

**THERMAL EVAPORATION OF COPPER DOPED TIN (II) SULFIDE
ABSORBER THIN FILM FOR SOLAR CELL APPLICATION**

BAKHTIAR RIDHWAN BIN BACHIRAN

UNIVERSITI TEKNOLOGI MALAYSIA

THERMAL EVAPORATION OF COPPER TIN (II) SULFIDE ABSORBER THIN
FILM FOR SOLAR CELL APPLICATION

BAKHTIAR RIDHWAN BIN BACHIRAN

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Untuk Yang Maha Mengetahui segala yang ada di langit dan di bumi; Dia.
Untuk wanita paling penyayang di dunia; Mama.
Untuk lelaki paling agung; Abah.
Untuk mereka yang sentiasa menyokong; Along, Angah, Alang.
Untuk anak buah yang sedang membesar bagai juara; Fayyadh, Kayla, Rania.
Dan sudah tentu isteri tercinta, Tun Teja.

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ABSTRACT

Recent reports shows that tin sulphide (SnS) is a promising material as an absorber layer in solar cell application. However, SnS had to be doped with Copper (Cu) which could help to decrease the high resistivity. SnS with various Cu weight percentage (wt%) from 5 to 20 had been deposited on glass substrate using thermal evaporation technique. The thin films were annealed in vacuum environment at 200 °C for 2 hours using tube furnace. The structural properties was characterized using X-ray diffraction, Scanning Electron Microscope, Energy Dispersive X-ray and Atomic Force Microscopy. Optical properties was determined using ultraviolet-visible spectrometer while the resistivity was measured using Four Point Probe method at standard room pressure and temperature. The thin films were matched with polycrystalline SnS having Herzbergite crystal structure and grain size estimated to be ~ 21 to 30 nm. It had almost near stoichiometry and dopant element was found in the doped thin films. The deposited thin films had good surface coverage, good crystallinity and no pinhole or cracks on the surface. The thin films had low transmission at visible light region and absorption coefficient were above 10^5 cm^{-1} . It also revealed energy band gap around 1.52 to 2.03 eV. Doped thin film has lower band gap energy than the undoped whereas high dopant concentration caused the energy band gap to increase compared to low dopant percentage. Meanwhile, annealed thin films had lower energy band gap. The resistivity range from 0.59 to $1.80 \times 10^3 \Omega \text{ cm}$. Doped thin films has less resistivity than the undoped and annealing process tends to lower the resistivity. It was observed that the properties of SnS thin films when Cu was introduced had changed and tend to improve at lower weight percentage. This demonstrated doping could modify the optical and electrical properties of SnS thin films precisely in lowering band gap energy and resistivity, thus have potential to be used as solar cell application.

