SYNTHESIS AND CHARACTERIZATION OF LEAD-FREE PEROVSKITE THIN FILM DEPOSITED USING SPIN COATING TECHNIQUE

AIN AJEERAH BINTI RAMLI

UNIVERSITI TEKNOLOGI MALAYSIA

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AIN AJEERAH BINTI RAMLI

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DEDICATION

I dedicate this thesis to family especially my parents, Ramli bin Pit and Siti Eira binti Mohd Shah. I also dedicated this work to my supportive mentors, PM Dr Wan Nurulhuda binti Wan Shamsuri, PM Dr Abd Khamim bin Ismail, Ts. Dr Rosnita binti Muhammad. Special thanks also to my best labmates who always support me physically, Muhammad Faiz bin Hashim and Md Nazrul Khan bin Md Shaharudin Khan. All of them taught me not to give up and always be consistent in performing work until the end even though it was quite challenging to complete the thesis. From weakness to strength, from grass to grace and from nothing to something. The knowledge and support from you have imparted upon me has been a great asset throughout my work.

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ABSTRACT

Perovskite solar cell (PSC) technologies are viewed as promising innovation and have sparked a lot of interests due to their efficiency, ease of manufacture, and low energy and environmental impacts. The performance of PSC has improved quickly in recent years, with the current record of 25.6 % power conversion efficiency (PCE). The purpose of this thesis is to fabricate methylammonium tin triiodide, $CH_3NH_3SnI_3$ perovskite thin film using spin coating technique. By manipulating spin rate and the precursor concentration, the structural and optical properties of microscope perovskite thin film were investigated and characterised using scanning electron - SEM, atomic force microscope-AFM, X-ray diffraction-XRD, and Ultraviolet-Visible spectroscopy respectively. The XRD result showed that $CH_3NH_3SnI_3$ perovskite material exhibits intense peaks corresponding to the plane (100) and (200) at the angles of 14º and 28º. The results from AFM revealed that perovskite film fabricated at 2000 rpm with 1.0 M of precursor concentration showed a uniform and consistent surface structure with a root mean square roughness (R_{rms}) of 20.70 nm. From SEM analysis, perovskite thin film fabricated at 2000 rpm with precursor concentration of 1.0 M showed a significant homogeneous and uniform layer. From UV-Vis data, the highest absorption spectra was demonstrated by the perovskite film with 1.0 M concentration and fabricated at 2000 rpm spin rate. By controlling the spin rate and precursor concentration during the fabrication process, it was shown that 2000 rpm and 1.0 M are the best parameters for good perovskite thin film quality for solar cell application.

ABSTRAK

Teknologi sel suria perovskit (PSC) dilihat sebagai inovasi yang bagus dan telah mencetuskan banyak minat kerana kecekapannya, kemudahan pembuatan dan tenaga serta kesan alam sekitar. Prestasi PSC telah meningkat dengan cepat dalam beberapa tahun kebelakangan ini, dengan rekod kecekapan penukaran kuasa (PCE) terkini sebanyak 25.6%. Tujuan tesis ini adalah untuk menghasilkan filem nipis perovskit metilammonium tin triiodide, $CH_3NH_3SnI_3$ menggunakan teknik salutan spin. Dengan memanipulasi kadar putaran dan kepekatan prekursor, sifat struktur dan optik filem nipis perovskit telah disiasat dan dicirikan menggunakan mikroskopi elektron penskanan-SEM, mikroskopi daya atom-AFM, pembelauan sinar x-XRD, dan spektroskopi ultraungu-nampak. Keputusan XRD mendapati bahawa bahan perovskit $CH_3NH_3SnI_3$ mempamerkan puncak keamatan yang selari dengan (100) dan (200) pada sudut of 14^o and 28^o. Keputusan daripada AFM mendedahkan bahawa filem perovskit yang difabrikkan pada 2000 rpm dengan kepekatan prakursor 1.0 M menunjukkan struktur permukaan yang seragam dan konsisten dengan punca min kekasaran kuasa dua (R_{rms}) 20.70 nm. Daripada analisis SEM, filem nipis perovskit yang dihasilkan pada 2000 rpm dengan kepekatan 1.0 M menunjukkan lapisan seragam yang ketara. Dari data UV-Vis, spektrum penyerapan tertinggi ditunjukkan oleh filem perovskit dengan kepekatan 1.0 M dan penghasilan pada kadar putaran 2000 rpm. Dengan mengawal kadar putaran dan kepekatan prekursor semasa proses fabrikasi, ia menunjukkan bahawa 2000 rpm dan 1.0 M adalah keadaan terbaik untuk kualiti filem nipis perovskit yang lebih baik untuk aplikasi sel suria.

