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GRAIN BOUNDARY DEFECT PASSIVATION OF MIXED CATION PEROVSKITE
SOLAR CELL TO IMPROVE DEVICE PERFORMANCE

BY
SHEIKH IFATUR RAHMAN

A thesis submitted in partial fulfillment of the requirements for the
Master of Science
Major in Electrical Engineering
South Dakota State University
2020
This thesis is approved as a creditable and independent investigation by a candidate for the master’s degree and is acceptable for meeting the thesis requirements for this degree. Acceptance of this does not imply that the conclusions reached by the candidate are necessarily the conclusions of the major department.

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ABSTRACT

GRAIN BOUNDARY DEFECT PASSIVATION OF MIXED CATION PEROVSKITE SOLAR CELL TO IMPROVE DEVICE PERFORMANCE

SHEIKH IFATUR RAHMAN

2020

Rigorous research on perovskite solar cell for more than ten years all over the world has led the rapid development of perovskite technology giving us device efficiency of 25.2%, surpassing the performance of traditional thin-film solar technologies on small scale devices (<1cm²). Perovskite material has excellent electronic and optical properties making it greatly suitable for PV application. The device fabrication process being simple with low cost and solution processability has led the researchers to visualize high efficiency scalable devices. Due to solution process fabrication method the defects in the materials causes the devices perform less than anticipated. These defects at the absorber material can come through as grain boundaries, surface defects, interfacial mismatch thus reducing photocurrent, open circuit voltage, fill factor and device stability. However, efforts and concentration has been highly directed on diminishing these detrimental defects from the perovskite crystals. Passivation engineering like interface interlayers, 2D perovskites, 2D/3D hybrid perovskites, secondary layers, grain engineering have been reported as a retaliation to minimize defects. Motivated by the outcomes of these works, a simple secondary growth of passivation layer on top of perovskite surface at the hole transport layer interface is studied here in this work showing enhanced device performance resulted from the treatment. Optical, surface morphological and different electronic study on both
perovskite films and perovskite devices have been extensively studied and presented in this work to reveal the properties of the grain boundaries in triple cation mixed perovskite materials for simple planar n-i-p devices. With the secondary treatment of post perovskite deposition, the device performance enhanced to 20.6% efficiency from the control device efficiency of 17.4%, short circuit current density increased from 21.71 mA/cm$^2$ to 24.49 mA/cm$^2$, open circuit voltage improved to 1.13V from 1.11V and fill factor rallied to 0.75 from 0.72. Overall, this study provides elaborate in depth understanding on the grain boundaries, their detrimental effects, and successful passivating route to improve device performance.
Chapter 1 Introduction

1.1 Background

The global energy sector is beholding a gradual transition from conventional power generation medium toward cleaner energy solutions. With ever dynamic geopolitical circumstances renewable energy is creating a bright opportunity for the global opportunity to create a self-dependent energy economy. In recent past years, the growth rate of renewable energy markets has accelerated beyond the conventional fuel market due to rise in the discovery of renewable energy and development of this market. The renewable energy targets set by most countries globally are ambitious and the way they have been working relentlessly to achieve it is breathtaking. The renewable share was 8.6% in the global energy mix in 2010 and now it anticipated to increase substantially to 22.5% in 2020 as per the thematic research report by GlobalData.\(^1\)

![Renewable energy market globally in 2010, 2017 and 2020.\(^1\)](image)

In the early quarter of 2020, the global use of renewable energy was higher than the use in the first quarter of 2019 by 1.5% and the most contributing factor to this rise is the
generation of 3% more renewable electricity generation. This increase was facilitated by 100GW extra Solar PV electricity generation and 60GW of wind power projects completion.\textsuperscript{2} Figure 1.1.b shows the graph of annual growth of different renewable energy generation from 2018 to 2020.

![Figure 1.1.b Global Annual Renewable Electricity Generation.\textsuperscript{2}](image)

Figure 1.1.b Global Annual Renewable Electricity Generation.\textsuperscript{2}

Figure 1.1.c shows the renewables generation by source in terawatt-hours.

![Figure 1.1.c Renewable electricity generation in 2019.\textsuperscript{3}](image)

Figure 1.1.c Renewable electricity generation in 2019.\textsuperscript{3}
The world’s primary renewable energy sources are solar, hydro, wind, biomass, and agricultural waste. And among all these great opportunities of sources solar energy from PV is the fastest growing and more cost-effective technology. Figure 1.1.d and 1.1.e shows the efficiency chart of research solar cell devices and PV module efficiencies respectively tracked by NREL for over 30 years illustrating the rise of PV devices in terms of efficiencies and the latest technologies in PV research. Among all the PV technologies in market and research, Si solar cells have been mostly studied and widely marketed. Since the birth of solar cells in 1954, multiple technologies have been developed over the years creating potential device efficiencies with opportunities to commercialization but only Si inorganic solar cell has survived the most. After Silicon solar cells, there has been Cadmium Telluride (CdTe) solar cells, Copper Indium Gallium Selenide (CIGS) solar cells which are considered as second-generation solar cells. The third and emerging PVs are polymer solar cells, dye sensitized solar cells (DSSCs), organic and inorganic hybrid perovskite solar cells (PSCs) which are still under high research development.
Among all the generations of solar cells, the most researched technology in last decade is Perovskite solar cells. Since its first display as a PV device in 2009 by Kojima et al\textsuperscript{6} this device has been in the center of the research of solar cell devices and due to the effort of numerous labs and research groups all over the world the device efficiency of PSCs has risen from 2.5% to 25.2% in just 10 years. A decade of rigorous research on perovskite solar cells (PSCs) through film growth control, interface engineering, transport layer engineering and perovskite compositional engineering has led to certified efficiency of 25.2% which outperforms the widely deployed multi-crystalline silicon and CIGS, CdTe thin film technologies.\textsuperscript{6, 7, 8, 9, 10, 11, 12, 13}

1.2 Perovskite Solar Cells

Organic-inorganic halide perovskite material based solar cells have attracted the most research interest due to their ability to provide high-power conversion efficiency and low-cost device manufacturing process.\textsuperscript{14,15,16,17,18} Perovskite structure has typically an
ABX$_3$ structure where A is organic (MA, FA) or inorganic (Cs) cation, B is divalent cation (Pb, Sn) and X is a halide (Cl, Br, I). The reason behind the enhancement in power conversion efficiency (PCE) for perovskite solar cells can be attributed to superior traits of the perovskite materials because of their absorption coefficient, long charge carrier diffusion length, high mobility, defect tolerance and low exciton binding energy. Perovskite films are produced through low temperature processes which makes them polycrystalline in nature and adamantly have grain boundaries (GBs). Because of these GBs, polycrystalline films usually possess defect density several orders of magnitude higher than their single-crystalline materials. GBs comprise of structural defects such as dangling bonds and vacancies which form electronic traps and these trap sites in the GBs of the perovskite films are responsible for deteriorating the lifetime, mobility and diffusion length of the charge carriers which eventually decreases the PCE and stability of the PSCs. Both surface and GB defects in perovskite solar cell can cause non radiative energy loss, ultimately lowering the open circuit voltage ($V_{OC}$) much below its Shockley-Queisser limit. These defects in perovskite materials occur during the deposition process of the absorber layer as they contain organic content in their structure which are susceptible to heat and they evaporates out with the annealing process during the post processing thus creating multiple defects in the crystals. Previous multiple studies have reported different types of ammonium cations to constrain the charge carrier recombination losses occurring at the interfaces or in bulk of the film during the fabrication process. Formamidinium lead bromide has been employed as electron blocking layer as a passivating layer through which a significant improvement in open circuit voltage was
obtained. Similarly, there has been report of methylammonium iodide being thermally evaporated at the perovskite/hole transport layer interface enhancing the PCE from 14.5% to 17.2% and recently, it has been narrated that quaternary ammonium halides could significantly decrease the ionic defects at the perovskite surface which has significantly improve PCE and stability. Furthermore, conductive aromatic ligands processed from benzylamine and benzoic acids have also been used as passivating agent to neutralize the detrimental effect of methylammonium lead bromide QDs perovskites to achieve higher stability. In addition, phenylalkylamine molecules, polymers, ethylammonium, guanidinium, imidazolium have been arrayed to passivate the defects in perovskites which led to improve device performance. Here in this work, we investigate a novel lab synthesized organic ammonium halide salt, Phenyl Hydrazinium Iodide (PHI), for post-treatment of the mixed cation perovskite film \(((\text{FA}_{0.83}\text{MA}_{0.17})_{0.95}\text{Cs}_{0.05}\text{Pb(I}_{0.83}\text{Br}_{0.17})_3)\) to suppress the surface and grain boundary defects. Particularly, the PHI post-treatment was observed to reduce the current at the grain boundaries, reduce the trap state density, and facilitate an electron barrier indicating suppression of leakage pathways and charge recombination, thus passivating the grain boundaries. The optimized condition of the treatment allowed us to achieve higher short-circuit current density (JSC), higher VOC and fill factor (FF) and lower hysteresis for the perovsktie solar cells which resulted in device PCE enhancement from ~17% to 20.6%.
1.3 Motivation

To provide a low cost, solution processed, low temperature methodology to fabricate high efficiency PSCs in faster possible time implementing interface passivation engineering.

1.4 Objectives

The goal of the research thesis was to investigate the grain boundary defects of Triple Cation or Mixed Cation perovskite material and to research means to improve the device performance through engineering the grain boundary defects creating better interface ultimately resulting better device performances.

To achieve the objective the following assignments were performed:

1. Fabricate and set up a protocol to prepare control device with triple cation perovskite material with lower temperature and less time.
2. Investigate the grain boundary defects of the fabricated control perovskite films using Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM).
3. Fabricate devices treated with Phenylhydrazine Iodide (PHI) layer using different concentrations and optimize the treatment layer.
4. Characterize the treated films investigating the nature of defect passivation using SEM, AFM, Photoluminescence (PL), Transient Measurements.
5. Characterize the devices to determine the device parameters through PCE test, External Quantum Efficiency (EQE) measurements.
6. Fabricate enough devices to ensure the repeatability of the treatment and the stability of the devices under different conditions.
Chapter 2. Device Physics of Solar Cells

2.1 Introduction

Solar cells are energy conversion electronic device which converts sunlight energy in a single step to generate electrical energy. Photons, packets of energy, when incident on solar cells can excite electrons, bound into solids to higher energy levels where they can move freely which are later fed to an external circuit. The extra energy of this excited electrons can create a potential difference which thrusts the electrons through a load in the external circuit. Generally, when light or photons are absorbed by matter, electrons from lower energy states are excited to higher energy states within the materials, but excited electrons then quickly relax back to their ground state. Solar Cells are designed in such a way that they can extract these excited electrons away before they relax back to ground state and are fed to the circuit connected to it.

![Figure 2.1: Cross section of a solar cell](image)

The operation of a solar cell involves four basic steps:

- Generation of light-generated carriers
- Collection of light-generated carriers to generate a current
- Generation of large voltage across the solar cell
- Dissipation of power in the load and in parasitic resistances

The energy conversion process for photovoltaics encompasses the following basic processes:\textsuperscript{49}:

- Absorption of incident photons (sunlight)
- Generation of free electron-hole pairs in the absorption layer
- Transport of the photo-generated carriers in the absorption layer
- Collection of the photo-generated carriers in the collection site

The following sections of this chapter will have detailed discussion on these physical phenomena backed by semiconductor device physics theory.

