REDUCED THERMAL DEGRADATION IN PEROVSKITE SOLAR CELLS BY INTERFACIAL ENGINEERING USING SOLUTION PROCESSED POLYMER LAYER

M.Sc. Thesis

By **PIYUSH KALRA**



DISCIPLINE OF PHYSICS INDIAN INSTITUTE OF TECHNOLOGY INDORE JUNE, 2019

REDUCED THERMAL DEGRADATION IN PEROVSKITE SOLAR CELLS BY INTERFACIAL ENGINEERING USING SOLUTION PROCESSED POLYMER LAYER

A THESIS

Submitted in partial fulfillment of the requirements for the award of the degree of

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by PIYUSH KALRA



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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled "Reduced Thermal Degradation in Perovskite Solar Cells by Interfacial Engineering Using Solution Processed Polymer Layer" in the partial fulfillment of the requirements for the award of the degree of MASTER OF SCIENCE and submitted in the DISCIPLINE OF PHYSICS, Indian Institute of Technology Indore, is an authentic record of my own work carried out during the time period from July 2017 to July 2019 under the supervision of Dr. Parasharam M. Shirage, Associate Professor, Head, Discipline of MEMS and Dr. Ulrich W. Paetzold, Senior Researcher, KIT, Germany.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

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Abstract

Persistent R&D to get alternatives to the market-dominating expensive & heavy silicon solar cells has led to the development of thin film technologies, one of which is perovskite solar cells (PSC). After being introduced in 2009 they have shown an unprecedented increase in efficiency – from <10% in 2012 to over 23% [1-7] in just seven years. These solar cells can be manufactured with less energy and toxic material than traditional silicon solar cells.

On the downside, PSCs have stability challenges with all major environmental stress factors namely oxygen, humidity, light and temperature. The purpose of this thesis is to produce high-performance perovskite solar cells and make them more robust to temperature degradation. We started with optimizing the cation mixture for our standard recipe and moved forward to introduce a new polymer i.e. PMMA to the recipe. This layer, when inserted between perovskite and HTL showed an increase in open-circuit voltage which motivated us to do more experiments with it. First, we added post-annealing in the spincoating process of this layer and there was an increment in both power conversion efficiency and open-circuit voltage with it compared to the cells with non- annealed PMMA layer. This indicated the enhancement in thermal stability of cells because of PMMA. We went ahead to apply thermal stress to the cells by heating the perovskite with and without PMMA at 50°C for the first test and at 100°C for the second one before coating HTL. From these experiments, a clear improvement was visible in efficiency and open-circuit voltages of cells which can be attributed to PMMA helping the perovskite structure to maintain its crystallinity and reducing its degradation to PbI₂. X-ray diffraction (XRD) and Field Emission Scanning Electron Microscope (FE-SEM) characterizations have been done on the overnight heated substrates, one with PMMA on top of perovskite and other with the only perovskite from

both 50°C and 100°C heating experiments. The XRD plots clearly show the reduced degradation of perovskite when PMMA is used. From the FE-SEM images, the bigger grain size of perovskite with PMMA is clearly visible and also the difference in PbI₂ content can be seen which is consistent with the XRD results. So we concluded that the addition of a PMMA layer between the perovskite and HTL (spiro –OMeTAD) has reduced the thermal degradation in PSCs till 100°C.

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Abbreviations

PV	Photovoltaic
PSC	Perovskite Solar Cell
ITO	Indium Tin Oxide
FTO	Fluorine doped Tin Oxide
ETL	Electron Transport Layer
ETM	Electron transporting material
HTL	Hole Transport Layer
IPA	Iso-propyl alcohol
DMF	Dimethylfomamide
DMSO	Dimethyl sulfoxide
GBL	Gammabutyrolactone
ACN	Acetonitrile
СВ	Chlorobenzene
РММА	Poly(methyl methacrylate)
MPP	Maximum Power Point
FF	Fill factor
PCE	Power conversion efficiency
FAI	Formamidinium Iodide
MACl	Methylammonium Chloride
MABr	Methylammonium Bromide
BAI	Butylammonium Iodide
BABr	Butylammonium Bromide

CHAPTER 1 Introduction

1.1 Solar energy

The electromagnetic radiations coming from the sun possess energy in the form of light and heat. This energy can be used directly or converted to other forms for utilization. The solar energy received on earth every day is 200,000 times more than the world's daily electricity generating capacity. Although the energy received is totally free but high costs of collection and storage prevent it from complete exploitation. Thermal and electrical energy are the two main forms of energy it can be converted to. Flat plate collectors are generally used to capture thermal energy which is then used for heating applications like water heaters and house heating. Solar energy is directly converted to electricity using photovoltaic cells and the phenomenon is known as the photovoltaic effect. The most common type of the material commercially used for PVs is silicon, cells produced from which are expensive and heavy. Persistent R&D to get alternatives to the market-dominating expensive & heavy silicon solar cells has led to the development of thin film technologies, one of which is perovskite solar cells which have shown remarkable growth in their efficiencies.

1.1.1 Photovoltaic effect

When electromagnetic radiation is incident on a photovoltaic cell with photons of energy equal or greater than the energy bandgap, a voltage or electric current is generated in the cell and this is called photovoltaic Effect. The difference of energy between the valence band and conduction band in a material is called bandgap. The energy levels of electrons in the outermost orbitals form the valence band and conduction band is the energy level to which electrons excite for making the material conductive. It is not occupied by any electron in the ground state. For organic semiconductors, this energy gap is described as the energy difference between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). The energy required to excite an electron from HOMO to LUMO is specific to the material. The energy of electromagnetic radiation (E) is related to its wavelength (λ) by the following relation:

$$E = \frac{hc}{\lambda}$$

Where h is the planks constant and c is the speed of light. When the electrons absorb photons with energy greater than the material's energy gap, they are excited to LUMO from HOMO leaving holes behind. The internal electric filed prevents the excited electron from recombining with the holes. This movement of electrons and holes generates the current and the energy band gap of the material produces the voltage.