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LIST OF ABBREVIATIONS

PCE	-	Power Conversion Efficiency
PSC	-	Perovskite Solar Cell
Sn	-	Tin
Pb	-	Lead
2D	-	Two-dimensional
3D	-	Three-dimensional
RMS	-	Root mean square
rpm	-	Revolutions per minute
AFM	-	Atomic Force Microscope
SEM	-	Scanning Electron Microscope
XRD	-	X-Ray Diffraction
UV-ViS	-	Ultraviolet-Visible

LIST OF SYMBOLS

A	-	Absorption
c	-	Molar concentration
l	-	Optical path length
ε	-	Molar absorption

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CHAPTER 1

INTRODUCTION

1.1 Research Background

Advances in solar cell technology are increasing gradually due to high demand in energy consumption for humans living. In recent years, there will be an incredible consideration in the advancement for renewable energy sources that makes ecological contamination. Solar energy is a prominent source of energy that led to global generation of electricity. A solar cell device is a p-n junction diode made of p-type and n-type semiconductors. When the light hits the solar cell, some of the photons of the light rays are absorbed and release electrons. The light energy supplies efficient energy to the junction and creates electron-hole pairs. The free electrons in the depletion region move to the n-type side of the junction while holes in the depletion move to the p-type side of the junction. When the concentration of electrons and holes becomes higher in n-type and p-type, the p-n junction will act like a battery cell. As a completed circuit is connected to the electrodes, the free electrons will travel through the circuit creating a flow of electricity and voltage called photovoltage.

In solar cell, there are three elements that complete the main features, which is light absorber, carrier collector and metal contact. Perovskite absorber layer works as a main functionof solar cell that convert photons (light energy) into electrical energy. Over the years, perovskite materials caught the attention most of the researchers because of the abundant in nature, strong solar absorption, low non-radiative carrier recombination and non-toxic material of solar cell (Green et al., 2014; Noel et al., 2014; Rahul et al., 2018; Sahoo et al., 2018; Yu et al., 2016).

It has led to the development of science studies especially in telecommunication and microelectronics field such as superconductivity, magneto resistance and ionic conductivity (Sahoo et al., 2018). The most significant parts of perovskite solar cell fabrication for successful commercialization are simplicity, low manufacturing cost, higher power conversion efficiencies (PCE) and easiness of production (Galindo et al., 2015; Jamal et al., 2018; Mourtada Elseman, 2019; Xiao et al., 2014; Yue et al., 2016).

Perovskite material is typically based on Group IV such as silicon, lead, tin, and germanium. The structure of perovskite is generally cubic unit cell. Silicon-based solar cell is currently dominated as perovskite material for the solar cell application. However, the high cost for the pure silicon production became a complex preparation and construction for silicon solar cell. Other than that, lead (Pb) is also proven as the best material for absorbing layer in the solar cell by its's excellent visible absorption, adjustable bandgap and high carrier diffusion length (Schileo and Grancini, 2021). Over recent years, lead-based perovskite absorbing layer present a huge contribution to the solar cell technologies.

An excellent capacity for the energy conversion into electricity is one of the upsides of lead material. Due to these advantages, Pb-based solar cell still caught an attention of many researchers. In recent years, the fabrication of Pb-based perovskite solar cell (PSC) using spin coating technique have been reported by several researchers. Previous report reveals that pre-heated treatment onto Pb-based PSC deposited using two-step deposition spin coating technique could produce almost 8.4% of PCE (Hongsith et al., 2019). At this point, the photocurrent of the perovskite solar cell is higher, and the morphology of the perovskite is said to be smooth and pinhole free.

The researchers claim that high performance of solar cell could be affected by pre-heated treatment on the material during the fabrication process. Similar works also carried out by other researcher which discovered the different between one-step and two-step deposition spin coating technique. Although the number of deposition step of spin coating are compared, this technique is able to produce void-free perovskite layer with completed pore-filling (Al-Asbahi et al., 2020). Therefore, this indicate that spin coating technique is one of the promising deposition techniques for good morphology and coverage of perovskite thin film.

