

**Mixed halide perovskite solar cells: Influence of fabrication and post
fabrication conditions on the device performance.**

A Dissertation Presented to
the Faculty of the Department of Physics
University of Houston

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy

by
Aida Torabi
December 2016

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fabrication conditions on the device performance.**

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Abstract

Organic-inorganic hybrid perovskite solar cells have attracted tremendous attention due to the dramatic improvement in efficiency from 3.8% to 22% during the past seven years. The technology, however, faces several challenges such as degradation due to the effect of humidity, hysteresis in the current-voltage characteristics, and lead toxicity. These problems adversely affect the commercial viability. In perovskite solar cells, 2,2',7,7'-tetrakis-(N,N-di-p-methoxyphenyl-amine)-9,9'-spirobifluorene which is generally termed as spiro-MEOTAD, is commonly used as the hole transport layer. It is well known that spiro-OMeTAD shows high conductivity in oxidized form and it needs chemical dopants in order to promote the oxidative reaction between spiro-OMeTAD and oxygen. Some of the common dopants such as tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine)cobalt(III) bis(trifluoromethylsulphonyl) imide (FK dopant) are expensive. Low materials cost and fabrication cost is a pre-requisite for the commercialization of a solar cell technology.

We developed a surface-treatment process for enhancing hole transport properties of spiro. The as-fabricated cells consisting of a spiro layer at the top was treated with an oxygen plasma. This post-fabrication treatment dramatically improved the performance of the cells without causing any degradation. The studies revealed that the enhancement in the device performance was due to increase in the concentration of oxidized spiro-OMeTAD. The presence of oxygen in the spiro-OMeTAD was revealed using XPS studies. Our method of doping could be used as a low-cost alternative to the conventional FK doping. This process is clean, fast, safe and environmentally friendly.

In order to understand the factors influencing the cell performance, we made a comprehensive study on the effect of fabrication parameters as well as post-fabrication conditions. We developed a chamber for the solar cell characterization in a well-controlled atmosphere. Impedance spectroscopy studies were done to understand the carrier transport and recombination characteristics. The studies revealed that charge transport through the bulk was affected by plasma treatment depending on plasma conditions. We attributed it to the interaction of oxygen with perovskite layer. Nevertheless, the spiro-OMeTAD conductivity and charge transfer at interface with perovskite improved with treatment and thus giving a significant overall improvement in the device performance.

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List of publications

1. **A. Torabi**, M. Paulose and O.K. Varghese. “Enhanced efficiency of simple planar perovskite solar cell with short post fabrication oxygen plasma treatment”. (Under preparation).
2. **A. Torabi**, M. Paulose and O.K. Varghese. “Studies on the effect of fabrication and testing atmosphere on the performance of perovskite solar cells”. (Under preparation).
3. M. R. Banki, **A. Torabi**, O.K. Varghese. “Anodically grown functional oxide nanotubes and applications”. MRS Communications. DOI:10.1557/mrc.2016.46
4. M. S. Mohamed, **A. Torabi**, M. Paulose, D.S. Kumar and O.K. Varghese. “Anodically grown titania nanotube induced cytotoxicity has genotoxic origins”. (Scientific reports, revised version submitted).

Conference Proceedings

1. **A. Torabi**, M. Paulose and O.K. Varghese. “Role of Post-Fabrication Treatments on the Performance of Perovskite Solar Cells”. Materials Research Society Meeting, Boston, MA, December 1-5 (2014).
2. **A. Torabi**, M. Paulose and O.K. Varghese. “Role of chlorine in the performance of mixed halide perovskite solar cells”. American Physical Society Meeting, San Antonio, TX, March 2-6 (2015).
3. **A. Torabi**, M. Paulose and O.K. Varghese. “Effect of Ambient on the Performance of Mixed Halide Perovskite Solar Cells”. Materials Research Society Meeting, Boston, MA, November 28- December 2 (2016).

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Abbreviation

Ag	Silver
DMF	N, N-dimethylformamide
DSSC	dye sensitized solar cell
ETM	electron transporting medium
FF	fill factor
FK	tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine)cobalt(III) bis(trifluoromethylsulphonyl)Imide
FTO	fluorine doped tin oxide
FTO	fluorine-doped tin oxide
HCl	hydrochloric acid
HTM	hole transport medium
IPCE	incident photon to current efficiency
I_{sc}	short circuit photocurrent density (mA/cm ²)
I-V	current-voltage
Li-TFSI	Bis (trifluoromethane)sulfonamide lithium salt
OCVD	open circuit voltage decay
PbCl₂	lead chloride
PbI₂	lead iodide
PCE	power conversion efficiency
PSC	perovskite solar cell
PV	photovoltaic
RF	radio frequency
RH	relative humidity
SEM	scanning electron microscopy
Silicon Si	
Spiro-OMETAD	(2, 2', 7, 7'-tetrakis-(N, N-di-p-methoxyphenylamine) 9, 9'- spirobifluorene
TBP	tert-butylpyridine
UV	ultraviolet
V_{oc}	open circuit voltage
XPS	X-ray photoemission spectroscopy
XRD	X-ray diffraction

1. Introduction

1.1. Solar cell technologies

Sustainability demands reduction in greenhouse-gas emission, especially the release of carbon dioxide into the atmosphere beyond a level that can be maintained by the land and ocean uptake.^{1, 2} A paradigm shift from fossil fuels to renewable energy has long been recognized as a solution to this problem. Sun is the largest renewable energy source and hence, future energy system is believed to be primarily based on solar energy. Photovoltaic (PV) technology offers the most-effective means to convert solar energy into electrical energy. An often-quoted metric is that the entire world's energy demand could be met by covering only 0.4% of the earth's surface with 15% efficient PV panels.³ There are three primary factors that decide the commercial viability of a PV technology, which are efficiency, cost and stability. Silicon (Si) technology offers the most desirable characteristics as far all these features are concerned. Since their introduction in the 1950s, Si solar cells have been extremely well studied and rigorously optimized, leading up to a current lab-scale efficiency record of about 25% and a module lifetime of at least 25 years.⁴ This technology holds about 90 % of the market share. Even though the price per watt-peak has decreased to below 1 USD, the achievement of global grid parity is still a challenge. Cost effective thin film technologies such as CdTe/CdS, amorphous silicon and Copper indium gallium selenide (CIGS) were developed at the end of the last century, but only CdTe/CdS technology became true commercial success. Excitonic type technologies such as dye sensitized and organic polymer solar cells also emerged in

recent years as low cost alternative to Si technology. Unfortunately, the record efficiency in these cells is only 12%. Furthermore, poor stability came out as stumbling block in their path to commercialization.⁵⁻⁸ In this aspect, the recently emerged organic-inorganic hybrid perovskite solar cell (PSC) technology is also not better, if not worse, but the certified efficiency of these cells (small area) has reached 22.1%, which is at par with CdTe solar cells. These technologies share the ability to be solution processed from low cost materials and are compatible with flexible solar cell technology. For the perovskite cell technology to be commercial reality, stability must be improved and all process used in the cell fabrication should be fast and scalable.³

1.2. Hybrid organic-inorganic perovskite solar cells

Organic-inorganic halide PSC have quickly become the most efficient of solution-processed PV technologies.^{9,10} Within a short time, it has become the most important new candidate for next generation PVs.¹¹⁻¹⁴ One advantage of perovskite materials over Si and more expensive Gallium Arsenide (GaAs) for large area solar cell application is that they can be solution processed, which allows researchers to use existing solution-deposition methods, such as slot-die coating and roll-to-roll fabrication, for large area PSC fabrication.¹⁵ These cells are able to combine the advantages of both inorganic thin film and organic PVs. The organometal trihalide perovskite absorbers, such as methylammonium lead halide, $\text{CH}_3\text{NH}_3\text{PbX}_3$ ($\text{X} = \text{I}, \text{Cl}, \text{Br}, \text{or I}$), are highly crystalline even when processed at temperatures as low as 70–100 °C.¹⁶ Their favorable PV characteristics include:

1-tunability of optoelectronic properties,¹⁷ which can be done in simple way by tuning the halide anion or the organic cation compositions.¹⁸

2- High optical absorption (absorption coefficient $\approx 10^5 \text{ cm}^{-1}$). This superior light absorption coefficient facilitates creation of a high density of photoexcited charges and use of only sub-micrometer size perovskite film for sufficient light harvesting.¹⁹⁻²²

3- Low exciton binding energy,^{22, 23} $\sim 0.03 \text{ eV}$, so most of them turn to free charges very fast.

4- Long range charge transport.²⁴ Long electron and hole diffusion lengths in thin-film ($>1 \text{ }\mu\text{m}$) and single-crystal ($>175 \text{ }\mu\text{m}$) perovskite enables efficient carrier extraction.²⁵⁻²⁷

5- Efficient charge collection at the contacts.²⁸

Furthermore, this structure is an ambipolar semiconductor, which can transport holes and electrons to their corresponding collector electrode. That is why PSC can operate even when no hole transport layer^{29, 30} or electron conductor^{31, 32} is used. These unique properties combined with its low cost and easy processability make it promising for efficient and cheap third-generation PV solar cells.³³

1.3. Perovskite structure

The mineral perovskite, calcium titanate (CaTiO_3), was discovered in 1839. More recently, the term perovskite refers to any material with the general chemical formula ABO_3 , and similar crystal structure to CaTiO_3 . For the hybrid perovskites, the formula is most often represented as ABX_3 [(Figure 1.1. (a)], where A is a monovalent cation, B is a divalent metal cation, and X is a halogen anion. Given the wide variety of elements

which fit these criteria, it is no surprise that a myriad of different perovskites have been synthesized and characterized.³ The most commonly used organic–inorganic perovskite for semiconductor device applications is generically $\text{CH}_3\text{NH}_3\text{PbI}_{3-x-y}\text{Br}_x\text{Cl}_y$, unit cell of $\text{CH}_3\text{NH}_3\text{PbI}_3$ is shown in [(Figure 1.1.(b)].³⁴

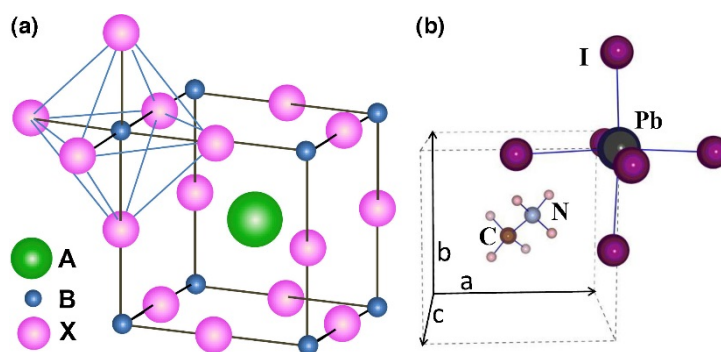


Figure 1.1. (a) ABX_3 perovskite structure showing BX_6 octahedral and larger A cation occupied in cubo-octahedral site. Reprinted with permission from [35]. Copyright (2014) Elsevier Ltd. (b) Unit cell of cubic $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite. Reprinted with permission from [36]. Copyright (2013) American Chemical Society.

1.4. Perovskite cell efficiency limit

The basic structure of solid-state PSC comes from the solid-state DSSC employing organic hole-transport material (HTM) of 2,2',7,7'-tetrakis(*N,N*-dimethoxyphenylamine)-9,9'-spirobifluorene (spiro-MeOTAD).³⁷ A compact TiO₂-blocking layer deposited on a transparent conductive oxide substrate, such as fluorine-doped tin oxide (FTO), followed by mesoporous TiO₂ as the electron-transporting material (ETM).¹⁸

CH₃NH₃PbI₃ was first used in DSSCs by Myasaka et al.³⁸ and delivered only 3 % PCEs, partly because the perovskite was unstable in the liquid redox electrolyte used in DSSCs; the perovskite degraded during characterization. When the liquid electrolyte was replaced by a solid-state hole transporter however, Park and co-workers^{39, 40} were able to achieve PCEs over 10% without any observable degradation on the short time scale. Since then there has been a surge of research activities on perovskite solar cell due to superb photovoltaic performance.⁴¹ Shortly thereafter, a meso-superstructured solid-state PSC employing Al₂O₃ as a scaffold layer was reported⁴², where the thin perovskite layer transported photoexcited electrons that were collected by an electrode via a thin hole-blocking TiO₂ layer. As a result, a certified PCE of 22.1% was reported in 2016 on the National Renewable Energy Laboratory's best efficiencies chart.⁴³ Unlike other devices on such a chart, PSCs are marked as 'not stabilized', indicating that validations with stable devices are still required.⁴⁴

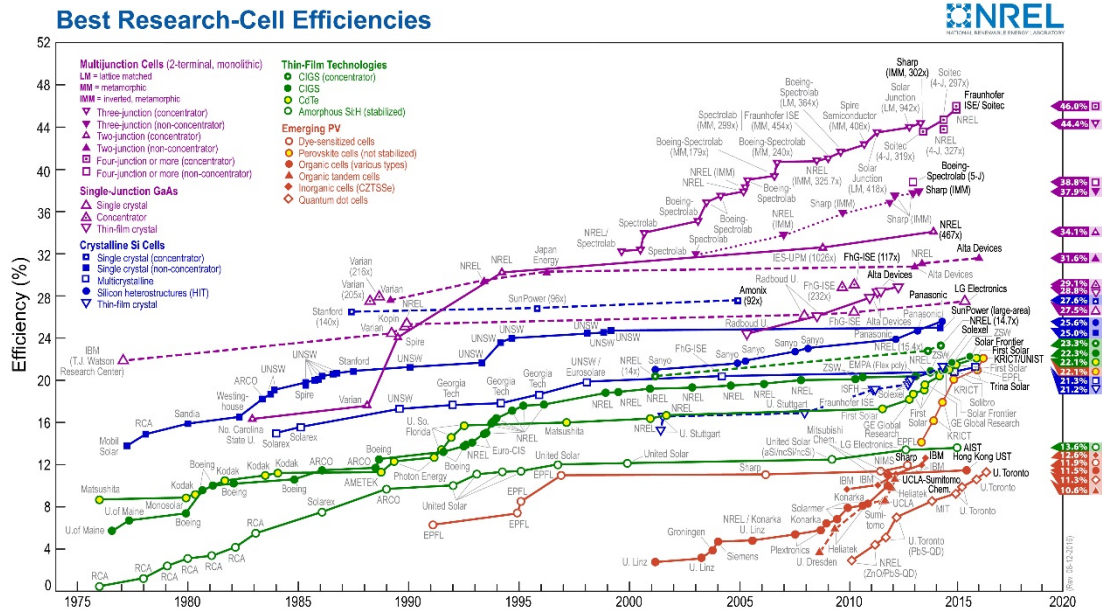


Figure 1.2. National Renewable Energy Laboratory's best-efficiencies chart, 2016. ¹¹

The PCE limit of the perovskite cell is about 31%, which approaches the Shockley-Queisser limit (33%) achievable by gallium GaAs solar cells. Compared to 500 nm-thick flat GaAs solar cells with fill factor (FF) of 0.89, open-circuit voltage (V_{oc}) of 1.16 V, and short-circuit current (I_{sc}) of 29.5 mA/cm², perovskite cells have comparable FF, larger V_{oc} , and smaller I_{sc} .⁴⁵

1.4.1. Device configuration

All solid-state organometal perovskite solar cells can be divided into two categories (Figure 1.3.). The first type belongs to the mesoporous metal-oxide heterojunction

perovskite solar cells, in which nanoparticle films of metal oxides, such as TiO_2 , ZnO and Al_2O_3 ,⁴⁶⁻⁴⁸ serve as scaffolds for more perovskite loading and/or as ETM [Figure 1.3. (a)]. The second class will be the planar [Figure 1.3. (b)] perovskite solar cells,⁴⁹ in which both carriers are generated and transported in the perovskite itself to respective electrodes.⁸ TiO_2 nanoparticle scaffold layer is absent and the perovskite absorber layers are directly deposited on TiO_2 compact layer.⁵⁰

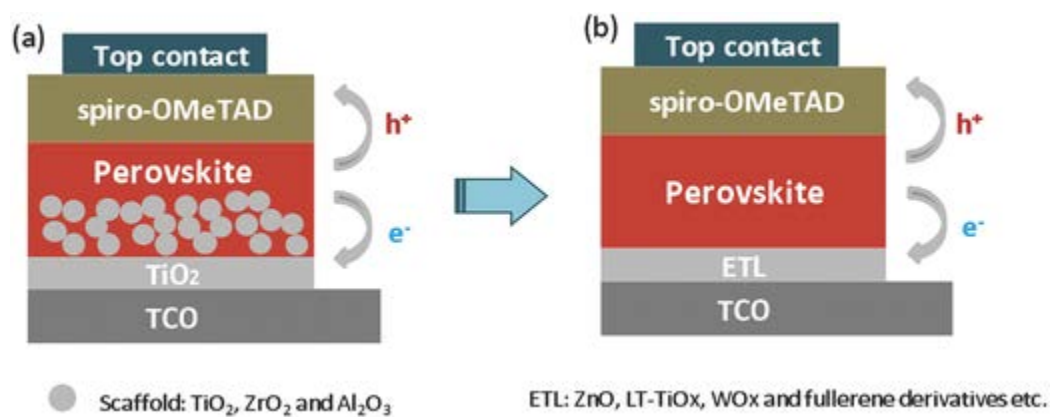


Figure 1.3. Device configurations of a) mesoscopic and b) planar perovskite solar cells. Reprinted with permission from [51]. Copyright (2015) WILEY-VCH Verlag GmbH & Co.

1.5. Device-fabrication methods

Perovskite films can be deposited easily onto the substrates via various methods such as solution method which can be described as one-step or two-step solution deposition⁵²⁻⁵⁵ or by vapour deposition method.^{56,57} There has been a rapid development and understanding in both methods. With the one-step method, Snaith and coworkers showed the importance of the coverage with perovskite layers to get high V_{oc} .⁵⁸⁻⁶⁰ Seok and coworkers achieved the 17.9% PCE with additional solvent engineering.⁶¹ These studies suggested that an optimum structural design of the perovskite layers is the key factor to get high efficiency. The two-step method is another way for reproducible deposition of perovskite layers which was reported by Burschka et al.⁵⁴ It is known that this technique enables an excellent coverage of perovskite absorbers on the mesoporous-TiO₂ surface, which leads to a high PCE.⁶³ The perovskite layer can be fabricated by methods such as vacuum evaporation,⁶⁴ vapor assisting⁶⁵ which can result in an extremely homogeneous perovskite layers⁶⁶ but it is likely to increase the manufacturing cost. So the solution preparation methods still receive much attention.⁶⁷

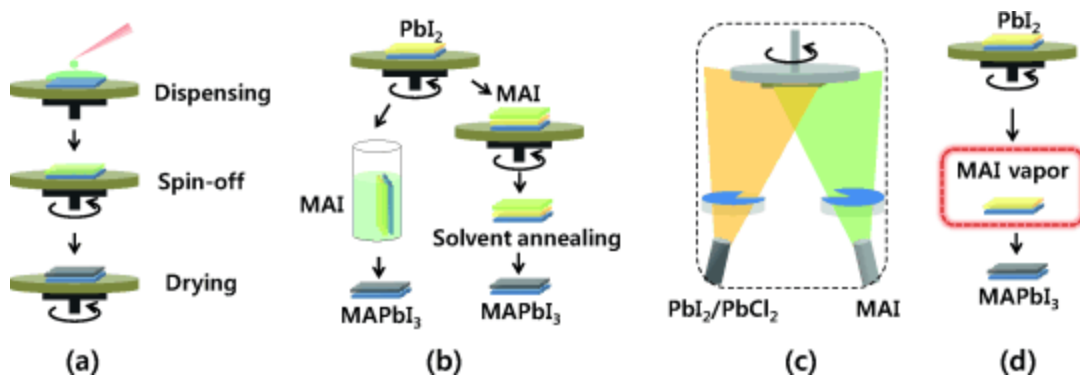


Figure 1.4. Schematic of different deposition methods for perovskite (a) One-step spin-coating method; (b) sequential deposition method; (c) dual-source vapour deposition; and (d) vapour-assisted solution process. Reprinted with permission from [68]. Copyright (2015) WILEY-VCH Verlag GmbH & Co.

