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TAILORING THE GRAIN BOUNDARIES OF WIDE-BANDGAP PEROVSKITE
SOLAR CELLS BY MOLECULAR ENGINEERING

BY

KHALID EMSHADI

A dissertation submitted in partial fulfillment of the requirements for the

Doctor of Philosophy

Major in Electrical Engineering

South Dakota State University

2020

TAILORING THE GRAIN BOUNDARIES OF WIDE-BANDGAP PEROVSKITE
SOLAR CELLS BY MOLECULAR ENGINEERING

KHALID EMSHADI

This dissertation is approved as a creditable and independent investigation by a candidate for the Doctor of Philosophy degree in Electrical Engineering and is acceptable for meeting the dissertation requirements for the degree. Acceptance of this dissertation does not imply that the conclusions reached by the candidate are necessarily the conclusions of the department.

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ABSTRACT

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Due to the attraction of fabricating highly efficient tandem solar cells, wide-bandgap perovskite solar cells have attracted substantial interest in recent years. However, polycrystalline perovskite thin-films show the existence of trap states at grain boundaries, which diminish the optoelectronic properties of the perovskite and thus remains a challenge. This research demonstrates a one-step solution-processing of the $[MA_{0.9}Cs_{0.1}Pb(I_{0.6}Br_{0.4})_3]$ wide-bandgap perovskite using Phenylhydrazine Iodide with amino groups to successfully passivate the trap density within grain boundaries and increase the perovskite grain size. The reinforced morphology and grain boundaries treatment considerably enhanced the photovoltaic performance from an average of $10.7 \pm 0.6\%$ for pristine to an average of $14.15 \pm 0.32\%$ for the treated devices. This strategy can be quickly adapted to other perovskites and help realize highly efficient perovskite solar cells.

Chapter 1: Introduction

1.1 Overview

Fossil fuels are the most important source of energy since the start of the industrial revolution, which leads to growth in global carbon dioxide (CO₂) emissions from energy use. The result of increasing the use of fossil fuels for energy production has increased the atmospheric CO₂ emissions from 270 ppm in 1890 to 400 ppm in 2015 [1]. Fossil fuels provide approximately two-thirds of the electric energy demand for the entire globe. The fact is that fossil fuels are nonrenewable; at current power consumption rate; scientists have reported that in 2018 the demand for oil increased by 1.3% putting all the estimations to run out of fuel in 2052 and other known deposits of coal and natural gas will be gone by 2060 [2]. Many problems need to be addressed when the demand for energy supplies has increased. The difficulties for demanding energy are related to not only global warming, but also air pollution, ozone depletion, forest destruction, and emission of radioactive substances. Due to the use of residential heating and industrial electric power consumption, more sulfur dioxide pollution increased to be the primary source of acid precipitation [3]. The main two reasons to advance the search for renewable energy are the endless energy supply, and the restriction of power contributes to climate change. The population with a lack of access to electricity estimated to be 1.4 billion people, and the number of rural communities relying on the general use of biomass is projected to surge from 2.7 billion in 2016 to 2.8 billion in 2030 [4].

With a modern, comfortable lifestyle, energy is dramatically increasing to sustain the essential community's needs. Due to the rapid increase of populations and industrialization, the energy demands are escalating and expected to increase from 14 terawatt (TW)

nowadays to 50 TW at the end of this century [5]. Heightening the concern of greenhouse emissions and escalating the demand for clean and replenishment energy are opening up new opportunities for the utilization of renewable energy resources. Not to mention, solar energy is the most abundant, endless, and clean of all the renewable energy resources today. About 1.8×10^{17} W (Joule per second) is the power received by the earth directly for the sun [6]. It means less than 15 minutes of sunlight (if fully utilized with 100% efficiency) can support the energy consumption of the entire world. For thousands of years, solar energy has been used and utilized by humankind as a radiant light and heat source. Sun as an endless source of energy, which offers us the solution to solve most energy problems now faced by humankind via supplying power in many types such as solar heating, solar photovoltaic, solar thermal electricity, and solar architecture.

Photovoltaic knowledge is one of the most excellent ways to harness solar power via the direct conversion of sunlight into electrical energy to be delivered either to the utility grid directly or isolated loads [7]. The photovoltaic effect was discovered in 1839 for the first time by Becquerel, and Fritz fabricated the advancement of the first photovoltaic cell in 1883, and its efficiency was less than 1% [8]. Further improvements were made on photovoltaic cells, where photovoltaic technology was introduced on the principle of electron-hole creation. Also, modern photovoltaic technology introduced fabricating multi-junctions devices; each of them consists of two different layers of semiconducting materials, i.e., p-type material with holes as majority carriers and n-type material with electrons as majority carriers. Figure 1.1 shows the history of improvement, and the advances in photovoltaics technology are reported in terms of power conversion efficiency for different types of solar cells.

The usage of different materials in photovoltaic solar cells has categorized the solar cells to mainly three generations. Crystalline silicon (Si) wafers are used to fabricate the first-generation of solar cells. This type is the oldest and the most common due to high power efficiencies [9].

Figure 1.1 Progress in solar cells research efficiency over the last four decades.

(Source: National Renewable Energy Laboratory (NREL), 2019)

These were the first commercialized rooftop solar panels. First-generation fabricated by using silicon crystalline to be the photovoltaic material in the solar cell. The first-generation exhibits a typical efficiency of about 25% [10]. First-generation solar cells have the advantage of excellent photoconversion efficiency, but they have high manufacturing costs, and solar cells are not flexible. The second-generation is thin-film solar cells, which could be fabricated by Si. Also, other materials could be used, such as cadmium telluride (CdTe), copper, indium, gallium, selenide (CIGS), and gallium arsenide (GaAs) [11]. These alternative materials have higher absorption coefficients than silicon leading to much absorption within a thinner layer (thin-film) of material [12]. Second-generation solar cells

have lower-cost production than the first-generation. However, they have lower efficiencies in comparison to the first-generation [13], and the relative scarcity of those elements in nature [11]. Third-generation solar cells are new promising technologies and still not commercialized yet.

Figure 1.2 Various types of solar cell technologies[9, 13]

The third-generation of solar cells can be nanocrystal-based solar cells, polymer-based solar cells, dye-sensitized solar cells, or organic/inorganic hybrid perovskites[14]. Organic-inorganic hybrid perovskite solar cell has attracted more interest over silicon-based solar cells due to the rapid increase in power conversion efficiency (PCE) and manufacturing cost [15].

1.2 Previous Work

1.2.1 Perovskite Solar Cell

Organic-inorganic lead halide perovskites $[ABX_3]$, where A can be cesium Cs, Methylammonium (MA), or Formamidinium (FA); B is lead (Pb) or Tin (Sn); and X is Iodide (I), Bromide (Br) or Chloride (Cl)] have rapidly become known as new promising photovoltaics (PV) due to their exceptional optoelectronic attributes [16], long carrier

diffusion lengths [17], strong optical absorption [18], and low processing costs. The certified PCE for perovskite solar cells (PSCs) started from 3.8% in 2009 when Kojima and his team fabricated first PSC [19] and reached 25.2% in 2019 [20], and this rapid increase and improvement in PCE of single-junction devices is unique in the history of photovoltaic development and have attracted tremendous interest [21, 22].

Figure 1.3 Perovskite crystal structure for photovoltaic devices

The perovskite crystal structure is illustrated in figure 1.3. The tolerance factor (t) and octahedral factor (μ) are the two main important factors that can determine the crystallographic stability and probable structure.

$$t = \frac{(R_A + R_X)}{\sqrt{2}(R_B + R_X)} \quad (1.1)$$

The tolerance factor is known as the ratio of the distance A-X to the distance B-X in the solid-sphere model. Here, R_A , R_B , and R_X are the Goldsmith ionic radii of the equivalent ions. Where octahedral factor μ represents the ratio of R_B/R_X . Perovskite crystal structure generally has $0.81 < t < 1.11$ and $0.44 < \mu < 0.90$. To have more stable perovskite crystal structure thus one more condition needs to be met which is $R_A > R_B > R_X$.

The interest in perovskite comes to the unique properties of perovskite, such as high absorption coefficient, high dielectric constant, long-range charge diffusion length, and high carrier mobility. It is important to show different device architectures used in fabricating PSCs before we go in detail to discuss perovskite processing parameters.

Figure 1.4 Schematic of two PSCs architecture were (a) p-i-n and (b) n-i-p

There are two main different device architecture configurations that have been developed to fabricate perovskite-based solar cells, n-i-p, and p-i-n.

The first architecture is an n-i-p structure (figure 1.4 b) where the light enters the solar cell first from the glass substrate and goes through the electron transport layer (n-type material), then passes through perovskite thin-film and exiting for the hole transport layer (p-type material). Whereas p-i-n architecture (figure 1.4 a) the light goes through the substrate first and then enters the hole transport layer (p-type material), then passes through the perovskite thin-film and goes to the electron transport layer (n-type material).

Perovskite materials have many advantages over other materials used in photovoltaics technology, and those advantages are:

- These materials are relatively easy to process [23].
- Low-temperature fabrication process [18].
- Low-cost solution processing and scalable processability [24].
- Perovskite materials have outstanding optoelectronic properties [25].
- It has broad-spectrum light absorption [19].
- High carrier mobility[17, 19].
- High carrier diffusion length[17].
- Perovskite materials are direct bandgap semiconductors [26].
- Low exciton binding energy [27-29].
- High dielectric constant [30, 31].
- Excellent radiative efficiency and photon recycling [32, 33].
- Perovskite materials have the ability to tune the bandgap from 1.2 - 2.5 eV [18, 34].

Such excellent properties make perovskite material potential candidates for the fabrication of photovoltaic devices with high efficiency. Moreover, PSCs have been

investigated for an integrated system that includes both energy generation and energy storage for the purpose of battery charging [35-38]. Among the organic-inorganic halide perovskite materials, $CH_3NH_3PbI_3$ is the well-known material used in single junction solar cells that can have PCE close to the Shockley-Queisser limits, which is 33.7% at 1.4 eV in a single-junction device [39, 40].

However, there are still some technical complexities that PSCs need to overcome before they can be commercialized and introduced to the market, such as:

- The presence of hazardous substances such as Pb, which makes these PSCs toxic and dangerous to humans and the environment [41].
- High hysteresis in the photovoltaic device owing to ionic-electronic behavior [42-44].
- PSCs have less stable performance in comparison to other thin-film solar cells and silicon-based solar cells due to moisture sensitivity [41].
- Degradation.
- PSC devices fabrication, and overall performance primarily depend on synthesis conditions with appropriate preparation methods.

There are various methods to perform the perovskite thin-film in photovoltaic solar cells such as vapor phase deposition [45-47], sequential deposition method [48, 49], spin-coating of perovskite precursor [50], doctor blading [51, 52], slot die deposition [53], and spray coating [54-56]. Some of these methods involve more steps and have more complicated procedures compare to others, the spin-coating method requires only prepare the perovskite precursor and then spin-coated on top of charge extraction layer in no more than one step.