### 2.2 Absorption Process

The absorption of the incident photons from the sunlight takes place in the main absorber layer of the solar cell. The absorption process is dependent of the quantum energy of the incident photons and the band energy of the absorber material. Photon with sufficient energy can promote electrons from lower energy level to higher energy level. Since the energy levels in a material is quantized and has distinct energy condition, the photon must possess enough energy to get absorbed otherwise, the photon passes through the material. Electronic bands are formed from periodic potential which is created from the interaction of the electrons with the ions and other electrons. Each electron has their individual wave function and when multiple electrons are brought close to each other, their wave function interact with each other and individual wave functions of the electrons overlap and by the principle of exclusion, they cannot stay in the same quantum state and results the split of
original equivalent energy level in to different energy levels. The energies of these levels are dependent on the interatomic distance. When these electrons are brought together from large number of atoms, a continuous bands of energy levels are formed which is known as energy band. Although allowed states of energy and wave number are still quantized but since there are a large number of atoms are placed together, they are considered to be continuous or in continuum. Each energy band is separated from the other band by a gap which is known as band gap and highest band that is filled is known as valence band and the next available band in the energy structure is known as conduction band. For an electron to jump from valence state to conduction state the incident photon must have energy equal or more than the band gap of the material. In semiconductors, when very large number of atoms are brought together in a solid, atomic orbitals split into very large number of levels, which being so close to each other can be considered as continuous energy states or allowed states of band. The energy distribution of the bands is dependent on the electronic properties and the strength of the bonding between each atom. The energy band diagram of any materials can be accurately modelled using Schrodinger’s equation.

\[ -\frac{\hbar^2}{2m} \nabla^2 \psi + (U - E)\psi = 0, \psi(k, r) = u_{jk}(r)e^{ikr}. \]  \hspace{1cm} (2.2.1)

With periodicity in crystal lattice, the electric potential energy \((U(r))\) becomes periodic and thus makes the function \(u_{jk}(r)\) periodic. For each atomic orbital \(j\), a continuous set of solutions with different \(k\) values create the wavefunction in the \(j^{th}\) crystal band. The \(u_{jk}(r)\) (amplitude) and \(E(k)\) (eigen energy) are derived from Schrodinger equation for each of \(j\) and each of \(k\). The map of \(E\) (energy) versus \(k\) (wavevector) is called the band structure of crystal.\(^{50}\)
The movement of electron from valence band to conduction band takes place inside materials in two different methods:

I. Band to band transition

II. Transition by mid-gap trap states

Figure 2.2.1: Absorption process in band-to-band transition

Figure 2.2.2 Energy-band structures of (a) GaAs and (b) Si. 

\(^{50-52}\)
Figure 2.2.3 Band Structure of MAPbI$_3$ perovskites at (a) points $1^c_{111}$, (b) $1^c_{110}$, (a=b=c=6.32 Å)

Figure 2.2.1 demonstrates the phenomenon of absorption happening from band to band directly and it only occurs only when the incident photon has equal or higher energy than that of the band gap creating electron-hole pairs. With sufficient high energy from photon, electrons can be transitioned to even higher state than the conduction band energy level, which again comes back to conduction band through relaxation process dissipating excess energy. Band to band transition can be again described in two different ways where the band energy minimum of conduction and maximum of valence band occurs at two different position of $k$ vectors. Figure 2.2.2 depicts two types of band structure, direct band, and indirect band structures. GaAs (Figure 2.2.2.a) band structure where the maximum of valence band and minimum of conduction band are aligned at the same vector $k$ position which makes the transition of electron from valence band to conduction band without forgoing any change in the momentum of the electrons and holes. From the energy
conversion rule, the photon energy thrusts the transition along with the kinetic energy of the resulting electrons and photons. So,

\[ E_{ph} = E_g + \frac{p^2}{2} \left( \frac{1}{m_n^*} + \frac{1}{m_p^*} \right) \quad (2.2.2) \]

Where \( p = \frac{\hbar}{\lambda} \), \( \lambda \) is the wavelength of the incident photon) is the momentum, \( m_n^* \) is the effective mass of electron and \( m_p^* \) is the effective mass of holes.

In Figure 2.2.2 (b), band structure of Si is shown which has indirect band structure as the minimum of conduction band and maximum of valence band are not aligned in the \( k \) vector space. In this condition, momentum of photons is much smaller compared to that of the electrons requiring assistance or another third particle to balance the momentum difference. Usually this extra momentum is supplied by phonons, lattice vibrations of the correct momentum. The phonon gives up its momentum to the electron at the moment of photon absorption so that both energy and momentum are conserved in the process. By this compensation of momentum from phonon enables the transition creating hole and electron. This electron excitation can be stimulated simultaneously with the absorption of emission of a phonon to maintain the conservation of energy. In case of phonon emission (when \( E_{ph} > E_g \)),

\[ E_{ph} - E_{phn} = E_g + \frac{p^2}{2} \left( \frac{1}{m_n^*} + \frac{1}{m_p^*} \right) \quad (2.2.3) \]

where, \( E_{phn} \) is the energy from phonon.

In case of phonon absorption (when \( E_{ph} < E_g \)),

\[ E_{ph} + E_{phn} = E_g + \frac{p^2}{2} \left( \frac{1}{m_n^*} + \frac{1}{m_p^*} \right) \quad (2.2.4) \]
Figure 2.2.4: Absorption through mid-gap states

Figure 2.2.4 portrays the transition of electrons from valence band to conduction band with the assist of trap states in the band gap. When the photon energy is less compared to that of the band gap electrons transits through the tail states or mid states or both. Sometimes when the photon energy is way low to initiate band to band or trap assisted movement, the photon transmits through the materials contributing to the loss mechanism of a photovoltaic device. Figure 2.2.3 demonstrates a typical band structure of MAPbI$_3$ perovskites.

Absorption coefficient is a key factor for solar cells as this parameter determines how deep into a material light of particular wavelength can travel before it is absorbed. For a material with low absorption coefficient and low thickness, light is inadequately absorbed and can appear transparent for particular wavelength of light. Figure 2.2.5 shows that for different photon energy each material does not have constant absorption coefficient. The probability of a photon being absorbed is dependent on the phenomenon of a photon and an electron interaction in such a manner so that electron can transfer from one band to another. With increasing photon energy, the probability of electron having energy close to the band gap have higher chances of interaction and thus large number of electrons can interact resulting to photon absorption. In a direct band gap semiconductor, absorption coefficient ($\alpha$) is
directly proportional to the probability of transition of electron from valence band to the conduction band, density of available electrons at valence band and the density of the available empty states at conduction band.

\[ \alpha(E) = \alpha_o \left( E - E_g \right)^2 \quad (2.2.5) \]

Where, \( \alpha_o \) is a frequency-independent constant of a material, \( E_g \) is the band gap and \( E \) is the photon energy.

Figure 2.2.5: Effective absorption coefficient of MAPbI\(_3\) perovskite thin film compared to other photovoltaic materials at room temperature.\(^5^3\)

During Indirect band transition, the absorption coefficient varies depending on the phonon absorption or emission along with photon energy. For phonon absorption,

\[ \alpha = K_{i,a} \frac{(E_g - E - E_{phon})^2}{e^{E_{phon}/k_B T} - 1} \quad (2.2.6) \]

And for phonon emission,

\[ \alpha = K_{i,e} \frac{(E_g - E - E_{phon})^2}{1 - e^{-E_{phon}/k_B T}} \quad (2.2.7) \]
Where, constant $K_i$ represents the probability of phonon absorption or emission in indirect band materials, $k_B$ represents Boltzmann’s constant and $T$ represents temperature in Kelvin. The net absorption coefficient is the sum of the contributions from each type of phenomenon.

For absorption coefficient of transition using the tail states or mid-gap states is generally very low due to their low density of sates, although it provides information on distribution of sub-gap states. The equation for such absorption coefficient,

$$\alpha = \alpha_o e^{\frac{h\nu}{E_U}}$$  \hspace{1cm} (2.2.8)

where, $E_U$ is called the Urbach energy, a function of tail and mid states distribution.\textsuperscript{54}

### 2.3 Generation of electron-hole pairs

Generation is an electronic excitation episode which creates the rise in the number of free carriers available to carry charge in materials. Free charge carriers can be both electron and hole. The creation of electron-hole pairs through the absorption of solar energy is an important step to the operation of solar cells. Absorption of photon promotes an electron from valence to conduction band creating an electron-hole pair as electron travels from valence band to the conduction band through localized state in the band gap or directly. The leaving of an electron creates an empty position which the electron was occupying in the valence band creating a hole in the process. The pair of electron and hole generated in the same absorption process are bound together by an attractive coulomb force gains stability to an energy level slightly below than that of unbound electron hole pairs to satisfy the minimization of energy in nature.
Photons may also be absorbed in other processes to increase the kinetic energy of the mobile carriers or to generate phonons or to transfer electrons to localized states inside band gaps or even they may get scattered. Usually near to band gap, band to band and localized states to band are ascendant in this transition process. Increase in kinetic energy of free charge carriers occur only when there are high carrier densities while phonon generation and transition to localized states are important only when the photon energies are very less than the band gap usually <100 meV. Scattering process is undesirable as this process eliminates light from the incident beam at interfaces and by inhomogeneities in non-uniform media without generating carriers. Nonetheless this process can be exploited to trap light and amplify photon field in solar cell structures.

\[ I = (1 - R)I_S e^{-\alpha x} \]

Figure 2.3.1 Weakening of light intensity in a block of absorption \( \alpha \) and thickness \( x \). A fraction of light (1-R) is reflected in the process of the light \( I_s \).

The macroscopic absorption coefficient (\( \alpha \)) defines the depth of photon’s ability to pass. \( \alpha(E) \) may be considered as the sum of the absorption cross sections per unit volume of material for various optical processes. Assume, photon beam of energy (\( E \)) and intensity (\( I_0 \)) is normally incident on a slab of absorbing materials. For a material of non-uniform \( \alpha \)
the intensity at a depth of x, with fractional absorption of \( E \) photon energy, the intensity \( I(x) \) can be defined by (Figure 2.3.1),

\[
I(x) = I(0)e^{-\int_0^x \alpha(Ex')dx'}
\]  

(2.3.1)

Where \( I(0) \) is the intensity just inside the surface and the attenuation factor being \( e^{-\alpha(E)dx} \).

For materials with uniform \( \alpha \) this reduces to a simple Beer-Lambert law,

\[
I(x) = I(0)e^{-\alpha x}
\]  

(2.3.2)

If we assume all the photons being absorbed to generate free carriers then the generation rate can be defined at per unit volume, at a depth of x below the surface by,

\[
g(E, x) = b(E, x) \alpha(E, x)
\]  

(2.3.3)

Where, \( b \) is the photon flux at x.