1.6. Challenges in the field

Despite the inspiring results and impressive efficiency achieved, a deeper understanding of the fundamental working mechanisms of PSC is lacking.⁶⁹ The technology faces several challenges and these must be addressed effectively for it to be commercially viable. Humidity dependence,⁷⁰ hysteresis behavior in the current -voltage curves,⁷¹ the effect of voltage sweep rates on short circuit current,⁷² stability of devices⁷³, lead toxicity⁷⁴ and control of the light-harvesting and electronic properties and identifying the role of the different components of the photovoltaic cells and their contribution to higher efficiency⁷⁵ cost of HTM and reproducibility of devices⁷⁶ are some among them. There are two main challenges encountered in the fabrication of single solution-processed perovskite films, controlling the crystallization process and ensuring high quality film.

Generally, the fast crystallization of perovskite materials with solvent evaporation may result in uncontrollable film morphology. Pinhole formation and poor coverage of the perovskite film, may cause low-resistance shunting paths, thus poor performance, especially in perovskite solar cells.⁷⁷ Even though the perovskite film morphology has been investigated as a function of parameters such as the initial precursor concentration, the kinds of solvents used, the solvent evaporation rate, and the time and temperature of annealing, wide morphological variation has resulted in significant differences in the photovoltaic performance, regardless of differences in the fabrication method and device configuration.^{78-80,45} The perovskite solar cells with high efficiencies, low cost, high stability, nontoxicity and reproducibility are the final goal to pursue.¹⁸

1.7. Structural-characterization techniques

1.7.1. Scanning electron microscopy

The morphology of the surface and crystallites was studied using a field emission scanning electron microscopy (FESEM; LEO 1525) with in-lens detector. SEM uses a finely focused electron beam to produce a high resolution image of the sample. The high energy incident electrons generate secondary electrons in the material by transferring their energy and ionizing the atoms. The secondary electrons are collected by a detector to give an image of sample surface.

1.7.2. X-ray diffraction

The crystal structure was identified using X-ray diffraction (XRD); Rigaku, Smartlab, Cu K-alpha). Diffraction peak occurs when x-ray light on material and Bragg's law $\lambda=2d\sin\theta$ is satisfied where d is lattice spacing of the crystal and θ is angle of incidence with λ as wavelength.

1.7.3. X-ray photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) measures the elemental composition, and the chemical and electronic states of the elements that exist within a material. We used Physical Electronics, model 5700 for our research. Photo-electrons were produced via a monochromatic Al-K α x-ray source (1486.6 eV) operated at 300 W. The analyzed area, collection solid cone and take off angle were set at 800 μm , 5° and 45° respectively. Data processing was carried out using the MultipakTM software package.

1.8. Device characterization techniques

1.8.1. Current-Voltage characteristics

Current-Voltage (I-V) characteristics were measured with a solar simulator (Newport, USA) equipped with 500 W Xenon lamp (Oriel) and a Keithley 2100, 6 1/2 digit multimeter, CHI instrument cyclic voltammeter/impedance spectrometer Model 604E.

Before each measurement, the exact light intensity was determined using a National Renewable Energy Laboratory (NREL) calibrated silicon solar cell.

The most important parameter of a solar cell is power conversion efficiency (PCE), which is determined by equation (1) and shown in Figure 1.5. I_{SC} is short circuit current which can be defined as the current density at zero voltage, V_{OC} is the open circuit voltage where current is zero and FF is fill factor which can be calculated by equation (2).

$$PCE = I_{SC} \times V_{OC} \times FF \quad (1)$$

$$FF = \frac{I_{mp} V_{mp}}{I_{sc} V_{oc}} \quad (2)$$

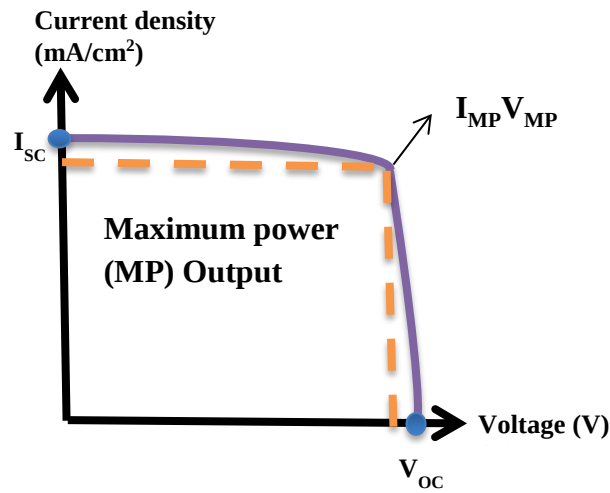


Figure 1.5. I-V characterization.

1.8.2. Hysteresis

One of the challenges in the PSC technology is to address the observed discrepancy in the I-V measurement between forward and reverse scan (Figure 1.6), known as hysteresis. Such behavior can lead to a considerable error in evaluating cell efficiency, since reliable cells should exhibit coincident curves from both scan directions.⁸¹

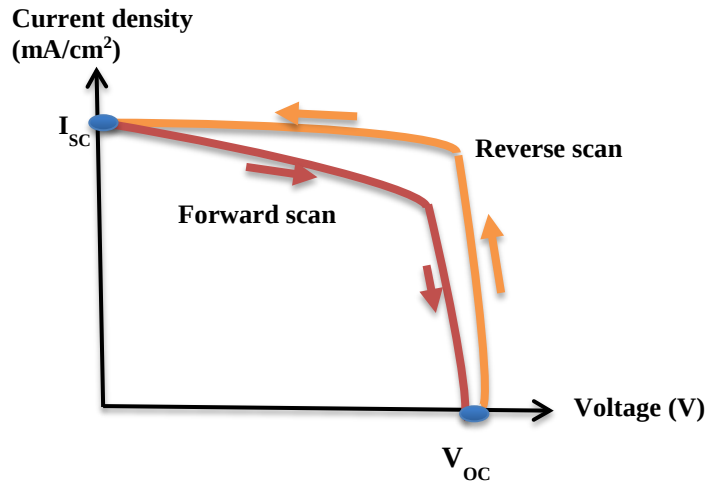


Figure 1.6. Hysteresis in I-V characterization.

In this regards several groups studied the possible origin for it. Results showed hysteresis can be caused by several factors such as trap states originating from either inherent defects in the perovskite or from grain boundaries,⁸²⁻⁸⁵ interfacial contact resistance at either the perovskite interfaces with ETM and HTM.⁸⁶ Other possibilities include ferroelectricity,^{87, 88} low frequency capacitance,⁸⁹ dipoles,⁹⁰ as well as mobile ion screening.⁹¹⁻⁹³ On the other hand it has been reported also that hysteresis may not only

depend on the ferroelectric ⁹⁴ and ion migration ⁹⁵ properties of perovskite material itself, but also on solar cell construction including film deposition techniques ⁹⁶ and device architectures. ⁹⁷ However, the origin of the I-V hysteresis behavior is still under debate. O'Regan et al. ⁹⁸ proposed that the I-V curve hysteresis is ascribed to the band offset at the interface. Tress et al. ⁹⁹ suggested that the hysteresis is due to the screening of built-in field by ionic migration, changing the effective difference in work functions of two contacts. Leguy et al. ¹⁰⁰ proposed a similar decrease of work functions difference due to an alignment of ferroelectric domains. At the same time, several groups have fabricated devices without significant hysteresis, for example, by using mesoporous TiO₂ layers instead of a compact TiO₂ layer, ^{102,103} solvent annealing to obtain large crystalline grains, ¹⁰³ as well as a fullerene passivation method. ¹⁰⁴ Hysteresis can also be less prevalent in devices with a high quality perovskite film. This has been achieved either by careful control of the crystal quality during deposition, ¹⁰⁴⁻¹⁰⁶ or by a post-treatment acting to passivate traps and reduce trap-mediated recombination. ¹⁰⁷⁻¹⁰⁹ It is now thought that fullerenes may be both a passivating agent and an efficiently extracting contact. ¹¹⁰⁻

1.8.3. Incident photon to current conversion efficiency

Incident photon to current conversion efficiency (IPCE) spectra were recorded at zero bias using a monochromator (Connerstone 260) – power meter (Newport, USA) system assembled in the lab. IPCE is the number of charge carriers flowing through the external circuit per incident photon at a given wavelength which can be calculated using equation (3). (Figure 1.7.) In order to check the quality of device the integrated current (I_p) can be calculated from IPCE spectra, this value should match with I_{sc} measured from I-V characterization. I_p can be calculated using equation (4).

$$IPCE = \left(\frac{hc}{e}\right) \frac{I_p(\lambda)}{P(\lambda)\lambda} = 1240(Wnm / A) \times \frac{I_p(\lambda)}{P(\lambda)\lambda} \quad (3)$$

$I_p(\lambda)$: Photocurrent density (A/m^2)

$P(\lambda)$: Incident power density (W/m^2)

$$I_p = \int_{\lambda_{min}}^{\infty} I_p(\lambda) d\lambda \quad \text{where} \quad I_p(\lambda) = IPCE \times P(\lambda) \lambda \left(\frac{e}{hc}\right) \quad (4)$$

I_p : Integrated current

$p(\lambda)$: Solar irradiance

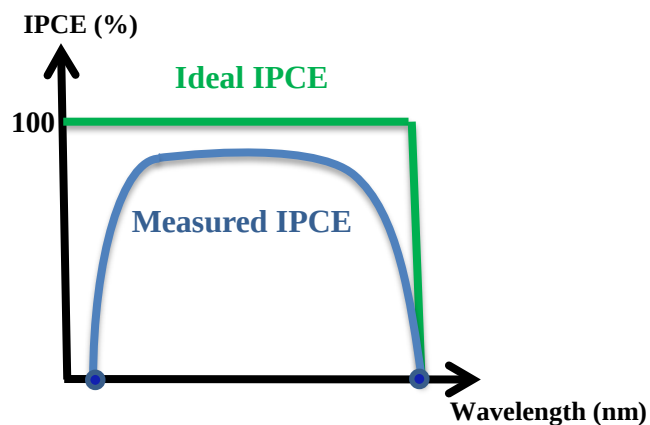


Figure 1.7. IPCE characterization.

1.8.4. Open-Circuit Voltage Decay

Open-circuit voltage decay (OCVD) was measured with a solar simulator (Newport, USA) equipped with 500 W Xenon lamp (Oriel) and a Keithley 2100, 61/2 digit multimeter, CHI instrument Model 604E. For this study, the voltage measurement was started with cell in the illuminated condition followed by switching the illumination off and continue recording the voltage in the dark as it decays with time. (Figure 1.8.).

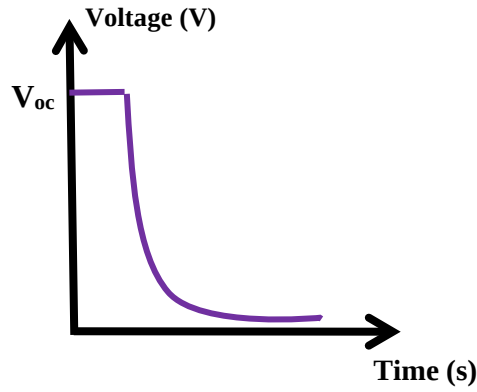


Figure 1.8. OCVD characterization.

This technique gives a continuous reading of lifetime of charge carriers which can be calculated using equation (5), where K_B is the Boltzmann constant, T is the temperature during measurement, e is the positive elementary charge and t is time.

$$\tau_n = -\frac{K_B T}{e} \left(\frac{dV_{oc}}{dt} \right) \quad (5)$$

$K_B T$: Thermal energy

1.8.5. Impedance Spectroscopy

Impedance Spectroscopy (IS) is a commonly used technique to understand dynamic operating parameters on solar cells. This measurement will record current in response to a small-amplitude voltage. Regular method is to fit and derive a circuit which describes

the internal elements. The measurement was done using a CHI instruments Model 604E cyclic voltammeter/impedance spectrometer in the illuminated using 500 W Xenon lamp source or in the dark conditions and applying a forward bias equal to open circuit voltage. Impedance is the ability of a circuit to resist the flow of electrical current, but unlike resistance, it is not limited by the simple properties. It can be defined as $Z = (\text{Real } Z) + i(\text{Im } Z)$. Nyquist plot (Figure 1.8) is defined as $-\text{Im } Z$ vs. $\text{Real } Z$ where each point on plot is the impedance at one frequency and arc shape is related to capacitance effect.

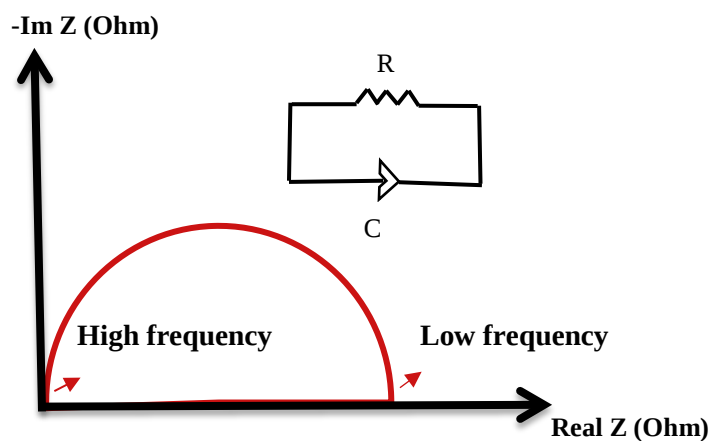


Figure 1.9. IS characterization, Nyquist plot.

1.9. Research objectives

This dissertation explores the influence of fabrication and post-fabrication conditions on the characteristics of mixed-halide perovskite solar cells. A comprehensive literature survey is done and is discussed in chapter 1. It is organized as follows. Chapter 1 will be an introduction, Fabrication details are given in chapter 2. The experimental setup and procedures used for characterization are described in first part of chapter 2. Here we have identified some of the important factors influencing the solar cell performance. Also structural characterization studies are discussed. Effect of fabrication and measurement ambient humidity are discussed in chapter 3. Effect of short post fabrication oxygen plasma treatment on the device is presented in chapter 4. Impedance spectroscopy studies on the effect of measurement oxygen, humidity and plasma doping on PSC are presented in chapter 5. Finally, the main conclusions of the dissertation and recommendations for the future work are presented in chapter 6.

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2. Device fabrication, characterization and parameters optimization

2.1. Perovskite solar cell fabrication

In this research we studied mixed-halide PSC with planar structure. All the chemicals used in this work were purchased from Sigma-Aldrich and Alfa Aesar and used as received. Spiro-OMeTAD was obtained from Borun New Material Technology Co., Ltd, China and Pilkington Tec-10 Fluorine doped Tin Oxide (FTO) glass from Hartford Glass Co., IL, USA. The substrates were ultrasonicated in Micro-90 and thoroughly cleaned in distilled water and isopropanol. Compact TiO₂ layer of 100-120 nm was formed by spin coating TiO₂ sol at 2000 RPM for 30 s. Sol was prepared by mixing titanium isopropoxide in ethanol with 200 μ L of hydrochloric acid (HCl) and refluxing at 180 °C for 15 hours. Coated films were annealed at 500 °C for 2 hours under oxygen ambient. Methyl ammonium iodide CH₃NH₃I (MAI) powder was prepared by process described in ref 1. Device fabrication under ambient lab conditions where humidity levels varied from 15 % to 65 % was affecting the solar cell performance badly. The I-V characteristic were never predictable. Thus the fabrication was transferred to a glove box under the air/nitrogen ambient under controlled humidity levels. A schematic picture of the prepared device is provided in Figure 2.1. (a) and a SEM cross-sectional image in Figure 2.1. (b) to show the different layers. Sequential deposition method ² was used to form the perovskite layer. A 3:1 molar ratio of lead iodide (PbI₂) and lead chloride (PbCl₂) was dissolved in N, N-dimethylformamide (DMF) by stirring at 70 °C. Hot solution was spin

coated Spin-coating on the substrate at 6500 RPM for 30s and annealing at 100 °C for 15 min. MAI in 2-propanol (10mgml^{-1}) was spun at 3000rpm for 20s and annealed at 100 °C for 15 min. We used undoped spiro-OMeTAD as the hole transport material (HTM). Solution was prepared according to procedure of Burschka et al. with the omission of cobalt dopant.² Spiro-OMeTAD was deposited at different spinning speeds to obtain the optimum thickness for the best performance. Back contacts of 2mm diameters were taken by sputtering silver (Ag) through shadow masks. The SEM images of top view of perovskite and spiro layer is presented in Figure 2.1. (c) and (d).

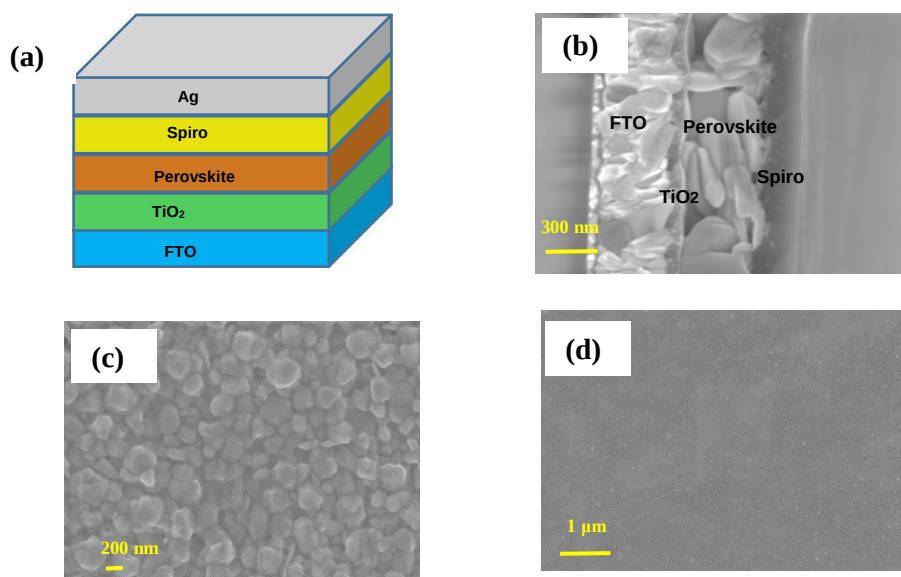


Figure 2.1. (a) Schematic illustration of perovskite solar cell. (b) Cross-section SEM image of the prepared cell. Top view of (c) perovskite and (d) spiro layer.