In every technique to fabricate the perovskite thin-film, there are many processing factors and parameters that control the perovskite layer to give the desired performance in the photovoltaic devices. For example, in the spin-coating technique, the perovskite film thickness can be controlled via optimize the angular speed, angular acceleration, and spinning time of the spin deposition process. Anti-solvent dripping amount and time have a considerable impact on perovskite thin-film crystallinity and thin morphology to boost the device performance.

Regardless of the increase in the overall performance of PSCs, the single-junction solar cells PCE is restricted by the Shockley-Queisser efficiency limits, which directed the scientists and researchers to go another route to develop tandem solar cells that can reach PCE of more than 42% under normal solar irradiance [57].

Wide-bandgap perovskite solar cells with bandgaps between 1.7 and 1.9 eV have been used in junction with low-bandgap solar cells in tandem applications. The bandgap can be tuned up to the desired bandgap by partially substituting Br for I in iodide-based perovskite[58, 59]. Wide-bandgap perovskites in comparison to low-bandgap perovskites ($E_g < 1.5$ eV) have high open-circuit voltage V_{oc} and low short-circuit current density J_{sc} . Also, wide-bandgap perovskite exhibits high V_{oc} -deficits as a result of the defects at the grain boundaries and in bulk, energy mismatch of Fermi level between hole selective layer (HSL) and electron selective layer (ESL) with wide-bandgap perovskite, and photoinduced phase segregation[60].

$$V_{oc} - \text{deficits} = \frac{E_g}{e} - V_{oc} \quad (1.2)$$

Where E_g is the bandgap, and e is the elementary charge.

The tunability of the perovskite materials was first initiated by Noh et al. and Eperon et al. back in 2013 when they worked to investigate and prove the bandgap tunability for perovskite material from 1.5 to 2.3 eV, and that opened new research areas such low-bandgap and wide-bandgap to form a new type of tandem solar cells [61, 62].

1.2.2 Defect Passivation in Wide-bandgap Perovskite

The solution-based fabrication method of perovskite devices via low-temperature process gives this type of photovoltaic device a promising future to reduce the cost of manufacturing the next-generation of photovoltaic solar cells. Nevertheless, the low-temperature processing brings low formation energy, and as a result of that, defects and trap states can be formed within the grain boundaries, inside grains, and on the surface of the perovskite thin-film [63]. These defects can affect the perovskite as they cause an energy band mismatch between the carrier transport materials and perovskite thin-film as an absorber layer in the PSC device [21]. Furthermore, some of these defects cause the negative impacts on the performance of the full device, such as the ionic defect movements, which stimulates higher hysteresis in the solar cell performance and causes the fast degradation [64-66]. For those reasons and more, passivation to reduce the number of these defects and charge carrier traps is very important to achieve high-efficiency PSCs as the performance of PSCs with passivation is reported much higher compare to PSCs without passivation. There are many research and efforts have been done to improve the PSCs' performance by reducing the defects and deep trap states within grain and grain boundaries in perovskite thin-film.

In 2014, L. Wang et al. reported the advantageous effects of including additional PbI_2 in the fabrication of PSCs. The formation of PbI_2 passivates the perovskite film and leads to longer carrier times therefor PbI_2 is an excellent material for perovskite passivation [67].

In 2015, Bo Wu et al. reported that the passivation process for trap states reduces the charge accumulation at the interface between the electron transport layer (ETL) and perovskite film. Passivation can reduce and eliminate the ETL trap states as well as reduces the ETL/perovskite interface defects to lessen the device hysteresis[68]. Another work was done in 2015 by Xu et al. in which they used phenyl- C_{61} -butyric acid methyl ester (PCBM) as an additive for perovskite precursor solutions to show that the deep trap sites in grain boundaries of perovskite film can be passivated by PCBM [69].

In 2016, W. Ke et al. reported that the fullerenes such as C_{60} and PCBM as excellent acceptors were used to boosting the performance of PSCs via passivation of the defects of perovskite layer and promote electron transfer. In this work, they use a spin-coating method to introduce an ultra-thin fullerene layer to remain on the top of ETL to penetrate into perovskite film and passivate the grain boundaries. Via this thin layer of fullerene, they were able to passivate the ETL/perovskite interface and perovskite grain boundaries [70]. As reported in many works before, fullerene derivatives have been used and developed to passivate perovskite as well as passivate the ETL surface [71, 72]. Fullerene derivatives are responsible for developing the physical barrier to reduce the charge accumulation at the ETL/perovskite interface as a result of the reduction of ETL trap states.

In 2016, Y. C. Kim et al. reported the advantages of adding excess PbI_2 into the perovskite precursor solution, which could be used to passivate grain boundaries. Further

investigation with KPFM analysis showed that the excess PbI_2 reduced the ionic defect migrations, diminished the hysteresis, and improved the overall PSCs performance [73].

In 2016, Hadadian et al. did the passivation for perovskite surface by using a perovskite solution mixed with N-Doped graphene to reduce the non-radiative recombination. It was confirmed by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and elemental mapping and X-ray photoelectron spectroscopy (XPS) to find the graphene was positioned on top of the perovskite film [74].

In 2016, Yu et al. reported the addition of lead thiocyanate $[Pb(SCN)_2]$ to the perovskite precursor will passivate the film and increase the grain size, which leads to the increase of carrier lifetime. With that additive to perovskite precursor, the team was able to increase the V_{oc} , FF, and enhance the overall performance of PSCs [75].

In 2017, Li et al. introduced new passivation materials that accelerate the carrier extraction and transportation and reduce the charge recombination. Low-cost caprolactam as Lewis base was introduced to the fabrication of PSCs, which produced stable planar PSCs with highly efficient PSCs. The residual of caprolactam is beneficial to passivate perovskite grain and grain boundaries by the chemical interaction with PbI_2 forming a thick perovskite film with massive grains [76].

W. Yang, and his group in 2017, investigated the introduction of additional iodide ions into the perovskite precursor solution. By the oxidation of isopropyl alcohol, they were able to prepare the triiodide ion. The deep-level transient spectroscopy (DLTS) was used to confirm that the addition of iodide ions led to a reduction in the concentration of the deep-level defects in the film. The best PSCs reached a certified PCE of 22.1% [58].

In 2017, Y. Zhou et al. reported the molecular passivation method to achieve high thermal-stability for wide-bandgap perovskite. Perovskite thin-film decomposition and phase segregation found to be results of the collaborative effect of light and heat. Furthermore, after perovskite deposition, the team introduced passivation procedure treatment with benzylamine (BA) to passivate the highly defective areas such as grain boundaries and surface. BA efficiently passivated the surface and the grain boundaries of the perovskite film and eliminated the trap states and reduced V_{oc} deficit [77].

In 2018, Seo et al. reported the usage of CsBr as a treatment of ETL (TiO_2) to strengthen the contact in the ETL/perovskite interface. This treatment allows rapid photogenerated electrons extraction resulting in higher fill factor close to 80% [78]. Also, in 2018, Peng et al. showed that they achieved a V_{oc} for passivated PSC as high as 1.2 V after passivating a spiro-OMeTAD/perovskite interface with an ultra-thin layer of poly(methyl methacrylate) PMMA [79].

In 2018, Cho et al. reported the passivation method of perovskite interface for a better reduction in interface defects to enhance carrier transportation. Also, they reported that the enhancement of both device stability and overall performance. Cho and his group used a mixture of iso-butylammonium iodide (iBAI) and formamidinium iodide (FAI) as a mixed passivation treatment to reduce the ionic transport via the formation of energetic interfacial barrier and inactivate of the interfacial trap sites [80].

In 2019, K. Zhu et al. reported the passivation method to reduce the defect concentration as they cause poor performance of the solar cell due to the ability to form in absorber layers and generate more traps. Ethylamine alcohol chloride was introduced to the perovskite precursor solution. Ethylamine alcohol chloride has the hydroxyl group and

ammonium group; both can easily interact with perovskite halogen to suppress and oppose ion migration by creating more hydrogen bonds. Here, hydrogen bonds improved the grain size via working as a crosslinking agent to bring more adjacent grains together and form bigger grains [81].

In 2019, C. Chen et al. reported a strategy for tuning the work function of the surface layer of wide-bandgap perovskite by incorporating guanidinium bromide (*GABr*) into the precursor solution. The results were observed as larger grain size due to chemical heterogeneity, which increases the Gibbs free energy barrier for nucleation and the reduction of V_{oc} deficits, which attributed to decreases of defect density [82].

1.3 Motivations

There is a need for additives to passivate the perovskite grain boundaries to reduce the trap states and improve current density, fill factor, and overall photoconversion efficiency of PSCs. This work investigates the use of different concentration of Phenylhydrazine Iodide [PHAI ($C_6H_7N_2I$)] as an additive to passivate the wide-bandgap perovskite grain boundaries for a more efficient device.

1.4 Objectives

The objectives of this study are to improve the wide-bandgap perovskite solar cell efficiency by more than 2% by using the PHAI as an additive. In addition, the improvement in overall photovoltaic device performance will be another objective as the grain boundaries passivation improves the fill factor. These objectives could be achieved if the following tasks were performed:

1. Fabricate twelve wide-bandgap PSC devices with PHAI additive for each concentration: 0, 1, 2, and 3 mg/mL.
2. Characterize the surface morphology of all the fabricated wide-bandgap PSCs using SEM and Atomic Force Microscopy (AFM).
3. Perform the current density-voltage (J-V) measurement, external quantum efficiency (EQE), UV-Vis absorption spectroscopy, current sensing atomic force microscopy (cs-AFM).
4. Measure the XRD, steady photoluminescence (PL), transient photovoltage (TPV), transient photocurrent (TPC), electrochemical impedance spectroscopy (EIS), and Mott-Schottky (MS) measurement for fabricated wide-bandgap perovskite devices.

Chapter 2: Theory

2.1 Solar Energy

Solar energy is known as one of the cleanest energy available in the universe. It is the alternative energy to fossil fuel energy, such as coal and oil. Without add to global warming, the sun radiates energy in one second more than the entire world has used from the beginning of life on earth until nowadays. The increasing shortage of fossil fuels makes the demand much higher to explore new energy types that have minimum environmental and biological threats to the earth. Solar energy is getting more attention to be the best solution for the problems of increasing the demand for energy worldwide due to population growth and industrial progression. Many reasons make solar energy the best option for a future energy source for the entire world, such as solar energy, which is an infinite energy source of all renewable energies. The sun produces energy at the rate of $3.8 \times 10^{23} \text{ kW}$, of which approximately $1.8 \times 10^{14} \text{ kW}$ reached to the surface of the earth [83]. The increasing demand for energy can quickly meet by using photovoltaic technology.

The solar spectrum extends over the wavelength corresponding to ultraviolet (UV) with the wavelength range between 10 nm to 380 nm, visible light (Vis) with a wavelength range between 380 nm to 750 nm, and near-infrared (NIR) with a wavelength range between 750 nm to 2,500 nm. Figure 2.1 shows the solar radiation spectrum for direct sunlight at the sea level and at the top of the earth's atmosphere. The solar spectrum radiation is similar to the (5250 °C, which is approximately the temperature of the sun) blackbody spectrum. In the spectrum of the sun radiation measured at sea level, we see some radiation gets absorbed by gases as the radiation passes through the atmosphere.

Figure 2.1 Solar Radiation [84].

