EFFECTS OF ANNEALING TEMPERATURE ON BISMUTH OXYIODIDE THIN FILM FOR LEAD-FREE PEROVSKITE SOLAR CELLS.

ASYRAF HAKIMI BIN AZMI

MASTER OF SCIENCE
(PHYSICS)

UNIVERSITI PERTAHANAN NASIONAL MALAYSIA

2022

EFFECTS OF ANNEALING TEMPERATURE ON BISMUTH OXYIODIDE THIN FILM FOR LEAD-FREE PEROVSKITE SOLAR CELLS.

ASYRAF HAKIMI BIN AZMI

Thesis submitted to the Centre for Graduate Studies, Universiti Pertahanan Nasional Malaysia, in fulfilment of the requirements for the Degree of Master of Science (Physics)

2022

ABSTRACT

Perovskite solar cells based on lead (Pb) halide has demonstrated the rapid increased in efficiency and advanced in photovoltaic technology in the last decade, but the toxicity issue impede the large-scale industrial production. Bismuth oxyiodide (BiOI) has been recognized as suitable candidate of less-toxic material to replace Pb in conventional Pb-halide perovskite solar cells (PSCs), without adversely impacting performance in perovskite solar cells. Thin films of BiOI were synthesized and deposited using Successive Ionic Layer Adsorption and Reaction (SILAR) on the glass substrates, the BiOI films were characterized with all these characterizations prior to find the optimum annealing temperature and used it for fabrication of solar cells device and accessed its perfomance. The samples were annealed at various annealing temperature for optimization of the performance which influenced on crystallization, morphology and leads to improving the electrical properties of BiOI films from 250 °C, 350 °C, 450 °C and 550 °C, for 20 minutes. The physical observation, microstructure, thickness, optical, structural, and electrical properties of BiOI thin films were characterized. From the physical observation, the colour of the films changed from the orange-yellow to yellowish with increasing annealing temperature. The microstructure study demonstrated the BiOI thin films have flakes morphology structure. The average thicknesses of BiOI films were in ranged of 3.479 - 8.082 µm with the optical band gap, E_g in range 1.59 to 2.10 eV. From XRD characterization, sample annealed below 350 °C demonstrated single crystalline structure, but with further higher annealing, BiOI film changed to polycrystalline with mixed phases of BiOI. The crystallite size was calculated in range from 27.74 to 29.31 nm. Finally the

BiOI thin films were measured its conversion efficiency using I-V measurement. The sample annealed with 350 °C shows the highest efficiency with 1.67 %. By referring to all the results in this study, we conclude that the optimum annealing temperature for BiOI thin film is 350 °C with 1.67%.   This study provided the clue on BiOI thin film properties for active layer in low-toxicity perovskite solar cells.

Keywords:

Bismuth Oxyiodide, SILAR, Thin Film, Lead-free Perovskite Solar Cell, Annealing Temperature.

ABSTRAK

Sel suria perovskit berdasarkan plumbum halida diperlihatkan sebagai satu sel suria yang mempunyai kecekapan yang tinggi dalam teknologi fotovolta dan perkembangan yang singkat sedekad ini. Namun, sel suria perovskit dengan isu toksik plumbum yang tinggi menghalang pengeluaran perindustrian yang berskala besar. Bismuth oxyiodide (BiOI) adalah bahan yang tidak mempunyai plumbum dan kurang bertoksik jika dibandingkan dengan plumbum, telah dikenali sebagai pengganti yang amat selaras untuk mengantikan sel suria perovskit yang berdasarkan plumbum tanpa memberi impak dalam prestasi kecekapan penukaran. Filem nipis BiOI telah disintesis menggunakan teknik penjarapan dan tindak balas lapisan ionik berturutan (SILAR) diatas substrat kaca. Kesemua sampel disepuhlindapan pada beberapa suhu iaitu 250 °C, 350 °C, 450 °C, dan 550 °C selama 20 minit. Kesemua filem BiOI di analisa, seperti pemerhatian fizikal, mikrostruktur, ketebalan, optik, struktur dan sifat elektrik. Daripada pemerhatian fizikal, warna filem nipis berubah daripada jingga kepada kuning dan menjadi lebih kekuningan dengan pertambahan suhu sepuhlindapan. Untuk analisa mikrostruktur pula, imej pancaran medan mikroskop elektron pengimbas (FESEM), menunjukan filem BiOI mempunyai morfologi berbentuk struktur serpihan seperti struktur kepingan bunga yang bersaiz dalam lingkungan 1 µm. Ketebalan filem nipis pula, adalah diantara 3.479 µm sehingga 8.082 µm manakala untuk optik pula, jurang jalur adalah diantara 1.59 ke 2.10 eV. Daripada analisa XRD, sampel yang disepuhlindapan dengan pada suhu 350 °C mempunyai struktur hablur yang tunggal manakala, untuk suhu lebih daripada 450 °C, mempunyai struktur bahan yang polihablur. Saiz hablur adalah diantara 27.747 hingga 29.314 nm. Seterusnya, kecekapan penukaran untuk kesemua filem nipis BiOI dianalisa menggunakan pengukuran arus voltan. Sampel filem nipis BiOI yang disepuhlindapan pada 350 °C menunjukan kecekapan penukaran yang tertinggi dengan 1.67 % berbanding dengan sampel-sampel yang lain. Kesimpulannya, dengan merujuk daripada kesemua bahagian hasil dalam kajian ini, BiOI 350 °C adalah suhu sepuhlindapan yang paling sesuai untuk digunakan dalam fabrikasi sel suria perovskit dan suhu sepuhlindapan yang melebihi 450 °C tidak sesuai dalam kajian ini. Kajian ini juga memberi petunjuk dan maklumat tentang sifat filem nipis BiOI yang telah disepuhlindapan dengan suhu yang sesuai sebagai lapisan aktif untuk fabrikasi sel suria perovskit.