2.2. Parameters optimization

2.2.1. Chlorine concentration in the perovskite layer

MAPbI₃ is a common structure for PSC. Another structure is obtained by adding other halides like chlorine (Cl). Snaith et al. first used PbCl₂ and named compound MAPbI_{3-x}Cl_x.³⁻⁵ Other groups have shown this full or partial replacement as a method to change band gap from 1.57 to 2.29 eV.^{7,8} MAPbI_{3-x}Cl_x are reported to show good performance even in devices using a simple planar structure.^{6,9-12} these devices showed remarkably high Voc¹³ and extraordinary long charge transport distances of over 1 mm.^{7,14} performance of mixed halide structure strongly depends on processing parameters like RH, fabrication ambient, temperature, etc.¹⁵⁻¹⁷ Recent theoretical calculations by Mosconi et al. showed that the presence of Cl at the perovskite/TiO₂ interface leads to an increased binding strength of the perovskite film to the TiO₂ surface.¹⁸ In turn, this leads to stronger interfacial coupling between the titanium d- and lead p-bands that aids electron injection, increases electron accumulation at the interface, and causes a slight shift in the TiO₂ conduction band to higher energies.¹⁷ Experimental evidence for the presence of Cl at the perovskite/TiO₂ interface was recently obtained and supported by density functional theory (DFT) calculations.¹⁹ It predicted a chloride-induced band-bending at the perovskite/TiO₂ interface that may improve the efficiency of charge collection.¹⁹

The presence of Cl may lead to improved electronic properties of the perovskite/TiO₂ interface in multiple ways. If the Cl is located at the perovskite/TiO₂ interface this may quench oxygen vacancy defect states that act as charge traps in the band gap of the TiO₂ surface, and facilitate charge transfer across the interface.¹⁷ In addition to enhancing the

electronic properties of the perovskite/TiO₂ interface region, the presence of Cl may provide a better template for perovskite film growth leading to less disorder in CH₃NH₃PbI_{3-x}Cl_x perovskite films compared to Cl-free films.²⁰ A defect-free perovskite layer would likely provide a better path for charge transport than a highly defective layer.^{14,21} This helps to explain the observed low efficiencies of devices made with Cl-free, CH₃NH₃PbI₃ absorber layers when combined with nanostructured TiO₂.^{7,22} Based on these reports there were impressive attempts in the field to increase the content of Cl and explain role of Cl on the performance, however Cl amount in final device was still negligible and undetectable but role of Cl was undeniable.^{21,23,24}

In order to find an optimum Cl concentration needed for a better performing perovskite solar cell, Cl concentration were varied in the precursor solution for the mixed halide film. Devices were made with pure PbI₂ and three different concentration 0.1, 0.3 and 0.6 M of PbCl₂. PbI₂ concentration was fixed at 1M in all solutions. The I-V and IPCE plots of these devices are shown in Figure 2.2 and calculated photovoltaic parameters are given in Table 2.1. V_{oc} was higher in case of mixed halide. I_{sc} and FF improved with concentration and reached a maximum at 21.6 mA/cm² for the sample with 0.3 M concentration, further increase of Cl caused reduction in I_{sc} and FF values, which means an excessive PbCl₂ content could degrade the performance.⁶ So 1M PbI₂ and 0.3 M PbCl₂ ratio was used for mixed halide films for further experiments.

In the IPCE measurement curves showed deterioration in long wavelength region for single halide and low concentration of Cl which was an indication of degradation of perovskite due to humidity effect. Improvement upon adding Cl showed that device tolerate higher humidity level.

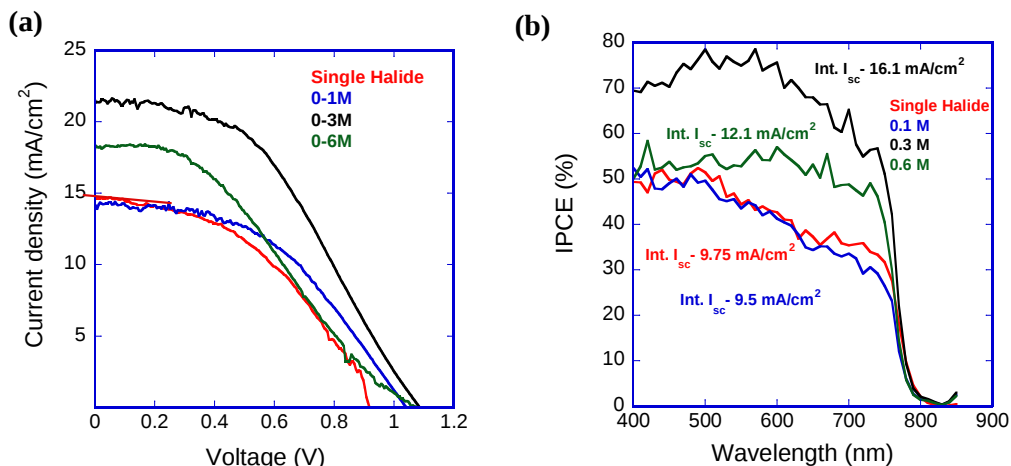


Figure 2.2. (a) I-V and (b) IPCE curve for devices fabricated with different Cl concentration.

Cl concentration (M)	V _{oc} (V)	I _{sc} (mA/cm ²)	FF	PCE (%)	R _s (Ohm)	R _{sh} (Ohm)
Single Halide (PbI ₂)	0.92	14.72	0.42	6.02	1050	9508
0.1 M	1.05	14.17	0.47	6.89	1182	17500
0.3 M	1.09	21.6	0.44	10.19	1200	13157
0.6 M	1.07	18.2	0.35	6.79	2272	250104

Table 2.1. Calculated photovoltaic parameters for devices fabricated with different Cl concentration.

XPS was done to detect the presence of Cl in the films. Cl was absent in the surface profile measurement. A few monolayers of the surface were removed by sputtering and a depth profile measurement for Cl was conducted on the sample. Sputtering was done with argon ion gun with voltage of 2 kV and current of 0.1 μ A for varied durations. In high resolution scans, Cl 2p peaks could be detected in film. (Figure 2.3. (a)). Cl was present

throughout the film, but it was almost double in the scan which was done after 60 s sputtering. (Figure 2.3. (b)). This could be due to segregation of Cl to top part of perovskite layer during annealing. Yang Yang et al.²⁵, could hardly detect Cl in the film with XPS measurements, pointing toward the loss of $\text{CH}_3\text{NH}_3\text{Cl}$ during the preparation process.

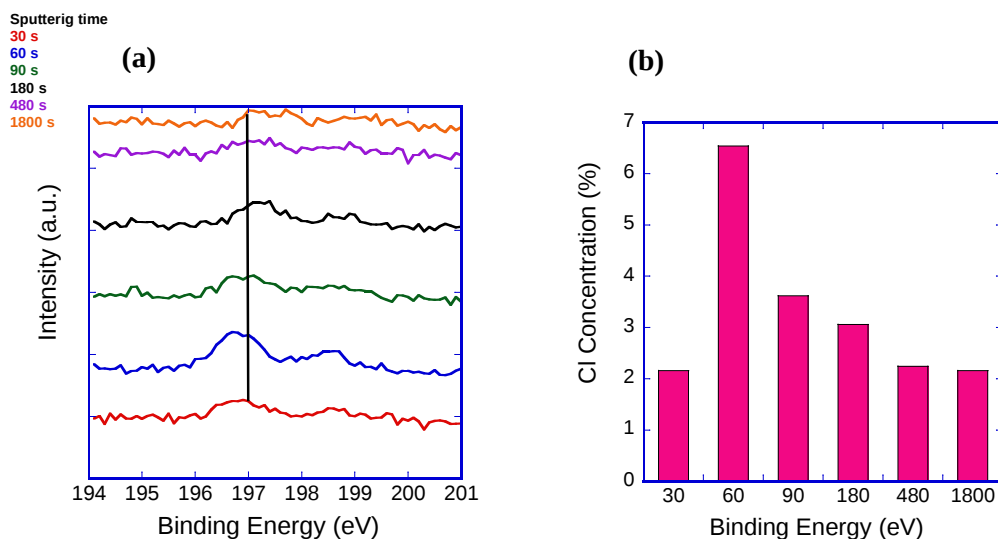


Figure 2.3. (a) XPS spectra for detecting Cl. (b) bar graph for Cl concentration vs. sputtering time.

It is possible to lose Cl in gas form during annealing process. This may also occur when annealing perovskite films in inert atmospheres, since Cl_2 is a gas at ambient conditions.²⁶ This loss of Cl can be controlled by choosing proper annealing condition. Annealing could also cause redistribution of Cl. Thus we see a small amount of Cl distributed evenly in the bulk.

2.2.2. Perovskite layer annealing temperature

As Eperon et al. and Dualeh et al. have shown, both annealing temperature and time can result in variation of performances due to morphological evolution.^{27, 28} For perovskite films, slow and low-temperature heating not to cause phase change is potentially necessary for crystal growth with few grain boundaries, microvoids, pinholes and little internal stress. ²⁹ So it is necessary to study the effect of temperature on device performance. In this section, we will report our investigations on effect of annealing temperature on the crystallinity and performance of PSC. Samples were annealed at different temperatures: 90 °C, 110 °C, 120 °C and 150 °C. Structural changes with annealing were analyzed from the powder XRD patterns in Figure 2.4. XRD spectra gave all the main perovskite peaks at 14.1 °, 28.4° and 32 °. The intensity of 12.56° peak of PbI₂ increased with annealing temperature which was attributed to perovskite decomposition and in case of 14.01° (the strongest peak of perovskite) highest intensity was from sample annealed at 90° and reduced in higher temperatures. But the ratio of the perovskite to PbI₂ peak decreased with increase in annealing temperature.

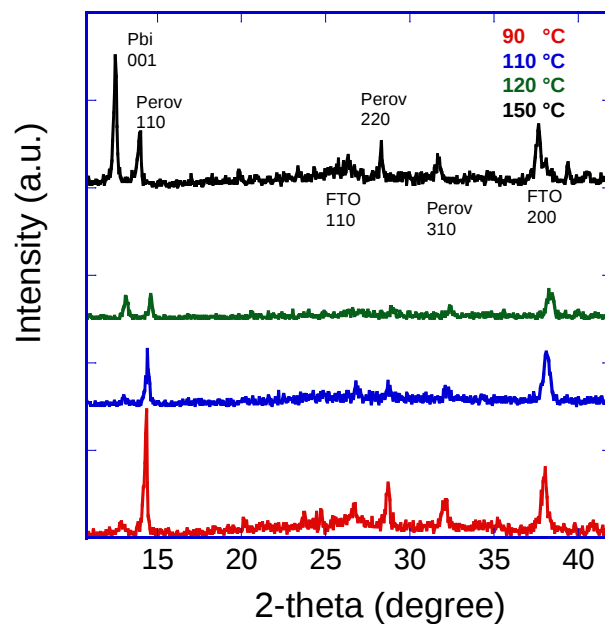
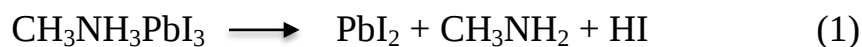


Figure 2.4. XRD pattern for perovskite films prepared on Tec 10 FTO glass under various annealing conditions.

IV curve is presented in Figure 2.5 and calculated parameters is shown in Table 2.2. V_{oc} , I_{sc} and FF showed same behavior as they increased upon increasing annealing temperature from 90 °C to 110 °C and reduced after increasing temperature further. It has been reported that partial decomposition of perovskite could happen at 130 °C according to according to the expression (1) ³⁰:



This temperature could change boundaries of perovskite and consequently would reduce coverage according to the previous investigations.³¹⁻³³ Thus the performance of the 110 °C annealed devices were good in comparison even though the ratio of perovskite to PbI₂ peak was slightly low compared to 90 °C. Presence of small amounts of unreacted PbI₂ didn't affect the device badly. But when the amount of PbI₂ increased significantly with temperature, device performance deteriorated.

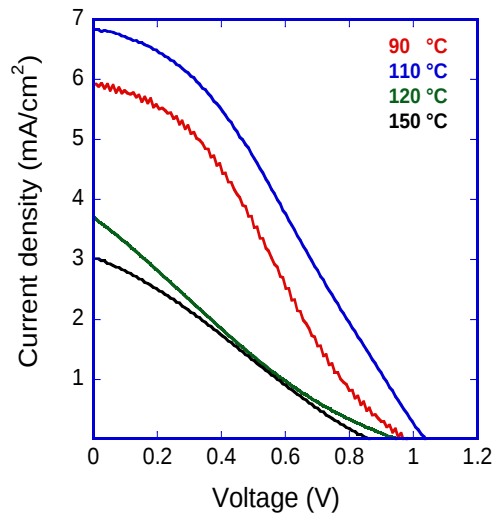


Figure 2.5. I-V curve for devices fabricated with different annealing temperature of perovskite layer.

Temperature (°C)	V _{oc} (V)	I _{sc} (mA/cm ²)	FF	PCE (%)	R _s (Ohm)	R _{sh} (Ohm)
90	0.97	5.93	0.32	1.85	7166	14210
110	1.03	6.82	0.34	2.36	4166	14130
120	0.94	3.7	0.21	0.74	6870	7142
150	0.85	3.04	0.27	0.7	6964	6913

Table 2.2. Calculated photovoltaic parameters for devices fabricated with different annealing temperatures of perovskite layer.

2.2.3. Spiro-OMeTAD layer thickness

PSC works on electron-hole generation upon radiation followed by transfer of electrons to ETM and holes to HTM and continues by injecting hole to metal electrode.³⁴⁻³⁸ In addition to extracting photogenerated positive charges from the perovskite and transporting these charges to the back contact metal electrode, the HTM helps to minimize recombination losses at the TiO₂/perovskite and perovskite/HTM interfaces and thus, leads to improved device performance.³⁸ Employing an HTM improves the V_{oc} which in a solar cell with a given absorber depends mainly on the recombination in the device.³⁹ The ideal positive charge extraction layer should have a highest occupied molecular orbital (HOMO) energy level that is compatible with the valence band of the perovskite. In addition, good hole mobility, minimal absorption in the visible and near-IR region of the solar spectrum, as well as excellent thermal and photochemical stability are required.³⁹ The most-commonly used hole transport material in PSCs is spiro-MeOTAD, which exhibiting impressive photovoltaic performance when used in PSC with a PCE of over 15% by using a sequential deposition⁴⁰ or a dual source thermal evaporation of the perovskite layer.⁴¹ Several desirable properties, favorable glass transition temperature, solubility, ionization potential, and transparency in the visible spectral range make spiro-MeOTAD a suitable candidate for this application. The electronic properties of the material have been extensively investigated,^{42,43} but the focus of those studies was mainly on the optimization of the performance by chemical p-doping of spiro-MeOTAD.⁴⁴ Although, it was demonstrated that Spiro-OMeTAD is an excellent small molecule HTM, its high cost accompanied by multi-step synthesis and difficult purification steps curtail

its commercial viability.³⁸ Malinauskas et al. argued that the fully symmetrical spiro-OMeTAD tends to be easily crystallized, which can affect the contact between the perovskite and the HTM.⁴⁵ Abate et al. also found that the HTM has a dramatic influence on the stability of the device^{46, 47}

It is essential to find the optimum HTM thickness to reduce R_s and simultaneously create a pinhole-free layer.⁴⁸ Uncovered perovskite can be pathway for faster deterioration of device due to interaction with environmental humidity. In this section, we will report our study on the role of spiro-OMeTAD thickness on the performance of PSC. Spiro-OMeTAD layer was coated with three different spinning speeds of 1000, 2000 and 4000 RPM (by keeping all the other fabrication parameters same) which was giving thicknesses of 500, 400 and 200 nm respectively. I-V and IPCE curves are presented in Figure 2.6. Calculated solar cell parameters are shown in Table 2.3. V_{oc} were not influenced much by thickness variation of spiro-OMeTAD, it was slightly reduced with increased spiro which could be attributed to increased recombination. Both I_{sc} and FF showed drastic improvement as thickness reduced to 200 nm with spinning speed of 4000 RPM, which could be mainly due to reduced R_s . Same trend was observed in IPCE as well, reducing spiro thickness showed improvement in IPCE in all wavelengths. A sufficiently thick HTM (200 nm) does not only increase the charge carrier collection efficiency, but also the light-harvesting efficiency due to an enhanced reflection from the smooth HTM/Ag interface.⁴⁹

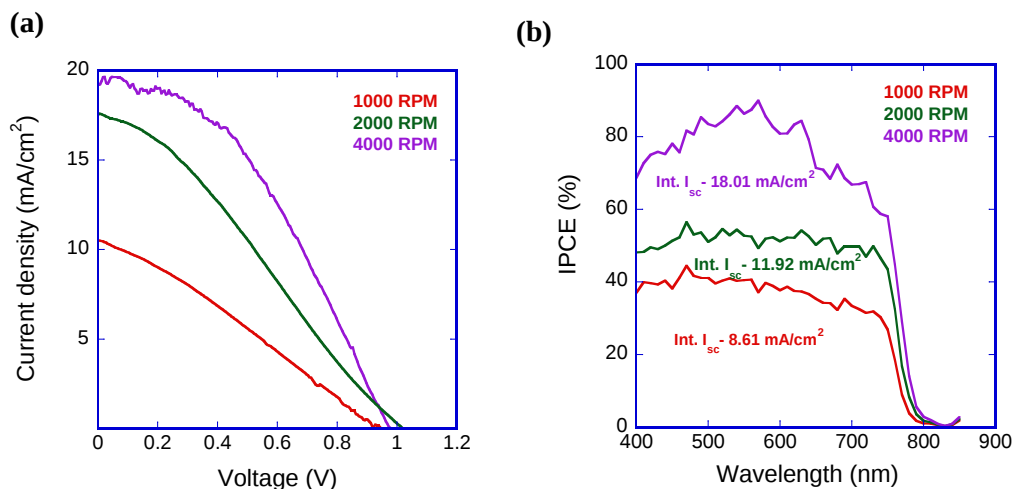


Figure 2.6. Effect of variation of spiro-OMeTAD thickness on (a) I-V and (b) IPCE of fabricated devices.

Spinning speed (RPM)	Thickness (nm)	V_{oc} (V)	I_{sc} (mA/cm^2)	FF	PCE (%)	R_s (Ohm)	R_{sh} (Ohm)
1000	500	0.92	10.5	0.12	1.2	2488	3954
2000	400	1.01	17.1	0.1	1.18	2142	5934
4000	200	0.98	19.1	0.42	7.7	1200	6774

Table. 2.3. Calculated photovoltaic parameters for reverse scan of samples with different spiro-OMeTAD thicknesses.