To find the total generation rate at x we sum over the photon energies,

\[
G(x) = \int g(E, x) dE
\]  

(2.3.4)

2.4 Transport mechanism of photo-generated carriers

The generated carriers from the photon source in a solar cell are separated and collected to create electricity. The two charge transport phenomena that contribute to the process are drift-based transport and diffusion-based transport. A drift-based transport occurs in presence of an electric field whereas the diffusion-based transport is powered by the gradient of carrier concentration. For a photovoltaic device, the operation is biased at maximum-power condition where the presence of external electric field is significantly smaller than that of in a short-circuit condition and the current generation is mostly dominated by diffusion transport mechanism. For this reason, the photon absorbing
materials must provide a superior diffusion length, charge collection. If a device demonstrates weak diffusion process, to improve charge transfer and collection a drift-based transport mechanism can be implemented instead of diffusion-based transport.

If both diffusion and drift based transport are considered, usually known as ambipolar transport, the equation turns out to be\textsuperscript{56,57},

\[
\frac{\partial \Delta n}{\partial t} = D' \frac{\partial^2 \Delta n}{\partial x^2} + \mu' \varepsilon \frac{\partial \Delta n}{\partial x} + G - R \tag{2.4.1}
\]

Where, $\Delta n$ is the excess of electron concentration, $\mu'$ is the ambipolar mobility, $\varepsilon$ is the net electric field, $D'$ is ambipolar diffusion coefficient, $G$ is generation rate and $R$ is the recombination rate.

The ambipolar mobility can be stated as,

\[
\mu' = \frac{\mu_n \mu_p (p-n)}{n \mu_n + p \mu_p} \tag{2.4.2}
\]

The ambipolar diffusion coefficient can be given as,

\[
D' = \frac{n \mu_n D_p + p \mu_p D_n}{n \mu_n + p \mu_p} \tag{2.4.3}
\]

Where, $\mu_n$ and $\mu_p$ are electron and hole mobilities respectively, $D_n$ and $D_p$ are electron and hole diffusion coefficients respectively, $n$ and $p$ are electron and hole concentration respectively.

When an n-type material with minority charge carriers as holes and no excess charge generation with internal electrical filed inside the material, the transport of the minority charge carrier holes is dominated by diffusion process of these carriers. The continuity equation in equation 2.4.1 becomes,
\[
\frac{\partial \Delta p}{\partial t} = D_p \frac{\partial^2 \Delta p}{\partial x^2} - \frac{\Delta p}{\tau_p} = 0
\]

(2.4.4)

The solution to the equation 2.4.4 gives us the hole diffusion length,

\[
\Delta p = \Delta p (x = 0) e^{-\frac{x}{L_p}}
\]

(2.4.5)

Where, \(L_p\) is the diffusion length and is defined by,

\[
L_p = \sqrt{D_p \tau_p}
\]

(2.4.6)

Similarly, with p-type material with electrons as minority charge carriers and no excess charge due to internal electric field the continuity equation turns as,

\[
\frac{\partial \Delta n}{\partial t} = D_n \frac{\partial^2 \Delta n}{\partial x^2} - \frac{\Delta n}{\tau_n} = 0
\]

(2.4.7)

And similarly, the solution to equation 2.4.7 gives us the diffusion length of electron,

\[
\Delta n = \Delta n (x = 0) e^{-\frac{x}{L_n}}
\]

(2.4.8)

Where, \(L_n\) is the electron diffusion length,

\[
L_n = \sqrt{D_n \tau_n}
\]

(2.4.9)

By the definition it is understood that, higher the diffusion length, the probability for the charge carriers being collected at the collection layer increases. To efficiently satisfy the charge collection the absorber layer thickness, \(t\) must be \(L_n, L_p \gg t\).

The drift-based transport process in a material is solely influenced by electric field inside the material. When the diffusion length inside a material is low, electric field is required to
assist the charge transport. For a n-type material the continuity equation transforms during drift-based transform as,

\[ \frac{\partial \Delta p}{\partial t} = \mu_p \frac{\partial \Delta p}{\partial x} - \frac{\Delta p}{\tau_p} = 0 \quad (2.4.10) \]

And the solution to the equation 2.4.7 gives us the drift range of holes,

\[ \Delta p = \Delta p (x = 0)e^{-\frac{x}{R_p}} \quad (2.4.11) \]

Where, \( R_p \) is the drift range of holes,

\[ R_p = \mu_p \tau_p \varepsilon \quad (2.4.12) \]

Similarly, for p-type material where the minority charge carriers are electron and electric field is required for excess carrier generation, the continuity equation becomes,

\[ \frac{\partial \Delta n}{\partial t} = \mu_n \frac{\partial \Delta n}{\partial x} - \frac{\Delta n}{\tau_n} = 0 \quad (2.4.13) \]

Where the solution to equation 2.4.13 gives us the drift range of electrons,

\[ \Delta n = \Delta n (x = 0)e^{-\frac{x}{R_n}} \quad (2.4.14) \]

Where, \( R_n \) is the electron drift range and is given by,

\[ R_n = \mu_n \tau_n \varepsilon \quad (2.4.15) \]

When both drift and diffusion add to the charge transport of the carriers an electric field can be defined to determine whether the transport is dominated by diffusion or drift. This electric field is given by,

\[ \varepsilon_c = \frac{kT}{qL_{n,p}} \quad (2.4.16) \]
In case of p type material, drift transport of charge carrier occurs when net electrical field, $\varepsilon$ is greater than $\varepsilon_c$ and diffusion transport dominates when $\varepsilon < \varepsilon_c$. On the contrary for a n-type material, drift transport occurs when $\varepsilon > \varepsilon_c$ and diffusion transport occurs when $\varepsilon < \varepsilon_c$.

### 2.5 Recombination

Recombination of generated carriers has a big detrimental effect in solar cell performance as it simply reduces the photocurrent, short circuit current, fill factor and open circuit voltage of photovoltaic devices. Recombination rate ($R$) in a semiconductor can be simply defined as the number of recombined charge carriers per unit volume per second. Recombination lifetime ($\tau_r$) of charge carriers is defined as the density of charge carriers by recombination rate. In direct band gap semiconductor, recombination is driven by direct recombination of electrons in conduction band and holes in valence band. Whereas, in case of indirect semiconductors, recombination takes place through defect states or intermediate trap states. There are three main types of charge recombination. They are:

1. Band to band: Radiative recombination
2. Auger recombination
3. Shockley-Read-Hall Recombination: Trap-assisted recombination.

Recombination in a bulk semiconductor can be modelled as the summation of all three recombination.

$$R = R_{Rad} + R_{Aug} + R_{SRH}$$

$$\frac{\Delta n}{\tau_r} = \frac{\Delta n}{\tau_{Rad}} + \frac{\Delta n}{\tau_{Aug}} + \frac{\Delta n}{\tau_{SRH}}$$
\[ \tau_r = \frac{1}{\tau_{Rad} + \tau_{Aug} + \tau_{SRH}} \]  \hspace{1cm} (2.5.3)

Where, \( \tau_{Rad} \) is Radiative lifetime, \( \tau_{Aug} \) is Auger recombination lifetime, \( \tau_{SRH} \) is Trap assisted recombination lifetime.

### 2.5.1 Band to Band Recombination

![Diagram of Band to Band Recombination](image)

Figure 2.5.1 Band to band recombination

When a free electron in the conduction band directly travels down to the valence band and recombine with a free hole direct recombination takes place. In this process, emission of photon occurs with same energy that of the band gap of the semiconductor as a result it is known as radiative recombination. This process is likely to occurs mostly in a direct band gap semiconductor. The equations to define direct band to band recombination rate and recombination lifetime are,

\[ R_{rad} = B(np - n_0p_0) = B\Delta n(n_0 + p_0 + \Delta n) \]  \hspace{1cm} (2.5.4)

\[ \tau_{rad} = \frac{\Delta n}{R_{rad}} = \frac{\Delta n}{B\Delta n(n_0 + p_0 + \Delta n)} = \frac{1}{B(n_0 + p_0 + \Delta n)} \]  \hspace{1cm} (2.5.5)

Where B is the recombination coefficient and \( n_0 \) and \( p_0 \) are the concentrations of electrons and holes respectively of doped materials under thermal equilibrium before disturbance such as excitation (illumination) or electrically injection. \( \Delta n \) and \( \Delta p \) are raised
concentrations of electrons and holes respectively after disturbance such as excitation (illumination) or electrically injection.

### 2.5.2 Auger Recombination

Auger recombination generally takes place when the material is heavily doped, whether n type or p type in both direct and indirect type materials. The mechanism is illustrated in Figure 2.5.2 where it shows the recombination process in both heavily n-type doped material and p-type doped material. In this process band to band recombination will create an excited carrier in conduction or hole in valence band and after further relaxation the carrier reaches the bottom of the conduction band or the top of the valence band. Auger recombination is modelled using following equations,

\[
R_{Aug} = (p_0^2 + 2p_0 \Delta n + \Delta n^2)\Delta n + C_n(n_0^2 + 2n_0 \Delta n + \Delta n^2)\Delta n \tag{2.5.6}
\]

\[
\tau_{Aug} = \frac{1}{C_p(p_0^2 + 2p_0 \Delta n + \Delta n^2)+C_n(n_0^2 + 2n_0 \Delta n + \Delta n^2)} \tag{2.5.7}
\]
2.5.3 Trap-assisted recombination (SRH)

Traps are intermediate localized states deep in the band gap region which involves in change of electron and hole momentums creating phonon emission. When an electron and a hole is trapped in the same trap states they recombine and each of these transitions create phonon emission. This process can also occur in both direct and indirect band gap materials. The phenomenon is illustrated in Figure 2.5.3.

The SRH recombination can be expressed as,

\[ R_{SRH} = \frac{p n - n_i^2}{\tau_p (n + n_i) + \tau_n (p + p_i)} = \frac{p_0 \Delta n + n_0 \Delta p + \Delta n \Delta p}{\tau_p (n_0 + \Delta n + n_i) + \tau_n (p_0 + \Delta p + p_i)} \]  \hspace{1cm} (2.5.8)

\[ \tau_{SRH} = \frac{\Delta n}{R_{SRH}} = \frac{\tau_p (n_0 + \Delta n + n_i) + \tau_n (p_0 + \Delta n + p_i)}{p_0 + n_0 + \Delta n} \]  \hspace{1cm} (2.5.9)
2.6 Basic Operation of Solar Cells

2.6.1 Electrical model

A solar cell can be modelled as an electrical equivalent circuit with electrical elements like p-n junction diode. Figure 2.6.1 shows a double diode model of solar cells which includes the recombination of the device at the surface and has ideality factors closed to two. The model also includes series and shunt resistances which are key parameters in device performance. The series resistance \( R_s \) occurs due to bulk semiconductor resistance, bulk metal contact resistance, interconnects, etc and shunt resistance \( R_{SH} \) represents the recombination of holes and electrons, impurities, defects etc. For an ideal solar cell, \( R_{SH} \) should be infinite thus providing alternate current route while \( R_s \) should be zero creating zero voltage drop before the current flow reaches the load. Fill factor (FF) and maximum power in a solar cell will be reduced if the \( R_s \) increases with decreasing \( R_{SH} \). Again, if \( R_{SH} \) is decreased way too much, the open circuit voltage \( (V_{OC}) \) will drop and if \( R_s \) increases too much, it will cause the short circuit current to drop.