Kata kunci:

Bismuth Oxyiodide, SILAR, Filem Nipis, Sel Suria perovskit tanpa plumbum, Suhu sepuhlindapan.

ACKNOWLEDGEMENTS

All praise to ALLAH the Almighty because without His command, I did not get to finish my master’s degree. I do want to offer my heartfelt gratitude to my main supervisor, Dr Nor Azlian binti Abdul Manaf, since she's so important in ensuring my thesis submission and research ongoing very well. I cannot imagine how my research would have progressed without her assistance and guidance. Besides that, I would like to give a special thanks to my co-supervisor, Dr Wan Yusmawati binti Wan Yusoff and Dr Azuraida Binti Amat as they greatly useful to me in terms of improving my research analysis skills and improve my presenting skills.

Besides that, I would like to thank my father Mr. Azmi bin Ajid and my mother Mrs. Wahida binti Ismail for helping me in form of mental and physical to further my study after degree. I also want to give my gratitude to them because giving their blessing to continuing my master’s degree. Also my sibling for helping me directly or indirectly during my master degree. Next, all my friends in UPNM Nadia, Hisyam, Falihan and Nasuha support me throughout my research study, discussion about the data and helping me with the PPS and PPPI business. Only ALLAH can repay what they did to me and may they always get blessing from Him.

Lastly, I would like to thank KPT for the FRGS grant to sponsoring my allowance and expense during this two years research study. In Sya Allah will be continuing my PhD next.

APPROVAL

The Examination Committee has met on **Date of Viva Voce** to conduct the final examination of **Asyraf Hakimi Bin Azmi** on his degree thesis entitled **Effects Of Annealing Temperature On Bismuth Oxyiodide Thin Film For Lead-Free Perovskite Solar Cells.**

The committee recommends that the student be awarded the of Master of Science (Physics).

Members of the Examination Committee were as follows.

Prof Madya Ts. Dr. Norhana Binti Abdul Halim
Centre of Foundation Defence
Universiti Pertahanan Nasional Malaysia
(Chairman)

Dr. Siti Zulaikha Binti Ngah Demon
Centre of Foundation Defence
Universiti Pertahanan Nasional Malaysia
(Internal Examiner)

Dr. Wan Maisarah Binti Mukhtar
Faculty of science and technology
Universiti Sains Islam Malaysia
(External Examiner)

APPROVAL

This thesis was submitted to the Senate of Universiti Pertahanan Nasional Malaysia and has been accepted as fulfilment of the requirements for the degree of **Master of Science (Physics)**. The members of the Supervisory Committee were as follows.

Dr. Nor Azlian Binti Abdul Manaf
Centre of Foundation Defence
Universiti Pertahanan Nasional Malaysia
(Main Supervisor)

Dr. Wan Yusmawati Binti Wan Yusoff
Centre of Foundation Defence
Universiti Pertahanan Nasional Malaysia
(Co-Supervisor)

Dr. Azuraida Binti Amat
Centre of Foundation Defence
Universiti Pertahanan Nasional Malaysia
(Co-Supervisor)

UNIVERSITI PERTAHANAN NASIONAL MALAYSIA

DECLARATION OF THESIS

Student's full name : Asyraf Hakimi Bin Azmi

Date of birth : 29/04/1994

Title : Effects Of Annealing Temperature On Bismuth Oxyiodide Thin Film For Lead-Free Perovskite Solar Cells.

Academic session : 2020 / 2021

I hereby declare that the work in this thesis is my own except for quotations and summaries which have been duly acknowledged.

I further declare that this thesis is classified as:

☐ **CONFIDENTIAL** (Contains confidential information under the official Secret Act 1972)*

☐ **RESTRICTED** (Contains restricted information as specified by the organisation where research was done)*

☐ **OPEN ACCESS** I agree that my thesis to be published as online open access (full text)

I acknowledge that Universiti Pertahanan Nasional Malaysia reserves the right as follows.

1. The thesis is the property of Universiti Pertahanan Nasional Malaysia.
2. The library of Universiti Pertahanan Nasional Malaysia has the right to make copies for the purpose of research only.
3. The library has the right to make copies of the thesis for academic exchange.