2.2.4. Relative humidity and ambient gases

The performance of PSC is dependent on the morphology and crystallinity of the perovskite films. Morphologies of the films are influenced by the ambient, RH and temperature during deposition of the film, pre and post treatments on the device. Thermodynamic and kinetic processes involved in crystallization are influenced by deposition parameters, humidity and heat treatments of films.⁶³⁻⁶⁹ The coverage of perovskite layer is also influenced by many factors, such as the choice of solvent, substrate, spin-coating rate and time, precursor concentration, annealing protocol, and so on. These parameters control the nucleation and growth of perovskite films and determine the ultimate crystallinity and morphology. Many tried to improve perovskite morphology and crystallinity by adjusting the above parameters.⁷⁰⁻⁷² Perovskite film is known to have pin-holes, incomplete coverage and high roughness which can be controlled in formation step.⁷³⁻⁷⁶ The pinholes not only weaken the light absorption ability of perovskite films but also deleteriously impact charge transport and recombination.⁶³ Perovskite with larger grain size should have lesser electronic trap states as compared with the smaller ones. Such films could help realize devices having PCE >20% .⁷⁷ Smaller grain domains means higher density of grain boundaries in the film, which create higher number of electronic trap states. Hence, the grain size should be large to lower electronic traps in the film and improve the performance of the cell.⁷⁷ By using P₃HT as HTM Gangishetty et al showed that RH is a key factor in both the growth and the degradation of perovskite crystals due to the highly hygroscopic nature of CH₃NH₃PbI₃.⁷⁸

We found that the RH during fabrication and measurement affect the performance of solar cell significantly. In this section we will show our results on role of fabrication RH on devices prepared at room temperature.

I-V and IPCE obtained from devices fabricated in nitrogen and air ambient are shown in Figure 2.7. and 2.8. The details of the photovoltaic parameters are listed in Table 2.4. and 2.5. The highest PCE obtained from air ambient fabricated devices was 11.6 % with I_{sc} 17.94 mA/ cm² and V_{oc} 1.08 V, and FF 0.6. The highest I_{sc} was seen in device fabricated in 9 % RH but with slightly less PCE of 10.34 % .The highest PCE for nitrogen ambient fabricated devices was 7.09 % with an I_{sc} of 15.89 mA/ cm², a V_{oc} of 1.08 V, and a FF of 0.41 for the device fabricated in 9 % RH. All parameters improved upon increasing RH from 5 % to 9 %.

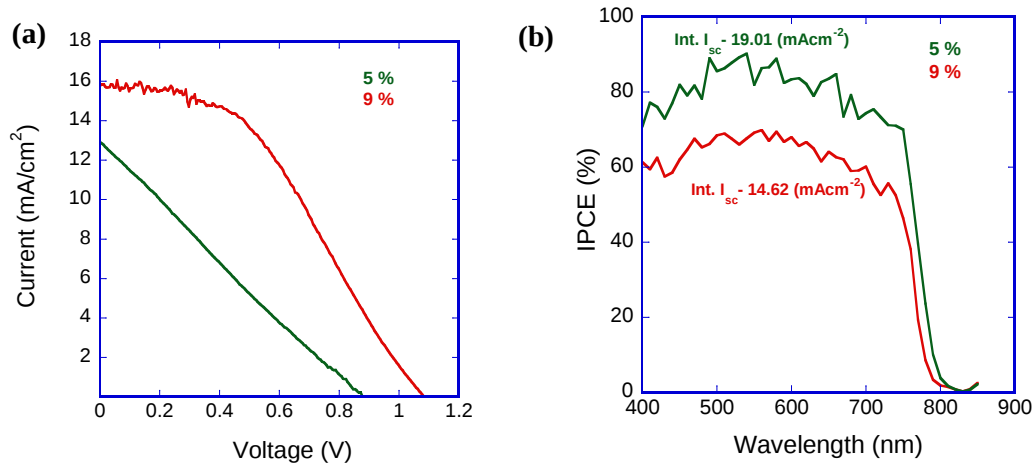


Figure 2.7. (a) I-V and (b) IPCE results of devices fabricated in nitrogen ambient with RH 5% and 9 %.

RH (%)	I_{sc} (mA/cm ²)	V_{oc} (V)	FF	PCE (%)	R_s (Ohm)	R_{sh} (Ohm)
9	15.89	1.08	0.41	7.09	1500	19230
5	12.83	0.88	0.24	2.73	1462	2610

Table 2.4. Calculated photovoltaic parameters for devices fabricated in nitrogen ambient with different RH levels.

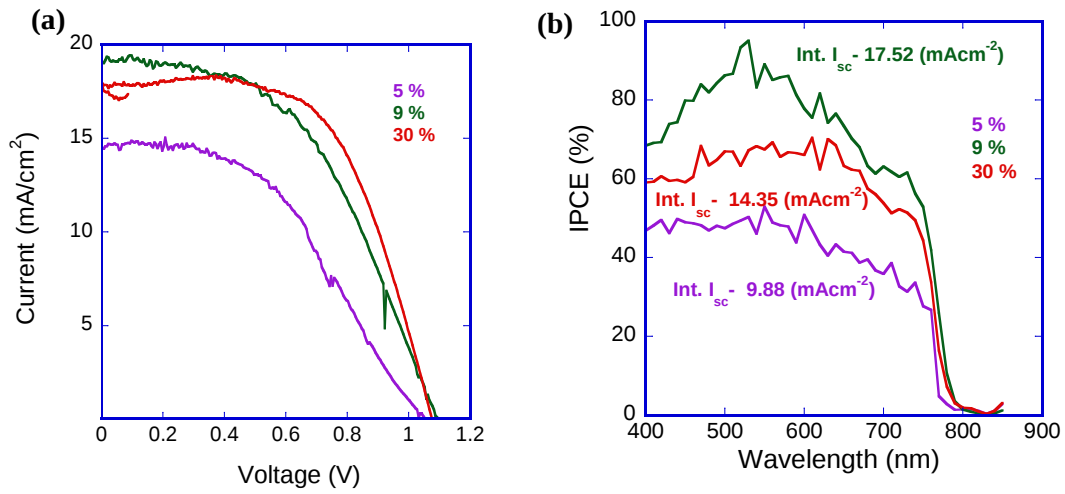


Figure 2.8. (a) I-V and (b) IPCE results of devices fabricated in air ambient with different RH levels.

RH (%)	I_{sc} (mA/cm ²)	V_{oc} (V)	FF	PCE (%)	R_s (Ohm)	R_{sh} (Ohm)
5	14.45	1.04	0.47	7.04	1500	28865
9	19.03	1.09	0.5	10.34	769	25417
30	17.94	1.08	0.6	11.6	533	28774

Table 2.5. Calculated photovoltaic parameters for devices fabricated in air ambient with different RH levels.

IPCE spectrum showed matching current with Rh of 9 % in both ambient. Generally low RH level (less than 5 %) showed better results in IPCE for samples fabricated in nitrogen ambient. Increase in RH in both air and nitrogen atmosphere deteriorated IPCE drastically. These results indicated that certain amount of humidity was necessary in these perovskite films in order to give high-performance devices that yield matching current.

We studied the effect of fabrication ambient on the morphology of PbI_2 - PbCl_2 and perovskite layer. SEM images of PbI_2 - PbCl_2 by keeping RH at 9 %. SEM images is shown in Figure 2.9. In air environment the films were found to have a mixture of smaller and larger grains with diameters ranging from 75 nm to 150 nm. In nitrogen ambient, the coverage was better and had more large size grains with average diameter ranging from 110 nm to 330 nm. Higher coverage PbI_2 - PbCl_2 films would lead to more unreacted PbI_2 - PbCl_2 left and located in the interface of ETM and $\text{CH}_3\text{NH}_3\text{PbI}_2\text{Cl}$ layer. The effect of unreacted PbI_2 on suppressing charge recombination could not be excluded. It was evident that the device performance could be changed drastically by changing the morphology of the PbI_2 underlayer.⁷⁹

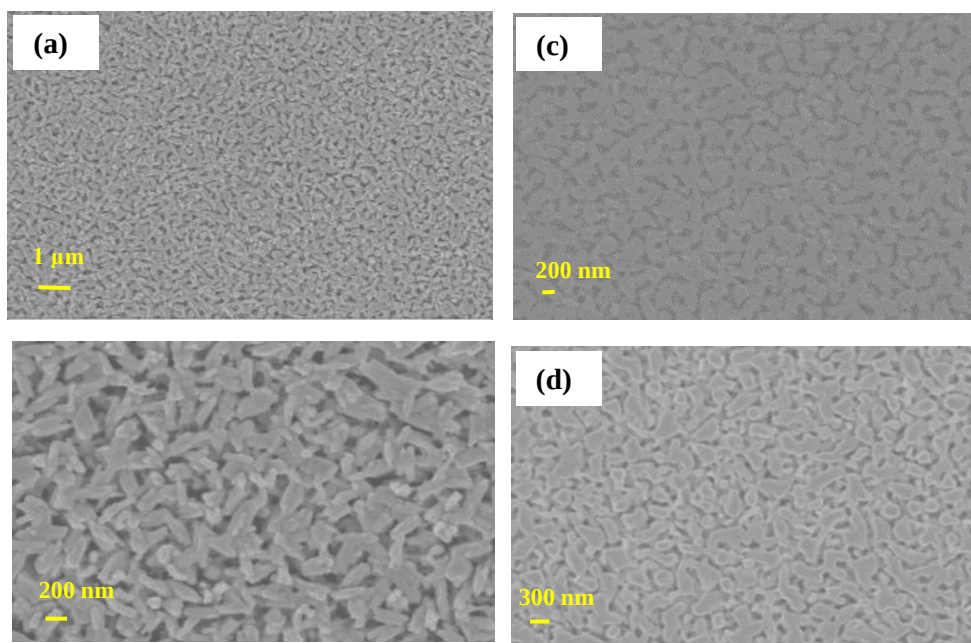


Figure 2.9. SEM images of $\text{PbI}_2\text{-PbCl}_2$ film prepared in 9 % RH with (a),(b) air ambient and (c),(d) nitrogen ambient.

The SEM images of the perovskite film prepared in different ambient condition are shown in Figure 2.10. Grain size ranged between 150 nm-290 nm for both nitrogen and oxygen environment.

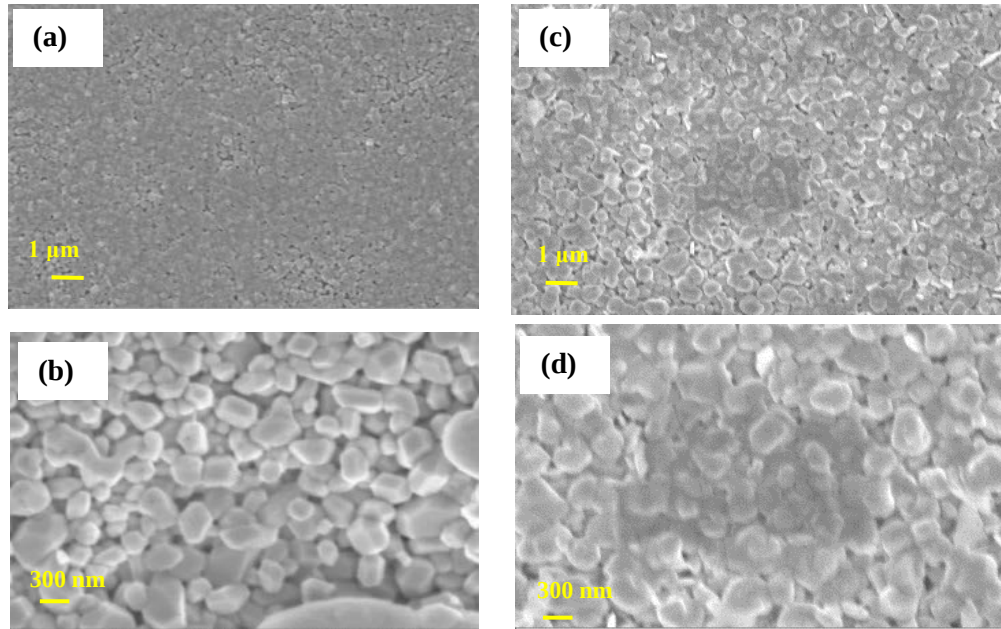


Figure 2.10. SEM images of $\text{CH}_3\text{NH}_3\text{PbI}_2\text{Cl}$ film prepared in 9 % RH with (a),(b) air ambient and (c),(d) nitrogen ambient.

High-coverage $\text{CH}_3\text{NH}_3\text{PbI}_3$ films could suppress charge recombination by reducing the detrimental direct contact between ETM and HTM.³²

2.2.5. Relative humidity and ambient during measurement

One of the main objectives in solar cells research is to have device working under actual atmospheric condition specifically in presence of oxygen and humidity. This is one of the major issues in the field to be addressed as many commonly used semiconductors for photovoltaics are readily oxidized in the ambient condition.⁸⁰⁻⁸³ Perovskite materials generally degrades very quickly upon exposure to outside ambient⁸⁴⁻⁸⁶ Two components

in ambient air, H₂O and O₂, affect the chemical stability of PSCs, accompanied by color change from dark brown to yellow.^{87, 88} A thorough understanding of the influence of the atmosphere on the material is of the utmost importance to solve the challenges. There are reports that for PSC, the relative humidity is detrimental to the device performance.⁸⁹⁻⁹¹ Exposing perovskite films to high levels of moisture leads to formation of hydrate phases;⁹²⁻⁹⁶ this led to the failure of the devices.⁹⁷ Kamat et al. reported that perovskite gets hydrated [(CH₃NH₃)₄PbI₆·2H₂O] under a humid environment in the dark and it forms PbI₂ under a humid environment in light.^{98,99} Leguy et al. further identified the formation of monohydrate CH₃NH₃PbI₃·H₂O first, which is reversible, before giving rise to dehydrate crystal and causing degradation.¹⁰⁰ The crystallographic deterioration is mainly responsible for the degraded device performance. However, another study on MA-based perovskites¹⁰¹ showed that a moderate moisture level (~35% relative humidity) could enhance the recrystallization of perovskites during the normal film formation process which could yield a high-quality perovskite film and solar cell performance. The degradation mechanism of perovskite materials in water condition was studied by Wang et al.¹⁰² The hydrolysis reaction of CH₃NH₃PbI₃ occurs when the material is exposed to the humid condition. The consumption of hydroiodic acid (HI) drives the whole decomposition process and causes the decrease in efficiency of PSC.¹⁰² Frost et al. proposed two reversible reactions, where both methylamine, CH₃NH₂ and HI could exist in gas state at room temperature, which could easily drive the degradation further in a non-encapsulated device.¹⁰³ Understanding the root cause of ambient dependent inconsistent performance of PSCs is of paramount importance for ultimately solving this issue. We studied the effect of characterization ambient on the performance

of these cells. I-V and IPCE results are presented in Figure 2.11. with parameters in Table 2.6.

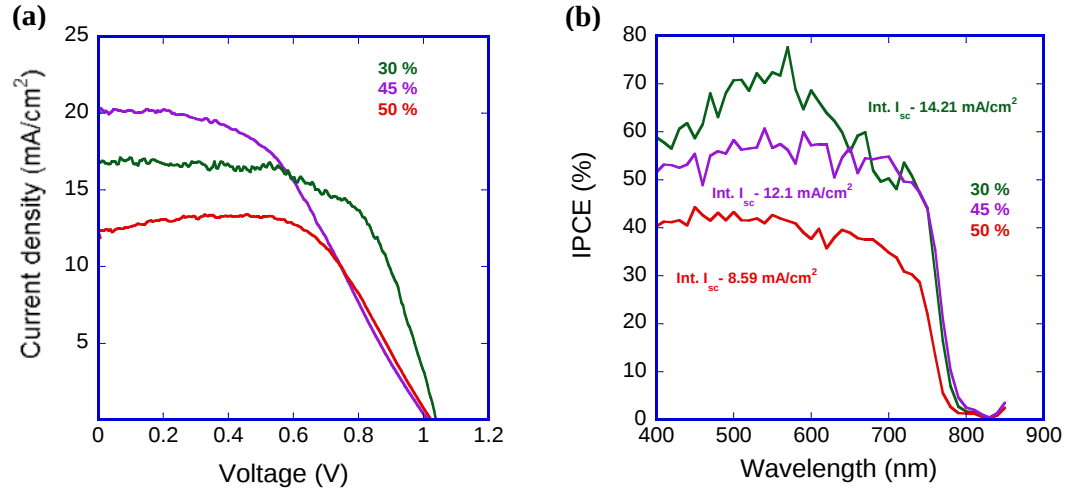


Figure 2.11. (a) I-V and (b) IPCE results of devices measured in different RH.

RH (%)	I _{sc} (mA/cm ²)	V _{oc} (V)	FF	PCE (%)	R _s (Ohm)	R _{sh} (Ohm)
30	16.74	1.03	0.63	10.9	675	19230
45	20.21	1.01	0.46	9.4	1076	22835
50	12.36	1.01	0.62	7.9	1069	18538

Table 2.6. Calculated photovoltaic parameters for devices measured in different RH.

PCE reduced from 10.9 % to 9.4 % upon increased measurement RH from 30 % to 45 % and further reduced to 7.9 % with measurement RH of 50 %, which means not only RH

in fabrication but in measurement step also had role on stability and deterioration of devices. Spiro layer could serve as penetration path of outside humidity during measurement due to its affinity towards oxygen. As long as the oxygen and RH stays within the spiro layer IPCE of device would be high. When it penetrates into the perovskite layer the IPCE degrades and eventually the short circuit current.

2.2.6. Influence of scan rate and fabrication humidity on hysteresis

Here we are presenting our results on possible reasons for observed hysteresis. Magnitude of observed hysteresis depends on the scan rate of I-V sweep, we noticed in general with very fast scan rate hysteresis was reduced, while in slow scan rate it was increased, but exact dependency was not same for all devices. Slow scan rate could be considered as the most-accurate way for measuring efficiency¹⁰⁴ but at the same time it was deteriorating device performance fast. Figure 2.12 shows the results of four different scan rates: 0.5, 0.05, 0.02 and 0.01 V/s. by reducing scan rates mainly I_{sc} value was reduced, V_{oc} was almost same but although hysteresis was reduced device behavior was not stable.

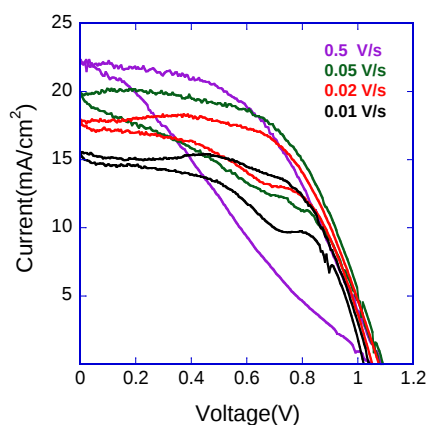


Figure 2.12. Effect of scan rate on hysteresis.