Considering the double diode model with a load \( R_L \) in the open end, the current equation becomes,
\[ I = \frac{V-IR_s}{R_{sh}} + I_{01} \left( e^{\frac{q(V-IR_s)}{kT}} - 1 \right) + I_{02} \left( e^{\frac{q(V-IR_s)}{2kT}} - 1 \right) - I_L \] (2.6.1)

Where, \( I \) is the current flowing through the load, \( I_{01} \) and \( I_{02} \) are the saturation current of two diodes and \( I_L \) is the current created through photoexcitation.

### 2.6.2 Current-Voltage (IV) measurement

From Figure 2.6.1 and equation 2.6.1 we can understand the current voltage relation of the solar cell. Figure 2.6.2 shows the current-voltage relation characteristics with single diode with ideality factor of 1 and the electrical power of the solar cell with respect to its voltage.

![Current density-voltage characteristics of solar cell and maximum power dissipation of solar cell with respect to its voltage.](image)

The open circuit voltage equation, when there is no load considered in the circuit,
$V_{OC} = \frac{nK_B T}{q} \ln \left( \frac{J_L}{J_O} + 1 \right) \quad (2.6.2)$

Where, $J_L$ and $J_O$ are photogenerated current and diode saturation current, respectively.

For organic or perovskite type solar cells where the band gap is defined by the difference between the HOMO and LUMO level of the absorber layer, the equation for $V_{OC}$ becomes,

$V_{OC} = \frac{1}{q} (E_{FN} - E_{FP}) \quad (2.6.3)$

Where $E_{FN}$ and $E_{FP}$ are the fermi level at the conduction band and fermi level at the valence band, respectively.

When the voltage across the solar cell is considered zero, that is the solar cell is short circuited instead we obtain the short circuit current density, $J_{SC}$. For a certain device area, the current density can be obtained as,

$J_{SC} = \frac{J_{SC}}{area} \quad (2.6.4)$

In general, the current density of a solar cell can be written as follows,

$I = J_L - J_O \left( e^{\frac{qV}{nK_B T}} - 1 \right) \quad (2.6.5)$

### 2.6.3 Fill Factor

At the operating points of open circuit voltage and short circuit current, the output power of the solar cell is zero. Fill Factor (FF) is the parameter which tells us where the device will run at maximum power. Comparing the point of $V_{OC}$ and $I_{SC}$, FF determines the maximum power from the cell. The FF is defined as follows,

$FF = \frac{P_{MAX}}{V_{OC} \cdot I_{SC}} \quad (2.6.7)$
Figure 2.6.3 shows the fill factor measurement process for a solar cell.

Figure 2.6.3 Graphical representation of Fill Factor.

2.6.4 Power Conversion Efficiency

Power conversion efficiency (PCE) is one of the most used parameters to determine the final behavior of the device. Moreover, to determining the performance of the solar cell, this parameter is well dependent on the solar spectrum, solar intensity, temperature of the cell and many other factors. Efficiency is usually determined by the ratio of the output power to that of the input power. In this case, input power is the power of sunlight which is incident on the device and is measured using the terrestrial AM1.5 conditions at a temperature of 25 degree Celsius and the output power of the solar cell is determined the other electrical parameters V_{OC}, I_{SC}, and FF. So, the equation stands as,

\[ P_{MAX} = V_{OC} * I_{SC} * FF \] (2.6.8)

\[ \eta = \frac{V_{OC}I_{SC}FF}{P_{in}} \] (2.6.9)

Where, \( \eta \) is the efficiency.
2.7 Perovskite solar cell: Working Principle

2.7.1 Perovskite Crystal Structure

Since the discovery of perovskite structure there has been many perovskite compounds reported in numerous scientific works, but the most primary perovskite structure compound used to fabricate perovskite solar cells specifically is CH$_3$NH$_3$PbI$_3$. The universal formula of perovskite structure is ABX$_3$ where A represents either inorganic or organic cation like methylammonium, formamidinium, Cesium, Rubidium, B letter is for divalent metal ions like lead, tin, germanium and the letter X sets the position for halides like chloride, bromide, iodide and sometimes their mixtures. The perovskite structure is usually evaluated by their tolerance factor, t. The equation of t stands as,

$$ t = \frac{R_A + R_X}{2\varepsilon(R_B + R_X)} \quad \text{and} \quad 0.81 < t < 1.11 $$

(2.7.1)
Where $t$ is defined as the ratio of the distance between A-X to the B-X and $R_A$, $R_B$, and $R_X$ are the corresponding atomic radii for different ions. High quality cubic perovskite structure has a tolerance factor $t$ of 1.\textsuperscript{63,64} For octahedral factors of perovskite materials the tolerance factor should range for 0.81 to 1.11. The stability of the perovskite material, structural deformation of the material, reaction mechanism, ionization and other properties are related to the quality of the perovskite materials which is the tolerance factor, $t$. Figure 2.7.1 depicts the general structure of MAPbI$_3$ perovskite materials showing positions of different cations and anions in the structure and their importance. The first solar cell with perovskite material, MAPbI$_3$ was reported by Kojima et al in their publication\textsuperscript{65} in 2006 and the first perovskite solar cell was reported by the same group in their publication\textsuperscript{6} in 2009.

### 2.7.2 Working principle of n-i-p perovskite solar cell

![Planar n-i-p perovskite solar cell](image)

Figure 2.7.2.a Planar n-i-p perovskite solar cell

Figure 2.7.2.a depicts a planar n-i-p structure of perovskite solar cell where the electron transport layer is comprised of simple tin oxide(planar) and PCBM layers and the hole transporting material is prepared with Spiro-OMETAD. Figure 2.7.2.b shows the energy band diagram of a typical perovskite of n-i-p structure of TiO$_2$ as electron transport layer,
MAPbI₃ as absorber perovskite materials and Spiro-OMMETAD as hole transport layer. The main absorber perovskite material deposited on top of electron transport layer goes through photoexcitation when photons of matching band gap are incident on and are absorbed through the electron transport layer. Then photoexcited electrons in the Lowest Unoccupied Molecular Orbital (LUMO) of the perovskite material are transferred to the conduction band of electron transport layer and travels through the electron transport layer to the Fluorinated Tin Oxide or Indium Tin Oxide coated glass substrate. During this process, the behavior of hole transport layer can also be described as electron blocking layer as it stops electrons from traveling to the LUMO of hole transport material. The generated holes in the Highest Occupied Molecular Orbital (HOMO) of the perovskite material when the absorber material is photoexcited are collected by the hole transport material and at the same time the electron transport layer blocks the hole from travelling through it to minimize the recombination of electrons and holes. When connected to an external circuit, the electron travels to the cathode where it combines with oxidized species of the electrolyte. It is imperative that we investigate the band gaps of each of this material and their HOMO and LUMO level so that enough potential is created to drive the block holes and electrons in respective junctions. The back-metal contact, Gold (Au) or Silver (Ag) should also be matched with the HOMO level hole transport layer so that the recombination can take place when the circuit is completed. Each of electron and hole transport layers should be thin enough to facilitate faster travel of the electrons and holes, respectively.
2.7.3 Grain Boundary (GB) Defects in perovskite material

Perovskite materials for solar cell application are generally solution processed and thus are polycrystalline in nature. During the deposition of perovskite layer, defects are formed in the polycrystalline thin films due the processing mechanism and deposition techniques.
and these defects play an important role in optoelectronic properties of the perovskite absorber material and thus affect the electrical output behavior of the device made with them. These defects have been present and reported previously for GaAs, CdTe, poly-Si and CIGS solar cells. The defects in the materials cause significant change in charge carrier dynamics due to vacancies, interstitials, bond angles, bond distances, dangling bonds at the GBs. This behavior at GBs can be created by incomplete broken bonds, lattice mismatch, depletion enhancement because of impurities. The defects at GBs can work as a site of recombination and trap-state centers of minority carriers. GBs with defects and impurities craft the regions where the majority carriers get depleted creating an electrostatic potential barrier for the majority carrier to move across the region. Figure 2.7.3 shows different possible defect types at GBs in perovskite materials. Schottky and Frenkel defects create Pb, I, and MA vacancies although do not create trap states but they create diminished carrier lifetime in the crystals. Pb vacancies, I vacancies, A-site cation vacancies, Pb-I antisites and interstitials are randomly created at GBs creating both shallow and deep traps in the crystal. Furthermore, these vacant sites facilitate ion migration although some reported that the activation energy of these ion migration at GBs are lower compared to that of the bulk. These defects are significantly correlated with the electrical properties of the semiconductor properties, so different treatment and passivation mechanisms have been developed over the years to reduce the detrimental effects of GBs defects. These vacant GBs also create doors for the oxygen and moisture to enter the main absorber material causing the long term stability to deteriorate, which is one of the biggest hindrances in commercialization of perovskite solar cells. Electrical properties like open circuit voltage (V_{oc}) is directly affected by recombination when the carriers are trapped at
the trap states. Nonradiative recombination takes place at GBs when charge carriers are trapped in its defects thus reducing the $V_{OC}$. Studies have shown that, when the GBs are compact, they have nonthreatening effect$^{21}$ but it is debatable that engineering the size of the grains in perovskite is related to the improvement of the $V_{OC}$. GBs can affect the current-voltage (J-V) hysteresis, as different previous studies reported that ionic movement through the crystal due to electric field is the main cause of hysteresis in the device. When the density of GBs increase, meaning the increasing GBs in the crystal have worsen the hysteresis behavior of the device as the halide travels easily through the vacant surfaces.$^{35}$

$^{81}$ There are different passivation mechanism that have been deployed over the years to address this issue in perovskite absorber materials, such as large crystal engineering where solvent-annealing$^{82, 83}$, hot-casting method$^{84}$, additive introduction$^{85}$ etc. methods are applied. In many cases two-dimensional (2D) perovskite materials are used in the interface of ETL/PVK or PVK/HTL to cover the surface at the interface for better charge transport.$^{86-88}$

$^{88}$ 2D/3D hybrid structures have also been utilized with an aim to passivate the GBs.$^{89-91}$ Surface passivation with an aim to passivate the GBs simultaneously has been proven to be very promising in most cases and have been widely utilized to study the GBs of different types of perovskite materials.
Chapter 3. Device Fabrication Experimental Procedures

3.1 Materials

Materials used in the experiments for film fabrication and device fabrication are listed below in the Table 3.1.