1.2 Perovskite

In 1839 the crystal structure of Calcium Titanate was discovered by German mineralogist Gustav Rose and was named after Russian mineralogist Lev Perovski as "Perovskite". Since then all compounds with the same crystal structure are referred to as perovskites. The general chemical formula of perovskite is ABX₃, where A and B are cations of different sizes and X is an anion. ABX3 structure consists of cornersharing [BX6] octahedra as shown in the fig. 1.1. The eight octahedra

Form a site in the middle of the cube which is occupied by A cation with 12-fold coordination.



Figure 1.1: structure of Perovskite ABX₃

The ideal structure of Perovskite illustrated in Fig. 1.1[1] has a cubic lattice although the unit cell of most perovskites is slightly distorted caused by different combinations of ion radii and steric constraints. Only SrTiO₃ possesses a perfect cubic unit cell.

In Perovskite structure, *A* or *B* lattice positions can be occupied by all the elements except noble gases. The ratio of ionic radii of *A* and *B* cations determines the stability of the structure. Not only size but the nature of A and B atoms determine the structure. If the "A" cation is monovalent, then the "B" cation must be divalent if "X" is a halogen and all sites are fully occupied.

In the generalized Perovskite structure ABX₃, on the basis of selected A, B & X keeping in mind the stable stoichiometry we can categorize perovskites as following

• According to the representation of X

1. Oxide-based Perovskites: In these, X is represented by element Oxygen and A & B can be either inorganic or organic-inorganic compounds.

- Halide-based Perovskites: Here X is represented by Halide ions (Cl⁻, Br⁻ and I⁻) and A & B are the same as Oxide-based. These are the most promising materials for PSCs.
- According to the representation of A & B
- 1. Inorganic Perovskites: In these, both A & B are inorganic compounds e.g. CsSrI₃.
- 2. Organic-inorganic (Hybrid) Perovskites: The most studied PSCs are organic-inorganic halide perovskites based in which A is a monovalent organic cation $(CH_3NH_3^+ = MA^+, CH(NH_2)_2^+ = FA^+)$ but may also have some sites occupied by inorganic metal cation $(Cs^+ \text{ and } Rb^+)$, B is a divalent metal cation $(Pb^{2+}, Sn^{2+}, Ge^{2+}, Mg^{2+}, \text{ and } Ca^{2+})$ and X is a halide ion, e.g. MAPbI₃, FAPI₃.

1.3 Hybrid Organic-Inorganic Perovskites (HOIP)

It all started when in 2012; M. Grätzel and N. G. Park et al. made PSCs device using methylammonium lead iodide (MAPbI₃) perovskite films as the photoactive absorber layer and achieved an efficiency of 9.7% [9]. Although MAPbI₃ is considered as a great light harvester, it suffers from a harmful 56 °C tetragonal-cubic phase transition at approximately while the operational temperature of solar cells is considered up to 85 °C. Due to this phase transition, the band structure is affected and the band gap of MAPbI₃ due to Shockley-Queisser theory causes negative impacts on photovoltaic behavior. Due to all these issues, the attention is diverted to formamidinium lead iodide (FAPbI₃) [10, 11].MAPbI₃ and FAPbI₃ have been extensively studied both theoretically and experimentally in recent years [12, 13]. The perovskites have become promising material for PSCs due to following advantages:

a) *Tunable Band Gap*: Schokley-Queisser (SQ) limit is the maximum theoretical value for efficiency of a solar cell using a single p-n junction. Rühle *et al.* [14] calculated t to be 33.7% at 1.34 eV. A study [15] has shown that varying the halide composition between iodide and bromide in

The methylammonium trihalide system the bandgap can be tuned between 1.55 and 2.3 eV, which can be used for variation in color and for incorporating in multi-junction solar cells but for a single junction solar cell the optimal bandgap is between 1.1 and 1.4eV. Although by changing the size of A cation by using formamidinium narrows the bandgap to 1.48eV [16] bringing it closer to the ideal bandgap.

a) Diffusion lengths exceed 1 µm for electrons and holes [17].

b) Low- cost, easy and scalable manufacturing process.

1.4 Degradation in Perovskites

a) Degradation due to moisture: When exposed to humidity methylammonium based perovskites degrades which was recognized as the main extrinsic factor for degradation of PSCs. It exhibits intrinsic thermal instability due to its low formation energy and volatility of the organic cations [18, 19]. The formamidinium (FA)-based FAPbI₃ perovskite, although more thermally-stable than MAPbI₃, has both a photoactive trigonal α -phase and an undesired hexagonal δ -phase. The photoactive trigonal α phase tends to convert to the δ -phase at room temperature, and this conversion is accelerated in the presence of moisture [20]. Although with a molecule passivated 3D/ Ruddlesden-Popper (R P) heterostructure Niu et al [21] achieved a PCE as high as 20.62% and remarkable long-term ambient stability with a t_{80} lifetime more than 2880 hours without encapsulation which is exceptional for PSCs but quite low when compared to 20000 hours lifetime of Silicon solar cells.

b) *Thermal degradation*: Typically, device temperatures can reach over 45° C higher than ambient temperatures when solar cells operate under direct sunlight. According to International Standard long-term stability at 85° C is required to compete with other solar cell technologies. Therefore, the study of the thermal stability of PSCs is utterly important for their commercialization. The surface of MAPbI₃ is degraded at a temperature as low as 85° C and the exact mechanism for degradation is