The solar spectrum that reaches the sea level is not the same as the measured at the top of the atmosphere due to the reflection, absorption effects, atmospheric scattering, and the path length that the spectrum takes to reach the earth's surface. The path length depends on the zenith angle, θ_z , which is the angle measured between the vertical and the direct sunbeam. Also, the solar spectrum path to any point of the earth's surface is generally compared with the vertical path directly to sea level at that point. The vertical path directly to the sea level is known as Air Mass (AM1), which has a zenith angle (θ_z) = 0° . When the solar spectrum passes through no atmosphere, the extraterrestrial spectrum is known as (AM0). The American Society for Testing and Materials (ASTM) published three spectra, AM 0, AM 1.5 direct, and AM 1.5 global when the zenith angle at 37.00° . As the intensity of the global radiation at the top of the atmosphere reduces from 1367 W/m^2 to

1000 W/m^2 at sea level, the following equation can be used to find the global radiation intensity via using AM,

$$I = 1367(0.7)^{(AM)^{0.678}} \quad (2.1)$$

Where AM can be calculated from the secant of the zenith angle,

$$AM = \text{Sec } \theta = \frac{1}{\cos \theta} \quad (2.2)$$

Figure 2.2 Solar Zenith Angle [85].

Figure 2.3 Solar Reference Spectra. Modified from ref [86].

2.2 Photovoltaic Effect and Solar Cells

The photovoltaic effect is the basic process of converting sunlight into electricity using photovoltaic devices. In other words, the photovoltaic effect is the process where the photovoltaic cell generates an electric current when it is exposed to the sunlight. It is the effect that makes the solar panels useful by converting the sunlight to electrical energy. A French experimental physicist Edmond Becquerel discovered the photovoltaic effect in 1838, only nineteen years old at that time [87]. The sunlight is just photons carry energy, and this energy depends only upon the wavelength of the incident light. The light-generated electrons (E) and holes (H) will be collected by the p-n junction, where the electrons move to the n-type side, and the holes move to the p-type side of the junction. A conventional

photovoltaic solar cell is constructed based on the p-n junction, where p-type and n-type materials are getting in physical contact with each other so that electrons and holes can move from one region to the other and creating electric field within the p-n junction. Figure 2.4 illustrates the primary photovoltaic solar cell created as a p-n junction.

Figure 2.4 Photovoltaic cell structure and operation schematic. Modified from ref [88].

The band diagram of a p-n junction is shown in figure 2.5. The concentration of the holes is higher in p-region compare to n-region, and this makes the p-region has a higher work function (E_{fp}) when it measured from the vacuum level. On the other hand, n-region has a higher concentration of electrons. Therefore, the work function (E_{fn}) in n-region is lower than the work function in n-region. When there is no contact between p-region and n-region, there will be no band bending and or charge diffusion or drifting from one region to another. As you can see in figure 2.5, the electrons diffuse into the p-type region, and the holes diffuse into the p-type region to create a depletion region between the hole-rich material and electron-rich material. On each side of the depletion region, on each side of the junction, there will be a quasi-neutral region (QNR) with no electric field. The quasi-

neutral region in the p-type region contains the majority charge carriers of holes, and in n-type contains the majority charge carriers of electrons [89, 90].

Figure 2.5 Schematic band diagram of a p-n junction with the regions. Modified from ref [91].

Electrons have moved from n-type to the p-type, and the holes move from p-type to n-type. As a result, the n-type region has a positively charged donor (N_D), and the p-type region has filled with a negatively charged acceptor (N_A). To maintain a neutral charge condition in a p-n junction, the total charge number on each side must be equal to the opposite side. The depletion region has a distance of the penetration (D_p) of the positive

side and the negative side has a penetration distance of (D_n) . In order to maintain charge equilibrium, one condition must be valid as represents in the following equation:

$$D_n \times N_D = D_p \times N_A \quad (2.3)$$

Now, the free charges need extra energy to pass the barrier, which is built-in potential. The charge carrier diffusion process from both sides of the p-n junction created an electric field, which creates the built-in potential difference within the depletion region. This built-in potential difference with an open-circuit potential can be calculated from this equation:

$$E_0 = V_T \ln \left(\frac{N_D \times N_A}{n_i^2} \right) \quad (2.4)$$

E_0 is the zero bias junction voltage, V_T is the thermal voltage, and n_i is the intrinsic concentration.

The depletion region width of the p-n junction depends on the built-in potential difference and the impurity concentrations of acceptor and donor. Hence, the depletion region width can be found from the following equation:

$$w = \sqrt{\frac{2\epsilon V_{bi}}{q} \times \left(\frac{1}{N_A} + \frac{1}{N_D} \right)} \quad (2.5)$$

Where ϵ represents the dielectric permittivity of the semiconductor, V_{bi} is the built-in potential difference between the quasi-Fermi level of p-type and n-type regions.

The diffusion distance that the minority carriers traveled for holes and electrons can be calculated via this equation:

$$D_p = \sqrt{K_p \tau_p} \quad (2.6)$$

$$D_n = \sqrt{K_n \tau_n} \quad (2.7)$$

Here, K_p and K_n are the diffusion coefficients for hole and electron, respectively, τ_p and τ_n are the recombination lifetime for hole and electron inside n and p side, respectively.

2.3 Electrical Model of Solar Cells

The electrical model of p-n junction solar cells can be represented by a simple equivalent electric circuit, such as the primary example shown in figure 2.6. In this model, I_D is the diode dark current, I_{ph} is the current source in the circuit, R_s and R_{ph} are the series and shunt resistances, respectively. R_L Represent resistance of the load.

From figure 2.6, the net current $J_{(V)}$ through the solar cell can be written as:

$$J = J_{ph} - J_{dark} \quad (2.8)$$

Where J_{ph} represents the photocurrent, which is weakened by J_{dark} , dark current.

Dark current can be found from this equation:

$$J_{dark} = J_0 \times \left(\exp \frac{qV}{nkT} - 1 \right) \quad (2.9)$$

Where J_0 is the reverse saturation current density, V is voltage, q is the electron charge, n is the identity factor, k is Boltzman's constant, and T is the temperature. When the applied voltage is zero, the dark current becomes zero.

Figure 2.6 Schematic diagram for the equivalent circuit of the photovoltaic cell with a load. Modified from ref [92].

Now, substituting equation 2.9 into equation 2.8, we get:

$$J = J_{ph} - J_0 \times \left(\exp \frac{qV}{nkT} - 1 \right) \quad (2.10)$$

The voltage across the load takes the maximum value when the current density of the circuit is zero, and this voltage known as open-circuit voltage (V_{oc}) of the solar cell. When the solar cell reaches the V_{oc} , then $J_{ph} = J_{dark}$ and then J equals zero. The current density of the solar cell called circuit current density (J_{sc}) when the load resistance is zero, and the voltage is zero.

One can write the open-circuit voltage as follow:

$$V_{oc} = \frac{nkT}{q} \ln\left(\frac{J_{ph}}{J_0} + 1\right) \quad (2.11)$$

Equation 2.9 could be modified to:

$$I(V) = \frac{V - IR_s}{R_{sh}} + I_o \left[e^{\frac{qV}{nkT}} - 1 \right] - I_{ph} \quad (2.12)$$

2.4 Solar Cell Parameters

Short circuit current I_{sc} is the current flowing in the external circuit when the voltage across the solar cell is zero. It depends on the incident photon flux density due to light intensity, and the solar cell area. To avoid the reliance on I_{sc} on cell area, the short circuit current density was introduced to be used as a unit to represent the maximum current in the solar cell.

Figure 2.7 Typical J-V curve of a photovoltaic device in the dark and under illumination conditions. Modified from ref [93].

The current density of a solar cell depends on the optical properties of the device and the absorption spectrum of the absorber layer. Next equation calculates the current density in the solar cell device:

$$J_{sc} = e \int_{\lambda_0}^{\lambda_n} N_{ph}(\lambda) \times EQE(\lambda) d\lambda \quad (2.13)$$

Where e is the electron charge in the unit of Coulombs, E_g is the bandgap of the material in the unit of electron volts, n is the maximum wavelength of the spectrum range, N_{ph} is the photon flux per unit wavelength ($\frac{conts}{m^2.s.nm}$) for the light that falls on the solar cell device and EQE is the external quantum efficiency. The higher the bandgap of the material, the lower the current density will be, due to the fact that higher bandgap materials absorb less spectrum of sunlight in comparison to materials with low-bandgap.

Open-circuit voltage (V_{oc}) happens when there is no current flowing in the external circuit and can be calculated from equation 2.11. In the case of organic photovoltaics (OPV), V_{oc} is defined by the difference between the two energy levels, Highest Occupied Molecular Orbital (HOMO) level of donor and the Lowest Unoccupied Molecular Orbital (LUMO) of the acceptor material.

The maximum upper limit of V_{oc} in organic photovoltaics devices is giving by the following equation:

$$V_{oc} = \frac{1}{e} [LUMO_{Acceptor} - HOMO_{Donor}] \quad (2.14)$$

When the empirical value can be calculated as following [94]:

$$V_{oc} = \frac{1}{e} [LUMO_{Acceptor} - HOMO_{Donor}] - 0.3 V \quad (2.15)$$

Where 0.3 is an empirical value for the difference between V_{oc} and the built-in potential (V_{bi}).

Another parameter used in the characterization of a photovoltaic device is the fill factor (FF). It determines the maximum power from a photovoltaic device. FF is described as the proportion of maximum power to the product of V_{oc} and J_{sc} for a giving solar cell. FF can be found from this formula:

$$FF = \frac{P_M}{J_{sc}V_{oc}} = \frac{J_M V_M}{J_{sc}V_{oc}} \quad (2.16)$$

Figure 2.8 Schematic of output current (red line) and power (blue line) as a function of voltage. Modified from ref [95].

The fill factor depends on the series and shunt resistances. Increasing the shunt resistance and decreasing series resistance found to improve the FF of the solar cell [96]. Whereas series resistance happens at the interfaces between different layers and occurs along the current path through the cell, shunt resistance is due to misshape in cell

fabrication. Both resistances are exhibited as a reduction in fill by pulling in of the J-V curve, as shown in figure 2.9.

Figure 2.9 the effects of R_s and R_{sh} on the fill factor in the I-V response.

One significant factor in judging the overall performance of the solar cell is by measuring efficiency. The efficiency of the solar cell is the measurement of how good the photovoltaic device can convert the incident light to electrical energy. This term is known as the overall power conversion efficiency, η . It can be calculated via this equation:

$$\eta = \frac{I_{sc} V_{oc} FF}{P_{in}} \times 100 \quad (2.17)$$

In other words, the efficiency of the solar cell is represented as the ratio of maximum power to the power of the incident light under standard illumination condition.

$$\eta = \frac{P_{max}}{P_{in}} \quad (2.18)$$

As a critical parameter, external quantum efficiency (EQE) used in the quantitative characterization of photovoltaic devices, which defines the ratio of the numbers of the generated electrons to the number of incident photons with a given wavelength.

$$EQE = \frac{\text{Number of collected electrons}}{\text{Number of incident photons}} \quad (2.19)$$

$$EQE = \frac{h \times c \times J_{sc}}{e \times \lambda \times P_{in}} = \frac{1240 \times J_{sc}}{\lambda \times P_{in}} \quad (2.20)$$

Where h is Plank's constant ($6.626 \times 10^{-34} J \cdot s$), c is the speed of light in a vacuum ($2.998 \times 10^8 m \cdot s^{-1}$), and e is the electron charge.