In order to choose the right scan rate for getting the real efficiency of device we used information from IPCE results and integrated current to see if it is matching with I_{sc} . Value of scan rate depends on stability of cell also. One of the other possible reasons for hysteresis could be fabrication RH level, as shown in Figure 2.13 for two devices fabricated in 9 % and 30 % RH. Both were measured with same scan rate (0.5 V/s). Although increased RH level enhanced performance in reverse scan, it also showed more hysteresis. Thus more hydrated devices display strong hysteresis, consistent with the presence of a higher concentration of mobile ions. ¹⁰⁵⁻¹⁰⁷

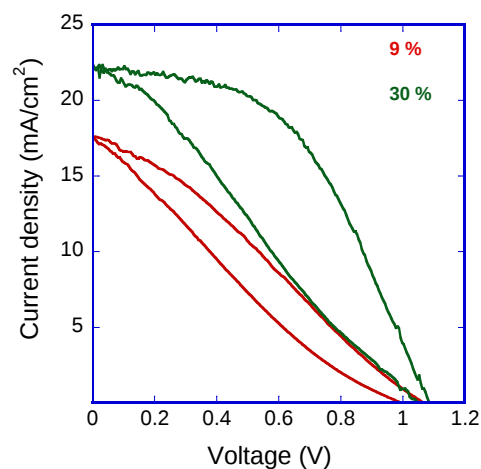


Figure 2.13. Effect of fabrication RH on hysteresis.

This means fabrication condition and specifically RH plays an important role in amount of hysteresis and it was exacerbated in high level of RH.

2.3. Conclusion

In summary we noticed fabrication parameters such as annealing temperature of perovskite, Cl concentration in perovskite layer, spiro-OMeTAD thickness and during fabrication humidity level are critical. Each of them need to be controlled in order to get a device with high performance and stability.

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3. Enhancement of device performance by modifying Spiro-OMeTAD layer

3.1. Spiro-OMeTAD layer-doping methods

3.1.1 Chemical doping

Spiro-OMeTAD layer containing Bis(trifluoromethane)sulfonamide lithium salt (Li-TFSI) and tert-butylpyridine (TBP) additives, which are known to improve hole mobility, is generally used for hole transport in perovskite cells.¹ The TBP additive can increase the polarity of HTM and enhance the interfacial contact between perovskite and HTM, leading to a high V_{oc} and PCE.¹ Unfortunately, the polarity of TBP makes it dissolve perovskite materials, which means that perovskite can be corroded by TBP.¹ At the same time, the addition of Li-TFSI is known to promote the oxidation of spiro-MeOTAD in order to increase the hole mobility and conductivity.² One of the common ways for increasing the conductivity of spiro-OMeTAD is the use of tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine)cobalt(III) bis(trifluoromethylsulphonyl) Imide (FK dopant) as a chemical dopant. We compared the performances of devices with and without this dopant and are shown in Figure 3.1 and Table 3.1. We noticed an improvement in performance, especially I_{sc} which increased to 21.4 mA/cm². Contact area of the device was 0.0314 cm². The FK dopant is expensive and hence, it could increase the fabrication cost of PSCs. Here, we present our results on our efforts to find an alternative low cost solution to this problem.

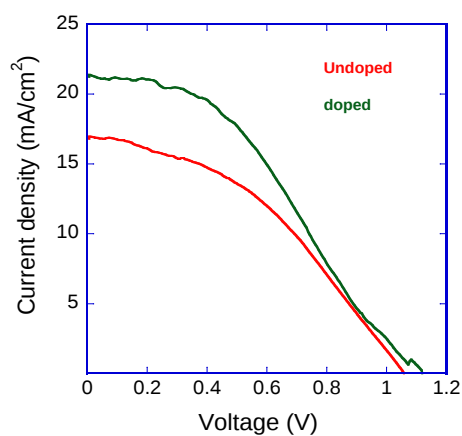


Figure 3.1. I-V characteristics of two devices, one having an undoped spiro-OMeTAD layer and the other having spiro-OMeTAD doped with FK dopant.

Spiro-OMeTAD	V_{oc} (V)	I_{sc} (mA/cm ²)	FF	PCE (%)	R_s (Ohm)	R_{sh} (Ohm)
Doped	1.1	21.4	0.39	9.07	1542	8378
Undoped	1.06	16.8	0.4	7.21	1454	7969

Table 3.1. Photovoltaic parameters calculated from the reverse scans of devices with and without FK dopant in spiro layer.

3.1.2 Molecular oxygen doping

Spiro-OMeTAD found its use as in HTM first in Solid-state dye-sensitized solar cells (sDSCs).^{4, 5} In contrast to organic solar cells, where oxygen caused degradation of devices,⁶ oxygen appeared to be necessary during device fabrication in order to obtain a working sDSC.⁴ Karlsson et al. suggested that poor device performance in devices fabricated in the absence of oxygen was due to a low spiro-MeOTAD conductivity and higher recombination rate.⁷ Oxygen presumably acted as an electron acceptor in spiro-MeOTAD.⁴ While neutral spiro-MeOTAD absorbs light in the ultraviolet (UV) region of solar spectrum (~ 390 nm), its oxidized forms show strong absorptions throughout the visible range, extending into the near-infrared (NIR; ~ 700 - 900 nm).⁸ The methoxy groups on the peripheral phenyl groups lower the spiro-MeOTAD oxidation potential, thus providing an optimal matching with the sDSC dye redox potential. Moreover, the methoxy groups stabilize the oxidized form, preventing the formation of polymeric species, as in the case of triphenylamine (TPA).⁸ It has been shown that the Poly(3-hexylthiophene-2,5-diyl) (P₃HT), typically used as the electron donor in polymer solar cells could form a charge transfer complex with oxygen, resulting in the oxidation of the polymer.⁹ In order to see exclusively the doping effect, the data shown in Figure 3.1 were collected without exposing spiro-OMeTAD to oxygen. In the results presented in Figure 3.2, we showed the effect of oxygen treatment in device fabricated with and without FK dopant. All of them were stored in oxygen for 120 minutes. In both cases we observed a drastic enhancement in the PCE. Both doped and Undoped devices showed PCE of about 13 % after treatment, which was believed to be due to the oxidation of spiro-OMeTAD.

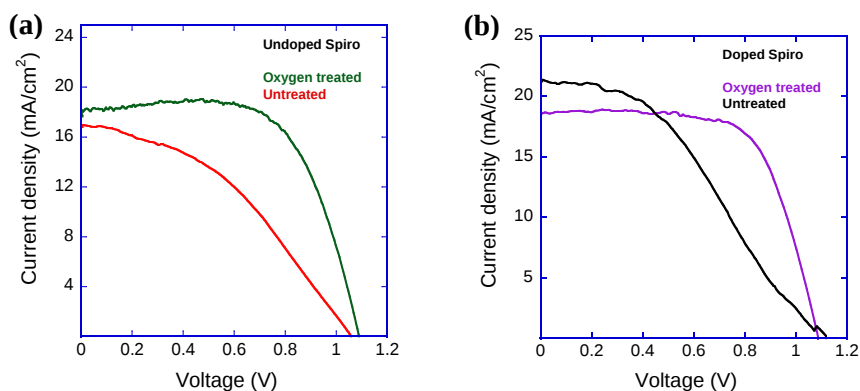


Figure 3.2. I-V plots showing the effect of oxygen treatment on devices (a) without FK dopant and (b) with FK dopant.

Spiro-OMeTAD	V_{oc} (V)	I_{sc} (mA/cm ²)	FF	PCE (%)	R_s (Ohm)	R_{sh} (Ohm)
Undoped-Untreated	1.06	16.8	0.4	7.21	1400	7666
Undoped-Treated	1.09	18.05	0.67	13.15	400	40909
doped-Untreated	1.1	21.4	0.39	9.07	1416	8629
Doped-Treated	1.08	18.61	0.68	13.64	416	38950

Table 3.2. Calculated photovoltaic parameters from reverse scans of devices, either untreated or treated with oxygen. The effects on devices having Undoped spiro-OMeTAD and that with FK dopant are shown.

3.2. Oxygen plasma treatment

3.2.1. Rationale

One of the major challenges in using oxygen treatment for improving the properties of spiro-OMeTAD as HTM is the time required for the treatment. We observed an enhancement in the device performance after 120 minutes of exposure to oxygen after device fabrication. Long exposure time reduces IPCE of the devices though the I-V will remain constant at least until the RH penetrates into the perovskite layer and transforms it. Many groups use overnight exposure to oxygen for stabilized performance. Such a long treatment duration could impair the commercialization possibilities of these devices. As mentioned before, oxygen treatment can be regarded as a low cost alternative to expensive FK doping. Considering the need of addressing the challenge, we investigated possible ways to reduce the oxygen treatment duration. Our hypothesis was oxygen plasma could drive oxygen into the material fast and more effectively in a controlled way.

At the end of these studies we proved that our hypothesis was indeed correct. We noticed a significant enhancement in the device performance after a very short (a few seconds) oxygen plasma treatment of the devices. We discovered that, oxygen had little impact on the degradation of devices. Nevertheless, the treated devices interacted with humidity very fast.^{10,11} The moisture in the preparation as well as measurement ambient known to cause degradation in PSCs.^{10,12} Thus, we studied the effect of our treatment on samples

prepared at different RH conditions as well as the devices tested under different humidity levels.

3.2.2. Effect of oxygen plasma treatment on device performance

Plasma treatment is probably the most-versatile surface treatment technique. Plasma treatment in gases such as argon, oxygen, nitrogen, fluorine, carbon dioxide and water can provide unique surface properties to various materials. For example, oxygen-plasma treatment can increase the surface energy of polymers, whereas fluorine plasma treatment can decrease the surface energy and improve the chemical inertness.¹³⁻¹⁵ Oxygen plasma treatment is a safe and environmentally friendly compared to other cleaning methods.

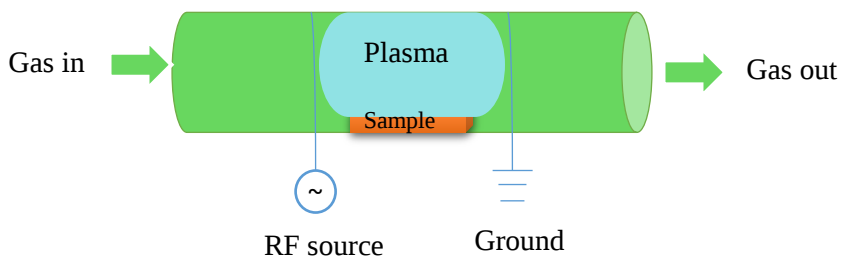


Figure 3.3. A schematic picture of plasma chamber.

The effect of plasma treatment on devices having chemically undoped spiro-OMeTAD is shown in Figure 3.4. Plasma treatment was done in two different power levels: 5-10W as low power plasma (LPL) treatment and 55-60W as high power plasma (HPL) and performance was compared to non plasma (NPL). The same enhancement as observed in

the molecular oxygen treatment (Figure 3.2) was noted. Nevertheless, the plasma treatment was only for 10s. Thus, it was indeed evident that oxygenation of spiro-OMeTAD happened quickly in oxygen plasma treatment. IPCE spectra (Figure 3.4. (b)) showed almost the same trend for both devices as expected because the short circuit current remained almost the same after treatment.

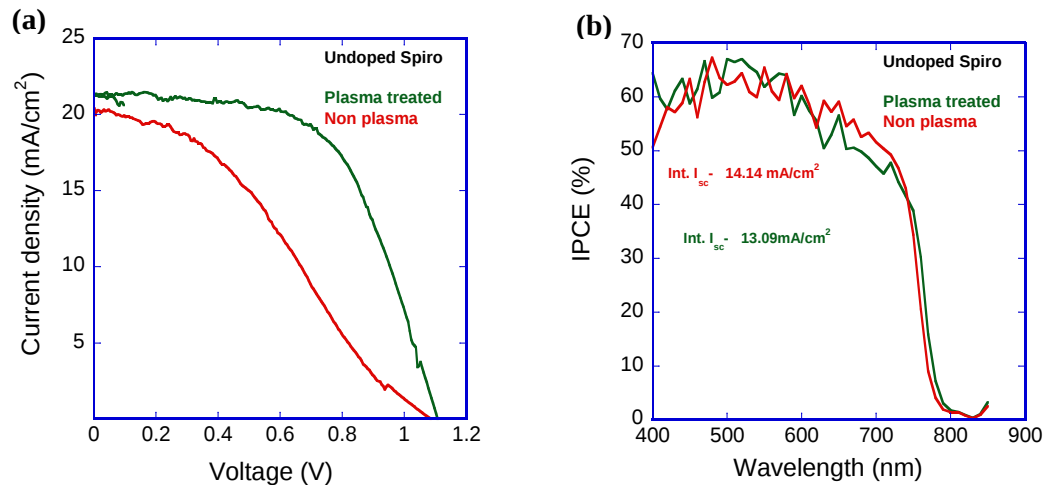


Figure 3.4. (a) I-V and (b) IPCE curves from devices (without FK dopant in spiro-OMeTAD) before and after treatment with oxygen plasma.

Spiro-OMeTAD	V _{oc} (V)	I _{sc} (mA/cm ²)	FF	PCE (%)	R _s (Ohm)	R _{sh} (Ohm)
Non plasma	1.07	20.14	0.35	7.58	2600	5117
Plasma treated	1.1	21.25	0.59	13.85	500	18421

Table 3.3. Calculated photovoltaic parameters from reverse scans of devices (without FK dopant in spiro-OMeTAD) before and after oxygen plasma treatment.

The same enhancement was not observed in I-V and IPCE when devices having FK doped spiro-OMeTAD were subjected to oxygen plasma treatment (Figure 3.5). Moreover, oxygenation in addition to chemical doping caused deterioration of the sample. Thus, the oxygen plasma treatment could replace FK doping although both of them could not be applied simultaneously.

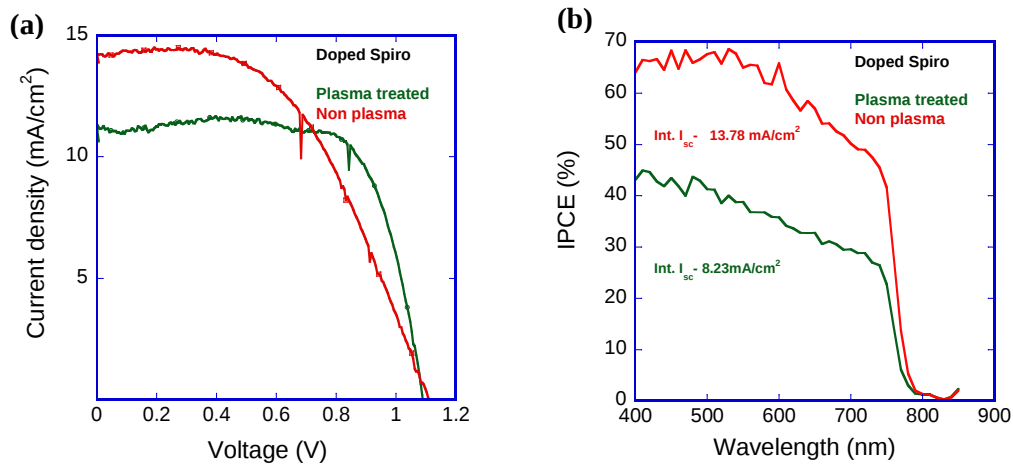


Figure 3.5. (a) I-V and (b) IPCE curves from devices with FK dopant before and after exposing to oxygen plasma.

Spiro-OMeTAD	V _{oc} (V)	I _{sc} (mA/cm²)	FF	PCE (%)	R _s (Ohm)	R _{sh} (Ohm)
Non plasma	1.1	14.16	0.52	8.06	1200	40000
Plasma treated	1.08	11.25	0.73	8.87	416	65909

Table 3.4. Calculated photovoltaic parameters from reverse scan of devices with FK doped spiro-OMeTAD before and after oxygen plasma treatment.

3.2.3. Morphology and transmittance

In order to understand if plasma treatment changed the thickness of the spiro-OMeTAD layer and the observed betterment in the performance had any relation with the change in spiro-OMeTAD thickness, the transmittance measurements were done. The transmittance spectra of spiro-OMeTAD before and after treatment (both LPL and HPL conditions) are presented in Figure 3.6. Measurement was done in 300 nm to 400 nm interval as the light absorption of spiro-OMeTAD is maximum in the UV region and hence, transmittance in this region is very sensitive to spiro-OMeTAD thickness. Since there was no difference in transmittance spectra of LPL device compared to NPL, it indicated that low-power plasma was not effecting spiro-OMeTAD layer thickness. An increase in transmittance was observed in the case of HPL, which indicated a reduction in spiro-OMeTAD thickness as a result of high power plasma treatment. Evidence provided by SEM images shown in Figure 3.7 supported this finding. While as prepared spiro-OMeTAD layer had a thickness of 210 nm, the thickness became 200 nm for LPL and 170 nm for HPL.

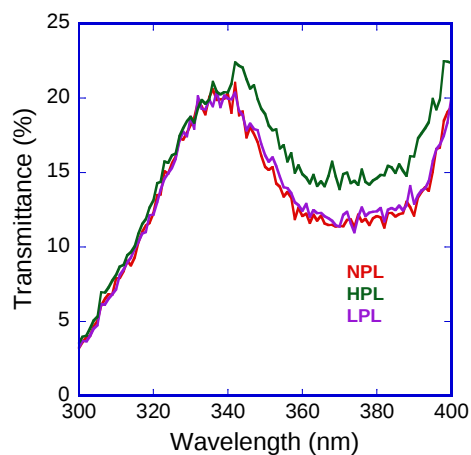


Figure 3.6. Transmittance spectra obtained from untreated and plasma treated spiro-OMeTAD layers.

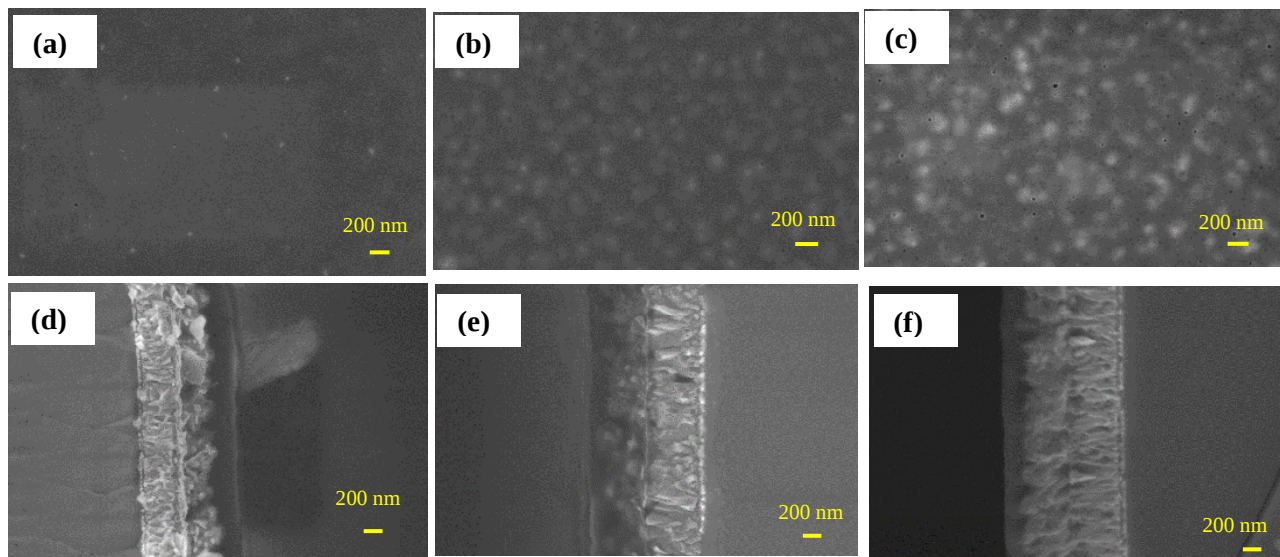


Figure 3.7. SEM image of spiro-OMeTAD layer top view from (a) NPL (b) LPL and (c) HPL. Cross-sectional images for (d) NPL (e) LPL and (f) HPL.