Still debated upon but the remarkable light harvesting properties of the material is lost over time because it degrades into PbI_2 after a little loss of MAI (CH₃NH₃I). This degradation from MAPbI₃ to PbI2 is believed to occur by a release of gases i.e. ammonia & methyl iodide via simple sublimation. The first step during the thermal degradation of MAPbI₃ is shown in reaction 1 and the second reaction shows the further decomposition of MAI under an inert atmosphere which proceeds as:

$$CH_3NH_3PbI_3 \rightarrow CH_3NH_3I + PbI_2 \qquad \dots (1)$$

$$CH_3NH_3I \rightarrow NH_3 + CH_3I$$
(2)

After this NH₃ and CH₃ gases evaporate from the structure leaving only PbI₂ as residue. But Cs+ & formamidinium cations are the possible replacement for the methylammonium cation. Cesium lead halides & FA lead halides are stable up to temperatures of 300° C & 200° C [23, 24]. However, as mentioned above pure FAPbI3 undergoes a phase transition to a hexagonal structure when cooled to room temperature called as δ -phase which is yellow & not photoactive. But by blending formamidinium with methylammonium this transition can be reduced to a great extent [25, 26].

1.5 Perovskites in Photovoltaics



Figure 1.2: Basic layered structure of a PSC

The basic structure of a Perovskite solar cell is shown in Fig 1.2. The lowest layer is a transparent electrode which has ITO or FTO on a glass. The radiation first goes through this layer. Over it is the ETL sometimes also called as electron collection layer where electrons enter from the absorber layer, transported through it and collected by the ITO/FTO. They are usually transition metal oxides (TiO₂, SnO₂, etc.) and metal oxide nanoparticles. On top of the ETL is Perovskite which is the active layer where the incident photons are absorbed and an electron-hole pair is generated. On top of it is the HTL which extracts holes from the perovskite and lastly, there is a metal electrode usually made of gold on the very top. To create a closed circuit for operating the solar cell, the transparent and gold electrodes are connected with a load in between. When the radiation is incident upon the junction, the generated charge carriers flow through the circuit generating a photocurrent in the circuit and a voltage across the load.

1.6 Interface engineering in PSCs using polymer

Formation of large pinholes has been observed in the perovskite layers [27] which can produce shunt-leakage thus reducing the photovoltaic performance. Because of these the HTL and ETL might come in direct contact and act as a parallel diode thus decreasing the open-circuit voltage and fill factor of the cells because of the increased recombinations. Also, degradation in the performance of the solar cells occurs due to non-radiative recombination losses caused by surface traps [28]. A compact layer of polymer like PMMA has been widely used to protect devices from oxygen and moisture [29]. Wang et al. reported an improvement in the photovoltaic performance and stability of MAPbI₃ based PSCs with the use of a PMMA layer between the perovskite and spiro-OMeTAD [30].

1.7 Motivation

PSCs have stability challenges with all major environmental stress factors namely oxygen, humidity, light and temperature. Under operation, a solar cell is exposed to cyclic temperature variations during day and night which affect its performance. Studies have shown a temperature variation induced performance decline which is unique to PSCs. This is a major hindrance in their commercialization so to tackle this issue we plan to fabricate PSCs which are more stable when exposed to temperature variations. We plan to do this by using a standard PSC architecture ITO/ SnO₂/ Perovskite/Spiro-OMeTAD/Au and add another layer of PMMA polymer which has already shown stability against moisture. This layer will be optimized to obtain a more temperature stable PSC.

CHAPTER 2

Theory

2.1 Solar cell characteristics



Fig 2.1: (a) Equivalent circuit of a solar cell (b) I-V plot of a diode and a solar cell Fig. 2.1(a) shows the equivalent circuit of a solar cell [31] and using Kirchoff's current law we can write:

$$I = I_o - I_{ph}$$

Where I_o is the diode current and I_{ph} is the photocurrent generated in the cell. So net current I is diode current decreased by an amount of photocurrent. We can see from the fig. 2.1(b) [31] that due to this decrease in this current the I-V curve is shifted to the fourth quadrant and now has a finite area under the curve. Since the area under the I-V curve gives power it tells us that now the power is generated from the solar cell. The photocurrent is directly proportional to the intensity of the incident light.



Figure 2.2: I-V plot of a solar cell indicating MPPs

From the fig. 2.2, Short circuit current (I_{sc}) is the current which flows through the circuit when the two electrodes of the cell are shorted making the voltage zero and open circuit voltage (V_{oc}) is the voltage across the cell when the circuit is open. The current and voltage value on the curve at which maximum power is generated from the solar cell is $I_{m\&} V_m$ and that point on the curve is called as a maximum power point (P_m) . A solar cell is characterized by four parameters, two of them are $I_{sc} \& V_{oc}$ another two are fill factor & efficiency. Fill factor is given by:

$$F.F = \frac{I_m V_m}{I_{sc} V_{oc}}$$

And efficiency is given by:

$$\eta = \frac{I_{sc} * V_{oc} * F.F}{E * A_c}$$

Where E is the incident radiation flux and A_c is the active area of the cell.

2.2 Choosing the right layers for PSCs

The layers in perovskite solar cells are carefully chosen according to their band energy compared to the adjacent layers because when electrons are excited they will always try to minimize the energy by recombining with holes. But another property of the charge carriers is that they will always prefer the path of minimum resistance. So if the right layer structure is chosen, recombination can be decreased if charge carriers are made to take



Figure 2.3: Energy band diagram of PSC's layers

a different route. This is done by selecting an ETL which is having its LUMO lower than the LUMO of perovskite thus making a more attractive way for an electron to go. The same idea applies for the selection of HTL in which its HOMO should be higher than the HOMO of perovskites creating a more attractive way for holes to go. The same concept should be applied to all the layers of the PSC for the chain transportation of the charge carriers to occur as shown in fig. 2.3.