2.5 Operating Principles of Characterization Techniques

2.5.1 UV-Visible Spectroscopy

When the material absorbs energy in terms of UV-Vis light and that energy is higher than the energy of the bandgap of the material, that light will cause the excitation of electrons to move from lower energy states to empty higher states. The example of this excitation is that samples absorb the energy in the form of ultraviolet or visible or near-infrared light, which makes the samples undergo electronic transitions, then electrons excited from the valence band to conduction band states or from HOMO to LUMO energy states. UV-Vis spectroscopy is a technique used to measure electronic transition under the condition of illumination and allow us to measure the absorbance and to find the exact bandgap energy for the material. The UV-Vis spectrometer contains a light source generates light with wavelength in the range of 280 – 1200 nm. The spectroscopy has a

monochromator that consists of an entrance slit, a dispersion device, and an exit slit. The schematic diagram of UV-Vis spectroscopy is shown in figure 2.10.

Figure 2.10 Schematic of UV-Vis spectroscopy [97]

Figure 2.11 Possible Electronic Transitions of σ , π , and n electrons. Modified from ref [98].

The principle behind UV-Vis absorption spectroscopy is based on the Beer-Lambert law, which can be represented in terms of transmittance as following:

$$T(\lambda) = \frac{I}{I_0} = e^{-\alpha(\lambda)d} \quad (2.21)$$

Where I_0 is the incident light intensity, I is the transmitted light intensity, d is the sample thickness, and $T(\lambda)$ is the transmittance at a particular wavelength of light.

The Beer-lambert law can be used to determine the absorbance of the sample as following:

$$A(\lambda) = -\log[T(\lambda)] = -\log\left(\frac{I}{I_0}\right) = \alpha d = \epsilon dc \quad (2.22)$$

Where α is the absorption coefficient of the sample, ϵ is the molar absorptivity, and c represents the concentration of the compound in solution, expressed in mol/L. The absorption coefficient can be found as follow:

$$\alpha = \frac{1}{d} \ln T(\lambda) \quad (2.23)$$

2.5.2 X-Ray Diffraction (XRD)

The X-ray diffraction technique is widely used to identify and examine the material crystalline structure. XRD gives quantitative information regarding the crystallographic orientation of different materials, lattice spacing, and crystalline fraction. When a sample tested by XRD, the incident beam of X-ray beam scatters from the sample due to diffraction with varying intensities. Bragg's law is used to study the diffraction pattern, as shown next:

$$2d \sin \theta = n\lambda \quad (2.24)$$

Where d is the spacing between the crystal layers, Θ is the angle of the incident and reflected beams, and λ is the wavelength of the incident beam. Figure 2.12 shows a schematic diagram of the diffraction from a sample to an incident beam with an angle Θ .

Figure 2.12 X-ray Diffraction From Sample [99].

2.5.3 Atomic Force Microscopy

The atomic force microscopy (AFM) is a type of scanning probe microscopy (SPM), where it can image the surface morphology and topography of a sample. This scanning probe can measure local surface potential and conductivity and magnetic properties. AFMs use the force between the tip of the probe and the sample surface when measuring different properties. The measurement of the tip is 3-6 μm tall (pyramid shape), and 15-40 nm end radius depending upon the measurement.

Figure 2.13 shows the general components of atomic force microscopy. The position sensitive photodiode detects the laser beam reflected from the cantilever. As the cantilever moves vertical and lateral, it reflects the laser beam to the four-segment photo-detector to

indicate the position of the tip. When the position-sensitive photo-detector receives the signals, then the diode will send it to the controller and tip to maintain the force between the tip and the sample. From the deflection of the cantilever due to Van der Waals, electrostatic, and capillary and adhesive forces between the tip and sample, the topographic image of the sample can be obtained from the data processor.

Figure 2.13 (a) Schematic of an Atomic Force Microscope, Modified from Ref [100], and (b) interatomic Force Vs. Distance Between Tip and Sample [101].

AFM can be used in three different modes, depending on the interaction between the cantilever tip and the sample surface.

- i. **Contact mode:** happens when the tip is very close to the surface of the sample, and there is a mechanical contact between the cantilever tip and the sample. When the tip is touching the sample, the repulsive Van der Waals forces are dominant, and the net electrical force is positive. During this mode, there is a high risk of damaging the tip and the sample.

- ii. Tapping mode: consider to be the typical AFM imaging mode. In this mode, the tip moves further away or closer to the sample to generate oscillating attractive and repulsive forces. When tapping mode is used, the benefit is to provide a high-resolution phase and topographic imagery.
- iii. Non-contact mode: happens when the tip is away from the sample, and there is no mechanical interaction. After the distance between the sample and the tip becomes smaller but not contact, there are weak attractive forces that exist between tip and sample, and imaging will be obtained in non-contact mode.

2.5.4 Kelvin Probe Force Microscopy

Kelvin probe force microscopy (KPFM) is a type of scanning probe microscope technique to measure and map the local surface potential of a sample with high spatial resolution [102, 103]. In this technique, the imaging is done in non-contact mode to reduce the electrostatic interaction between the sample and the cantilever tip by applying an external bias voltage. This technique was developed by Lord Kelvin in 1898 [104].

KPFM work principle is based on the capacitor with parallel plates where one plate works as a sample, and the other plate works as a cantilever tip with a known work function. Figure 2.14 shows the schematic diagram of KPFM measurement. The KPFM has two lock-in amplifiers (LIA), which both are simultaneously used, as shown in figure 2.14. The first lock-in amplifier (Lock-in # 1) oscillates at a frequency (ω), then the capacitance will change as the distance between the plates changes. As a result, the alternating current will be generated in the circuit connecting the plates. If there is applied dc-voltage to either plate, the current will be reduced to zero, and this voltage known as the contact potential difference (CPD) of the two materials. The KPFM uses a compassionate force cantilever

tip, and therefore the electrostatic force is used instead of the current as a controlling parameter in the KPFM measurement.

Contact potential difference (V_{CPD}) between both the tip and the sample can be mathematically measured from this equation [105]:

$$V_{CPD} = \frac{\phi_t - \phi_s}{-e} \quad (2.25)$$

Where ϕ_t and ϕ_s are work functions for the tip of AFM and the sample, respectively. e is the electron charge.

Figure 2.14 Schematic Diagram of Kelvin probe force microscopy (KPFM) [106].

To induce the electrostatic force between the tip and the sample, KPFM applies a DC and AC electrical bias to the conductive tip via the second lock-in amplifier (Lock-in #2). The contact potential difference is the DC potential difference between the work function of the tip (ϕ_t) and the work function of the sample (ϕ_s).

The electric force (F_c) between both the tip and the sample can be calculated by the following equation:

$$F_c = \frac{1}{2} (V_{tip} - \phi_{CPD})^2 \frac{dc}{dz} \quad (2.26)$$

$$V_{tip} = V_{dc} + V_{ac} \sin(\omega_{elec} t) \quad (2.27)$$

Where ϕ_{CPD} is the contact potential difference between the sample and the tip, c is the capacitance, V_{dc} is the DC offset applied to the tip, and ω_{elec} is the frequency of AC bias applied to the tip. KPFM measurement offers topography and surface potential mapping instantaneously at the same time.

2.5.5 Scanning Electron Microscopy

There are many ways to determine the morphology of the sample's surface; a scanning electron microscope (SEM) is one of the best techniques to use. SEM uses a concentrated beam of electrons to generate signals that carry information representing the film surface morphology. Figure 2.15 shows the schematic diagram of the SEM device. There is an electron gun that generates a high-electrons beam, and then the beam gets into the condenser lens to get focused. Scanning coil works to focus the electron beam onto the sample. When the focused beam strikes the sample's surface, it scatters into signals such as secondary electrons, backscattered electrons, photons, and heat. The two useful signals are the secondary electron and the backscattered electrons due to the ability to provide a good quality surface image. These two types are commonly used to provide imaging for morphology and topography of the samples. SEM commonly used to perform the

nanometers to millimeters scale measurements due to the low wavelength of the electrons compare to visible light.

Figure 2.15 Basic Construction of an SEM. Modified from ref [107].

2.5.6 Transient Photocurrent Measurement

Transient photocurrent (TPC) technique is used to measure the charge carrier transport time (τ_{tp}). In this measurement, a nanosecond laser pulse device will be used to measure the photocurrent in the solar cell. The measurement requires to keep the photovoltaic

device in a short-circuited state by applying a small resistance of about $50\ \Omega$ across the device terminals. The transport time (τ_{tp}) represents the time needed for the charge carriers to reach the device electrodes. Figure 2.16 shows (a) the schematic setup TPC and (b) transient photocurrent decay produced across the $50\ \Omega$ load. Mathematically one can calculate transient photocurrent as given by the following equation [108, 109]:

$$I(t) = I_0 e^{-t/\tau_{tp}} \quad (2.28)$$

Where I is the current at any time $t \neq 0$, and I_0 is the initial current at $t = 0$.

Figure 2.16 (a) Schematic of Transient Photocurrent measurement, (b) Transient Photocurrent Decay.

2.5.7 Transient Photovoltage Measurement

Transient photovoltage (TPV) is a technique to measure the photoconductivity in which the photovoltaic device kept at open-circuit voltage by applying a significant resistance ($1\ M\Omega$) across the solar cell terminals. This technique used to measure the charge carrier

recombination lifetime (τ_{rec}). The exponential change in the voltage is expressed mathematically in this equation:

$$\Delta V(t) = \Delta V_0 e^{-t/\tau_{rec}} \quad (2.29)$$

Where $\Delta V(t)$ is the transient photovoltage at time $t \neq 0$, and ΔV_0 is the transient photovoltage at $t = 0$.

Figure 2.17 (a) Schematic of Transient Photovoltage Measurement, (b) Transient Photovoltage Decay.

The total charge carrier density can be mathematically calculated by using the differential capacitance, which is defined as:

$$dc = \frac{\Delta Q}{\Delta V_0} \quad (2.30)$$

Where ΔQ is obtained from TPC analysis while ΔV_0 is the amplitude of TPV transient under different illumination conditions.

Also, one can calculate the total number of charge carrier density under a particular illumination condition by the following equation:

$$n = \frac{1}{A \cdot e \cdot d} \int_0^{V_{oc}} c \, dV \quad (2.31)$$

Where A and d are the area and the thickness of the device, e is the electron charge.

From TPC and TPV, the diffusion length of the carrier can be found via the given equation:

$$L = \sqrt{D_n \tau_{rec}} \quad (2.32)$$

Where D_n is the diffusion coefficient and τ_{rec} is the recombination time found from TPV measurement.

All these measurements include charge carrier transport time, charge carrier recombination lifetime, the diffusion length of the carrier, and the total number of charge carrier density will help to identify and differentiate the performance of the solar cells and make a good judgment on which photovoltaic device has an excellent performance.