ABSTRAK

Laporan terkini menunjukkan bahawa stanum sulfida (SnS) adalah bahan yang berpotensi untuk digunakan sebagai lapisan penyerap dalam aplikasi sel solar. Walaubagaimanapun, bahan SnS perlu didopkan dengan kumprum (Cu) untuk membantu mengurangkan kadar rintangan yang tinggi. SnS dengan pelbagai peratusan berat (wt%) kuprum (Cu) telah diaplikasikan di substrat kaca menggunakan teknik vakum penyejatan haba. Filem-filem nipis telah sepuh lindap dalam persekitaran vakum pada 200 °C selama 2 jam dengan menggunakan tiub relau. Peranan proses penyepuhlindapan ke filem-filem nipis turut dikaji. Sifat-sifat struktur dicirikan menggunakan Pembelauan X-ray, Mikroskop Pengimbasan Elektron, Tenaga Serakan X-ray dan Mikroskop Daya Atom. Ciri optik telah ditentukan dengan menggunakan Spektrometer Ultraviolet Boleh Nampak manakala kerintangan diukur menggunakan kaedah Probe Empat Titik pada tekanan bilik dan suhu standard. Filem-filem nipis dipadankan dengan SnS polihabluran mempunyai struktur kristal Herzbergite dan saiz butiran dianggarkan ~ 21 hingga 30 nm. Ia mempunyai hampir persamaan stoikiometri dan unsur dopan terdapat dalam filem nipis yang didopkan. Filem nipis yang dianap mempunyai liputan permukaan yang baik, penghabluran baik dan tiada lubang kecil atau retak di permukaan. Filem nipis tersebut mempunyai transmisi yang rendah pada kawasan cahaya boleh nampak dan pekali penyerapan lebih daripada 10^5 . Ia juga mendedahkan jurang jalur tenaga sekitar 1.52-2.03 eV. Filem nipis yang didopkan mempunyai jurang jalur lebih rendah daripada filem yang tidak terdop manakala dopan yang tinggi kepekatan menyebabkan jurang jalur tenaga meningkat berbanding dopan yang rendah kepekatan. Sementara itu, filem nipis yang disepuh lindap mempunyai jurang jalur tenaga lebih rendah. Nilai kerintangan berjulat diantara $0.59-1.80 \times 10^3 \Omega \text{ cm}$. Saput tipis didopkan mempunyai kurang nilai rintangan daripada saput tipis yang tidak didop dan proses penyepuhlindapan cenderung untuk mengurangkan kerintangan. Dapat diperhatikan bahawa sifat-sifat saput tipis SnS telah berubah apabila Cu diperkenalkan dan cenderung untuk bertambah baik pada peratusan berat yang lebih rendah. Ini menunjukkan pendopan boleh mengubahsuai prestasi sifat optic and elektrik saput tipis SnS khususnya menurunkan jurang jalur tenaga dan rintangan, jadinya berpotensi untuk digunakan dalam aplikasi sel solar.

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LIST OF SYMBOLS AND ABBREVIATION

J	Joule
PV	Photovoltaic
GaAs	Gallium Arsenide
CdTe	Cadmium Telluride
CuInSe ₂	Copper Indium Diselenide
Si	Silicon
c-Si	crystalline silicon
CIGS	Copper indium gallium selenide
TiO ₂	Titanium Dioxide
SnS	Tin Sulfide
CO ₂	Carbon dioxide
Cu	Copper
Sb	Antimony
eV	Electronvolt
α	Absorption Coefficient
h	Planck's constant
E _g	Energy Band Gap
σ	Electrical Conductivity
ρ	Electrical Resistivity
ρ_s	Sheet Resistivity
$f(R)$	Correction Factor
t	Thickness
s	Probe spacing
wt%	Weight Percentage

at%	Atomic Percentage
XRD	X-Ray Diffraction
JCPDS	Joint Committee on Powder Diffraction Standards
XRF	X-ray Fluorescence
EDX	Energy Dispersive X-Ray Spectroscopy
SEM	Scanning Electron Microscopy
AFM	Atomic Force Microscopy
UV-Vis	Ultraviolet-Visible Spectrometer
NIR	Near Infrared Region
TFSC	Thin Film Solar Cells
PVD	Physical Vapor Deposition
CVD	Chemical Vapor Deposition
ECD	Electrochemical Deposition
TCO	Transparent Conducting Oxide
DC	Direct Current
V	Potential Difference
λ	Wavelength
θ	Diffraction Bragg Angle
\AA	Angstrom = 10^{-10} m
D	Estimated grain size derived from XRD
β	FHWM of 2θ
FWHM	Full Width Half Maximum

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CHAPTER 1

INTRODUCTION

1.1 Background of study

Energy plays a huge role in assisting mankind's way of life in industry, communication and transportation. Generally, energy can be supplied from fossil fuels (80%) such as oil (35 %), coal (23 %), and natural gas (22 %) and other energy sources (20%) such as biomass (11.5%), nuclear (6.5 %), and hydropower (2%). However, due to rapid growth of human population and modern industries, the total rate of global energy consumption has greatly increased and expected to triple by the year 2100. The demand for energy of modern society is constantly increasing. Moreover, several crisis that arise like rapid depletion of fossil fuels, global climate change and a worrying level of environmental pollution due to fossil fuel consumption have made the researchers to find a much more efficient usage of energy plus to develop an alternative, sustainable, and clean energy technologies such as solar cells, fuel cells, and biofuels to solve critical issues. For many reasons, solar energy has become an important technology that is worth paying attention (Bissels *et al.*, 2014; Edenhofer *et al.*, 2012).