____________________	____________________
Signature	**Signature of Supervisor/Dean of CGS/ Chief Librarian
Click here to enter text.	Click here to enter text.
IC/Passport No.	**Name of Supervisor/Dean of CGS/ Chief Librarian
Date:	Date:

*If the thesis is CONFIDENTAL OR RESTRICTED, please attach the letter from the organisation with period and reasons for confidentiality and restriction.
** Witness

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

CO_2	-	Carbon Dioxide
TW	-	Terawatts
Si	-	Silicon
Ge	-	Germanium
P	-	phosPhorus
B	-	Boron
CdTe	-	Cadmium telluride
CIGS	-	Copper Indium Gallium Diselenide
PSCs	-	Perovskite Solar Cells
Pb	-	Lead
Bi	-	Bismuth
WHO	-	World Health Organization
BiOI	-	Bismuth Oxyiodide
SILAR	-	Successive ionic layer adsorption and reaction
NREL	-	National Renewable Energy Laboratory
GaInP	-	Gallium Indium Phosphide
GaAs	-	Gallium Arsenide
CIGS	-	Copper Indium Gallium Diselenide
DSSC	-	Dye Sensitized Solar Cells
TiO_2	-	Titanium dioxide
SC	-	Simple Cubic
FCC	-	Face-Centered Cubic
BCC	-	Body Centered Cubic
SH	-	Simple Hexagonal
PCE	-	Power Conversion Energy
J-V	-	Current Density-Voltage
PV	-	Photovoltaic

$CH_3NH_3PbI_3$	-	Metyl Ammonium Pb-Iodide
Sn	-	Tin
In	-	Indium
CBD	-	Chemical Bath Deposition
E_g	-	Band gap
FTO	-	Fluorine-doped Tin Oxide
Au	-	Gold
$Bi(NO_3)_2$	-	Bismuth (III) nitrate
KI	-	Potassium Iodide
EDX	-	Energy Dispersive X-Ray Analysis
FESEM	-	Field Emission Scanning Electron Microscope
UV-Vis	-	Ultraviolet–visible
XRD	-	X-ray diffraction
SEM	-	Scanning Electron Microscope
FEG	-	Field Emitter Gun
TTIP	-	Titanium (IV) isopropoxide
HTL	-	Hole transport layer
Li-TFSI	-	Lithium bis(trifluoromethanesulfonyl)imide
EHT	-	Electron High Tension
I	-	Iodine
O	-	Oxygen
JCPDS	-	Joint Committee on Powder Diffraction Standards
MCO	-	Movement control order

LIST OF SYMBOLS

$h\gamma$	-	Light energy
η	-	Efficiency
Voc,	-	Open circuit voltage
Jsc/Isc	-	Short circuit current
FF	-	Fill factor
α	-	Alpha
β	-	Beta
γ	-	Gamma
°C	-	Degree Celsius
°	-	Degree
µ	-	Micro
θ	-	Theta
λ	-	Wavelength
α	-	absorption coefficient
c	-	constant of proportionality
h	-	Plank`s constant
v	-	frequency of light
σ	-	Conductivity

CHAPTER 1

INTRODUCTION

1.1 Background study

1.1.1 Three types of energy sources in the world

The world that we live in today, fast growing-technology is a good trend for better future for the human kind. Over the years, technology grows day after day and a lot of new devices and electrical appliance coming into the market with are increasing the energy consumption. The primary source of energy currently available can be classified to fossil fuels and renewable energy.

.

The conventional energy sources used widely around the world are based on fossil fuels such as petroleum, coal and natural gas (Economides et al., 2009). It is reported that the annual consumption of these sources is about 39 % from petroleum, 22 % from natural gas and 30 % from coal (Burnham et al., 2012). Fossil fuels are derived from the decomposition of plants and animals. These fuels are found in the Earth's crust and contain carbon and hydrogen, both of which can be burned to generate energy. Fossil fuel power plants generate heat by burning coal or oil, which is then used to generate steam, which drives turbines, which generate electricity. However, it is estimated that these sources will run out within 90 years and all the fossil fuels sources of petroleum, coal and natural gas will become ceased. On top of this, the issue on global warming pollution needs to be taken seriously when we burn petroleum oil, coal, and gas. In meeting our energy needs, and we have driven the current global warming crisis as well (Hansen et al., 2005). Fossil fuels produce large quantities of carbon dioxide (CO_2) when burned these carbon emissions trap heat in the atmosphere and lead to climate change for our world. Furthermore, burning fossil fuels releases harmful greenhouse gases into the atmosphere, primarily carbon monoxide (CO).

Thus, it is important to find alternative renewable energy that can provide reliable power supplies in the future and help to slow down the climate change. Renewable energy is the kind of energy that are renewable and naturally replenished on human timescale. It is a natural form of energy that is much cleaner and sustainable. A brief discussion on this area follows in section 1.1.2.

1.1.2 Renewable energy

Many researchers aim in using green technology and renewable energy sources to replace all the conventional energy sources that hold more disadvantages. By replacing renewable energy sources for traditional energy sources, renewable energy technologies offer a great chance to reduce greenhouse gas emissions effect and global warming. Renewable