2.5.8 Electrochemical Impedance Spectroscopy

Electrochemical Impedance Spectroscopy (EIS) is a potent tool to measure the electrochemical reaction to an AC potential $[V(\omega, t)]$ over a wide variety of frequencies $[f = \frac{\omega}{2\pi}]$, where ω is the angular frequency. EIS is a very prevalent technique to examine the charge extraction and charge recombination processes in PSCs [110-112]. During the measurement, the small amplitude of AC potential will be applied over a range of frequency (1 MHz – 1 Hz) to an electrochemical system and measuring the current of the

system $[I(\omega, t)]$. According to Ohm's Law, the impedance $[Z(\omega)]$ of the electrochemical system can be expressed by the equation:

$$Z(\omega) = \frac{V(\omega, t)}{I(\omega, t)}. \quad (2.33)$$

In complex numbers, the small AC potential can be written as:

$$V(\omega, t) = V_0 e^{j\omega t}. \quad (2.34)$$

Also, the measuring AC current of the system can be written in complex number formula as follow:

$$I(\omega, t) = I_0 e^{f(\omega t - \theta)}. \quad (2.35)$$

Where $j = \sqrt{-1}$, and f is the linear frequency. Now, equation (2.33) can be rewritten as:

$$Z(j\omega) = \frac{V(\omega, t)}{I(\omega, t)} = \frac{V_0}{I_0} e^{j\theta} = Z_0 e^{j\theta}. \quad (2.36)$$

Using Euler's relationship and representation, equation (2.36) can be as:

$$Z(j\omega) = |Z|(\cos\theta + j\sin\theta). \quad (2.37)$$

Thus, the general expression will be:

$$Z(\omega) = Z_{Re} + jZ_{Im} \quad (2.38)$$

EIS collected data generally represented in the form of the Nyquist plot, where the imaginary values are plotted against the real values over a range of ω . The result is semi-circular arc represents the high-frequency and low-frequency resistance characteristics of the PSCs.

Figure 2.18 shows the W-PSCs Nyquist plot with the equivalent circuit model. At high-frequency of EIS, the component signifies the charge transfer resistance (R_{tr}),

whereas at low-frequency the component represents the charge recombination resistance (R_{rec}) [113].

Figure 2.18. Nyquist Plot with Equivalent Circuit Model.

2.6 Phenylhydrazine Iodide [PHAI]

PHAI was selected as crosslinking agent due to its richness in amino groups [NH_2], which incorporate into the perovskite structure and attach to the surface of via supramolecular interaction of hydrogen bonds such as $C-H \cdots I$ and $N-H \cdots I$. These bonding make PHAI molecules more effective to crosslink neighboring perovskite grains to form one big grain. PHAI enables the growth of perovskite crystals with larger grain size and passivates grain boundaries resulting in improved photovoltaic performance.

Figure 2.19. Phenylhydrazine Iodide (PHAI)

Figure 2.20. Schematic of PHAI crosslinking method.

Chapter 3: Experimental Procedures

3.1 Materials and Device Fabrication Procedures

This section talks about the materials and the specific techniques and methods used in the fabrication process to achieve the full wide-bandgap perovskite solar cell, which is demonstrated in this work.

3.1.1 Materials

The transparent FTO substrates (sheet resistance of $14 \Omega / \text{sq}$ and a thickness of 2.2 mm) were obtained from Hartford Glass Co, Hartford City, IN, USA. The substrates were cut to a customized size of $1.5 \text{ cm} \times 1.5 \text{ cm}$. An aqueous solution of Clevios P VP AI 4083 PEDOT: PSS was obtained from Heraeus Precious Metals, North America Daychem LLC, Vandalia, OH, USA. Methylammonium iodide ($\text{CH}_3\text{NCH}_3\text{I}$) was ordered from Greatcell Solar Materials, Canberra, NSW, Australia. PbI_2 (99.99%, trace metals basis, for perovskite precursor) and PbBr_2 (>98%, for perovskite precursor) were purchased from TCI America. Anhydrous-DMSO (>99.7+%) extra dry was purchased from Acros Organics. PC60BM (99.5%) polymer was obtained from Nano-C, Inc. γ -butyrolactone (>99%), and Rhodamine both were obtained from Sigma Aldrich. All the materials were used as received.

3.1.2 Device Fabrication – Glass Substrate Preparation

The FTO coated glass substrates were cleaned in an ultrasonic bath while bathed in solutions of detergent, de-ionized water, acetone, and 2-propanol. Each bath lasted approximately 20 minutes. The FTO substrates were then exposed to UV-ozone for approximately 20 minutes.

3.1.3 Device Fabrication – Spin-Coating Process

After cleaning and UV exposure procedures were finished, PEDOT: PSS aqueous solution was spin-coated on top of FTO substrates at 5000 rpm for 40 seconds. Then, substrates were thermally annealed at 140 °C for 10 min in ambient air. After FTO substrates were cooled down to room temperature, all FTO substrates were transferred into an N₂-filled glove box to finish the fabrication process. For the spin-coating perovskite layer, the perovskite solution contained 143 mg of MAI, 184 mg of PbI₂, 220 mg of PbBr₂, and 26 mg of CsI; all were dissolved in 1 mL of a mixed solvent of γ -butyrolactone: DMSO at a volume ratio of 7:3. The prepared solution was stirred at 70 °C overnight. In addition, to control a wide-bandgap perovskite solution, the perovskite precursor was doped with PHAI to make three different concentrations, 1, 2, and 3 mg/mL. PHAI was added 1-2 hours prior to the spin-coating process.

Figure 3.1. The schematic diagram for fabrication steps, (a) Dropping perovskite precursor on top of the substrate, (b) spinning the substrate holder for spin-coating perovskite layer, (c) dripping of anti-solvent, (d) Thermal annealing at 100 °C for 10 min.

The perovskite layer was fabricated on the top of PEDOT: PSS via spin-coating with a two-step process, first at 2000 rpm with the ramping rate of 1000 rpm s^{-1} for 15 s and second at 5000 rpm with the ramping rate of 2000 rpm s^{-1} for 45 s. During the second step, 500 μL of extra dry toluene was poured on the center of the spinning substrates 20 s prior to the end of the whole spinning program. The samples were thermally annealed on a hotplate at 100°C for 10 min in an inert atmosphere (N_2). The change in perovskite color from yellowish to light brown confirms the film transformation from precursor to perovskite. The solution of 20 mg/mL of PC60BM in chlorobenzene was stirred overnight and then used as an ETL. PC60BM was spin-coated on top of perovskite film at 2500 rpm with the ramping rate of 2000 rpm s^{-1} for 40 s, then immediately annealed on a hotplate at 60°C for 15 min. A rhodamine dye solution of 0.5 mg mL^{-1} in dry IPA was then spin-coated at 4000 rpm with a ramping rate of 3000 rpm s^{-1} for 20 s on top of the PC60BM layer.

Figure 3.2. Schematic diagram of the device architecture.

Evaporator with a high vacuum of approximately 2×10^{-6} mbar was used to deposit the electrode. Silver was thermally evaporated as a top electrode with an active area of 0.13 cm^2 on top of the rhodamine layer. All steps were performed in an N_2 -filled glovebox, and some solvents vapor in the glovebox kept minimized during the spin-coating process to avoid any film damage. All single-junction w-PSC devices were constructed in the inverted (p-i-n) architecture.

3.2 Materials and Device Characterizations

3.2.1 UV-Visible Absorption Spectra Measurements

All the measurements of UV-Vis absorption for this work were done using an Agilent 8453 spectrophotometer running ChemStation software. This spectrophotometer equipped with two lamps, a tungsten lamp as the visible/near-infrared (VNIR) source, and a deuterium lamp as the ultraviolet (UV) source.

Figure 3.3 Schematic of UV-Visible absorption spectrophotometer [114].

Four sets of measurements were conducted. First, the control perovskite thin-film with 0 mg/mL of PHAI spin-coated on the FTO substrate. The second was a perovskite thin-film with 1 mg/mL of PHAI, third was 2 mg/mL, and finally, the last sample was perovskite thin-film with 3 mg/mL of PHAI.

The optical bandgap for wide-bandgap perovskite has been calculated from the UV-Vis spectra using Tauc's plot techniques [115]

$$\alpha h\nu = A(h\nu - E_g)^n \quad (3.1)$$

Where α is the absorption coefficient, $h\nu$ is the photon energy; A is a constant, E_g is the optical bandgap of the desired material, and n is the exponent coefficient, which denotes the nature of electron transition within the bandgap from the valence to conduction band. This coefficient (n) could take values of $1/2$ in case of direct bandgap material or 2 if the material has an indirect bandgap. Wide-bandgap perovskite has a direct bandgap, so n will take the value of Tauc plot $1/2$, the resulting plot [$(\alpha h\nu)^{1/2}$ vs $h\nu$] has a linear region. By extrapolating this linear region, the intercept represents the bandgap (E_g) of the material.

3.2.2 Current Density-Voltage (J-V) Characterization

All the J-V's measurements were completed under the illumination of a xenon lamp (Newport, Model 67005) as an illumination source with AM 1.5 filter. The xenon lamp, which has powered by the power supply (Newport Model 69911) to provide 300 watts, was turned on 20 minutes prior to the calibration of light intensity measurement takes place. Along with xenon lamp, Agilent 4155C semiconductor parameter analyzer equipped with

current and voltage source meters was used to sweep the voltage from 0 V to 1.2 V with an increment of 10 mV.

The light intensity was calibrated by optimizing the distance between the photodetector and the xenon lamp. The Hamamatsu mono-Si cell photodetector (S1133-14), which was NREL calibrated, was used to optimize the distance. The optimal distance was confirmed when the semiconductor parameter analyzer reads an equivalent I_{sc} of 1.63 mA and V_{oc} of 0.65 V. Current and voltage were simultaneously obtained, and a Microsoft Windows-based PC with Agilent desktop software was used to control and save the semiconductor parameter analyzer readings. From the data points that we saved, the J_{sc} , V_{oc} , FF, and PCE were calculated and measured.

Figure 3.4 Schematic of J-V Measurement Setup, adopted [116]

3.2.3 X-Ray Diffraction (XRD) Spectroscopy

In this study, all XRD characterization for the samples were obtained using a Rigaku SmartLab diffractometer (2.2 kW Cu-K α (1.54 Å) radiation). Wide-bandgap perovskite thin-films were deposited on top of PEDOT: PSS coated on top of FTO substrates. The values of 2θ were collected from 5° to 60° . As shown in Figure 3.5, the XRD spectrometer was equipped with a source of a copper tube that generates an x-ray of wavelength 1.54 Å when a voltage of 40 kV and a current of 44 mA was applied to it as accelerating voltage. While measuring the XRD, samples were held horizontally on stage with x-rays were incident, and samples were stationary. Both source and detector were rotated along the z-axis of the film using the goniometer, which gave the diffracted x-ray intensity for each value of 2θ that measured.

Figure 3.5 Photograph of Rigaku Smartlab X-Ray Diffractometer

3.2.4 External Quantum Efficiency Measurement

Newport IPCE measurement setup was used to perform all the external quantum efficiency (EQE) for all samples in this research. Figure 3.6 shows the EQE measurement system that was used in collecting data. The solar simulator coupled with a monochromator

(Cornerstone™ 260 ¼ m) to be used for a light source. The monochromator has a grating that produces a single wavelength wave with an accuracy of 0.35 nm. The monochromator helps to have wavelength range required for this measurement, which was from 280 nm to 1000 nm with an increment of 5 nm. Focusing lenses were used to focus the light on the reference photodiode. Lock-in amplifier was used to provide voltage output to the Agilent 4155C semiconductor parameter analyzer while the fabricated solar cell devices were under testing.