Solar energy is unlimited, abundant and clean of all the renewable energy resources on the earth up until now. The power from sun is tremendous energy

resources. The energy intercepted by the earth is about 4×10^{24} J. According to U.S Energy Information Administration, the world's total energy consumption was around 5.6×10^{20} J in 2010 (Energy Information Administration (US), 2012), meaning that the solar energy delivered to the earth in about one hour is sufficient to provide the energy needs by the global population for a whole year. Photovoltaic (PV) technology is one of the best ways to harness the solar energy. A recent report from the Intergovernmental Panel on Climate Change predicts PV will account for up to 30 % of the world's electricity production by 2050, even in the moderate developments. This shows that research in solar energy and solar cell need to be persuaded so that the energy can be harvested with high efficiency (Edenhofer *et al.*, 2012).

This research focusses on the absorber layer for solar cell using thin film technology. Generally, solar cells consist a light absorbing material within the cell structure which function to collect photons and release free electrons known as photovoltaic effect. The PV effect is the foundation of the conversion of electrical energy from light energy. Meanwhile, thin-film solar cells are mainly thin layers of semiconducting materials which possess photovoltaic properties deposited onto a solid backing material also known as substrate. The advantage of thin films is it prominently reduce the amount of semiconductor material required for each cell when compared to silicon wafers and therefore reduce the cost of production of PV cells (Parida *et al.*, 2011).

In previous study, gallium arsenide (GaAs), cadmium telluride (CdTe), copper indium diselenide (CuInSe₂) and titanium dioxide (TiO₂) are materials that have been greatly used to produce thin film solar cells. Although these materials show excellent achievement, the main drawbacks are lack of abundance and non-environmental friendly (Ogah *et al.*, 2009). Therefore, new promising materials are searched. Tin sulfide (SnS) has been reported as a potential material to be used as absorber layer due to its characteristics which has a direct energy band gap about 1.3 eV, around the optimum energy needed for conversion of PV solar energy. Additionally, the optical absorption coefficient is also high where most of the incident light can be absorbed by the layers thickness with only several microns (Bube, 1960). It can be deposited by a wide range of chemical and physical deposition methods. Moreover, the advantages

of tin sulfide is both of these essential elements are earth abundant, and environmental risk of Sn and S are low and non-toxic (Miles *et al.* , 2009).

A research conduct by Ogah *et al.* (2009) to determine whether tin sulfide could produce a stable and efficient cells using thermal evaporation has shown that it is possible to deposit SnS layers with thickness of numerous microns and free of pinhole that is conformal to the substrate. The layers of thin film have also has been made up of columnar grains that are densely packed. The structural properties show the deposited layers are mostly SnS which has the structure of orthorhombic crystal. For the optical properties, the absorption edges shown are consistent with direct energy band gap. The energy band gap value is in the range 1.3 to 1.7 eV, where the lower values are obtained for film with thicknesses less than 1 μm and suitable for use in thin film solar cell structures.

Another study done by Miles *et al.* (2009) shows that stoichiometric SnS thin films is possible to be produced using thermal evaporation technique with adherent to the substrate, consisting of densely packed columnar grains. The thickness of thin films produced has different band gap values (1.3–1.7 eV) due to the variation in the deposition conditions but still maintaining the optimum band gap energy range for PV energy conversion (1.5 eV) and having p-type layers (Miles *et al.*, 2009). However, further study need to be done on the optical and electrical properties. Besides that, the post-deposition annealing effect also need to be investigated.