Table 3.1 List of Materials used in Fabrication

<table>
<thead>
<tr>
<th>Name of Materials</th>
<th>Supplying company</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tin Oxide colloid precursor (Tin (IV) oxide, 15% in DI water colloidal dispersion liquid)</td>
<td>Alfa Aesar</td>
</tr>
<tr>
<td>PC&lt;sub&gt;60&lt;/sub&gt;BM</td>
<td>Nano-C</td>
</tr>
<tr>
<td>Lead Iodide (PbI&lt;sub&gt;2&lt;/sub&gt; extra dry 99.99%)</td>
<td>Alfa Aesar</td>
</tr>
<tr>
<td>Lead Bromide (PbBr&lt;sub&gt;2&lt;/sub&gt;) (extra dry 99.99%)</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Methyl Ammonium Bromide (MABr)</td>
<td>Great Cell</td>
</tr>
<tr>
<td>Formamidium Ammonium Iodide (FAI)</td>
<td>Great Cell</td>
</tr>
<tr>
<td>Cesium Iodide (CsI)</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Spiro-OMETAD</td>
<td>Lumtech</td>
</tr>
<tr>
<td>FK-209 Cobalt Salt</td>
<td>Great Cell</td>
</tr>
<tr>
<td>LiTFSi Salt</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>4-tert-butylpyridine (TBP)</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Anhydrous dimethyl sulfoxide (DMSO)</td>
<td>Acros Organic</td>
</tr>
<tr>
<td>Anhydrous dimethyl formamide (DMF)</td>
<td>Acros Organic</td>
</tr>
<tr>
<td>Anhydrous Isopropyl Alcohol (IPA)</td>
<td>Acros Organic</td>
</tr>
<tr>
<td>Chlorobenzene (CB)</td>
<td>Acros Organic</td>
</tr>
<tr>
<td>Silver (Ag)</td>
<td></td>
</tr>
<tr>
<td>ITO-Substrate</td>
<td>Hartford Glass</td>
</tr>
</tbody>
</table>
3.2 Fabrication Steps

3.2.1 Substrate Cleaning

Indium in oxide (ITO) coated glass substrate of dimension 1.5 cm by 1.5 cm were used in making devices. The ITO coated glass substrates came etched in one side where cathode material was deposited. The substrates were cleaned properly before the deposition of films. The samples were numbered and placed in a Teflon sample holder and placed in a beaker. The cleaning process involved the following steps in order:

I. Soap (Sodium Dodecyl sulfate) mixed with DI water ultrasonication for at least 20 minutes. Figure 3.2.1 shows the ultra-sonicator (FS30H) used in the cleaning process. To complete this process, the samples were rinsed in fresh DI water after the ultrasonication.

II. The substrates were then ultrasonicated with DI water only for 20 minutes at least.

III. The substrates were then ultrasonicated with Acetone for at least 20 minutes.

IV. Fresh IPA solution was used then to ultrasonicate the samples for 20 minutes.

Figure 3.2.1 Ultrasonicator
V. The last step involves putting the samples in fresh IPA solution and can be stored in dark and dry places with the beaker being covered.

The samples which are more than four days old after cleaning were not recommended to use. Even after cleaning, it was suggested that before the film deposition the substrates should be checked further to make sure that there were no small dirty particles on the surface.

3.2.2 Device Fabrication

![Fabrication steps of different layers](image)

Figure 3.2.2.a Fabrication steps of different layers

The full device fabrication for n-i-p structured perovskite solar cells involved multiple steps (Figure 3.2.2.a), carefully executed to maximize the possibility to obtain best quality devices. It is important to realize that, it is not possible to maintain the best fabrication environment every time, but effort should be made to make sure the presence of best
possible environment condition while depositing each layer. Each layer must be processed properly with utmost sincerity with their own processing procedures. The below steps will discuss the best possible procedures to fabricate each layer which is derived through multiple experimentation under various condition:

I. After cleaning the substrate, the ITO coated glass substrates are further cleaned through UV treatment, shown in Figure 3.2.2.b for at least 20 minutes.

![UV treatment on ITO surface](image)

Figure 3.2.2.b UV-treatment on ITO surface

II. SnO$_2$ colloidal dispersion in 15% water is diluted to 2.67% which is then deposited as the n-type electron extraction layer on top of the ITO surface. The diluted solution of SnO$_2$ is passed through a filter and two or three drops are dropped on the surface. The substrate is then spin coated using spin coater (MODEL) (Figure 3.2.2.c) at a speed of 3000 rpm/s with an acceleration of 2000rpm/s$^2$ for 30s. After
the end of spin coating the substrate is then placed on a preheated hot plate (Figure 3.2.2.d) of 150 degree Celsius and annealed in ambient air flow for 30 minutes. The substrates are then cooled to room temperature before further processing.

Figure 3.2.2.c Spin Coater

Figure 3.2.2.d Hot Plate

III. The samples are then carefully taken inside a Nitrogen glovebox (Figure 3.2.2.e).

It is recommended to have the Oxygen and Hydrogen saturation inside the glovebox
to be less than 0.1ppm. PC$_{60}$BM solution was prepared with 10mg/ml of Chlorobenzene at least 12 hours before the deposition. The prepared solution was kept stirred with a magnetic stirrer at 60 degree Celsius throughout the whole time but needed to cool before depositing. 60 microliters of solution were taken a pipette and dropped on the surface. It is suggested to make sure to have the whole surface covered before starting the spin coater. The spin coater was run at in two steps of 3000 rpm for 30s and 4000rpm for 5s. The sample was then annealed at 80 degree Celsius for 10 minutes and then cooled to room temperature before the next step.

Figure 3.2.2.e Nitrogen Glovebox

IV. The absorber materials, triple cation perovskite (FAMACs) was prepared right before the deposition of the layer. Triple cation perovskite precursor solution was prepared following the method described in [92]. First, stock solution of 1.5M PbI$_2$ and PbBr$_2$ in anhydrous DMF:DMSO 4:1 (v/v) were prepared. The PbI$_2$ solution
was heated at 180°C for 15 mins and PbBr2 at 180°C for 10 mins. The inorganic salt CsI stock solution was prepared with 1.5M per liter of DMSO and heated to 150°C for 10 mins. The FAPbI3 solution was prepared with 0.15 gm of FAI salt in 0.702 ml of PbI2 stock solution and 1.5 µL of DMF:DMSO 4:1 (v/v). The MAPbBr3 stock solution was prepared from 100 mg of MABr salt and 0.704 ml of PbBr2 stock solution and 16µL of DMF:DMSO 4:1 (v/v). The final perovskite solution results in addition of 0.5ml of FAPbI3 solution, 0.1ml of MAPbBr3 solution and 32 µL of CsI stock solution. The perovskite layer was then deposited on top of the PCBM layer with two-step spin-coating process of 1000 rpm for 10 sec and 6000 rpm for 25 sec. 200 µL of CB as antisolvent was dripped at 10 secs of the second step. After deposition, the films were then annealed at 100 °C for 45 mins and allowed to cool down to glovebox temperature.

V. PHI was synthesized from the reaction of phenyl hydrazine with hydriodic acid (HI) (57wt% in water) at 0°C (ice bath). 10 mL C6H5NH2NH2 was added into 25 mL methanol. 10 mL HI (57 wt%) was dropwise added into the C6H5NH2NH2 solution under vigorous stirring. The ice bath was removed, and the mixture was continuously stirred at room temperature for 2 hours. Then the solvent was removed by a rotary evaporator at 60°C. The crude powder was washed with diethyl ether for three times, and finally recrystallized from a mixed solvent of ethanol and diethyl ether. After filtration, the white solid was dried in vacuum at 60°C for 12 hours before use. The PHI solution was prepared with different concentrations in dry IPA. 50 microliters of the solution were dropped on the perovskite surface and
spin coated at 6000rpm for 20s with a ramp of 3000rpm/s². No further processing was done on this layer.

VI. The hole transport layer Spiro-OMeTAD was prepared by mixing 43mg Spiro-OMeTAD in 0.5 ml of chlorobenzene doped with 17 µL of TBP, 9.5 µL of Li-TFSI and 6.28 µL of FK209-Cobalt salt. 60 microliters of Spiro-OMeTAD was then spin coated on top of the PHI layer at 4000 rpm for 20 sec. The substrate with all the deposited layers was then kept in dark and dry condition for 12 hours to help the Spiro-OMETAD oxidize.

VII. The final back contact of 80 to 85nm of Silver (Ag) was deposited on top of the Spiro-OMETAD layer through thermal evaporation. Thermal evaporator (Figure 3.2.2.f) was first vacuumed to at least 6*10⁻⁶ mbar which took around 30-40 minutes and then silver was slowly deposited with varying deposition rate.

Figure 3.2.2.f Thermal Evaporator
3.3 Optoelectronic Characterization

3.3.1 Current density vs voltage (J-V) measurements

J-V measurements were done using a coupled system comprising Xenon Lamp (Newport 67005) (Figure 3.3.1.a) which imitates solar spectrum of AM 1.5G with Agilent 4155C semiconductor parameter analyzer (Figure 3.3.1.b). National Renewable Energy Laboratory (NREL) provided silicon photodetector is used to calibrate the whole system to get accurate measurements. The silicon photodetector named as Hamamatsu S1133-14 is always used every time before measurements to calibrate the distance between light source and sample to ensure accurate results and to maintain light intensity of 100 mWcm$^{-2}$. The sample device was scanned using the parameter analyzer at different scan rates, fast, medium, and slow with interval being at 10mV in every cases. Voltage was varied from 0 to 1.2V and current measurements were recorded for each voltage value. The scan from 0 to 1.2V is called forward scan and 1.2V to 0V is called reverse scan.

Figure 3.3.1.a J-V Measurement set up using Xenon Arc Lamp.
3.3.2 External Quantum Efficiency (EQE) measurements

Figure 3.3.2.a EQE measurement set-up.
Figure 3.3.2.b EQE Measurement Schematic representation.\(^9\)

Figure 3.3.2.a and Figure 3.3.2.b demonstrates the EQE measurement set up and schematic respectively which is a coupled system of Xenon Arc Lamp, monochromator, multiple lens, and semiconductor parameter analyzer. 7412 Oriel Cornerstone 260 1/4m monochromator, Xenon Arc Lamp, Newport Utility Software and Semiconductor Parameter Analyzer (Agilent 4155C) are connected as a system to measure EQE in a dark room. Very fine, targeted, and bright incident light was varied from 280nm to 1000nm wavelength at 5nm steps using Newport Utility software. Distances between the lenses and test devices were optimized using a reference cell, same Hamamatsu S1133-14 used for J-V measurements. Output current were measured during the full scan period.

### 3.4 Morphology Characterization

#### 3.4.1 Atomic Force Microscopy

For surface topological mapping images, AFM was operated in tapping mode using Agilent 5500SPM. The tip used in the process was Silicon (Budget Sensors, Multi75 Eg) which was coated with Chromium/Platinum having spring constant of ~1.4N/m and a tip radius of ~1Angstrom with a resonance frequency of 75KHz. The cantilever with an off-resonance frequency of 100-200Hz was applied to get needed resolution of resonance
frequency. Figure 3.4.1 shows the AFM set up (Agilent Nano-scope 5500 SPM) used to perform this measurement.

![Figure 3.4.1 AFM measurement set up](image)

A different combination of set up and experimental procedure was used to obtain surface potential measurements and current-sensing images.