The EQE of the tested solar cell device can be calculated using the following equation:

$$EQE_{sample} = \frac{V_{sample} \times EQE_{reference}}{V_{reference}} \quad (3-2)$$

Figure 3.6 Photograph of EQE setup

3.2.5 Scanning Electron Microscopy (SEM)

Figure 3.7 shows Hitachi S-3400N SEM that was used to examine the surface morphology and cross-section of the perovskite film samples of varying PHAI concentrations. The imaging process was performed immediately after the crystallization of perovskite films. Working distance of ~ 10 mm and the accelerating voltage of 4kV was used for the imaging procedure.

Figure 3.7 Photograph of Hitachi S-3400N SEM [117]

3.2.6 Electrochemical Impedance Spectroscopy (EIS)

In the measurement of EIS was carried out via Ametek VERSASTAT3-200 Potentiostat with a frequency analysis module (FDA). Then Nyquist plots for different concentrations were found at a zero bias voltage of 10 mV AC signal that has a frequency sweep from 1 Hz to 1 MHz.

3.2.7 Atomic Force Microscopy (AFM)

Atomic force microscopy measurement was obtained using Agilent 5500 probe microscope, as shown in figure 3.8. The topography images during the procedure were taken in tapping mode. AFM uses silicon tips coated with Cr/Pt from Budget Sensors (Multi 75E-G) with the resonant frequency of ~ 75 kHz and applied force constant of 3 N/m. The tip was oscillated at 150 to 200 Hz above its resonance frequency using a lock-in amplifier (MAC III controller) to make sure the interaction force of tip-sample is in the net attractive regime. Samples were examined in ambient air immediately after fabricated inside the glove box. All measurements were investigated and stored on PC uses Picoview 1.14.2 software provided by Agilent Technologies, after that, all images were analyzed using Gwyddion software.

Figure 3.8 Photograph of Agilent 5500 Scanning Probe system.

Chapter 4: Tailoring the Grain Boundaries of Wide-bandgap Perovskite Solar Cells by Molecular Engineering

4.1 Keywords

Additive materials, wide-bandgap perovskite solar cell, surface passivation, trap states suppression

4.2 Introduction

Organic-inorganic halide perovskites [ABX_3 , where A can be cesium Cs, Formamidinium (FA), or Methylammonium (MA); B is lead (Pb) or Tin (Sn); and X is Iodide (I), Bromide (Br) or Chloride (Cl)] have been considered as new promising photovoltaics (PV) due to their exceptional optoelectronic attributes [16], long carrier diffusion lengths [17], strong optical absorption [18], and potential low processing costs. Power conversion efficiency (PCE) for perovskite solar cells (PSCs) has rapidly increased from 3.8% in 2009 to a certified 25.2% in 2019 [20]. This rapid improvement in PCE of single-junction devices is unique in the history of photovoltaic development and thus has attracted tremendous interest [21, 22].

The low-temperature processing and tunable bandgap make metal halide perovskite a strong candidate for constructing tandem solar cells to overcome the Shockley-Queisser efficiency limit in single-junction cells [118, 119]. Wide-bandgap perovskites with bandgap ranging from ~1.7 to 2.3 eV have attracted considerable research attention to enable efficient monolithic tandem devices with mainstream silicon PV or creating an all-perovskite tandem [120] [22, 82, 121]. The established route of creating a wide bandgap metal halide perovskite has been established by partially replacing the iodide halide with bromide, with more bromide content resulting in a wider bandgap. An ideal combination for tandem devices requires the front cell with wide bandgaps of 1.7-1.9 eV in line with a

rear cell with low-bandgaps of 0.9-1.2 eV [121]. These tandem perovskite solar cells have shown excellent promise reaching high PCE of $\sim 21\%$ -28% [20, 122-124], but their PCEs still far below the theoretical limits of 40% [125].

Tandem solar cells can be structured in monolithic (2-T), or mechanically stacked (4-T), where PCE of $\sim 36\%$ is theoretically achievable in monolithically series tandem solar cells by using bandgap arrangement of 1.2 eV for rear cell and 1.82 eV for front cell [126]. In addition to the Shockley-Queisser efficiency limit, the fill factor (FF) for single-junction perovskite theoretically can reach as high as 90% at room temperature [127]. With the existence of the barriers within the Grain Boundaries (GBs) in which they cause less efficient charge extraction, w-PSCs have a low FF and J_{sc} , which indicates further improvement is needed to enhance the PSCs performance. Recently, several investigations and different attempts have been made to improve the FF of the device. W-PSCs suffer from small grain size and photoinduced phase segregation, letting to open-circuit voltage (V_{oc}) deficits [82]. Controlling interfacial microstructures and prepare perovskite precursor solution with excess PbI_2 are different methods for GBs passivation [128-130]. Defects states and trap states in w-PSCs can exist at the GBs and uncoordinated bonding on the surface, which facilitate charge recombination, thus hindering charge transport in perovskite thin-film [131, 132]. Due to the low-temperature fabrication process, most likely defects in perovskite films are inescapable [133]. GBs in perovskite films have shown shorter charge carrier lifetime and different optoelectronic properties in comparison to bulk [134]. Furthermore, Kelvin probe force microscopy studies have confirmed that the GBs have different electric potential compare to grain interior (GIs) [64]. Other theoretical studies have shown that the GBs composition that was stopped by either ammonium ion or

iodide affects the optoelectronic properties of perovskite film [135-137]. Different methods have been successfully demonstrated, such as fullerene passivation [138], Lewis-base passivation, and passivation via small molecules, such as pyridine and thiophene[139]. Many ammonia additives have been used to enhance perovskite crystal growth as these additives are integrated into the perovskite crystal structure and could passivate the GBs and conceivable crosslink grains [130, 140].

In this work, we successfully demonstrate the improvement of FF, V_{oc} , and the PCE of a 1.82 eV $MA_{0.9}Cs_{0.1}Pb(I_{0.6}Br_{0.4})_3$ w-PSC by chemically tailoring perovskite grains that result in passivating the GBs. Using an optimized ratio of phenylhydrazine iodide or PHAI ($C_6H_7N_2I$), this passivation strategy led to the enhancement of morphology and optoelectronic properties of the w-perovskite thin-films. As a result, the champion device exhibited an increase in FF to 0.76 and efficiency to 14.63% compared to FF of 0.73 and efficiency of 12.16% for control and the reported 1.82 eV wide-bandgap has a FF of 0.69 and efficiency of 12.5%; as a result of GBs passivation [124]. Further analysis shows that the use of PHAI reduces the defects and density of trap sites in the GBs, which facilitates the reduction in charge recombination and enhancement in charge transport in the perovskite thin-films.

4.3 Results and Discussion

Figure 4.1a shows the schematic diagram of the w-PSC, and figure 1b shows the graphic of probable chemical interaction with perovskite sheets. The crosslinking agent PHAI was selected because of its richness in amino (NH_2) groups, which known for its capability to incorporate into the perovskite crystals and anchor to the surface via a supramolecular interaction between hydrogen bonds ($\text{C-H}\dots\text{I}$, $\text{N-H}\dots\text{I}$) as shown in fig. 1c [141, 142]. Such bonding, the PHAI molecules, are able to crosslink neighboring perovskite grains [140, 143].

Figure 4.1 (a) Schematic diagram of the device architecture. (b) Chemical structure of PHAI. (c) Schematic diagram showing crosslinking of the PHAI with the perovskite.

Figure 4.2 SEM images of perovskite films with various PHAI concentration, (a) 0 mg/mL. (b) 1 mg/mL. (c) 2 mg/mL. (d) 3 mg/mL.

Figure 4.2 shows scanning electron microscopy (SEM) images for perovskite films with various PHAI concentration of 0-3 mg/mL.

Figure 4.3 (a, b) Top view SEM images of perovskite films treated with 0 and 2 mg/mL PHAI, respectively. (c, d) cross-sectional SEM images of full W-PSCs treated with 0 and 2 mg/mL, respectively

Figure 4.3 shows the pristine perovskite film with a small grain size compares to the one with additive. It can be observed that the PHAI incorporation with 2 mg/ml has led to morphology reinforcement with larger grain size as well as smooth and compact film compared to the pristine film. As shown in figure 4.4, films with none or less amount of PHAI, the grains show a smaller size in comparison to the optimal condition, which in this case 2 mg/mL of PHAI were added to perovskite precursor 2 hours prior to the spin-coating process. It was found that exceeding the optimal content leads to small grain size due to the exitance of more atoms and particles within the grain boundaries.

Figure 4.4 Perovskite films with different content of PHAI, (a, b) 1 mg/mL, (c, d) 2 mg/mL, and (e, f) 3 mg/mL.

Subsequently, extracted data from SEM images for all perovskite films was performed by using ImageJ software to give more statistical details about the grain size and corresponding PCE for each type. Table 4.1 shows the statistical data for grain size and PCE.

Table 4.1. Statistical data of grain size and PCE for different concentrations of PHAI.

PHAI Concentration [mg/mL]	Grain's surface area [μm^2] Max (Ave $\pm$ STDV)	PCE [%] Max (Ave $\pm$ STDV)
0	0.318 (0.0436 $\pm$ 0.0216)	12.16 (10.7 $\pm$ 0.6)
1	0.869 (0.1808 $\pm$ 0.0761)	13.17 (12.8 $\pm$ 0.41)
2	2.88 (1.785 $\pm$ 0.607)	14.63 (14.15 $\pm$ 0.32)
3	0.672 (0.4623 $\pm$ 0.101)	12.9 (11.97 $\pm$ 0.4)

Figure 4.5. Grains' surface area (a) histogram and (b) box chart for different PHAI concentrations.

Figure 4.6 shows the XRD pattern for all perovskite films, where both films reveal similar diffraction peaks at 2θ around 14° and 18° , which are the representation of (110) and (220) planes, respectively. XRD characterization shows narrower peaks, which supports the enhancement of crystallinity and grain size. However, when PHAI content

was increased to 3 mg/mL, spaces between the grains and pinholes were formed. As the 2 mg/mL concentration provided the optimized morphology, further characterizations of topography, conductivity, and current distribution were studied for the 2 mg/mL PHAI-based film versus the pristine.

Figure 4.6. XRD pattern of perovskite films treated with 0, 1, 2, and 3 mg/mL PHAI.

Figure 4.7 (a) J-V characteristics and (b) Forward and reverse scans of w-PSCs fabricated with 0 and 2 mg/mL PHAI. (c) PCE measured at maximum power point for 0 and 2 mg/mL PHAI treated device with time.

Figure 4.7 represents current density-voltage (J-V) curves for the best w-PSCs treated with different PHAI concentrations (0, 1, 2, 3 mg/mL) under 1.5 AM illumination at ambient conditions and the photovoltaic presentation parameters are briefed in table 4.2.