2.3 Hysteresis in PSCs

For the JV characteristics measurement is done in two directions, starting from the maximum preset value voltage towards the minimum preset value called as backward direction or vice-versa which is the forward direction. In PSCs, these two curves do not overlap as shown in fig. 2.4.1 which in turn gives two different values for each cell parameter. This is called hysteresis in PSCs. One of the most accepted reasons for it to happen is the ion migration. Weber et al. proposed the following mechanism for explaining the hysteresis [32].



Fig 2.4: (1) JV characteristics of a PSC showing hysteresis. **(2)** Proposed mechanism of hysteresis: (a) The perovskite layer has no internal field in equilibrium (b) When an electric field is applied, it is screened by the mobile Iodide ions released from the perovskite at the anode interface and positive ions are adsorbed at the cathode interface. (c) The entire electric field is screened by these charges and the net potential across the perovskite layer becomes flat. (d)When the external field is switched off, this reverse internal electric field helps in driving electrons and holes towards the anode & cathode [32].

The presence of strong hysteresis in PSCs can be directly explained by the dynamics of the internal electric field. During the forward scan, the applied electric field across the device drives electrons and holes to the opposite electrodes which reduce the extraction efficiency (Fig. 4.2a&b). When the electric field is relaxed in the perovskite, it was proposed that the charge distribution freezes at the spiro-OMeTAD/perovskite interface because the ions get adsorbed (Fig. 4.2c). During the downward scan, this stabilized charge distribution induces a strong reverse field which aids in the charge extraction thus generating a higher photocurrent (Fig. 4.2d).

2.4 Box plots

These statistical plots are a way to show the distribution of data based on a six number summary which includes minimum value, first quartile $(25^{th}$ percentile), second quartile $(50^{th}$ percentile) & third quartile $(75^{th}$

Percentile) together forming the interquartile range, maximum value, median value and mean value. These can be seen in fig. 2.5. We used it because it makes comparison across groups easier.



Fig 2.5: Box plot

CHAPTER 3 Experimental Techniques

3.1 Cell fabrication

Materials: 120 nm thick ITO layer coated on glass $(15\Omega m^{-2} \text{ sheet})$ resistance, Luminescence Technology, CAS: 50926-11-9), aqueous colloidal dispersion of SnO₂ nanoparticles 15 wt% (Alfa Aesar), 0.4mmol lead Iodide (TCI), Formamidinium Iodide (GreatCell Solar), Solar), Methylammonium bromide(GreatCell Methylammonium chloride((GreatCell Solar), Butylammonium bromide(GreatCell Solar), Butylammonium iodide(GreatCell Solar), all the following solvents are from Sigma Aldrich: acetone, IPA DMF, DMSO, ACN, GBL, CB were used without any purification, DI water, PMMA spiro-OMeTAD (Luminescence Technology), Lithium bis(trifluoromethanesulfonyl) imide, 4-tert-butylpyridine, gold nuggets.

3.1.1 Solution Preparation

- a) SnO₂: Precursor solution with concentration of 2.04 wt% was prepared: by diluting colloidal dispersion of SnO₂ in DI water.
- **b) PbI₂:** We prepared a 1.2M solution in a solvent mixture of DMF: DMSO 19:1(v/v). It was shaken and heated at 70°C until completely mixed and then left overnight for the particles to settle down. The solution was filtered just before use.

- c) Standard cation solution: 60mg Formamidinium Iodide, 6mg Methylammonium bromide, and 6mg Methylammonium chloride were mixed in 1ml IPA.
- **d) PMMA solution:** Two solutions with PMMA were prepared with concentrations 0.1mg/ml and 0.21mg/ml with CB as the solvent.
- e) Spiro-OMeTAD solution: 17.5 μ L lithium *bis*(trifluoromethanesulfonyl) imide (520 mg mL-1 in acetonitrile) and 4-*tert*-butylpyridine (28.5 μ L) were added with 80mg spiro-OMeTAD and dissolved in 1 mL chlorobenzene.

3.1.2 Cutting and cleaning of the ITO & FTO substrates

ITO coated glass come in 64mm x 64mm sheets which we cut into sixteen 16mm x 16mm substrates. Cleaning was performed in the following steps:

- 1.) Substrates were washed in DI water to remove any small glass pieces stuck to them.
- After that, they were ultrasonicated in acetone for 7 minutes and then dried with a nitrogen gun.
- 3.) In this step, they were again ultrasonicated with IPA for 7 minutes and dried with a nitrogen gun.
- 4.) In this final step, substrates were treated with oxygen plasma for 3 minutes.

3.1.3 Spin Coating Technique

It is the most common technique used for depositing thin films on the substrates. The apparatus used for it is called a spin coater. It has the ability to produce thin uniform films easily with varying thickness from nanometer to micrometers in range. It is widely used in semiconductor industries and other technological areas.

Working Principle: This technique uses centrifugal force to spread uniform films on flat substrates. A solution of material is dispensed onto

the center of the substrate, which is then rotated at high speed. Rotation is continued until the excess solution flung off the substrate and a film of desired thickness is achieved. Spin speed, acceleration, time of deposition and viscosity of the solution defines the film thickness. Evaporation rate of the solvent and wettability also affect the film quality. Although some part of the solvent evaporates while spinning but usually substrates are annealed to evaporate the residual solvent. There are two common methods of dispensing, static and dynamic. In static, the puddle of fluid is first dropped and then the substrate is spun but in dynamic the fluid is dispensed on a spinning substrate which is helpful when the fluid or substrate has poor wetting abilities.