**3.4.2 Scanning Electron Microscopy**

Hitachi S-4700 Field Emission Scanning Electron Microscope (FESEM) system (Figure 3.4.2) was used to observe the surface morphology at nanometer range. The sample was loaded to a chamber which was vacuumed to desired level and an accelerating voltage of 10KV and higher with a working distance of around 10-5mm was applied to extract a clear view of the surface. Different magnification was applied to observe the surface. Both cross-section and surface morphology were observed through this system.
3.4.3 UV-visible absorption spectroscopy

UV-visible absorption spectroscopy was performed with Agilent 8453 spectrophotometer with the utility software connected with a desktop. Figure 3.4.3 demonstrates the equipment involved in UV-visible absorption measurement. An empty blank ITO sample was always used as background sample to remove background noise due to air and ITO substrate. This measurement helped us to identify the band gap of the sample layer in visible range and to understand absorption quality of the film.
3.4.3 UV-visible absorption measurement set up.

3.4.4 X-Ray diffraction

Rigaku smart lab X-ray diffractometer was used to perform this characterization shown in Figure 3.4.4. The system was initiated by ramping the voltage to 40KV tube voltage and 20mA tube current to provide X-ray of 1.54 degree. The system was also calibrated to the thickness of the ITO substrate and medium resolution PB/PSA was used. With a step size varying 0.01 degree to 0.05 degree the measurements were done through optical alignment.
3.4.5 Transient Measurement

To determine the transient decay in devices, transient photo-voltage and transient photocurrent was measured using a coupled system of dye laser with nitrogen laser. The dye laser of Model 1011 with repetition rate of around 4Hz and pulse duration less than 1ns is combined with a nitrogen laser model OBB’s OL-4300, crisp pulse at 337nm is incident on the device which is connected to a oscilloscope of model Agilent MSO-X 4154A which records the device output data. A splitter was used to simultaneously transmit the laser on the sample device and the photodiode. The transient photocurrent was measured at short circuit with 50 ohm resistance while the photovoltage was measured at open circuit under
light illumination and steady condition of 1 Mega Ohm resistance. The recorded exponential data was then fitted with exponential decay function to derive the time constant. Figure 3.4.5 shows the experimental setup for this measurement.

Figure 3.4.5 Transient measurement set up.

3.4.6 Fourier-Transform Infrared Spectroscopy

A Thermo Scientific FTIR instrument of model Nicolet 6700 was used in this measurement. It is coupled with a desktop utility software which helps to run the instrument. For each sample data collection, a background sample was first collected at particular resolution and scan repetition. Similar settings were used for the sample films as well. The instrument used in the process is shown in Figure 3.4.6.
3.4.7 Contact Angle Measurement

The system for contact angle measurement was from Advanced Surface Technology video contact angle VCA 2000 system. DI water was used as droplet on sample surface to determine the contact angle at left and right edge of the water droplet on the surface. The system is shown in Figure 3.4.7. The brightness of the lamp is properly adjusted to obtain good images.
Chapter 4. Results and Analysis

**This chapter was written from the results published in the research article in the journal of ACS Applied Materials and Interface with the following title**

“Grain Boundary Defect Passivation of Triple Cation Mixed Halide Perovskite with Hydrazine-based Aromatic Iodide for Efficiency Improvement”

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4.1 Characterization of Films

4.1.1 Possible Reaction Mechanism of Perovskite with PHI

Figure 4.1.1.a Possible working mechanism of PHI secondary post treatment layer on perovskite film.

Figure 4.1.1.a depicts the possible working or reaction mechanism of the PHI treatment on the perovskite surface. Organic components like MA (A-site cation) is known to evaporate due to thermal annealing. This causes development of under coordinated Pb atoms or iodide vacancies and also Pb-I anti-site defects where iodine takes the place of Pb thus terminating bonds with neighboring Iodine atoms resulting into disordering of the crystals. These anti-site defects and under-coordinated Pb atoms or iodide vacancies are the main source of trap states as the band edges of perovskites were described to be compromised of Pb and I orbitals. Besides, Pb-I anti-site defects showed lower formation energy than that of the bulk as a result of which they form more readily and prevail on the surface. The PHI molecules can provide abundant N-H groups and iodide to the perovskite surface and grain boundaries. Molecules with N-H group can fill up point defects or A-site vacancies for perovskite surfaces. The positively charged PH⁺ are
expected to compensate the MA⁺ loss in perovskite by taking their place in the MA⁺ vacancy sites. While, iodide in PHI can provide bond formation with the unreacted Pb²⁺ ions, thus reducing the number of under coordinated Pb atoms and controlling the lead iodide formation on the perovskite surface and grain boundaries. Besides, the iodide deficiency or vacancies can lead to point defects in perovskite, which is proposed to be treated with iodides supplied by the PHI passivation layer.

Figure 4.1.1.b FTIR spectroscopy measurement of control perovskite film, perovskite film with PHI layer and only PHI.

Investigation into the interaction between PHI and the perovskite film was performed by carrying out FTIR measurements (Figure 4.1.1.b). The FTIR spectra for the PHI treated perovskite film was obtained using control perovskite film as the background for the experiment. The FTIR spectrum of only PHI powder shows characteristic peaks at 1604 cm⁻¹, 1494 cm⁻¹, 893 cm⁻¹, 761 cm⁻¹ and 687 cm⁻¹. The treated perovskite film with PHI shows corresponding peaks where the 1604 cm⁻¹ peak was shifted to 1618 cm⁻¹, 1494 cm⁻¹ peak to 1467 cm⁻¹. 893 cm⁻¹ to 897 cm⁻¹ suggesting interaction between the perovskite
and PHI and that the PHI molecule can coexist with the perovskite molecules in the film alongside forming bonds with the perovskite. The observed shift in peaks may correspond to coordination bonds formation by PHI with the perovskite film.

4.1.2 UV-Visible Absorption

![UV-Visible Absorption Graph]

Figure 4.1.2 Ultraviolet-visible absorption of (FA$_{0.83}$MA$_{0.17}$)$_{0.95}$Cs$_{0.05}$Pb(I$_{0.83}$Br$_{0.17}$)$_3$ perovskite solar cells without and with perovskite layer modification. The band gap remains unchanged ~1.59 eV. Absorption of the structure remained similar in all conditions.

UV-Visible absorption (Figure 4.1.2) spectra was performed for different concentrations of PHI treated perovskite films. The structure used for this purpose was glass/ITO/SnO$_2$/PCBM/Perovskite and PHI treatment on top of perovskite layer for different concentrations. No significance change in the absorption spectra was observed
showing valleys at the same wavelength of 778nm, demonstrating a bandgap of \(\sim 1.59\) eV. This implies that the PHI treatment did not affect the structural integrity of the perovskite.

### 4.1.3 Scanning Electron Microscopy

![SEM images](image)

Figure 4.1.3. a), b), c), d) and e) are the SEM images of control perovskite film, perovskite films with 1mg/ml PHI, 2mg/ml PHI, 3mg/ml PHI and 4mg/ml PHI respectively.

The structure used to perform this characterization was glass/ITO/SnO\(_2\)/PCBM/Perovskite. Various concentration of PHI was spin-coated on top of the perovskite film and was further annealed. As can be seen in SEM images Figure 4.1.3 a), b), c), d), e), it was found that the perovskite layer was covered with the PHI layer. Figure 4.1.3 a) shows control perovskite film with varying grain size and numerous pin holes on its surface, whereas perovskite films treated with different concentrations (Figure 4.1.3 (b), (c), (d), (e)) show less or no such pinholes. However, with increasing concentration of PHI, there is development of unwanted white phases which are absent of carbon\(^{105}\) on the surface of the perovskites. The
films with PHI concentration of 2mg/ml shows minimum white facets on the surfaces and uniform grain size and distribution.

4.1.4 Atomic Force Microscopy (Surface Topography)

Figure 4.1.4 Atomic force microscopy (AFM) images of perovskite films without and with PHI treatment. a), c) AFM of perovskite film without PHI treatment and b), d) with 2 mg/ml PHI treatment. After PHI treatment, the roughness of perovskite layer reduced from 34 nm to 28.9 nm indicating smoother perovskite layer for better charge transport. From the surface topology performed using Atomic force microscopy it was found that the roughness of the perovskite layer was reduced from 34.0 nm to 28.9 nm, and this reduction can be attributed to the deposition of the PHI passivating layer on both the perovskite grains.
and in between grain boundaries reducing the height between the perovskite surface and grain boundary depth rendering less rough surface.

4.1.5 X-Ray Diffraction

![XRD spectrum](image)

Figure 4.1.5 XRD spectrum of the control perovskite films compared with the treated perovskite films with PHI.

X-ray diffraction (XRD) measurements was performed (Figure 4.1.5) to demonstrate the state of PHI on the surface of the perovskite layer. The diffraction peaks for the perovskite film with and without PHI layer did not show any dissimilarities except appearance of one new peak at 50.04°, which is consistent with the PHI XRD peak. Regular peaks of 3D perovskites are formed at 14° (110 plane) and 28° (220 plane) with PbI₂ peak at 12.56°. It
can be inferred that PHI was not converted to any other phase and it remained as crystals of PHI itself on the top of the perovskite surface.

4.1.6 Photoluminescence Spectra

![Photoluminescence spectra](image)

Figure 4.1.6.a Photoluminescence spectra of control perovskite film compared with treated perovskite films.

![Photoluminescence quenching](image)

Figure 4.1.6.b Photoluminescence quenching of the perovskite films both treated and control.

The steady-state photoluminescence (PL) spectra (Figure 4.1.6.a) was observed for the perovskite films with PHI treatment under various PHI concentrations. All the peaks are
obtained at around 778nm emission wavelength with excitation wavelength applied at 395nm. PL intensities evidently increased after PHI treatment without any thermal annealing which indicates that the recombination in the perovskite has been greatly suppressed. PL intensities with 2mg/ml and 3mg/ml concentration have intensities higher than that of control, while 1mg/ml and 4mg/ml concentration exhibit lower peaks. Steady-state PL (Figure 4.1.6.b) was also performed with Spiro-OMETAD hole extraction layer on top of the (for the control and treated perovskite films). 2mg/ml PHI concentration demonstrated the lowest peak intensity compared to 1mg/ml, 3mg/ml, 4mg/ml treated films and control perovskite film, indicating more efficient hole extraction at the absorber layer and Spiro-OMETAD interface with PHI treatment.

4.1.7 Contact Potential Difference Mapping
Figure 4.1.7. a) Contact Potential Difference (CPD) map in dark conditions of a) control perovskite and d) perovskite layer treated with 2mg/ml PHI. Grain boundaries considered for studies are identified by white lines across GB. b) and e) are line profiles extracted from the CPD mappings of control perovskite and perovskite layer treated with 2mg/ml PHI respectively. c) and f) are individual line profile to demonstrate the potential variation (ΔCPDGB) between GB and adjacent grain surfaces for bare perovskite and perovskite layer treated with 2mg/ml PHI, respectively.

To understand the effect of PHI as passivating agent particularly at GB region, we considered comparison of control (untreated) perovskite film with 2 mg/ml PHI-treated perovskite film. For this, surface potential mappings were performed using Kelvin probe microscopy (KPFM) where contact potential difference (V_{CPD}) between the tip and sample were measured along with the topography simultaneously. V_{CPD} between the tip and sample is defined as:

\[ V_{CPD} = \frac{\phi_t - \phi_s}{-e} \]  \hspace{1cm} (4.1.1)

where \( \phi_t \) and \( \phi_s \) are the work function of the tip and sample respectively, and \( e \) is the elementary charge. The difference between the grain surface (GS) and the GBs gives the GB potential barrier. It is important to mention that, the work function of the tip is constant as the same tip was used for measurement of all the samples.