The control device with 0 mg/mL of PHAI has an efficiency of 12.16%, whereas the highest efficiency was recorded to devices doped with 2 mg/mL of PHAI with 14.63%. Figure 4.7 b shows the J-V curves of the champion cells for pristine and treated conditions, where the w-PSC devices treated with 2 mg/mL PHAI show the highest PCE among all other different concentrations. The best devices achieved a photovoltaic performance when J_{sc} increased from 14.16 to 16.12 mA cm^{-2} , V_{oc} increased from 1.16 to 1.2 V, FF improved much when it increased from 68.3% to 75.5%, and PCE increased from 12.16% to reach a highest of 14.63%.

The improvement of J_{sc} in 2 mg/mL PHAI treated device is attributed to the recombination reduction in perovskite film, while the enhancement of FF in treated devices reflects the reduction of series resistance in the device due to the suppression of charge traps in the GBs.

Table 4.2. Photovoltaic parameters for w-PSCs using different concentrations of PHAI.

PHAI concentration [mg/mL]	J_{sc} [mA cm^{-2}]	V_{oc} [V]	FF [%]	PCE [%]
0	16.52 (14.17 $\pm$ 1.38)	1.16 (1.1 $\pm$ 0.04)	73.1 (68.3 $\pm$ 4.8)	12.16 (10.7 $\pm$ 0.6)
1	15.17 (14.86 $\pm$ 0.34)	1.18 (1.1 $\pm$ 0.02)	76.7 (74.5 $\pm$ 1.0)	13.17 (12.8 $\pm$ 0.41)
2	17.11 (16.12 $\pm$ 0.63)	1.2 (1.1 $\pm$ 0.03)	76.8 (75.5 $\pm$ 0.7)	14.63 (14.15 $\pm$ 0.32)
3	15.41 (14.63 $\pm$ 0.47)	1.16 (1.1 $\pm$ 0.02)	78.2 (72.3 $\pm$ 3.0)	12.9 (11.97 $\pm$ 0.4)

Figure 4.7 c reports the stabilized power output (SPO) of w-PSCs for 200 s for both control and 2 mg/ml PHAI treated devices at the maximum power points (MPP). Whereas

the treated device shows higher SPO with a value of 14.15%, the control device shows only 10.6%. ... Figure 4.7 d shows the external quantum efficiency (EQE) spectrum for control and 2 mg/mL PHAI-doped w-PSCs. With perovskite films having the same thickness of about 200-220 nm as evaluated by thin-film profilometry and confirmed via SEM cross-sectional images, the treated cells show higher EQE than the primary cells.

The integrated photocurrent density of control and treated are 14.65 mA cm^{-2} and 15.75 mA cm^{-2} , respectively; both are in good agreement with the J_{sc} 's derived from the J-V measurement. Figure 4.11 shows the statistics of all photovoltaic performance parameters obtained for 12 w-PSCs treated with 0, 1, 2, and 3 mg/mL of PHAI.

Table 4.3. Photovoltaic parameters for w-PSCs with 0 mg/mL and 2 mg/mL of PHAI.

PHAI content [mg/mL]	Scan Directions	J_{sc} [mA cm^{-2}]	V_{oc} [V]	FF [%]	PCE [%]
		Max (Average)	Max (Average)	Max (Average)	Max (Average)
0	FS	16.13 (14.16)	1.16 (1.1)	72.1 (67.5)	11.8 (10.45)
	RS	16.52 (14.17)	1.16 (1.11)	73.1 (68.3)	12.16 (10.71)
2	FS	17.01 (16.03)	1.19 (1.16)	76.7 (74.66)	14.46 (13.87)
	Rs	17.11 (16.12)	1.2 (1.16)	76.8 (75.49)	14.63 (14.15)

An in-depth investigation of the GBs of the perovskite films was carried out using KPFM and c-AFM tools to comprehend the role of PHAI as a passivation agent on reducing the trap states. KPFM was used to study and determine contact potential difference or surface potential (V_{CPD}), while c-AFM was used to calculate local photocurrent of thin-films. These two methods provide nanometer-scale precise measurement of spatial mapping on GIs and GBs to analyze the built-in potential and charge-transport behavior

anywhere within the thin-films. All the measurements of AFM, c-AFM, and KPFM for perovskite films with 0 and 2 mg/mL PHAI were based on the perovskite films deposited on glass/FTO substrates. The surface of the perovskite film has no capping layer or electron transport layer on top, so the surface was scanned directly via the AFM tip. Figure 4.8 shows the AFM images of surface morphology and photocurrent mapping for pristine (fig. 4.8 a, e) and incorporated perovskite film with 2 mg/mL of PHAI content concentration (fig. 4.8 b, f). As can be noticed from the AFM morphology images (Fig. 4.8 a, b), there is an increase in the grain size as a result of doping with PHAI, figure 4.4.

AFM topography images show that in case of 0 mg/mL PHAI content, the grain

Figure 4.8 (a-d) AFM topography images (a & c pristine, b & d 2 mg/mL PHAI). (e, f) c-AFM images for pristine and 2 mg/ml PHAI, respectively. (g, h) KPFM images for pristine and 2 mg/mL PHAI, respectively.

size is less than 500 nm, whereas in samples doped with 2 mg/mL PHAI the grain size is more than 1 μm. Figures 4.8 e, f show the c-AFM mapping for films with 0 mg/mL and 2 mg/mL of PHAI, respectively. Lower current in GBs was observed in the treated perovskite

films compared to untreated films. Further, the treated perovskite film showed higher current in GIs than in GBs. Perovskite films doped with PHAI have a higher current in GIs with an average absolute magnitude of 66.3 pA, and untreated films have an average absolute magnitude of 57.2 pA. This indicates surface and grain boundary passivation facilitated by the PHAI treatment [144]. Whereas ion migration leads to having more current flow within GBs, the GIs will be inefficient for charge transfer results in the poor overall performance of the photovoltaic device [144] [145]. These results show the change in the intensity of current flow as an indication of the significance of GBs passivation on improving w-PSCs performance [146].

. V_{CPD} was measured between the conductive tip of the KPFM and the perovskite film and calculated via the equation below[147-149]:

$$V_{CPD} = \frac{\Phi_{tip} - \Phi_s}{-e} \quad (1)$$

Where V_{CPD} is the measured contact potential difference, Φ_{tip} is the work function of the KPFM cantilever tip. Tip with a conductive coating of platinum/iridium (Pt/Ir) was used throughout the measurement to have constant Φ_{tip} , Φ_s is the work function of the wide-bandgap perovskite thin-film, and e is the elementary charge.

KPFM measurement was performed to investigate V_{CPD} which tells the work function difference between the AFM tip and the perovskite local surface. The variation of work function between GIs and GBs gives the GB potential barrier, which can further provide information on the passivation effects. [150, 151]. Pristine wide-bandgap perovskite film (fig. 4.8 g) shows the absolute value of the potential difference between GIs and GBs about 78 mV with a total absolute average value of 198 mV for the whole

sample. While the 2 mg/ml PHAI treated perovskite film (fig. 4.8 h) has an absolute value of 43 mV and a total absolute average of only 3.9 mV [Fig. S10]. This reduction in the grain boundary potential barrier further suggests the passivation effect induced by the PHAI treatment.

Mott-Schottky (MS) characterization was used to determine the flat band potential (V_{fb}), which is another technique to verify the change in the Fermi level position and the change in the work function of the material [147, 152, 153]. Figure 4.9a shows the MS plots for w-PSCs for pristine and 2 mg/ml PHAI treated film. The capacitance-voltage (C-V) measurement shows a higher built-in potential (V_{bi}) of 770 mV for the treated film compared to the pristine film with 736 mV. Heterojunction solar cell devices with higher V_{bi} have greater electric field in the depletion region, which is advantageous for boosting charge transfer [113]. This strong electric field thrusts mobile charge carriers to reach the corresponding electrodes, but if the electrical field is weak due to the small value of V_{bi} , charge extraction becomes less likely [154]. This suggests improved charge transfer in the PHAI treated device, which results in suppressed hysteresis and enhancement of device performance with an increase in V_{oc} and FF [155].

Figure 4.9 (a) Mott-Schottky plots. (b) EIS and equivalent circuit for the Nyquist plots. (c) Transient photocurrent decay. (d) transient photovoltage decay. All for w-PSCs treated with 0 and 2 mg/mL PHAI.

Electrochemical impedance spectroscopy (EIS) was performed to examine the behavior of charge transfer activity in the devices. The high-frequency of the EIS plot, the component indicates the charge transfer resistance (R_{tr}), while at low-frequency the component represents the charge recombination resistance (R_{rec}) [113]. It is well known that the bigger value of R_{rec} indicates less charge recombination in the device [113, 156,

157]. Figure 4.9 b shows the Nyquist plots of the pristine and treated devices under dark conditions, and the equivalent circuit used for data fitting. The treated device showed charge recombination resistance (R_{rec}) value of 22.1 k Ω versus the pristine device with 11.7 k Ω . This higher R_{rec} indicates lower charge recombination and efficient charge collection taking place in the treated device compared to the pristine device.

Steady-state photoluminescence (PL) measurements were performed to study the charge transfer and extraction characteristics of pristine and passivated perovskite films. In the recombination procedure, the photoinduced charge carriers have a radiative recombination rate that competes with the nonradiative loss [158].

Figure 4.10 Steady-state photoluminescence (PL) of perovskite film with different concentrations of 0 and 2 mg/mL of PHAI

As shown in Figure 4.10, compared with pristine perovskite thin-films, PHAI passivated films show enhanced PL intensity, which demonstrates that the nonradiative recombination of photo-generated carriers in passivated perovskite thin-films has been

suppressed [58, 134]. Figure 4.9 c shows transient photocurrent (TPC) measurements of w-PSCs treated with 0 and 2 mg/mL PHAI. TPC measurement was implemented to identify and evaluate the charge transport time (τ_{tr}) within and between the interfaces of the device. During the measurement, the full devices were kept under short circuit current condition and excited by a nanosecond laser pulse, where low input impedance of around 50 Ω was used with no background light. All the values of the τ_{tr} were calculated and fitted from TPC curves using the mono-exponential function:

$$y = A \exp(-x/\tau) \quad (2)$$

τ_{tr} values were calculated from the mono-exponential fitted results. It was found that the τ_{tr} value decreased from 0.61 μ s for w-PSCs with pristine perovskite films to 0.54 μ s for that treated with 2 mg/mL PHAI. This indicates efficient charge transport and extraction process enabled by the PHAI passivation. Figure 4.9 d shows transient photovoltage (TPV) measurements of w-PSC devices

treated with 0 and 2 mg/mL PHAI. TPV measurement was carried out to calculate the charge carrier lifetime or recombination lifetime (τ_{rec}). An open-circuit condition with continuous illumination was applied where a large input impedance of 1 M Ω was used during the measurement. The results from TPV measurements were plotted and τ_{rec} values were computed from the fitting of TPV exponential decay curves with a mono-exponential function (equation 2). It was estimated that the w-PSC devices passivated with 2 mg/mL of PHAI have longer τ_{rec} of 0.81 μ s compared to pristine devices with only 0.63 μ s. The higher charge carrier lifetime values further support the reduction in recombination facilitated by PHAI passivation.

