project.

Materials that are contributing to the solar cells properties are playing a vital role in determining the behavior of solar cells. Researchers continue to develop and improve the materials such as Silicon (Si), GaAs, InP, CdTe, CuInS (CIS), $Cu(In,Ga)Se_2$ (CIGS) to ameliorate the solar cells efficiency (A.R. Jha, 2010). Several parameters such as temperature, pH, reaction time, concentrations, and types of solvents have been investigated to obtain high purity of the samples.

1.2 Previous study

Properties of the materials such as morphology, electrical, optical band gap and thermal vary differently according to the methods used. Based on the recent research, different methods such as solid state method, coordinating solvent method, hot injection method, electrodeposition method and other methods have been used to synthesize $Cu_2ZnSnSe_4$ (CZTSe) (Zhou et al., 2013; Du et al., 2012; Li et., 2012; Adhi Wibowo et al., 2010). Small sphere-like CZTSe particles with rough surface formed using solvothermal method under 250°C for 24 hours (Du et al., 2012). Small and unequal size of CZTSe grains formed using solid state method (Adhi Wibowo et al., 2010). Smaller CZTSe grains with approximately sizes of 1µm are formed using electrodeposition method (Chen et al., 2011). Parameters such as reaction time, reaction temperature, types of precursors and solvents, pH of the medium and volume of the solvents are the factors that influence the behavior of the materials. Different volume of Ethylenediamine (En) will produce samples in different thickness (Shi et al., 2011).

1.3 Problem statement

At first, researchers are trying to develop solar cells which are made from cadmium telluride. However, due to its low absorption coefficient and toxicity issue, cadmium telluride has been stopped. Group III-V semiconductor compounds such as Galium Arsenide (GaAs) and Indium Phosphorus (InP) have been developed due to its high absorption potential. Thin film ternary and quaternary compounds such as Copper Indium Sulfide (CIS), Copper Indium Gallium Sulfide (CIGS) and Copper Indium Gallium Selenide (CIGSe) have been introduced as well. However, Indium and Gallium are rare earth and expensive elements. Researchers tend to utilize the abundant elements with an affordable price to optimize the properties of the materials. As a result, Zinc and Tin has been introduced to substitute the Indium and Gallium elements from CIGSe to become Copper Zinc Tin Selenide (CZTSe). As a vital quaternary compounds with high capability for photovoltaic, CZTSe, a p-type semiconductor, has high absorption coefficient ($10^5 cm^{-1}$) and optimum direct band gap energy of 1.0 to 1.5eV. (Du et al., 2012; Shi and Li, 2011). Many research have been concentrated on synthesizing CZTSe compounds with different methods such as pulsed laser ablation, magnetron sputtering, co-evaporation, hot injection method, coordinating solvent method and solid state method (Zhou et al., 2013; Du et al., 2012; Li et al., 2012; Adhi Wibowo et al., 2010). Some of these reported that the methods required the complicated setup of the apparatus and the expensive apparatus. Therefore, solvothermal method has been introduced to synthesize CZTSe. This method is able to produce crystalline phases, manipulate the particle size easily, simple equipment, catalyst free growth, low cost, large area uniform production, environmental friendliness and less hazardous (Aneesh et al., 2007). Conductivity or resistivity is another concern in determining the properties of the materials. Conductivity defines how easily electron can move in the materials when the voltage is applied. The higher the conductivity, the electrons move easily in the material. Different synthesizing method will produce materials with different properties. So in this research, conductivity of CZTSe prepared by solvothermal method will be investigated.

1.4 Objectives of study

The objectives of current research are:

a) To synthesize stoichiometric and non-stochiometric Copper Zinc Tin Selenide, $Cu_2ZnSnSe_4$ (CZTSe) quaternary chalcogenide semiconductor through solvothermal route by adjusting the concentrations of $CuCl_2{\cdot}(H_2O)_2$, $Zn(CH_3COO)_2{\cdot}(H_2O)_2$ and $SnCl_4{\cdot}5H_2O$ respectively.

b) To analyze the conductivity of $Cu_2ZnSnSe_4$ quaternary chalcogenide semiconductor.

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