Despite the success of Pb-based perovskite, previously the researchers claim that the concern with materials is the toxic nature of lead, poor stability and scientific challenge to replace it with less toxic materials (M. Chen et al., 2019; Chu et al., 2019; W. Ke and Kanatzidis, 2019; Noel et al., 2014). Compared to other issues, the toxicity of lead became a challenge in commercializing this perovskite absorbing layer thus restricted from various specialized application. For example, it raises toxicological concerns that could negatively affect human health and the environment. This is owing to the insolubility of Pb-based materials, which could cause leakage from the solar panel. Despite lead-based perovskite demonstrate a significant attraction in solar cell technology, it could produce toxicological concerns that could affect both human beings and the environment. Therefore, due to perilous and lack of adaptibility to human life, further research on perovskites material remains debated.

By taking into account this issue, Sn-based perovskite is a lead-free material that most likely substitute to Pb as it is present at the same group as Pb in Periodic Table, hence its properties are comparable to one another based on its satisfactory performance. Tin (Sn) present highcharge mobility and smaller optical bandgaps than Pb (P. Wang et al., 2020). Various studies are implemented to obtain good data describing the character of perovskites thin film. Sn-based perovskite proposed good films properties, thus its characterization should be comparable to Si and Pb material. Moreover, Sn is a non-toxic material that has a good charge-carrier mobility and small band gap which display an excellent optoelectronic property.

Indeed, Sn-based which also known as lead-free material also shows an excellent morphology which is smooth surface, densely packed grains, good surface coverage and preferred crystal orientation (Yu et al., 2016). Therefore, lead-free material such as Sn-based halides is a good choice for new future solar cell technologies due to its low-toxicity property (W. Ke and Kanatzidis, 2019) and present an excellent semiconducting property (Noel et al., 2014). In this spirit, it leads the research in the exploration of perovskite solar cell technology at higher quality, properties, stability, and efficiencies.

Generally, Sn-based halide such as $CH_3NH_3SnI_3$ has an optical bandgap of 1.3 eV. It is also known as p-type metal with low carrier density and act as lead-free light absorbing material because of it's potential (Iefanova et al., 2016). In the last few years, work on $CH_3NH_3SnI_3$ perovskite solar cell was discovered by many researchers using various parameters and techniques of deposition. The properties of the $CH_3NH_3SnI_3$ perovskite showed promising results in context of its morphology, optical and structural. However, studies using spin coat techniques in the production of $CH_3NH_3SnI_3$ thin film were not much was reported within recent years.

In other point of view, changes in morphological and optical properties of the perovskite thin film are affected by several manipulated parameters such as precursor concentration, annealing temperature, spin speed, type of substrate as well as time taken during the fabrication process. These parameters were studied to determine the performances and quality of lead-free perovskite film. Recently, research on the effects of annealing temperature, precursor concentration and spin speed towards Pb-based solar cell efficiency has been extensively studied by researchers to understand its impact on the film's properties. Nevertheless, the research on lead-free $CH_3NH_3SnI_3$ materials is still lacking until now.

To the best of our knowledge, SnI_2 concentration effect on the n-based perovskite has not been reported in the last few years. More attention should be focused to study on the impacts of SnI_2 precursor concentration, annealing temperature and spin rate towards $CH_3NH_3SnI_3$ perovskite thin film. Thus, this research remains deficient in recent years. In order to produce the best quality of the film, it is importance to analyze the correlation of the parameters that influences the production of perovskite material and able to solve all the outstanding issues such as, what is the optimum deposition condition to fabricate highly efficient lead-free perovskite thin film, how to enhance the structural and optical properties of $CH_3NH_3SnI_3$ thin film, what is the optimum spin coating speed that indicate the best quality $CH_3NH_3SnI_3$ thin film, how molar concentration of SnI_2 influence the structure and optical of $CH_3NH_3SnI_3$ thin film, and how the properties observed is correlated to one another.

1.2 Problem Statements

The main issue of solar panel generation is its relatively low performance but requires high maintenance for the fabrication process for large area photovoltaics. Previously, silicon and lead based perovskites which are major contributors to solar cell technology are not economical relative to grid-based energy supplies. The traditional silicon-based raw materials and the toxicity issue of lead-based turned into an obstacle to bring these products in the market. Therefore, Sn is a possible substitute for Si and Pb as it has more efficient charge transport features compared to the others. The halide $CH_3NH_3SnI_3$ perovskite layer has high potential as light absorbing materials compared to others (Iefanova et al., 2016).