Here, we demonstrate the formation of positive barrier or electron transport barrier at perovskite film GBs by applying PHI as the passivating layer. Figures 4.1.7 a, d show the surface potential images of control and PHI treated perovskites respectively with a scanned size of \(~1.5 \, \mu\text{m} \times ~1.5 \, \mu\text{m} \), where ten different GB areas were randomly selected for line
profile measurements marked by white lines for each perovskite film. Figures 4.1.7 b, e show variation in the CPD profile obtained through the line profiles at different GBs and their adjacent GS for control and PHI treated perovskites films, respectively. As can be seen from Figure 4.1.7 c, for the control perovskite, GBs exhibit negative potential compared to GS. The average value of the potential difference ($\Delta CPD_{GB} = CPD_{GB} - CPD_{GS}$) observed at ten areas is $-35.68$ mV indicating negative potential barrier or hole barrier at the GBs. Whereas, for the PHI treated perovskite, the ten different line profiles (Figure 4.1.7 e and f) and average $\Delta CPD_{G}$ on the PHI treated perovskite surfaces interestingly shows positive potential difference between GBs and GS, suggesting an electron barrier at the hole collection side of the perovskite film. The average $\Delta CPD_{GB}$ shows the potential value at $+88.2$ mV. This concludes that the PHI helps to transform hole barrier into an electron barrier, indicating suppression of shunting, or leakage paths, thus passivating the GBs.\textsuperscript{106} Similar correlation was deduced by Nicoara et. al in their recent studies \textsuperscript{88} on CIGSe thin films where they investigated the work function variation between different passivating materials by analyzing the GB potentials and adjacent surface potentials. It was concluded that downward band bending (i.e. hole transport barrier) have negative impact on the device as it leads to increased electron density at GBs forming a shunt path to the collection layers thus reducing overall device performance.

### 4.1.8 Current-Sensing Atomic Force Microscopy

![Current-Sensing Atomic Force Microscopy](image)
Figure 4.1.8 a) Topography and b) C-AFM images of control perovskite. c) Line profiles of current for the five different locations indicated by white lines for the control perovskite, which shows higher current at grain boundaries compared to the grain surface. d) Topography and e) C-AFM images of 2 mg/ml PHI-treated perovskite. f) Line profiles of current for the five different locations indicated by white lines for the PHI treated perovskite, which shows lower current at grain boundaries compared to grain surfaces.

Conductive AFM(C-AFM) mapping (Figure 4.1.8 b, e) with corresponding AFM topography (Figure 4.1.8 a, d) was implemented to measure surface current along with the current at grain boundaries of the perovskite films. Five different random locations were chosen in each film to determine the line profiles for differentiating the current on the surface to that at the GBs. The average current of control perovskite was 1.67 nA, whereas the average current for the treated perovskite reduced to 0.88 nA. As is evident from the line profiles for the control perovskite (Figure 4.1.8 c), the current at the GBs is higher than that of the adjacent surface, while on contrary, for the treated perovskite (Figure 4.1.8 f), the current at GBs is lower compared to that of the adjacent surface. This reduced current at the GBs suggests that the PHI layer effectively passivates the GBs by suppressing the electrical leakage pathways through the GBs. Previous reports suggests that, thin insulating
passivation layer on perovskite surface and GBs can successfully suppress charge recombination at leakage paths and thus increase carrier transport.\textsuperscript{107, 108, 109, 110}

4.2 Characterization of Devices

4.2.1 Efficiency Variation with different concentrations

![J-V characteristics of control device and devices of PHI treatment with different concentrations.](image)

Figure 4.2.1.a J-V characteristics of control device and devices of PHI treatment with different concentrations.

![Efficiency variation with different concentrations of PHI.](image)

Figure 4.2.1.b Efficiency variation with different concentrations of PHI.
Figure 4.2.1.c J-V characteristic of control and best treated device with 2mg/ml PHI concentration.

Table 4.2.1. Device performance summary in different PHI concentration.

<table>
<thead>
<tr>
<th>PHI Concentration (mg/ml)</th>
<th>Scan Direction</th>
<th>Voc (V)</th>
<th>Jsc (mA/cm²)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>Average</th>
<th>H-index</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>RS</td>
<td>1.11</td>
<td>21.71</td>
<td>0.72</td>
<td>17.43</td>
<td>16.39%</td>
<td>11.93%</td>
</tr>
<tr>
<td></td>
<td>FS</td>
<td>1.09</td>
<td>21.73</td>
<td>0.65</td>
<td>15.35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>RS</td>
<td>1.13</td>
<td>23.96</td>
<td>0.68</td>
<td>18.46</td>
<td>18.04%</td>
<td>4.55%</td>
</tr>
<tr>
<td></td>
<td>FS</td>
<td>1.11</td>
<td>23.69</td>
<td>0.67</td>
<td>17.62</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>RS</td>
<td>1.13</td>
<td>24.49</td>
<td>0.75</td>
<td>20.62</td>
<td>20.34%</td>
<td>2.76%</td>
</tr>
<tr>
<td></td>
<td>FS</td>
<td>1.13</td>
<td>24.30</td>
<td>0.73</td>
<td>20.05</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>RS</td>
<td>1.14</td>
<td>23.4</td>
<td>0.66</td>
<td>17.71</td>
<td>17.26%</td>
<td>5.02%</td>
</tr>
<tr>
<td></td>
<td>FS</td>
<td>1.13</td>
<td>23.26</td>
<td>0.64</td>
<td>16.82</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>RS</td>
<td>1.11</td>
<td>22.28</td>
<td>0.69</td>
<td>17.15</td>
<td>16.80%</td>
<td>4.02%</td>
</tr>
<tr>
<td></td>
<td>FS</td>
<td>1.09</td>
<td>22.32</td>
<td>0.68</td>
<td>16.46</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

H-index = (PCE_{reverse} − PCE_{forward}) / PCE_{reverse}
To further investigate the positive effect of the PHI secondary treatment, perovskite devices with structure ITO/SnO$_2$/PCBM/Perovskite/spiro-OMETAD/Ag was fabricated. Varying the concentration of PHI, the best device performance was determined, where the device treated with 2mg/ml concentration of PHI exhibited the best photovoltaic performance (Figure 4.2.1.a, 4.2.1.b, 4.2.1.c and Table 4.2.1). From Figure 4.2.1.c, we can see that the device performance enhanced with increase in concentration but started to decrease towards higher concentration. The typical current density-voltage (J-V) curves of the devices with PHI (2mg/ml concentration) and without PHI treatment are shown in Fig 4.2.1.b. Significant improvement can be observed in the J$_{SC}$, while V$_{OC}$ and FF also improved after the PHI treatment when compared to the control device. The PHI treatment also contributed to hysteresis reduction of the perovskite devices (Table 4.2.1). Both these improvement in device performance and suppression of hysteresis can be attributed to reduction or passivation of the surface and grain boundary defects by the PHI treatment, which consequently suggests suppression of charge recombination, charge accumulation, band alignment and ionic defect accumulation.$^{111}$ Our champion PHI-treated device delivered PCE of 20.62% with V$_{OC}$ of 1.13 V, J$_{SC}$ of 24.49 mA/cm$^2$ and FF of 75% under reverse scan with almost no hysteresis, whereas the control device showed PCE of 17.43% with V$_{OC}$ of 1.11 V, J$_{SC}$ of 21.71 mA/cm$^2$ and FF of 72% under reverse scan with significant hysteresis.
4.2.2 External Quantum Efficiency

![External Quantum Efficiency Graph](image)

External quantum efficiency (EQE) measurements (Figure 4.2.2) was done on control and treated devices and integrated J_sc of 21.36 mA/cm^2 and 23.81 mA/cm^2 was obtained for the untreated and treated respectively which are consistent with the J-V measurements. The EQE difference was highly noticeable from wavelength of 450nm to 780nm as the treated device showed higher EQE percentage compared to that of treated device. As a result, the integrated J_sc for treated device increased for AM 1.5 solar simulator spectrum.
4.2.3 Transient Photo-voltage and Transient Photo-Current

![Diagram of transient photovoltage](image1)

Figure 4.2.3.a Transient Photovoltage

![Diagram of transient photocurrent](image2)

Figure 4.2.3.b Transient Photocurrent

The charge recombination and transport time constants (τ₁ and τ₂ respectively) were studied from the transient photovoltage (Figure 4.2.3.a) and transient photocurrent (Figure
4.2.3.b) decays measured at open and short circuit conditions of the device respectively. The $\tau_1$ of the control and PHI treated devices are 7.7 $\mu$s and 11.8 $\mu$s respectively. This higher value for charge recombination constant indicates slower surface charge recombination for the PHI treated PSCs. In addition, the PHI treated devices also demonstrated faster transport time $\tau_2$ of 1.15 $\mu$s compared to the control with 1.4 $\mu$s, thus indicating efficient and faster charge collection at the contacts.

4.2.4 Ideality Factor

Figure 4.2.4.a Light intensity vs open circuit voltage
The device performance under varying light intensities were studied. From the relationship between Voc and light intensity shown in Figure 4.2.4.a, it can be estimated that the control device shows a slope of $1.35K_bT/q$, while the PHI treated devices show a much smaller slope of $1.20K_bT/q$ where $K_b$ stands for Boltzmann constant, $T$ is the temperature and $q$ stand for the electric charge. It is well-known that defect-assisted recombination in the devices can be understood from $K_bT/q$ slope, where a smaller value indicates lesser recombination and vice versa. From these results, it is further proved that the recombination has largely been suppressed for the PHI treated perovskite device.\textsuperscript{39} Also, linear behavior for Jsc vs light intensity relationship (Figure 4.2.4.b) was observed for both the control and PHI treated devices. This is an indication that carriers can transport smoothly and that no induced charge barriers exist at the interface by introduction of the
PHI layer at the interface of perovskite/Spiro-OMETAD interface. The J-V characteristics used to obtain this result is shown in Figure 4.2.4.c.

![Figure 4.2.4.c J-V characteristics used to calculate ideality factor study.](image)

### 4.2.5 Dark J-V measurement

The dark J-V characteristics (Figure 4.2.5) of our devices, where the treated device showed reduced reverse saturation current of $5.15 \times 10^{-14}$ A compared to that of control device with
1.56\times10^{12} \text{ A}. The reduction in reverse saturation current can be attributed to the defect passivation of the perovskite surface and grain boundaries by the PHI treatment.

4.2.6 Charge Transport Study

![Graph showing charge transport study](image)

Figure 4.2.6 Photo-CELIV measurements to calculate the mobility for the control perovskite and treated perovskite devices.