3.2.4. Structure and chemical composition

In order to study the effect of plasma treatment on the bulk properties of the material, we used analytic techniques like XPS and XRD to characterize the material. XRD pattern is shown in Figure 3.8. Diffraction peaks at 14.12° , 20.04° , 28.45° , 31.89° , 40.67° and 43.34° can be assigned to (110), (112), (220), (310), (224) and (330) planes of perovskite, respectively. Thus we did not see significant changes in the crystal structure of perovskite in the plasma treated devices compared to untreated. That means crystallinity of perovskite was not influenced by the treatment. We, therefore, concluded that changes in device performance were related to modification of the surface properties. In order to find if the plasma induced strain the perovskite crystal lattice, we performed high resolution scan on the peak at 14.1° . As evident from Figure 3.8. (b), this main perovskite peak did not show any shift due to treatment, which implied that the oxygen treatment at the surface of spiro-OMeTAD did not cause any strain in the perovskite lattice. It was, however, not clear if oxygen was going in to the perovskite layer or staying in the spiro-OMeTAD layer.

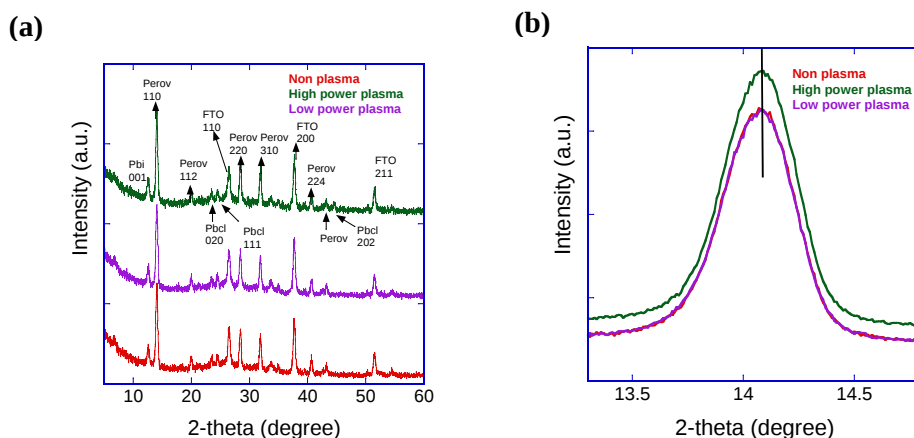


Figure 3.8. (a) XRD pattern from non-plasma and plasma treated samples.

(b)High resolution measurement for main perovskite peak.

XPS measurements were done to understand the change in composition of different layers as a result of exposing the devices to oxygen plasma. Figure 3.9. shows the oxygen (O) and carbon (C) core level spectra. The C1s core level of untreated device showed a peak at 286.5 eV on both surface as well as at a depth of 20-40 nm. This peak represents the sp^2 carbon which could be the adventitious carbon. Same peak was observed in the case of treated devices also, but with less intensity. This can be attributed to the removal of adventitious carbon in form of carbon dioxide by oxygen. Two other peaks observed in surface measurement of plasma treated devices at binding energy levels of 286 eV and 289 eV, which correspond to C-O and C=O respectively. These were, however, not detected in depth profiling. The O1s core-level scan showed highest value of oxygen (531 eV peak) in the surface scans of plasma treated devices. The depth profiling showed the same peak intensities from NPL and HPL, whereas at the surface, LPL sample showed

higher oxygen. This means that oxygen ions on the surface contributed to both etching and chemical modifications in HPL devices.

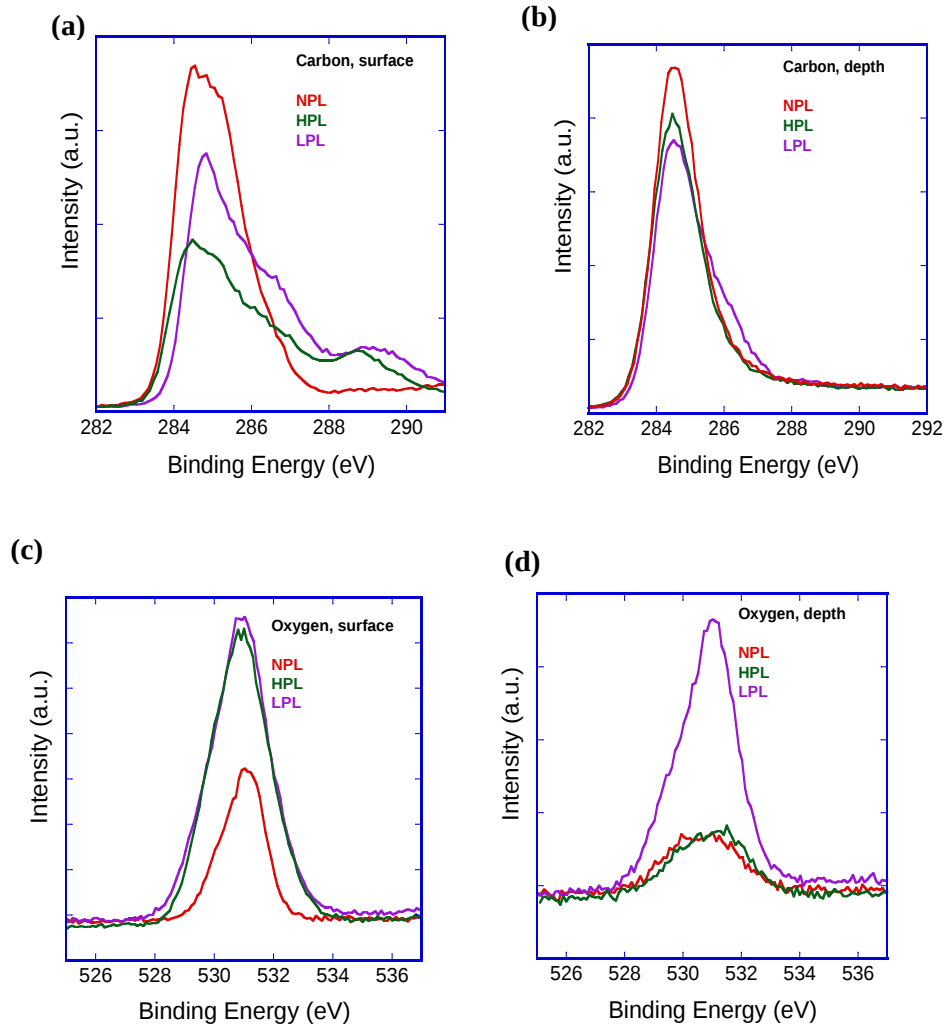


Figure 3.9. XPS spectra of C 1s on (a) surface (b) depth, O 1s on (c) surface and (d) depth.

3.2.5. Effect of plasma power on device performance

I-V and IPCE curves are presented in Figure 3.10. for all three devices. Detailed photovoltaic parameters are summarized in Table 3.5. As we noticed that atmospheric conditions, such as humidity, during device testing also was affecting the performance, we did these measurements in a controlled atmosphere in order to decipher the influence of oxygen plasma treatment.

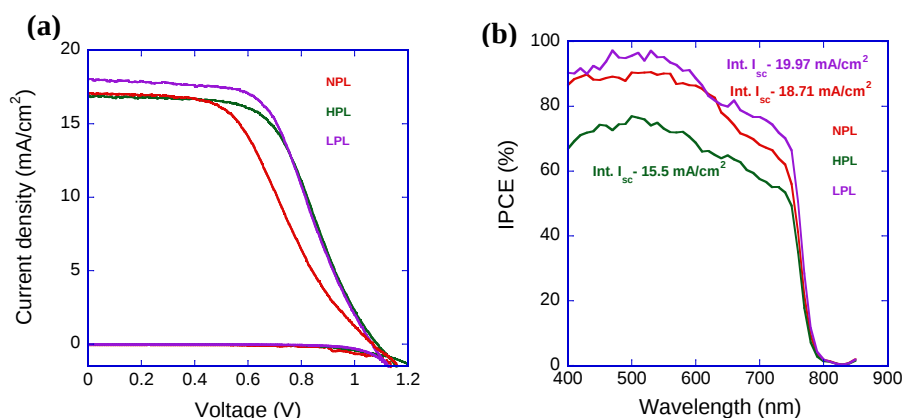


Figure 3.10. (a) I-V and (b) curve for non-plasma and plasma treated devices.

Device	V _{oc} (V)	I _{sc} (mA/cm²)	FF	PCE (%)	R _s (Ohm)	R _{sh} (Ohm)
NPL	1.09	17.33	0.33	6.24	1606	31500
HPL	1.09	16.89	0.56	10.33	1540	31940
LPL	1.05	18.05	0.57	10.8	1510	31700

Table. 3.5. Calculated photovoltaic parameters for reverse scan of non-plasma and plasma treated samples.

It was found that PCE increased dramatically by upon 70 % upon treating the device with oxygen plasma. While both LPL and HPL devices yielded almost the same PCE values, which are 10.8 % and 10.3 % respectively, the PCE of NPL device was only 6.2 %. V_{oc} was not influenced by the treatment, I_{sc} increased slightly for LPL treated sample and was almost the same in case of HPL. Primary improvement was in FF.

To investigate the limit for enhancement of the device, performance IPCE spectra were measured (Figure 3.10.b). The I_{sc} obtained by integrating IPCE over AM1.5G solar spectrum was 18.71 mA/cm² for NPL sample. It reduced to 15.5 mA/cm² for HPL sample and increased to 19.97 mA/cm² for LPL sample. This change was consistent with the observed trends in I_{sc} . In the IPCE measurement, wavelengths 300-400 nm were not included in order to avoid exposing the samples to UV light. Maximum IPCE value was 90%, which was observed in case of LPL device. $IPCE_{max}$ was 86 % in the case of NPL device and 66 % for HPL device.

The high V_{oc} and high IPCE point to unusually slow recombination of electrons and holes in the perovskite absorber layer. The second-order rate constants for uncontacted thin films reported to be four orders lower than the Langevin limit for bimolecular recombination.¹⁶ The reasons for such a slow recombination rate are currently a central topic of discussion^{17,18} and it has been suggested that the formation of ferroelectric domains may lead to spatial separation of electrons and holes.¹⁹⁻²²

In all measurements IPCE value were almost consistent till about 630 nm, but it showed degradation at higher wavelengths. IPCE dropped to about zero for wavelengths above

820 nm and hence, the band gap of the perovskite absorber was calculated as 1.51 eV. In the case of LPL the treatment improved charge collection efficiency, which indicated that the generated carriers were able to reach electrodes more efficiently. In case of HPL, increased charge carrier recombination due to the defects created by high power plasma could be main reason for the observed reduction.

When a polymer is exposed to an oxygen-containing plasma the surface changes to a high-energy state (increase in surface tension) as a result of the formation of polar groups. Oxygen and oxygen-containing plasmas are most commonly employed to modify polymer surfaces. It is well known²³ that an oxygen plasma can react with a wide range of polymers to produce a variety of oxygen functional groups, including C-O, C=O, O-C=O, C-O-O and CO₃ at the surface. In an oxygen plasma two processes occur simultaneously: 1) etching of the polymer surface through the reaction of atomic oxygen with the surface carbon atoms, giving out volatile reaction products and 2) the formation of oxygen functional groups at the polymer surface through the reaction between the active species from the plasma and the surface atoms. The balance of these two processes depends on the operation parameters of a given experiment.

Improvement with plasma treatment suggested that oxidation of spiro-OMeTAD happened faster. That means, the treatment increased hole concentration and hole transferring ability. An assumption is that oxygen species such as (O⁻, O²⁻, OH⁻), excited oxygen, and free electrons etc. are created by plasma at spiro-OMeTAD surface and energy of these species transferred to the solid by bombarding it. As a result of the reaction with organic contaminants, gases/vapors such as H₂O, CO, CO₂, and light

hydrocarbons could be formed. These products were sucked out by the vacuum pump during processing.²²

To determine if the spiro-OMeTAD conductivity was increased by oxygen plasma treatment, the HTM layer was characterized using four-point probe measurement. The configuration used for this measurement is schematically shown in Figure 3.11 and the measured conductivity values are shown in Table 3.6. While the conductivity of spiro-OMeTAD layer without using any dopant or additive was $1.2 \times 10^{-7} \text{ Scm}^{-1}$, it increased to $1.4 \times 10^{-5} \text{ Scm}^{-1}$ by adding Li-TFSI salt and 4-tert additive. The spiro-OMeTAD conductivity increased further to $1.4 \times 10^{-4} \text{ Scm}^{-1}$ after plasma treatment and it was in same order of magnitude as in the case of spiro-OMeTAD doped with FK. Pristine Spiro-OMeTAD is essentially a poorly conducting insulator, causing devices to suffer from high series resistance owing to poor hole transport through the device. This leads to poor charge collection efficiencies as charge recombination dominates over charge transport.^{24,25} Additive like Li-TFSI, does not directly oxidize Spiro-OMeTAD, but accelerate the reaction between Spiro-OMeTAD and oxygen.²⁶

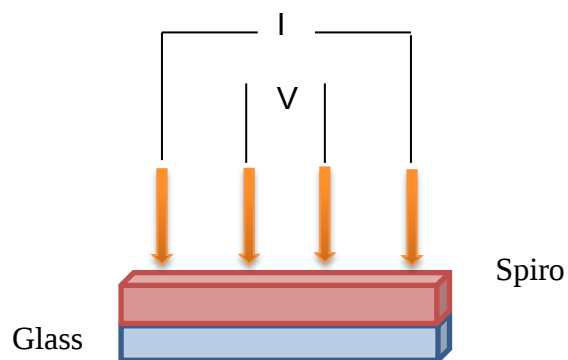


Figure 3.11. An illustration of the four-point-probe measurement configuration used for determining spiro-OMeTAD conductivity.

Solution	Conductivity (Scm^{-1})
Without additive and dopant	1.2×10^{-7}
With TBP, Li-TFSI	1.4×10^{-5}
With TBP, Li-TFSI plasma treated	1.4×10^{-4}
With TBP, Li-TFSI and FK dopant	5×10^{-4}

Table. 3.6. Calculated conductivity values.

3.2.6. Optimization of plasma power with respect to fabrication humidity

We investigated the effect of post-fabrication treatments on PSC and optimized conditions for best performance of the device. Since some of the parameters were interrelated, we had to be extremely cautious to find the right condition. All processes involving oxygen doping, modulates the conductivity of the spiro-OMeTAD. So we conducted experiments at 30 % and 9 % fabrication RH with two plasma treatment conditions. Results are shown in figure 3.12 and 3.13 with calculated parameters in Table 3.7 and 3.13. respectively.

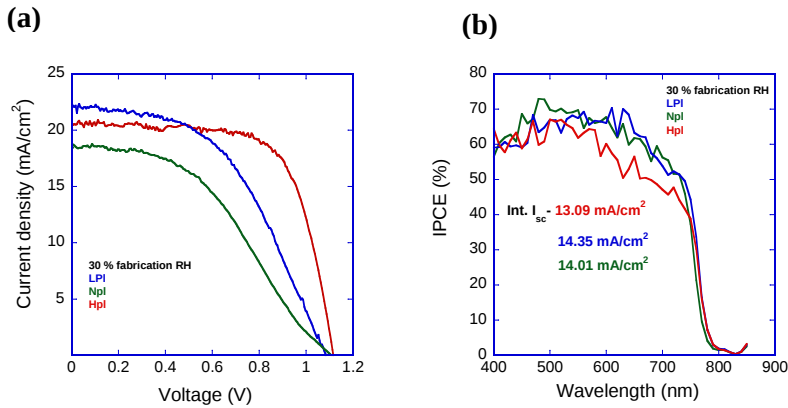


Figure 3.12. (a) I-V and (b) IPCE curve for devices without FK doped spiro-OMeTAD treated or untreated with oxygen plasma. The fabrication RH was 30 %.

Device	V_{oc} (V)	I_{sc} (mA/cm ²)	FF	PCE (%)	R_s (Ohm)	R_{sh} (Ohm)
LPL	1.08	22.22	0.49	11.79	529	10668
HPL	1.1	20.42	0.7	15.81	410	19757
Npl	1.1	18.68	0.42	8.7	740	10675

Table. 3.7. Calculated photovoltaic parameters for reverse scan of non-plasma and plasma treated samples.

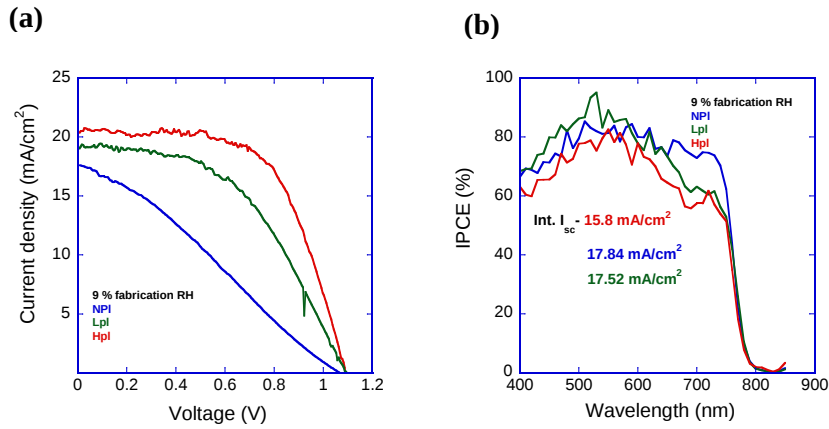


Figure 3.13. (a) I-V and (b) IPCE curves for devices without FK doped spiro treated or untreated with oxygen plasma. The fabrication RH was 9 %.

Device	V_{oc} (V)	I_{sc} (mA/cm ²)	FF	PCE (%)	R_s (Ohm)	R_{sh} (Ohm)
NPL	1.05	17.57	0.29	5.39	1924	5500
HPL	1.09	20.28	0.62	13.85	549	11912
LPL	1.09	19.3	0.49	10.34	675	11818

Table 3.8. Calculated photovoltaic parameters from the reverse scans of non-plasma and plasma treated samples.

In both fabrication RH conditions, PCE enhanced upon plasma treatment. The NPL device had PCE 8.7% in high fabrication RH while it was 5.39% in low fabrication RH, which is an indication of the influence of fabrication RH in the device performance as discussed in detail in chapter 2. Highest PCE 15.81 % was obtained for HPL device fabricated at 30 % RH. IPCE curves showed an overall reduction in high RH fabricated devices. The highest value was 70 % for high RH and 80 % for low RH devices. The highest I_{sc} were almost the same in both RH conditions. The integrated current in case of low RH devices matched with I_{sc} whereas it did not match in the case of high RH. The FF in the case of HPL was the best in both RH conditions, but our observation was that LPL with 9 % RH was the optimum condition as it was more stable compared to HPL. It had matching I_{sc} and lower hysteresis (discussed later in this chapter).