3.1.4) Deposition of the layers

a) SnO_2 : This ETL was deposited on the substrate by spin coating at 4000RPM for 30s followed by annealing at 250°C for 30 minutes in ambient air condition (30-40% humidity). and oxygen plasma treatment for 1 minute.

b) **PbI₂:** We use a two-step process for spin coating perovskite. In this first step, PbI_2 was spin coated at 1500RPM for 30s and afterward annealed at 70°C for 1 minute in an inert atmosphere.

c) **Cation mixture**: This is the second step in which the cation solution was spin coated at 1300RPM for 30s in inert atmosphere followed by annealing at 150° C for 15 minutes in ambient air condition (30-40% humidity).

d) **PMMA**: We deposited it by dynamic dispensing for spin coating at 4000RPM for 30s followed by annealing at 80°C for 6 minutes in an inert atmosphere. Although its annealing was not performed in some experiments and directly Spiro-OMeTAD was coated over the perovskite.

e) **Spiro-OMeTAD**: This was spin coated at 4000RPM for 30s and left for oxidation in dry air for 12-14 hours.

- f) **Contact swiping**: Edges of the substrate were swiped with GBL to remove the spin-coated layers and form contacts.
- g) **Gold (Au) evaporation**: Au electrode with a thickness of 60nm was deposited by thermal evaporation through shadow masks to define the active area to 10.5 mm².



Figure 3.1: Fabrication of solar cell

3.2) Device characterization

3.2.1) Current density – Voltage (J-V) measurements

Newport solar simulator (Oriel Sol3A) providing an AM1.5G solar irradiation spectrum was used to measure J-V characteristics in both forward and backward directions. We used a certified Si photodiode (Fraunhofer ISE) to calibrate it, equipped with a KG5 bandpass filter.

For measuring the stable PCE of perovskite solar cells, the power output at a constant voltage close to the maximum power point was determined. A Peltier element connected to a microcontroller kept the temperature of the device at a constant value of 25°C while conducting the J-V analysis and MPP tracking.

3.2.2) X-ray diffraction (XRD)

XRD is a common & powerful nondestructive technique for characterizing crystalline materials. It provides information on various structural parameters such as structures, grain size, crystal defects, unit cell dimensions & phases.

Working Principle: For X-ray wavelengths, crystal structure acts as a 3-D diffraction grating so when they are incident on the sample they are scattered at specific angles from the set of lattice planes. If these scattered beams interfere constructively X-ray diffraction peaks are produced. The distribution of the atoms within the lattice decides the peak intensities and since this distribution is specific to the structure, XRD acts as a fingerprint of periodic atomic arrangements. The condition for constructive interference is given by Bragg's law:

$$n\lambda = 2 d_{hkl} \sin \theta$$

where 'n' is the diffraction order(an integer > 0), ' λ ' is the wavelength of the incident X-ray, 'd' is the interplanar distances of the lattice planes hkl & ' θ ' is the angle of incident beam to the same set of lattice planes. Fig. 4.2 shows the X-ray diffraction in atomic planes



Figure 3.2: Schematic of X-ray diffraction

3.2.2.1) Instrumentation

X-ray diffractometers consist of three elements: an X-ray tube, a sample holder and a detector. For generating X-rays, the filament in a cathode ray tube is heated to produce electrons which are then accelerated towards the target by applying a voltage. Characteristic X-ray spectra are produced when accelerated electrons with sufficient energy bombard the target material and knock out the inner shell electrons. Copper with K_{α} radiation, $\lambda = 1.5418$ Å is the most common material for single-crystal diffraction. Those X-rays are then collimated and directed towards the sample which is rotated along with the detector and intensity of reflected X- rays are recorded. If those reflected rays interfere constructively, a peak

in intensity occurs. The detector detects and processes this X-ray signal which is converted to a count rate and then output to the user. Collimated X-ray beam hits the rotating sample at an angle θ and the detector collects the diffracted beams while rotating at an angle of 2θ as shown in figure 3.3.



Figure 3.3: Basic components of an X-ray diffractometer

3.2.3) Scanning electron microscope (SEM)

SEM is basically a high-resolution version of an optical microscope which takes highly magnified images of solid samples using focused scanned electron beam and can also determine the composition of the samples. We used the most common mode of SEM i.e. secondary electron image which is a map of secondary electron emissions as a function of spatial position. Since these emissions are dependent on the angle between the surface and the beam, it displays the topography of the sample.

Working Principle: Primary electrons are bombarded on the sample generating low energy secondary electrons which gives the topographic nature of the specimen.

3.2.3.1) Instrumentation

At first, an electron optical system is used to produce probe electrons which consist of an electron gun, a condenser lens, an objective lens, and a scanning coil. The electron gun produces the electron beam and the lenses are used to focus & control the diameter of the beam. After that, there is a specimen stage to place the specimen and then a secondary electron detector to collect secondary electrons. This data is shown as an image on The display unit is connected to an operating system for performing various operations. The schematic diagram is shown in figure 3.4.



Figure 3.4: Basic construction of an SEM (*Image source: www.jeol.co.jp*)

CHAPTER 4

Results and discussions

Firstly we tried to optimize the cations mixture in our cells. We took the recipe used by Jiang et al [33] and made more cation mixtures by varying its concentration and also by adding other cations. PSCs prepared from these seven cations were illuminated under the solar simulator and their solar cell characteristics were compared using statistical box plots. After selecting the best performing cation we went on checking the thermal degradation in our cells. In all the thermal stability testing experiments HTL and the top electrode are not included. We heated the perovskite coated substrates on a hotplate at 150°C for different time durations and compared their performance. For the next experiment, we introduced a layer of PMMA coated without post-annealing between perovskite and spiro-OMeTAD. We saw an improvement in the performance compared to the standard architecture with that so we went on to test two different concentrations of PMMA and also post-annealed it. The results clearly showed that annealing PMMA has given better performance than the nonannealed. Even though the post-annealing duration was only 6 minutes we came to know that thermal stress has improved the performance of the cells with PMMA. So for the next experiment, twe heated perovskite at 50°C with & without PMMA for different time durations going up till 14 hours where we saw an improvement in V_{oc} in the cells heated overnight with PMMA compared to the reference. The accepted minimum standard for the operational temperature of solar cells is 85°C so we repeated our last experiment but this time the perovskite heating temperature was

100°C.This time also we saw a significant improvement in the performance when PMMA was used thus with our architectural changes we have made the cells less prone to thermal degradation. We used two characterization techniques i.e. FESEM and XRD on the substrates from our last two experiments. FESEM images have been analyzed for the morphological changes in perovskite structure and also the difference in lead content can be seen on the surface. With XRD plots the difference in peak intensity of lead iodide and perovskite the degradation in the perovskite layer was analyzed.