To better understand the charge transport devices, Photo-CELIV measurements were carried out. The measurement (Figure 4.2.6 and Table 4.2.6) was carried out at 2 \mu s time delay with 40000 V/s ramp rate for both the devices. The control device shows charge carrier mobility of $1.67 \times 10^{-3} \text{ cm}^2/\text{Vs}$ whereas the treated device exhibited higher mobility of $5.26 \times 10^{-3} \text{ cm}^2/\text{Vs}$. The estimated higher mobility can lead to the observed enhanced $J_{\text{SC}}$ of the treated device.
Table 4.2.6 Charge Carrier Mobility Measurements

<table>
<thead>
<tr>
<th></th>
<th>$t_{max} ($\mu$s)</th>
<th>Mobility (cm$^2$/Vs)</th>
<th>Thickness (nm)</th>
<th>Voltage Ramp Rate (V/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>1580</td>
<td>$1.67 \times 10^{-3}$</td>
<td>500</td>
<td>$4 \times 10^5$</td>
</tr>
<tr>
<td>Treated</td>
<td>890</td>
<td>$5.26 \times 10^{-3}$</td>
<td>500</td>
<td>$4 \times 10^5$</td>
</tr>
</tbody>
</table>

4.2.7 Mott-Schottky measurement

The increase in $V_{OC}$ can be understood from the flat band potential ($V_{bi}$) obtained from Mott-Schottky plot (Figure 4.2.7 and Table 4.2.7). The measurements were taken at 20 kHz with a scan from 0 V to -1.2 V. The observed increase in the $V_{bi}$ by the PHI treatment can be related to the increase in the $V_{OC}$. The $V_{bi}$ increased from 0.96V to 1.00V for treated device.
Table 4.2.7 Flat Band Potential and Slope obtained from Mott Schottky Plot

<table>
<thead>
<tr>
<th></th>
<th>Slope</th>
<th>$V_{bi}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>$2.34 \times 10^{16}$</td>
<td>0.96</td>
</tr>
<tr>
<td>Treated</td>
<td>$2.88 \times 10^{16}$</td>
<td>1.00</td>
</tr>
</tbody>
</table>

4.2.8 Steady state power output and steady state current density

Figure 4.2.8.a Steady State power output comparison
The steady state power output measurements were performed at voltage of maximum power points are shown in Figure 4.2.8.a, which shows higher stable PCE of 20.36% for the treated device versus control with 17.23%. The maximum current densities for the control and treated devices as shown in Figure 4.2.8.b are 19.8 mA/cm$^2$ and 22.13 mA/cm$^2$ respectively. To perform this study the control device was biased at 0.87V while the treated device was biased at 0.92V for 120s in both cases.

4.2.9 Trap Density Measurements
Figure 4.2.9. Trap state density calculation: a) AFM-topography image of control perovskite film, b) KPFM mapping of control perovskite film, c) trap state density measurement using area profile for control perovskite, d) AFM-topography image of perovskite film treated with PHI, e) KPFM mapping of perovskite film treated with PHI, f) trap state density calculation of perovskite film treated with PHI from area profile.

By assuming that the grain boundary corresponds to a surface with a surface charge we can determine the net doping $P_{\text{net}}$ of the absorber material from the size of the band bending $\Delta \phi_{gb}$ and the SCR width $w$,

$$P_{\text{net}} = \frac{2 \varepsilon_0 \varepsilon \Delta \phi_{gb}}{e^2 w^2}$$  \hspace{1cm} (4.2.1)

where, $e$ is the elementary charge, $\varepsilon_0$ is the permittivity of free space and $\varepsilon$ is the dielectric constant of the perovskite. By the fact that the SCR width at the grain boundaries does not extend to the center of the grains, we can estimate the density of charged trap states $P_{gb}$, following a model originally proposed for transport across grain boundaries in polycrystalline silicon,

$$P_{gb} = \frac{1}{e} \sqrt{8 \varepsilon \varepsilon_0 P_{\text{net}} \Delta \phi_{gb}}$$  \hspace{1cm} (4.2.2)
The density of trap states was also calculated for control perovskite film and treated perovskite film using KPFM measurements area profile at the grain boundary region (Figure 4.2.9). The average charged trap state density for control perovskite film considering five different locations was $4.1(\pm 1.4) \times 10^{11}$ cm$^{-2}$ whereas the average charged trap state density of the treated perovskite film with 2mg/ml PHI reduced to $1.32 (\pm 0.65) \times 10^{11}$ cm$^{-2}$. This further reveals the defect passivation effect induced by incorporation of the PHI.

4.2.10 Contact Angle Measurement

Figure 4.2.10 Contact angle measurements of (a, b) control perovskite film and (c, d) perovskite film treated with 2mg/ml PHI.

Contact angle measurements shown in Figure 4.2.10 were performed on control perovskite film and perovskite film treated with 2mg/ml of PHI. The contact angles for control perovskite film are determined at 44º (left) and 42º (right) whereas the treated perovskite have higher contact angles of 55º (left) and 53º (right). This provides the evidence of the increase in the hydrophobicity of the treated perovskite film which can enhance the
possibility of blocking the permeation of moisture (i.e. water) into the perovskite and thereby contribute in improving stability.

4.2.11 Device Stability Tests

![Graph showing normalized PCE (a.u.) vs time (h) for devices outside and inside the glovebox.]

Figure 4.2.11.a Stability measurement in ambient condition outside glovebox

![Graph showing normalized PCE (a.u.) vs time (h) for devices inside the glovebox.]

Figure 4.2.11.b Stability measurement inside glovebox

The stability of the devices in ambient air and inside the glovebox were tested as shown in Figure 4.2.11.a and 4.2.11.b respectively. For the ambient stability, the devices were kept
in dark at temperature of 24-25 °C and relative humidity of ~35%. The treated device showed comparatively better stability retaining more than 93% of initial efficiency after 500 hours, while the control dropped below to 87% of initial efficiency. For the devices kept inside the N₂ glovebox with relative humidity of ~20% and temperature at 24 °C, the devices performed almost similarly for 500 hours with treated device showing a slightly better output performance.

4.2.12 Device Reproducibility

![Device efficiency distribution](image)

Figure 4.2.12.a Device efficiency distribution

Figure 4.2.12.a shows the statistical distribution of the PCE of the control and 2 mg/ml PHI-treated devices to demonstrate the reproducibility of our results. Furthermore, Figure 4.2.12.b and Table 4.2.12 demonstrate the statistical distribution of all the photovoltaic performance parameters for control and treated conditions. Overall, the PHI-treated devices exhibited superior average PCE of 19.71±0.36% than the control with
16.32±0.85%. From the statistical analysis it is evident that there are increases over all in all factors, but in two of them (Fill Factor and Open Circuit Voltages) the increase is not statistically significant at 5% level.

Figure 4.2.12.b Statistical Analysis of device parameters
Table 4.2.12 Statistical T Test Data of Control and Treated Devices (95% Confidence of Interval)

<table>
<thead>
<tr>
<th></th>
<th>Paired t-test (p value)</th>
<th>Control</th>
<th>Treated</th>
<th>Standard error of difference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Efficiency (%)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.015334</td>
<td>SD = 0.8652</td>
<td>SD = 0.3712</td>
<td></td>
</tr>
<tr>
<td></td>
<td>T-test metric</td>
<td>3.609593</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mean</td>
<td>16.315</td>
<td>19.713</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Standard error of difference = 0.191.</td>
</tr>
<tr>
<td><strong>Fill Factor</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>19.75829</td>
<td>SD = 0.0351</td>
<td>SD = 0.0138</td>
<td></td>
</tr>
<tr>
<td></td>
<td>T-test metric</td>
<td>0.850287</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mean</td>
<td>0.684</td>
<td>0.716</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Standard error of difference = 0.008.</td>
</tr>
<tr>
<td><strong>Current Density (mA/cm²)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.001581</td>
<td>SD = 0.7079</td>
<td>SD = 0.2251</td>
<td></td>
</tr>
<tr>
<td></td>
<td>T-test metric</td>
<td>4.161489</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mean</td>
<td>21.409</td>
<td>24.500</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Standard error of difference = 0.138.</td>
</tr>
<tr>
<td><strong>Open Circuit Voltage (V)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>8.278923</td>
<td>SD = 0.0154</td>
<td>SD = 0.0104</td>
<td></td>
</tr>
<tr>
<td></td>
<td>T-test metric</td>
<td>1.386552</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>Mean</td>
<td>1.106</td>
<td>1.132</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Standard error of difference = 0.004.</td>
</tr>
</tbody>
</table>
Chapter 5 Conclusion and Future Works

In this work, we have explored triple cation perovskite material which contains both organic and inorganic components and also studied the defects of this particular hybrid type perovskite structure. We have performed systematic procedures and optimized the device configuration with definite fabrication protocol based on our understanding of this particular material and developed a planar n-i-p perovskite solar cell with 20.67% power conversion efficiency which is a improved efficiency from it’s control device efficiency of 17.43%. While improving the device performance was the ulterior goal, we opted surface and grain boundary passivation mechanism to improve the film morphology and its electronic behavior resulting into better device performance. We used a secondary growth approach of hydrazine based aromatic halide (PHI) on top of the perovskite layer without further processing. We also provided different means to identify and study the electronic behavior at GBs for perovskite materials.

5.1 Conclusion

- A planar n-i-p control device fabrication protocol with low temperature, fully solution process on ITO substrate with an efficiency of 17.47% was developed.
- SEM and AFM (both KPFM and C-AFM) characterization methods were applied to identify the GBs in the perovskite crystal and GBs behavior were studied through the results.
- A secondary layer post treatment method was adopted successfully to passivate the GBs in perovskite layer using Phenyl Hydrazinium Iodide. The post processing treatment passivation was studied using PL, XRD, SEM, AFM on the surface to further verify the passivation effect.
By using 2mg/ml PHI in IPA, the passivation layer significantly improved device performance parameters. The short circuit current density enhanced to 24.49 mA/cm² from 21.73 mA/cm², open circuit voltage increased from average 1.10V to 1.13V and the fill factor improved to average 72% from 68%.

We studied and observed different improved device characteristics through transient photocurrent, transient photovoltage, ideality factor calculation, charge carrier mobility test, Mott-Schottky measurements, dark current measurements etc.

Stability of the device was also studied through contact angle measurements and testing device performance over 500 hours keeping devices both inside and outside glovebox.

5.2 Future Works
This work opens areas to investigate more intensely about the passivation mechanisms, passivating materials, grain boundaries, crystal defects, detrimental effects of GBs in device performance. More studies can be done to develop a better control planar n-i-p triple cation perovskite solar cell device following the protocol established in this work. From fabricating a control device with better performance, it is possible to establish a device of higher performance through defect passivation. Individual parameters like $V_{OC}$, $J_{SC}$, and FF can be investigated further to identify which parameters are affected mostly due to GBs and how those parameters can be engineered to improve. Despite the great deal in advancements of characterization techniques, mapping of higher resolution is important to study the film morphology at nanoscale ranges which is still not available at large. This work can be used to study further develop nanoscale studies on GBs. There are further passivation mechanisms are out there which can be employed for this kind of device as
well. For example, 3D/2D perovskite hybrid at the interface or wide band gap material with matching HOMO level can also be used at the interface. This type of planar structure provides easier way of fabrication with lesser time and high device performance. Besides, this type can be extensively used to multiple application like rechargeable battery application\textsuperscript{113, 114}, drone flights, sensor set ups, etc. Despite of different limiting factors, with further intense study the limits can be pushed to develop very high efficiency devices which can help commercialize Perovskite Solar Cells in near future and making it cost effective to the general consumers.
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