Later we found that air-fabricated devices were difficult to reproduce. So in order to produce stable devices we switched fabrication atmosphere to nitrogen. These devices were then air treated for a short time. LPL plasma condition was used for fabricating the devices. Effect of measurement ambient (chapter 4) was studied on these devices. Also OCVD and impedance studies were done on these devices to understand the transport and recombination mechanism.

We also investigated the reproducibility of the performances these devices treated with plasma. The histogram showing efficiency distribution is provided in Figure 3.14.

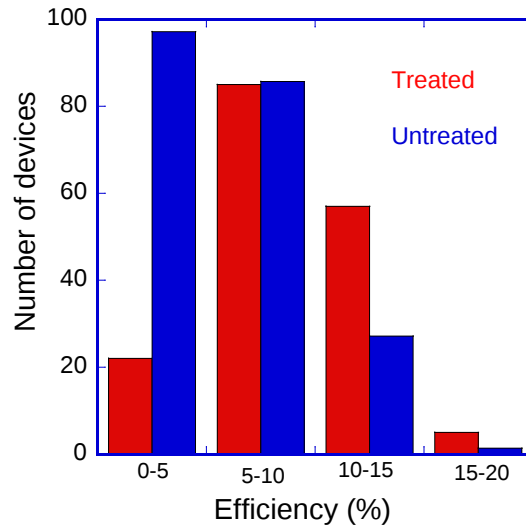


Figure 3.14. Efficiency distribution for non-plasma and plasma treated devices.

3.3. Hysteresis influenced by plasma treatment

We investigated the effect of oxygen plasma treatment on the hysteresis behavior of the devices, which is a major concern in PSCs. Results showed that though PEC enhancement was high in HPL devices, the increased plasma power made hysteresis worse. (Figure 3.15).

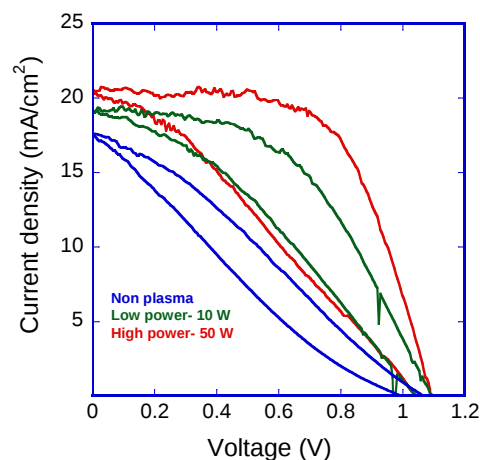


Figure 3.15. Effect of plasma treatment on hysteresis.

At higher plasma power, ions energy became higher. These energetic ions could penetrate more deep in to spiro-OMeTAD layer and reach the perovskite-spiro interface, cause degradation of the perovskite layer. From our studies we found oxygen in the perovskite layer also as one of the possible cause for hysteresis. The device architecture could be another cause for hysteresis. Anomalous hysteresis behavior was observed by various groups in a variety of configurations: planar PSCs on compact layer of TiO_2 , mesoporous/planar hybrid PSCs with perovskite capping layer, mesoporous PSCs on Al_2O_3 , HTM-free PSCs, and inverted polymeric perovskite devices.²⁷⁻³¹ But it was apparent that mostly the structures where the perovskite was infiltrated into a mesoporous titania scaffold had lower hysteresis problem compared to those fabricated in a planar configuration on compact TiO_2 or mesoporous Al_2O_3 .³²⁻³⁴ The compact TiO_2 and spiro-MeOTAD layers in the normal planar structure play critical roles in the electrode polarization and affect hysteresis.²⁷

3.4. Conclusion

In summary we have shown that plasma treatment can be a replacement for chemicals, which have been used as dopant for spiro. This treatment is fast, as well as conformal and environmental friendly. Also we demonstrate that, without effecting the bulk properties of device its performance can be enhanced by short plasma treatment.

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4. Mechanistic studies using impedance spectroscopy

4.1 Study on the effect of humidity and ambient during measurement

Unsealed devices always behaved differently in repeated measurements. Interaction of the constituent layers of the device with the outside ambient and humidity was playing a major role for this behavior. Deterioration was inevitable in devices exposed to humidity. But the time of deterioration depends on the level of humidity already incorporated during the fabrication time and the humidity at which the unsealed devices are characterized. In order to study these effects separately, a controlled environment measurement cell was used for further experiments to avoid any external interaction.

4.1.1 Air/Argon atmosphere at constant humidity

In order to investigate the effect of oxygen during measurements we performed solar cell characterization in air or argon environment under dry conditions ($RH < 2\%$) using the constant environment chamber that we fabricated. For this study, the devices were fabricated in 9% humid nitrogen and then exposed to 30% humid air for 30 minutes. No oxygen-plasma treatment was done on these samples. The I-V characteristics of the unsealed devices were measured in dry air first and then in dry argon. The devices were loaded in the chamber through which dry air was passed. The first measurement was done after 30 minutes and the second after 60 minutes. . I-V and IPCE results are presented in Figure 4.1 and corresponding parameters are shown in Table 4.1. The

measurement after 30 minutes exposure to dry air yielded a PCE 6.24% with V_{oc} 1.14 V, I_{sc} 17.31 mA/cm² and FF 0.31. The PCE increased to 8.55 % after another 30 minutes of exposure in air, which was primarily a result of the enhanced FF. Increased FF was attributed to reduced R_s value from 1698 ohm to 1650 ohm. This result confirmed the incorporation of additional oxygen in spiro-OMeTAD layer during the time of measurement. Among different layers in the cell, the spiro-OMeTAD is the one first affected by ambient conditions¹. In solid state DSSCs that employ LiTFSI-doped spiro-MeOTAD, the spiro-OMeTAD layer should be fabricated in ambient-air in order for it to work properly.^{2,3} Similarly, for PSC it is common to expose the device to ambient air after fabrication in order to obtain high PCE.³ Ambient air exposure results in electrical conductivity enhancement in LiTFSI-doped spiro-MeOTAD and is associated with light induced oxidation reaction.^{4,5} Common spin-coating method for spiro-MeOTAD coating create pinholes in the film, no matter how carefully the process is done. These pinholes are reported to accelerate inward diffusion of oxygen and humidity (if measurement is done in non-zero RH environment) from ambient into and outward diffusion of chemical elements/compounds, such as LiTFSI. Thus, it means that ambient air exposure results in a re-distribution of LiTFSI dopants across the spiro-MeOTAD film.⁶ This process is known to be the main reason for improved conductivity and enhanced performance.⁶⁻¹⁰

We observed in our experiments with different devices that exposing the device to dry air for longer time could degrade the devices. We understood this from the fact that IPCE values in the visible light range reduced with time and the integrated current no longer matched with I_{sc} . The degradation mechanism of perovskite in the presence of dry O₂ was studied by Aristidou et al.¹² As per their finding, superoxide O₂⁻ is generated when

O₂ reacts with photo-generated electrons, which leads to the deprotonation of perovskite, resulting in its decomposition into CH₃NH₂, PbI₂, I₂ and H₂O. Thus, combined action of light and molecular oxygen on photoactive layers results in the decomposition of the perovskite.^{11, 12}

In order to confirm whether oxygen was the cause of cell degradation, the environment was switched from dry air to dry argon after the second measurement in air (after 60 minutes) when the IV curves showed the maximum performance. The device was then kept in dry argon for another 30 minutes before taking another measurement. The IPCE spectrum showed a more or less a similar nature as the spectrum obtained after 60 minutes exposure to air. (results not shown here). The result indicated that the degradation was caused by oxygen reaching the perovskite layer. Nevertheless, we noticed that longer exposure to argon can make oxygen leave the spiro-OMeTAD layer, which adversely affected the device performance.

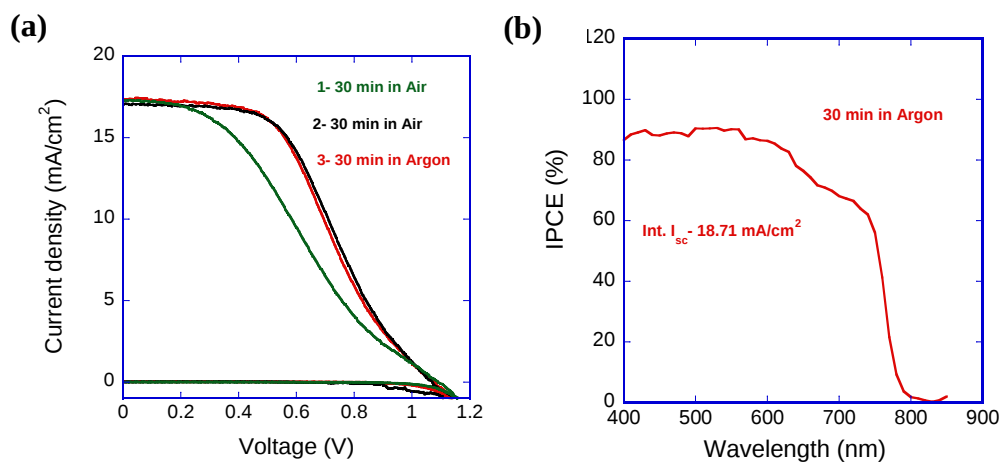


Figure 4.1. (a) I-V and (b) IPCE curve from a device tested in dry air or argon.

Sample	V _{oc} (V)	I _{sc} (mA/cm ²)	FF	PCE (%)	R _s (Ohm)	R _{sh} (Ohm)
1-30 min in Air	1.15	17.31	0.31	6.24	1698	24166
2-30 min in Air	1.13	17.05	0.44	8.55	1650	24137
3-30 min in Argon	1.13	17.4	0.42	8.4	1672	24120

Table. 4.1. Calculated photovoltaic parameters for devices tested in dry oxygen or argon atmosphere.

We collected the impedance data in the frequency range 1 MHz – 1 Hz from the same device under illumination after the I-V measurements. The measurement was done by giving a constant forward bias to the device equal to the open circuit voltage. Impedance was resolved into real and imaginary parts and Cole-Cole impedance plots were constructed. The arcs in the Cole-Cole plots were fitted with equivalent circuit models. The curves for the device under discussion are shown in Figure 4.2.a and the equivalent circuit model used for fitting in Figure 4.2.b. The values of the circuit model parameters obtained from fitting are given in Table 4.2.

Each curve in Figure 4.2 consists of one major arc and a spur. Our fitting results showed that the major curve consists of two semicircles: one at high frequency and the other at lower frequency. The semicircle at high frequency was attributed to the charge transport through the device (the bulk effect) and that at low frequency to the charge transfer at the spiro-perovskite interface and perovskite titania interface (the interface effect). A third

low frequency spur corresponding to the charge recombination/ion accumulation was present in the data. Upon fitting this spur (results not shown here) we obtained capacitance in the mF range. This super capacitance effect in perovskite cells is a topic of debate in the perovskite solar cell field ²¹. Due to the complexity in the analysis of the data in the light of ongoing discussions, we refrained from fitting the spurs and focused our discussion to the two higher frequency semicircles.

R_1 is the series resistance at the electrode, C_2 is the geometric capacitance, R_2 is the bulk charge transport resistance, C_3 is the interface capacitance and R_3 is the charge transfer/recombination resistance at the TiO_2 /perovskite and perovskite/spiro-OMeTAD interfaces. From Table 4.2, it can be seen that the time constants T_2 and T_3 for both processes are almost in the same range. That means, T_3 less likely to be associated with recombination.

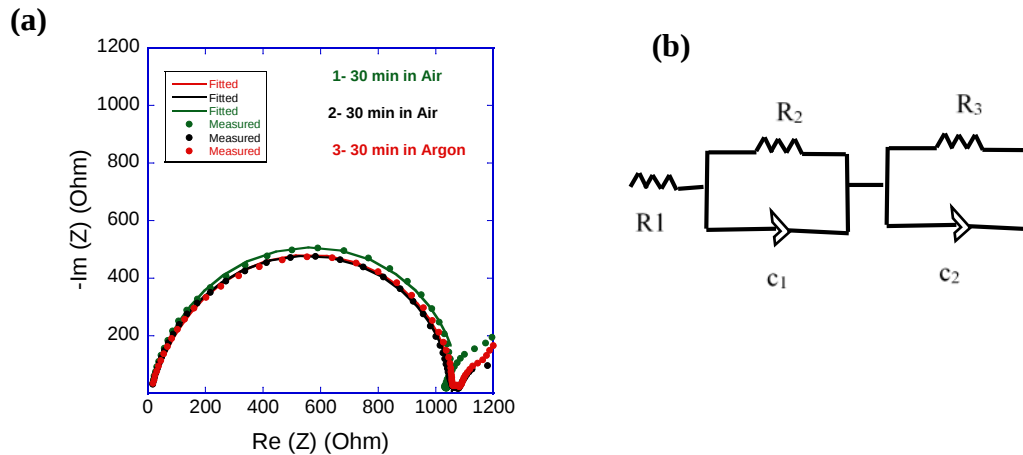


Figure 4.2. (a) Cole-Cole plots showing the influence of atmosphere used during device testing (b) equivalent circuit model used for fitting the arcs.

The measurement was done in dry atmosphere.

Ambient	R ₁ (Ohm)	R ₂ (Ohm)	R ₃ (Ohm)	C ₂ (F)	C ₃ (F)	T ₂ (s)	T ₃ (s)
1-30 min in Air	11	75	998	3.2×10^{-7}	4.3×10^{-9}	2.4×10^{-5}	4.3×10^{-6}
2-30 min in Air	14	75	967	1.2×10^{-7}	6.7×10^{-9}	8.8×10^{-6}	6.5×10^{-6}
3-30 min in Argon	12	89	959	2.6×10^{-7}	9.6×10^{-9}	2.3×10^{-5}	9.2×10^{-6}

Table. 4.2. Equivalent circuit parameters obtained from fitting of the curve in Figure 4.1. The measurement was done in dry ambient.

To verify this hypothesis, we performed voltage decay measurements by monitoring the open circuit voltage after shutting off the illumination. The results are in Figure 4.3 and showed almost same nature for measurement in air and argon. It can be seen that at the high-voltage range (near the value at illumination), the carrier life time was in the millisecond region. The lifetime rose to a few seconds as the photogenerated carrier concentration decreased under dark condition. In contrast, the time constants T₂ and T₃ obtained from impedance curves are in microseconds range. Hence, this result indicated that the high and medium frequency arcs were not arising from charge recombination. On analyzing the results in Table 4.2, it can be seen that R₂ remained same and C₂ reduced slightly when the device was kept for 60 min in air and it again increased upon keeping in argon. This might be due to the oxidation of spiro-OMeTAD in air and the slight removal of spiro-OMeTAD oxygen in argon environment. The interface resistance

R_3 reduced with time and capacitance C_3 increased with time. We believe that this change was caused by the changes in the spiro-OMeTAD /perovskite interface due to oxygen accommodation in air and its redistribution in argon environment.

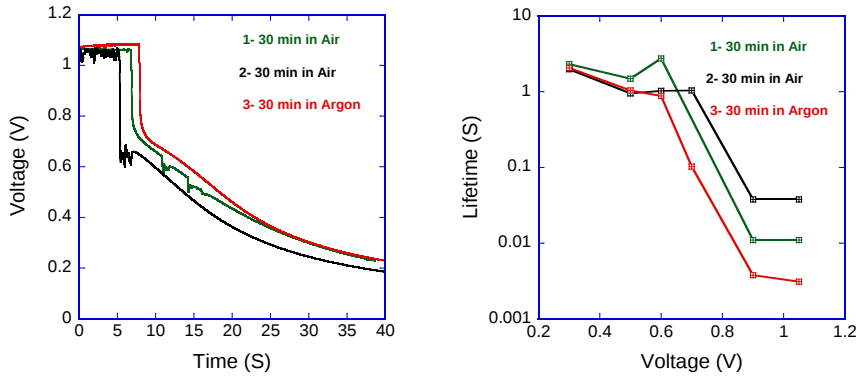


Figure 4.3. (a) Measured OCVD curves,
(b) Calculated lifetime for device measured in dry ambient.

4.1.2 Measurements in dry and humid air

In this section we discuss our results on effect of introducing humidity during measurement in presence of oxygen. The samples were prepared in 9% humid nitrogen and then exposed to 30% humid air for 30 minutes. The samples were treated with oxygen plasma under HPL conditions for 30 s. First measurement was done in dry air ambient then 30% of humidity was introduced in order to see its effect on performance as well as internal electrical properties. I-V and IPCE results are given in Figure 4.4 and corresponding parameters are shown in Table 4.3. I_{sc} and V_{oc} did not show any change after humidity exposure. There was, however, a slight improvement in FF. The IPCE spectra indicated degradation of the cell after exposure to humid oxygen environment.

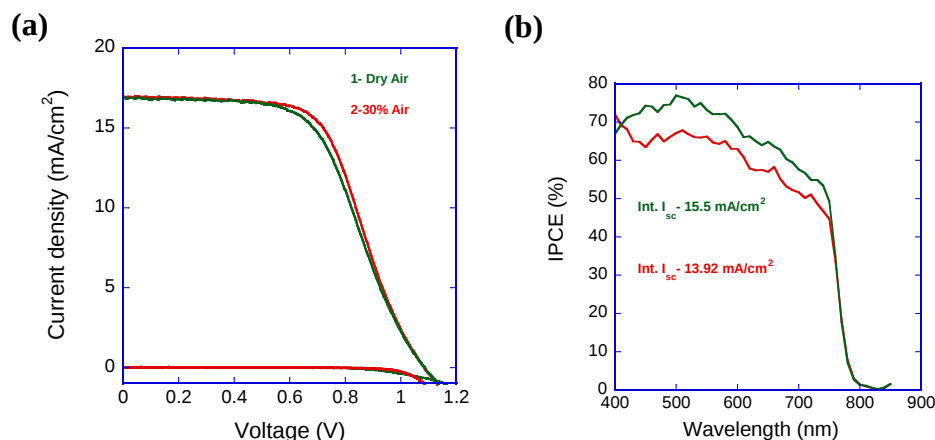


Figure 4.4. (a) I-V and (b) IPCE for sample measured in oxygen and humidity.

Sample	V _{oc} (V)	I _{sc} (mA/cm ²)	FF	PCE (%)	R _s (Ohm)	R _{sh} (Ohm)
1-Dry air	1.12	16.9	0.54	10.32	1285	30765
2- 30 % air	1.12	16.9	0.57	10.87	1283	30769

Table. 4.3. Calculated solar cell parameters for samples measured in dry and humid air environment.