4.1) Comparison of cells fabricated with different cations combinations

In this experiment, we used seven different cation solutions to process perovskite solar cells. Following are the compositions of the cations. The recipe of cation 5 is from Jiang et al. and all others are variations in that recipe. These compositions are mentioned in this section for the ease of comparison with the box plots.

Cation 1	119.1mg FAI, 12mg MABr, 12mg MACl &1mg BAI mixed in
	1mL IPA
Cation 2	117.4mg FAI, 12mg MABr, 12mg MACl &3mg BAI mixed in
	1mL IPA
Cation 3	120mg FAI, 11.3mg MABr, 12mg MACl &1mg BABr mixed in
	1mL IPA
Cation 4	10% increase in the concentration of cation 5
Cation 5	60mg FAI, 6mg MABr &6mg MACl mixed in 1mL IPA
Cation 6	5% increase in the concentration of cation 5
Cation 7	5% decrease in the concentration of cation 5

Table 4.1: Compositions of the cation mixtures

Following are the box plots of backward power conversion efficiencies (PCE) & ratio of forward & backward efficiencies for the cells based processed with these cations. The experiment was performed in two



Batches. In the first one cations 1, 2, 3 & 5 and in the second one cations 4,5,6 & 7 were used. All the solutions and processing were the same except the cations.

Figure 4.1: Box plots for cation optimization: (a &b) Backward efficiency plots, (c& d) Efficiency ratio (forward/backward) plots, (e & f) normalized backward PCE and PCE ratio plots. All the values normalized with the average value of cation 5 for each day.

From the two backward PCE plots, we can see that cation 1, 2, 5 & 7 have similar and highest average values. PCE ratio plots tell about the hysteresis in the device, if the ratio value is one it means there is no hysteresis and if it is less than one (or greater than one) it means hysteresis (reverse hysteresis) is present. In those plots cation 1, cation 2,

cation 3 and cation 7 have average values less than one signifying the presence of hysteresis. Cation 1 & 2 have an almost equal amount of FAI, MACl & MABr but cation 2 has three times the BAI in cation 1. Butylammonium which is a very big cation when used in perovskites does not get embedded in the 3D structured perovskites like FAI, MABr, and MACl but forms a separate layer [34] and are called 2-D perovskites. The thickness of this layer depends on the concentration of 2-D cation used. We suspect that the 1mg value of BAI was excessive for the cation mixture which has formed a thicker layer than required thus causing an imbalance in the charge carrier transfer, as a result, causing hysteresis. As for the cation 3 due to the higher content of BAI more hysteresis is present. In cation 3 also FAI, MABr, and MACl content are almost equal to the cation but the difference here is the use of BABr instead of BAI both of which were used in the same amount of 1mg. The possible reason behind it can be the size of BABr which is less than BAI thus the 2-D layer formed is less thick thus causing less hindrance. In the case of cation 7 the concentration of cation is less compared to the standard cation 5 which means more PbI₂ was present in the perovskite comparatively which has more crystalline structure compared to the cation so it aids in ion migration [33] thus causing more hysteresis.

The conclusion from this experiment is that cation has performed well with high PCE and negligible hysteresis so we will use it as the standard cation for our future experiments.

4.2) Applying thermal stress on PSCs for various time durations

In this experiment, we wanted to study the effect of thermal stress i.e. temperature on the perovskite layer. After the formation of perovskite layer on the substrate, we heated substrates at 150°C for different time durations and compared their performances. The parameters in the following experiment used in the box plots are

ref	Reference cells
10min	Cells with perovskite layer heated for 10 minutes at 150°C
60min	Cells with perovskite layer heated for 60 minutes at 150°C
834min	Cells with perovskite layer heated for 834 minutes at 150°C

Table 4.2: Heating time durations at 150°C



Figure 4.2: Box plots for thermal degradation at 150°C: (a) PCE backward plot (b) PCE ratio plot (c) V_{oc} backward plot (d) J_{sc} backward plot

The decline in the PCE backward value with increasing time duration of heating clearly shows the effect of thermal degradation in perovskite solar cells. The same trend of performance decline can also be seen in V_{oc} and J_{sc} also but an interesting trend can be seen in the PCE ratio plot which is the reversal of hysteresis when the substrate is heated for 834 minutes. As discussed earlier in the degradation of perovskites that when MAPbX₃ based perovskites are heated CH₃X & NH₃ evaporates and PbI₂ is left as residue.

When our perovskite was heated for 834 minutes almost all of the perovskite was degraded to PbI_{2} and probably an energetic extraction level is formed at the ETL/ perovskite interface due to a mismatch in their energy level alignment. This causes the pile-up of photogenerated charges at barrier under the reverse scan. This reduces the built-in potential and charge transfer causing more recombination thus lowering $V_{oc} \& J_{sc}$ during the reverse scan in J-V curves. So the ratio of forward & backward becomes greater than one which we call reverse hysteresis.