In this research, we are going to prepare tin sulfide thin film as absorber layer with metallic-doping which is copper (Cu) using thermal evaporation method. Cu as metallic elements dopant has been proved to improve PV efficiency in dye sensitized solar cell (Nguyen *et al.*, 2014). The performance of this layer is determined by characterizing the structural, optical and electrical properties of the copper doped SnS. This study would like to find out the possibility for copper doped tin sulfide as potential absorber layer to be used in solar cell application.

1.2 Problem Statement

The current work regarding solar cell is for the accomplishment of an absorbing layer with maximum efficiency. The material should be environmental friendly and abundant. Our aim is to find out an absorber layer for solar cell with non-toxic and abundant constituent. Besides that, the absorber layer must possess most of these properties; a high conductivity and low resistivity, small band gap energy, E_g (near 1.3 eV) to maximize absorption of solar radiation, high absorption coefficient ($\alpha > 10^4 \text{ cm}^{-1}$) and low transmittance especially in the visible light spectrum (wavelength range 400 – 700 nm). Since SnS has been reported in previous study as a promising absorber material. However, SnS has drawback in electrical properties specifically resistivity which is high. This experiment want to improve the properties by introducing metallic-doping which is copper, Cu. Cu is cheap, abundance and known as good electrical conductor. By adding Cu, the thin film is expected to have lower resistivity, ρ than undoped SnS. The structural, optical and electrical properties of the thin film were characterized to find out whether it possess the requirement to be an efficient solar cell absorber layer.

1.3 Objectives of Study

The objectives of this project are as follows:

- i. To fabricate copper doped tin sulfide thin film at different weight percentage (wt%) from 5% to 20% using thermal evaporation technique
- ii. To determine the effect of annealing process on the sample surface
- iii. To characterize the optical and electrical properties of doped tin sulfide thin film

1.4 Scope of Study

The sample is made of tin sulfide powder with purity of 99.9% and copper powder with purity of 99.9%. It is to be prepared using thermal evaporation method with different copper-doping weight percentage which are 5%, 10%, 15% and 20% respectively. All the samples are annealed at 200°C for two hours under vacuum environment which could help to optimize the crystallinity and surface morphology of the thin film. Constant temperature is chosen as the tin sulphide could be oxidized at more than 200°C. The structural properties is characterized using X-ray Diffraction (XRD), Energy Dispersive X-ray Spectroscopy (EDX), Scanning Electron Microscopy (SEM), and Atomic Force Microscopy (AFM). The optical properties such as absorbance and transmittance is analysed using ultraviolet-visible (UV-Vis) spectrometer in the wavelength range (200-1800nm) with an incident light perpendicular to the surface plane of the films. The electrical properties is evaluated using Four Point Probe technique to determine the electrical resistivity.

1.5 Significance of the study

The findings of the research could be useful to improve the efficiency of solar cell nowadays. The suitable material composition could be identified. Besides that, the optimized conditions to grow the thin film will be determined. When all of this optimum parameters are understood, a solar cell with best characteristics such as low band gap energy and low resistivity could be produced using the same technique. Therefore, this research can be a reference for industrial field especially in photovoltaic field. Thus, this study could save cost and time in preparing the sample. As consequence, this may reduce the price of solar cell in the market. Other than that, this research may establish a standard value for the characterization.

1.6 Thesis Outline

This thesis is divided into five chapters. Chapter 1 presents the background study of the research and the problem statement that gives motivation to conduct the experiment. Objectives of this study are also shown in this chapter. Chapter 2 discussed the previous work that have been done by others and also explain the analysis that is used. Chapter 3 describes the methodology used to prepare the samples and the working of analytical instruments for the experiments. Chapter 4 presents the experimental results that is obtained from the analysis and further discussed with previous work. Lastly, chapter 5 summarize the findings and conclude the experiments. Some outlook that can be done for future work is also mentioned to further improve the experiments.

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