Despite more attempt for lead-free perovskite layer, especially $CH_3NH_3SnI_3$ film in recent years, its characteristics still far from understanding. A comprehensive understanding of its structural and optical properties is necessary for further optimization of the material. Secondly, the method of fabrication for perovskite absorbing layer is one of the factors that need to be emphasized as it affects the characters of the perovskite thin film. In thin film technology, thermal evaporator, printing or solution-processing technique are generally became preferable method. However, these methods required a complex and complicated with multi-step processes. In addition, these techniques allocate relatively high costs and some of the specification does not meet the requirement for film fabrication. For instance, thermal evaporation method is most likely suitable for high temperature.

On the other hand, spin coating technique is more applicable due to low cost and very easy to handle. The process of controlling the machine is very simple and fast. Also, this method capable to produce a quality of thin film with easy fabrication (Al-Asbahi et al., 2020). Therefore, the characteristics of $CH_3NH_3SnI_3$ perovskite film are technically explained by the deposition method. Henceforth those structure and optical characteristic for $CH_3NH_3SnI_3$ thin film that is fabricated using spin coating technique could be compared to $CH_3NH_3SnI_3$ thin film that is deposited using other techniques.

In this research, the spin coating technique will be applied to prepare lead-free perovskite thin film and its characteristic will be investigated. In addition to that, the properties and quality of perovskite thin film are depending on the parameters that affect the formation of the film. This is because one parameter is inadequate to confirm the best quality film. In this work, the concentration of SnI_2 and spin rate parameters will be considered to examine its impact to $CH_3NH_3SnI_3$ perovskite thin film. Hence, these factors should be considered in this work to determine the correlation of all results so that best product could be formed, and the stability issues could be oversome for the future sake.

1.3 Research Objectives

The objectives of the work are stated below:

i. To synthesize $CH_3NH_3SnI_3$ perovskite thin film using spin coating technique using XRD.
ii. To characterize the morphological and structural properties of $CH_3NH_3SnI_3$ perovskite thin films by varying the spin coating rates with different molar concentrations of precursor solution using AFM and SEM.
iii. To analyze the optical properties of $CH_3NH_3SnI_3$ perovskite thin films by varying the spin coating rates with different molar concentrations of precursor solution using UV-Vis.

1.4 Significance to Information

The discovery or finding of this research will provide conclusions about the importance of the quality of lead-free perovskites absorbing layer in the solar cell. By considering the spin coating deposition technique and several parameters that influenced the properties of perovskite absorbing layer and understand the current issues regarding to Sn-based material, a better film quality with an excellent morphological and optical properties could be produced hence present a good perspective for solar cell application in future.

1.5 Research Scope

In sequence to achieve the given objectives, the works have been focused on the fabrication of lead-free perovskite absorbing layer using methylammonium tin triiodide ($CH_3NH_3SnI_3$). The technique used for fabrication process is one step spin coating technique. This material will be deposited with spin rate between 2000 to 5000 rpm. This is because 2000 rpm is the best minimum spinning rate that could be run by VTC-100 Vacuum Spin Coater. The highest speed that could be set is 5000 rpm. Therefore, to determine the optimum spin rate, the range will be set to 2000 until 5000 rpm. The molar concentration of each precursor solution varies from 0.5 to 1.5 M based on previous research claiming that a concentration of 1.0 M should be the best value for perovskites.

So, to prove it, this experiment was conducted in the range of 0.5, 1.0 and 1.5 M. For the synthesis and characterization, the morphological and structural properties of the absorbing layer will be analyzed using Scanning Electron Microscope (SEM), Atomic Force Microscope (AFM) and X-Ray Diffraction (XRD). The absorption and transmittance spectrum of the perovskite thin films will be examined using Ultraviolet Visible (UV-Vis).

1.6 Future Outlook

The research regarding to this lead-free perovskite absorbing layer can be further developed by improving the stability of Sn-based perovskite. This is because Sn tends to oxidize quickly. In addition, the performance of lead-free perovskite solar cell also could boostby investigating the interface properties of the thin film. This can add to the knowledge of the properties of Sn-based perovskite solar cells.

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