4.3) Adding a layer of polymer PMMA between Perovskite and spiro-OMeTAD

In this experiment, we introduced a layer of PMMA (0.1 mg/ml) between SPIRO and perovskite. It was not post-annealed Also we tested a new batch of SnO_2 compared with an old batch. The parameters of the experiment are:

nps	new SnO ₂ with PMMA& SPIRO
ns	new SnO ₂ with SPIRO only
ops	old SnO ₂ with PMMA& SPIRO
OS	old SnO ₂ with SPIRO only

Table 4.3: Parameters for cells with & without PMMA



Figure 4.3: Box plots for the introduction of the PMMA layer: (a) PCE backward plot (b) V_{oc} backward plot

The most prominent result among these graphs is the increase in V_{oc} when PMMA is used. Fig. 4.4 shows the perovskite solar cells with and without a PMMA layer based on the results of Wang et al. with a carrier dynamics model [30].



Figure 4.4: (a) PSC layered structure without PMMA (b) PSC layered structure with PMMA

We can see in the fig. 4.4(a) that the pinholes and grain-boundaries in the perovskite solar cells are filled by spiro-OMeTAD. This may cause a direct connection between the HTL & ETL which will reduce the built-in potential of the cell. The holes transporting through the HTL have a tendency to combine with the electrons because of these pinholes causing carrier recombination losses. Also, electron extraction is reduced because of non-radiative recombination due to the trap states. PMMA, on the other hand, fills the pinholes and grain boundaries and also since it an insulator it prevents the shorting of ETL & HTL and passivates trap states which reduce the recombination losses and increases the V_{oc} .

4.4) Using two different concentrations of PMMA with and without post-annealing

In the previous experiment, we did not post-anneal PMMA after spin coating so we planned to anneal it at 80° C for 6 minutes and also used two concentrations of PMMA (0.1& 0.21 mg/ml). The parameters used in the experiments are

ref	Standard recipe without PMMA
PMMA1	Lower concentration PMMA(0.1) without annealing
PMMA1heat	Lower concentration PMMA(0.1) with annealing
PMMA2	Higher concentration PMMA(0.21) without annealing
PMMA2heat	Higher concentration PMMA(0.21) with annealing

 Table 4.4: Parameters for annealed & non-annealed PMMA with two concentrations

 each



Figure 4.5: Box plots for annealed & non-annealed PMMA with two concentrations each. (a) PCE backward plot (b) V_{oc} backward plot

We can clearly see the improvement in PCE backward & V_{oc} when PMMA is post - annealed compared to the non-annealed. It must have happened because the layer is evenly distributed and a more uniform film is formed compared to non-annealed. Because of this the interface between PMMA and spiro- OMeTAD is improved decreasing the trap states thus decreasing the non-radiative recombinations. There is no significant difference in PCE between the two concentrations but the average V_{oc} is higher with PMMA of 0.21mg/ml so we will use this as the standard concentration for future experiments.

4.5) Heating the substrates with & without PMMA for various time durations at 50°C

Earlier cells with PMMA gave better results when post-annealed for 6 minutes compared to when they were not annealed. Considering that, in the following experiment after 6-minute post-annealing we heated some substrates for longer time durations at 50° C to see that if PMMA still shows better performance. The parameters used in the experiment are

ref	Standard recipe without PMMA
ref60min	Reference cells heated for 60 minutes
ref14hrs	Reference cells heated for 14hours
PMMA	Cells with PMMA & no extra heating
PMMA14hrs	Cells with PMMA heated for 14 hours

Table 4.5: Parameters for cells with and without PMMA heated at 50°C for different times



Figure 4.6: Box plots for cells with and without PMMA heated at 50°C for different

In the PCE backward plot, there is very little difference in the average PCE of all the parameters but in the V_{oc} plot, the cells heated with PMMA for 14 hours have higher average value compared to the average value of reference cell which was heated for 14 hours. One of the two reasons behind it is less thermal degradation of perovskite to PbI₂ when PMMA is present which is evident from the XRD plot below. The diffraction peaks of the plot exactly match with the peaks from Jiang et al. whose recipe we had used for the PSC preparation. We can clearly see from the fig. 4.7 that the diffraction peak of PbI₂ at 12.6° is significantly lower when the PMMA is used and the peaks from the perovskite phases are quite higher which is evident of less thermal degradation with the use of PMMA. The peak for PMMA was not present, maybe because it is a very thin layer.



Fig 4.7: XRD plots of perovskite with & without PMMA heated at 50°C

The second reason is higher crystallinity and bigger grain size with the use of PMMA which can be seen in the FE-SEM images below that means the grain size has gotten smaller with thermal stress for reference cells. Bigger grain size means fewer grain boundaries which reduce the hindrance in charge-carrier transport. Also, the surface looks smoother from the passivation with PMMA which forms a better interface with spiro-OMeTAD thus enhancing the charge transport across it & reducing irradiative carrier recombination. The amount of white phase which is the PbI₂ is very high in the fig. 4.8(a) compared to the negligible amount in fig. 4.8(b) which is consistent with the XRD results.



Figure 4.8: FE-SEM images: (a) Perovskite without PMMA heated for 14 hours at 50°C (b) Perovskite with PMMA heated for 14 hours at 50°C

4.6) Heating the substrates with & without PMMA for various time durations at 100°C

The accepted minimum standard for the operational temperature of solar cells is 85°C so we repeated our last experiment but this time the perovskite heating temperature was 100°C. The parameters of the experiment are:

ref	Standard recipe without PMMA
ref60min	Reference cells heated for 60 minutes
ref14hrs	Reference cells heated for 14hours
PMMA	Cells with PMMA & no extra heating
PMMA14hrs	Cells with PMMA heated for 14 hours

Table 4.6: Parameters for cells with and without PMMA heated at 100°C for different times



Figure 4.9: Box plots for cells and without PMMA heated at 100°C for different durations

We can see from the plot 4.9(a) that the average PCE of the cells from all three reference parameters are almost equal but the with increasing time duration the second quartile is getting wider and moving towards lower values which means some cells have been degraded & are giving lower PCE values. Comparing the average PCE of overnight heated cells the one with PMMA has a higher value. In plot 4.9(b) the average V_{oc} value of 'PMMA14hrs' is significantly higher than the average values of all other parameters. Like earlier the reason behind it is less thermal degradation of perovskite PbI2 is when PMMA is present. It is also evident from the XRD plot.