Figure 4.11 Stability of w-PSC devices fabricated with perovskite film treated with 0 and 2 mg/mL PHAI, (a) J_{sc} , (b) V_{oc} , (c) FF, and (d) PCE.

Figure 4.11 shows the stability for w-PSC fabricated devices with perovskite film treated with 0 & 2 mg/mL of PHAI. All devices were kept in an N₂-filled glovebox under dark. For w-PSC devices with pristine perovskite films, the PCE decreased from 12.16% to 8.15% after 15 days showing $\approx$ a 33% loss in device performance (figure 6d). On the other hand, the devices with perovskite thin-film that was treated with 2 mg/mL PHAI, the PCE showed much-reduced degradation from 14.63% to 13.64 after 15 days, thus exhibiting better stability than the pristine w-PSCs. FF and J_{sc} both followed the same trend

Figure 4.12 Statistics of all photovoltaic performance parameters (a) J_{sc} (b) V_{oc} (c) FF and (d) PCE obtained for 12 W-PSC devices treated with 0, 1, 2, and 3 mg/mL of PHAI.

of PCE for each condition, while the V_{oc} values showed much less change in both conditions.

4.4 Conclusions

In conclusion, an effective passivation method was established for engineering inverted planar w-PSCs by perovskite precursor doping with PHAI. This method led to a reduction in trap densities in perovskite thin-films, low nonradiative recombination of photo-generated carriers, enhanced charge transfer, and better charge extraction through the interfaces which improved FF and V_{oc} . The crosslinking $[MA_{0.9}Cs_{0.1}Pb(I_{0.6}Br_{0.4})_3]$ crystals by passivation with the amino groups of PHAI enables the growth of perovskite crystals with larger grain size and passivated grain boundaries. As a result, PHAI-passivated w-PSC devices showed improved photovoltaic performance with an average efficiency of $14.15 \pm 0.32\%$ compared to pristine devices with $10.7 \pm 0.6\%$. The strategy demonstrated in this work can be adapted to other perovskites and help realize high-efficiency perovskite solar cells.

4.5 Experimental Section

Materials: The transparent FTO substrates were obtained from Hartford Glass Co, the USA, with a custom size of $1.5 \text{ cm} \times 1.5 \text{ cm}$. An aqueous solution of Clevios P VP AI 4083 PEDOT: PSS was obtained from Heraeus Precious Metals. Methylammonium iodide (CH_3NCH_3I) was ordered from Greatcell Solar. PbI_2 (99.99%, trace metals basis, for perovskite precursor) and $PbBr_2$ (>98%, for perovskite precursor) were purchased from TCI America. Anhydrous-DMSO (>99.7%) extra dry was purchased from Acros Organics. $PC_{60}BM$ (99.5%) polymer was obtained from Nano-C, Inc. γ -butyrolactone (>99%), and

Rhodamine both were obtained from Sigma Aldrich. All the materials were used as received.

Device Fabrication: The FTO coated glass substrates were cleaned in an ultrasonic bath while bathed in solutions of detergent, de-ionized water, acetone, and 2-propanol. Each bath lasted approximately 20 minutes. The FTO substrates were then exposed to UV-ozone for approximately 20 minutes. After cleaning and UV exposure procedures were finished, PEDOT: PSS aqueous solution was spin-coated on top of FTO substrates at 5000 rpm for 40 seconds. Then, substrates were thermally annealed at 140 °C for 10 min in ambient air. After FTO substrates were cooled down to room temperature, all FTO substrates were transferred into an N₂-filled glove box to finish the fabrication process. For the spin-coating perovskite layer, the perovskite solution contained 143 mg of MAI, 184 mg of PbI₂, 220 mg of PbBr₂, and 26 mg of CsI; all were dissolved in 1 mL of a mixed solvent of γ -butyrolactone: DMSO at a volume ratio of 7:3. The prepared solution was stirred at 70 °C overnight. In addition, to control a wide-bandgap perovskite solution, the perovskite precursor was doped with PHAI to make three different concentrations, 1, 2, and 3 mg/mL. PHAI was added 1-2 hours prior to the spin-coating process. The perovskite layer was fabricated on the top of PEDOT: PSS via spin-coating with a two-step process, first at 2000 rpm with the ramping rate of 1000 rpm s⁻¹ for 15 s and second at 5000 rpm with the ramping rate of 2000 rpm s⁻¹ for 45 s. During the second step, 500 μ L of extra dry toluene was poured on the center of the spinning substrates 20 s prior to the end of the whole spinning program. The samples were thermally annealed on a hotplate at 100 °C for 10 min in an inert atmosphere (N₂). The change in perovskite color from yellowish to light brown confirms the film transformation from precursor to perovskite. The solution of 20 mg/mL

of PC₆₀BM in chlorobenzene was stirred overnight and then used as an ETL. PC₆₀BM was spin-coated on top of perovskite film at 2500 rpm with the ramping rate of 2000 rpm s⁻¹ for 40 s, then immediately annealed on a hotplate at 60 °C for 15 min. A rhodamine dye solution of 0.5 mg mL⁻¹ in dry IPA was then spin-coated at 4000 rpm with a ramping rate of 3000 rpm s⁻¹ for 20 s on top of the PC₆₀BM layer. Evaporator with a high vacuum of approximately 2×10^{-6} mbar was used to deposit the electrode. Silver was thermally evaporated as a top electrode with an active area of 0.13 cm² on top of the rhodamine layer. All steps were performed in an N₂-filled glovebox, and some solvents vapor in the glovebox kept minimized during the spin-coating process to avoid any film damage. All single-junction w-PSC devices were constructed in the inverted (p-i-n) architecture.

Characterization Method: Current density-voltage (J-V) curves of w-PSC devices were measured by adopting a semiconductor parameter analyzer (Agilent 4155C) equipped with current and voltage source meters under light source using xenon lamp (Newport Model 67005) equipped with an AM1.5G filter calibrated to 100 mW/cm² light intensity. National Renewable Energy Laboratory (NREL)-calibrated standard silicon solar cell (S1133-14-01) was used to calibrate the light intensity. All the J-V measurements were measured at a scan rate of 1400 mVs⁻¹ with step voltage of 10 mV from 0 to 1.2 V and then back to 0 V. EQE spectra were obtained with QE system (Newport Model 67005) with PC-controlled monochromator (Oriel Monochromator 74001) and focusing lenses on producing monochromatic beams with a wavelength between 300 nm and 800 nm, in increments of 5 nm.

SEM images were taken with a Hitachi-S4700 high-resolution field-emission scanning electron microscope (FESEM) at an applied bias of 3 kV. Absorbance spectra of

wide-bandgap perovskite films were measured by utilizing an ultraviolet-visible (UV-Vis) spectrophotometer (Agilent 8453 - G1103A). X-Ray Diffraction (XRD) spectra of perovskite films were recorded using the Rigaku Smartlab X-ray diffractometer to study the crystallization and phase identification of the films. Transient photovoltage and photocurrent measurements were performed using OBB's Model OL-4300 nitrogen laser pulse at 337 nm to pump model 1011 dye laser to generate a short pulse, which acts as an excitation source with a pulse duration <1 ns with repetition rate about 4 Hz. Results from c-AFM mapping in contact mode and KPFM in tapping mode were recorded using Agilent 5500 scanning probe microscopy (SPM) with a MAC III controller. Tip with platinum/iridium conductive coating was used for KPFM tapping measurement, and tip with chromium/platinum conductive coating was used in c-AFM contact mode measurement.

Electronic impedance spectroscopy (EIS) and Mott-Schottky (MS) measurements; the results were obtained from Ametek VERSASTATE3-200 Potentiostat. In EIS measurements, the AC signal with an amplitude of 20 mv and frequency from 0.1-1 MHz was applied to w-PSC devices. For MS measurements, the capacitance of the space charge region (C_{sc}) versus applied bias was studied by applying a 20 mV as AC voltage to w-PSCs, and the AC signal was fixed at 20 kHz.

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Chapter 5: Summary and Conclusions

5.1 Summary

The increasing demand and the cost of energy are very challenging problems nowadays to human civilization. As the oil embargo occurred in 1973/74, the interest in renewable energy and alternative energy source has tremendously increased. The environmental damage and impact due to CO₂ emissions and global warming are great reasons to stop burn more fossil fuels for energy and focus on finding new alternative ways to produce energy. Primary pollution-free renewable energy is solar energy, which can provide a sustainable and inexhaustible source of energy to all human communities around the world. Photovoltaic devices can harvest and transform the solar energy that reaches the earth's surface to electrical energy. The first-generation of photovoltaic devices was fabricated from Si wafers and still commonly used due to the high power conversion factor. However, solar cells fabricated from Si have some bulk production problems such as high cost, high purity wafers, and delicate. Diversely, the third-generation of solar cells, as discussed in the early chapter, shows new promising technologies and improvements over the Si-based solar cells with limited availability on the market. PSCs' efficiency has increased from 3.8% in 2009 to reach 25.2% in 2019. With all these improvements that have been done on PSCs to enhance the performance, there is still the ability to improve the overall energy conversion efficiency. More research has been done to improve the structural and optoelectronic properties of PSCs in many ways. Wide-bandgap perovskite solar cells have been used in junction with low-bandgap solar cells in tandem application to reach high overall PCE. Wide-bandgap perovskite solar cells demonstrate defects as trap states within grain boundaries and in bulk, which will result in high V_{oc} loss.

In this work, investigation and research have been done to apply a new engineered method and materials to reduce the charge trap states within grain boundaries to further improve the w-PSCs performance. This molecular engineered method used to tailor the grain boundaries aiming to improve the charge extraction, therefore, improve the device performance. The first objective of this study was to improve the efficiency of wide-bandgap perovskite solar cells by more than 2% as a result of using PHAI as an additive. The second objective was to enhance the overall photovoltaic characteristics as the fill factor increased by using different concentrations of PHAI for grain boundaries passivation.

5.2 Conclusions

Grain boundaries passivation process in w-PSCs with a bandgap of 1.28 eV with different concentrations of PHAI was studying, and optimal condition was tested. Defects and trap states within the GBs and GIs caused by low formation energy as the formation process involves low temperature can be reduced via different GBs passivation practices. Here, PHAI was used for passivating and reducing the number of these defects and charge carrier traps to achieve higher efficiency w-PSCs. Using PHAI as an additive to perovskite precursor benefits the overall photoconversion efficiency as the FF and J_{sc} showed quantifiable increases in the treated devices. The increase in the FF as the concentration of the PHAI resulted from the reduction in the trap states and defects in the GBs of the film. Also, J_{sc} was dramatically increased in treated devices as a result of increasing charge recombination resistance, which indicates lower charge recombination and efficient charge collection. The overall PCE (%) was substantially increased, from 12.16% for 0 mg/mL

PHAI to 14.63% for 2 mg/mL PHAI. Nevertheless, as the PHAI concentration increases beyond 2 mg/mL, the PCE (%) value dropped due to the excess amount of PHAI.

5.3 Future Work

This research shows the improvement in w-PSC devices' performance as a result of GBs passivation with different concentrations of PHAI. However, there is still some additional characterization that could be completed, such as extended time stability of the devices and degradation of the additive as it exposes to heat (sunlight).

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