Fig 4.10: XRD plots of perovskite with & without PMMA heated at 50°C

From the fig. 4.10 we can see the decrease in intensity of diffraction peak belonging to PbI₂ when PMMA is used but the decrement is not much which means a large amount of perovskite is still degraded. This can also be seen from the difference in the diffraction peaks perovskite phase which is not a lot. Still, the significant difference in performance can be because of the presence of this excessive PbI₂ in PMMA coated substrates as Jiang et al. has shown that a moderate residual of PbI₂ enhances performance by passivation of the surface or grain boundary defects but too much PbI₂ left in the perovskite can increase the ion movement which could lead to poor stability. In the SEM images below, it can be seen from the fig. 4.11(a) that most of the area is covered with a white phase of PbI_2 signifying that almost all of the perovskite on the surface is degraded. The amount of PbI_2 white phase visible in the fig. 4.11(b) is less and the amount black perovskite phase is more compared to fig. 4.11(a) which is consistent with the XRD results. Also, the grain size in fig 4.11(b) is bigger which means that PMMA has helped perovskite to retain its crystallinity under thermal stress.



Figure 4.11: FE-SEM images: (a) Perovskite without PMMA heated for 14 hours at 50°C (b) Perovskite with PMMA heated for 14 hours at 50°C

CHAPTER 5

Conclusion and Future scope

5.1 Conclusion

In this project, we started with the recipe from Jiang et al [33] for processing perovskite solar cells and we tried to optimize the cation from it. Six other cations were made by changing the concentrations and compositions of the original mixture. PSCs prepared from these seven cations were illuminated under the solar simulator and their solar cell characteristics were compared using statistical box plots. From this experiment, we saw that the addition of bigger cation like butylammonium to the mixture has increased the hysteresis which could be because of the amount we used was excessive. Also, the cells with cation mixture having less concentration of cation showed more hysteresis than the standard recipe which is due to the excessive PbI_2 in the substrate that promotes ion movement [33]. We concluded that the standard cation recipe gave the best performance and will be used in future experiments. Next, we applied thermal stress on the cells by heating them at 150°C for various time durations and a clear decrease is performance could be seen from the statistical plots. For the substrate heated for 834 minutes the hysteresis was reversed which was attributed to energetic extraction level formed at the ETL/ perovskite interface due to a mismatch in their energy level alignment causing a pile-up of photogenerated charges at barrier under the reverse scan and lowering V_{oc} and J_{sc} during the reverse scan. For next experiment where a layer of PMMA was introduced between the perovskite and spiro- OMeTAD which increased the V_{oc} of the cells compared to the standard recipe because PMMA fills the pinholes and

grain boundaries in the perovskite and since it an insulator it prevents the shorting of ETL & HTL and passivate trap states which reduces the recombination losses. It the last experiment the PMMA layer was not annealed after spin coating so we added post-annealing in the spin-coating process of this layer and we saw an increment in both power conversion efficiency and open-circuit voltage with it compared to the cells with nonannealed PMMA layer. It must have happened because the layer is evenly distributed on heating and a more uniform film is formed compared to non-annealed. Because of this the interface between PMMA and spiro-OMeTAD is improved decreasing the trap states thus decreasing the nonradiative recombinations. This indicated the enhancement in thermal stability of cells because of PMMA. So next We went ahead to apply thermal stress to the cells by heating the perovskite with and without PMMA at 50°C for different time durations going as high as 14 hours. From this experiment, t a clear improvement was visible in efficiency and open-circuit voltages of cells which can be attributed to PMMA helping the perovskite structure to maintain its crystallinity and reducing its degradation to PbI₂. To match with the industry standard for the operational temperature of solar cells which is 85°C we repeated the last experiment with 100°C and saw a more significant improvement in the performance with PMMA. X-ray diffraction (XRD) and Field Emission Scanning Electron Microscope (FE-SEM) characterizations have been done on the overnight heated substrates, one with PMMA on top of perovskite and other with only perovskite from both 50°C and 100°C heating experiments. The XRD plots clearly show the reduced degradation to PbI₂ by a decrement in its diffraction peak intensity when PMMA is used. From the FE-SEM images, the bigger grain size of perovskite with PMMA is clearly visible and also the difference in PbI₂ content can be seen which is consistent with the XRD results. So here we safely conclude that the addition of a PMMA layer between the perovskite and HTL (spiro –OMeTAD) has reduced the thermal degradation in PSCs till 100°C.

5.2 Future Scope

In this project, we have studied the effect of PMMA in reducing the thermal degradation of PSCs but a lot more experimentation is needed to get the best out of PMMA. The process of spin coating PMMA can be optimized by trying out different RPMs, acceleration & time duration of spinning to get the best spin coating parameters which will give a layer thick enough to passivate the pinholes completely but it should not cause insulation between perovskite and HTL. Different post-annealing temperatures and time durations can be tested for optimal values. Also, the concentration of PMMA can be varied more. After all these optimizations I suspect that the thermal stabilizing properties of PMMA can be significantly enhanced. Also, this optimization can be performed on 2D-3D perovskite-based PSCs which are highly moisture - stable so together the cell is less prone to degradation from humidity & temperature. Another thing that can be done is the change of HTL because it is coated directly over PMMA so it may affect the performance of the PSCs.

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