The Cole-Cole curves corresponding to conditions given in Fig. 4.4 are shown in Figure 4.5.a and the equivalent circuit model used for fitting in Figure 4.4b. The values of the circuit model elements obtained from fitting are given in Table 4.4. It can be seen from Table 4.5 that R_2 , C_2 and C_3 reduced whereas R_3 increased upon exposure to humidity. As the samples were exposed to HPL conditions, the spiro-OMeTAD layer is assumed to have sufficient oxygen. The slight reduction in R_2 could be caused by the combined effect

of water vapor and oxygen in spiro-OMeTAD causing its resistance to reduce. The increase in R_2 showed that water vapor reached the spiro-OMeTAD/perovskite interface and caused impediments for charge transfer due to perovskite restructuring. The OCVD measurements done on these samples showed a reduction in recombination life time upon exposure to humidity (see Figure 4.6), which means carrier recombination increased. Both IPCE and impedance results were in agreement. The water molecules cause problems first at the interface, which may not be immediately evident from I-V graph if the device has sufficient oxygen in the spiro-OMeTAD layer, as in the present case. The results also showed that the reduction in IPCE could be correlated with this interface phenomenon and device degradation.

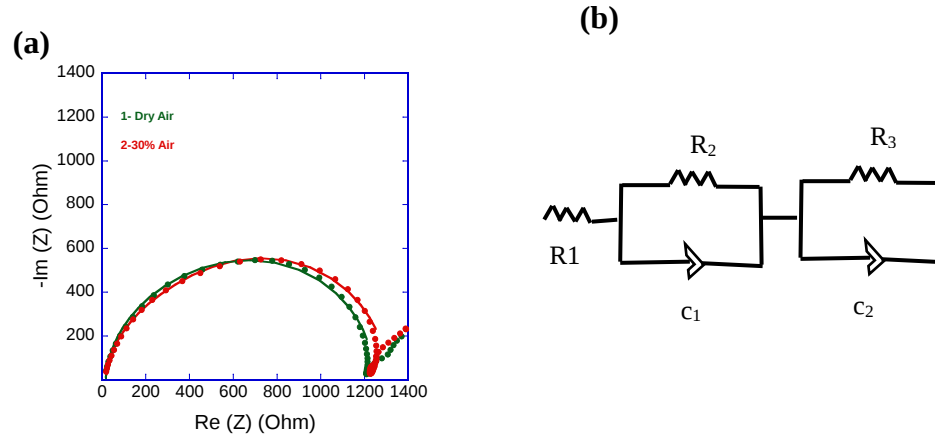


Figure 4.5. (a) Cole-Cole plots from impedance data collected from the device in Figure 4.4 under corresponding conditions. (b) equivalent model used for fitting the curves in (a).

Ambient	R ₁ (Ohm)	R ₂ (Ohm)	R ₃ (Ohm)	C ₂ (F)	C ₃ (F)	T ₂ (s)	T ₃ (s)
Dry air	16	399	831	6.7×10^{-7}	9.2×10^{-7}	2.7×10^{-4}	7.6×10^{-4}
30% air	19	342	943	1.6×10^{-8}	2.5×10^{-8}	5.5×10^{-6}	2.3×10^{-5}

Table. 4.4. Values of equivalent circuit elements obtained by fitting the data in Figure 4.5a with model in Figure 4.5.b.

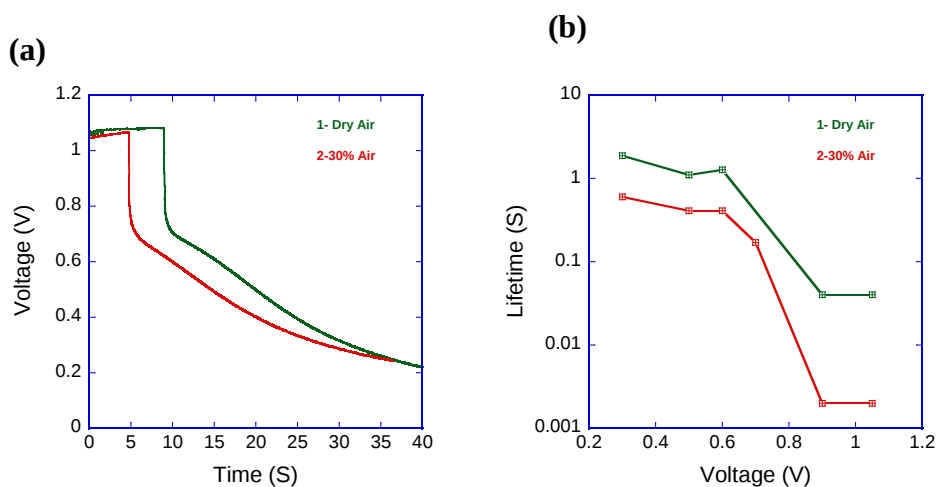


Figure 4.6. (a) Measured OCVD curves

(b) Calculated lifetime for sample measured in oxygen and humidity

4.1.3. Measurement at different humidity levels in argon environment

In this section we discuss our results on effect of introducing humidity during measurement in an inert ambient. The device was prepared in 9% humid N₂ and then treated with oxygen plasma under LPL conditions for 10 s. The devices were not exposed to humid air (as in the previous cases) to decipher the effect of humidity. First the measurement was done in argon ambient and then controlled level of humidity was introduced in order to see its effect on performance as well as internal electrical properties. The I-V characteristics and IPCE spectra are shown in Figure 4.7 and the cell parameters in Table 4.5.

While measurement in dry argon showed PCE 2.71% it enhanced to 6.32 % upon exposure to 10% humid argon and further improved to 8.5% on increasing humidity level to 30%. While V_{oc} did not show any change in this process both FF and I_{sc} were improved after introducing humidity. I_{sc} improvement was attributed to enhanced conductivity of spiro-MeOTAD while FF increased due to reduced R_s and increased R_{sh} . The results showed that although the sample treated under LPL conditions and have a certain amount of oxygen in spiro-OMeTAD, humidity acted almost the same way as oxygen and oxidized spiro-OMeTAD further. At the same time IPCE increased at 10% humid argon and reduced when humidity was increased to 30%.

It was reported that H₂O-vapor exposure resulted in an irreversible enhancement of LiTFSI-doped HTM conductivity mainly due to LiTFSI redistribution across the HTM. This observation was confirmed with XPS results¹². On the other hand, O₂ exposure

resulted in a reversible enhancement.¹² It means introducing 10% humidity started oxidation process of spiro-MeOTAD with same improvement trend observed in IPCE. Nevertheless, a further increase in humidity, although showed improved PCE, lowered IPCE values indicating that the water molecules reached spiro-OMeTAD /perovskite and started the device degradation process. As the humidity level increased, due to the same polarity between water and perovskite organic CH_3NH_3 unit encounters H_2O , bonds to two H_2O molecules will be formed and the organic–inorganic structure will be destroyed.¹³ When the humidity is reduced, the metastable monohydrated perovskite phase loses crystalline water and converts back to $\text{CH}_3\text{NH}_3\text{PbI}_3$.^{14, 15}

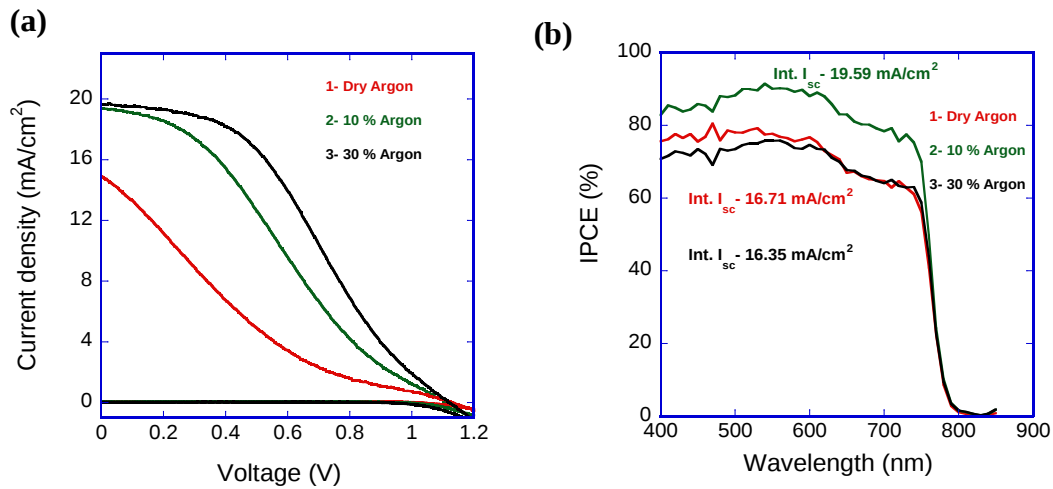


Figure 4.7. (a) I-V and (b) IPCE curve from device measured in inert ambient with different humidity levels.

Sample	V _{oc} (V)	I _{sc} (mA/cm ²)	FF	PCE (%)	R _s (Ohm)	R _{sh} (Ohm)
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1-Dry Argon	1.13	14.66	0.16	2.71	5209	1979
2- 10% Argon	1.13	19.2	0.29	6.32	2785	7380
3-30% Argon	1.13	19.67	0.38	8.5	2717	8421

Table. 4.5. Calculated photovoltaic parameters from device measured in inert ambient.

The Cole-Cole curves corresponding to the conditions given in Figure 4.7 and Table 4.6 are shown in Figure 4.8(a). The equivalent circuit model and the values of the circuit elements obtained from fitting are shown in Figure 4.8(b) and Table 4.7 respectively. It can be seen from Table 4.7 that C_2 and C_3 are high compared to the cases discussed before. The main difference between this case and the previous case (section 4.1.2) was the absence of humid-air treatment before the electrodes were fabricated. During this treatment water molecules could reach the perovskite layer and improve the charge transport properties.¹⁵ In the present case, water molecules started acting only when water vapor was introduced into the cell testing argon environment. R_2 was reduced due to penetration of water molecules through the electrode area to spiro-OMeTAD and improving its conductivity. Although R_3 decreased slightly at 10% argon, it increased to the original value at 30% argon. Hence, it can be inferred that at this stage water molecules started reaching the spiro-OMeTAD/perovskite interface. IPCE also showed

degradation in this condition. OCVD showed same trend for 10% humidity. The carrier life time was not significantly affected by humidity exposure. This shows that the influence of oxygen on recombination characteristics cannot be ignored. The recombination rate is likely decided by the interplay between oxygen and water molecules.

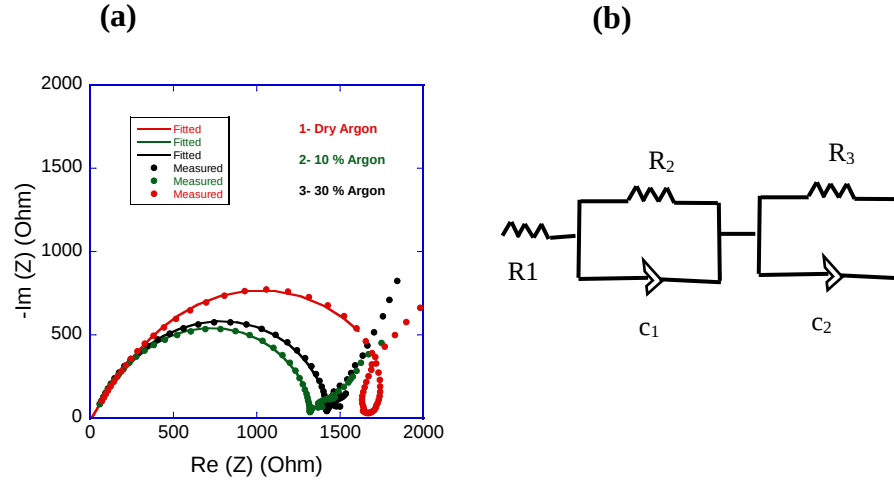


Figure 4.8. (a) Cole-Cole plot showing curves corresponding conditions given in Figure 4.7. (a). (b) equivalent circuit used for fitting. The device was measured in oxygen free environment.

ambient	R_1 (Ohm)	R_2 (Ohm)	R_3 (Ohm)	C_2 (F)	C_3 (F)	T_2 (s)	T_3 (s)
1-Dry Argon	9	705	1182	1.28×10^{-6}	1.6×10^{-6}	9.02×10^{-4}	1.9×10^{-3}
2- 10% Argon	8	280	1058	3.7×10^{-6}	4.2×10^{-6}	1.04×10^{-3}	4.45×10^{-3}

3-30% Argon	9	343	1086	1.3×10^{-6}	1.6×10^{-6}	4.46×10^{-4}	1.74×10^{-3}
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Table. 4.6. Values of circuit elements obtained from fitting. The testing was done in oxygen free ambient.

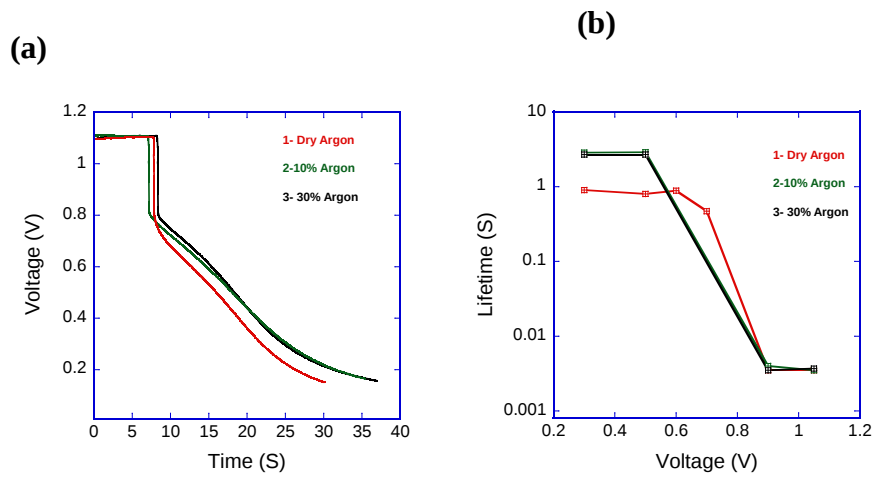


Figure 4.9. (a) Measured OCVD curves

(b) Calculated lifetime for device measured in oxygen free ambient.

4.2 Analysis of the plasma-power-dependent device performance

To obtain a clear picture of the role of plasma treatment conditions on the device performance, experiments similar to those discussed in the previous sections were done. The device is prepared in 9% humid nitrogen, treated with 30% humid air for 30 minutes and then subjected to LPL or HPL oxygen plasma treatment conditions.

I-V and IPCE curves of the device are shown in Figure 4.10. (a) and (b) respectively. The cell parameters are summarized in Table 4.8. As discussed in chapter 3, the improvement in fill factor with plasma treatment and the reduction in IPCE at HPL conditions are evident from the Figure 4.10. Also PLP condition is found to be the optimized one for the best performing solar cell.

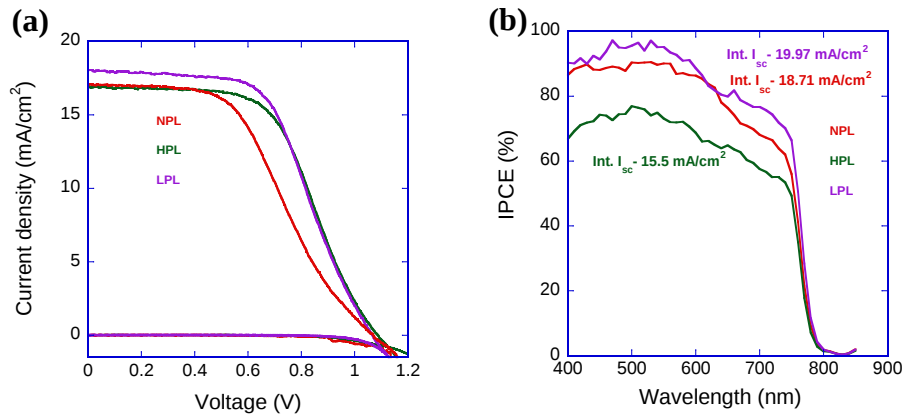


Figure 4.10. (a) I-V and (b) curves from untreated and plasma treated devices.

Device	V _{oc} (V)	I _{sc} (mA/cm ²)	FF	PCE (%)	R _s (Ohm)	R _{sh} (Ohm)
NPL	1.09	17.33	0.33	6.24	1606	31500
HPL	1.09	16.89	0.56	10.33	1504	31940
LPL	1.05	18.05	0.57	10.8	1510	31700

Table. 4.7. Calculated cell parameters from reverse scans for untreated and plasma treated devices.

The Cole-Cole plot and equivalent circuit model are given in Figure 4.11. The equivalent circuit parameters obtained from circuit model fitting are given in Table 4.9. It can be seen that R₂ increased with plasma power. C₂ and C₃ also increased in a similar way. Increase in R₂ was related to the changes made by oxygen in the perovskite layer. It is likely that plasma treatment drives oxygen to the spiro-OMeTAD layer. R₃ decreased at LPL condition and increased at HPL condition. Reduction in R₃ appeared to be responsible for the higher fill factor in LPL treated devices. That means, at LPL the interface got just the sufficient amount of oxygen for effective charge transfer. The XPS depth profile on a device with LPL condition showed an increased amount of oxygen compared to HPL and NPL. This supports our conclusion from the impedance studies that in case of LPL condition there is right amount of oxygenation in the spiro-OMeTAD which enhances its conductivity. In HPL conditions the interface would receive higher oxygen flux, causing harm to the perovskite layer and causing both R₂ and R₃ to increase. This is supported by the fact that C₃ increased dramatically with plasma power by two orders of magnitude.

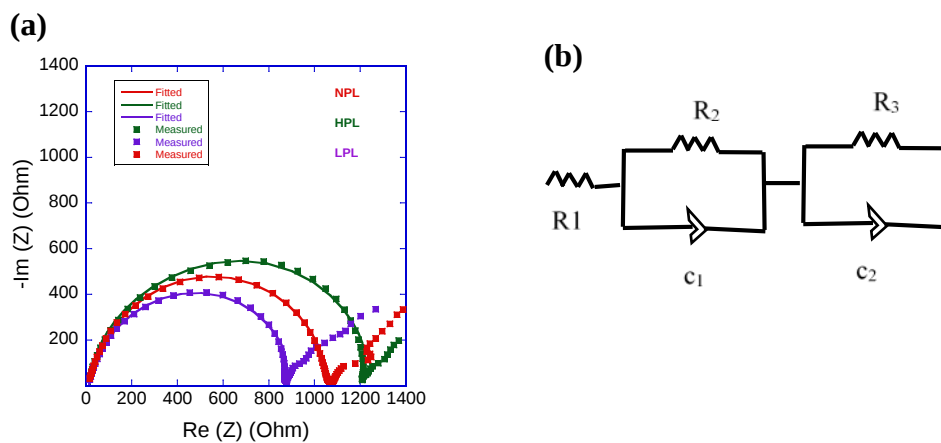


Figure 4.11. Measured and fitted IS curves for non-plasma and plasma treated devices.

Device	R ₁ (Ohm)	R ₂ (Ohm)	R ₃ (Ohm)	C ₂ (F)	C ₃ (F)	T ₂ (s)	T ₃ (s)
NPL	14	75	967	1.2×10^{-8}	4.5×10^{-9}	9.3×10^{-7}	4.3×10^{-6}
LPL	14	196	692	1.3×10^{-7}	9.4×10^{-8}	2.5×10^{-5}	6.5×10^{-5}
HPL	16	399	831	6.7×10^{-7}	9.2×10^{-7}	0.0002	0.0007

Table 4.8. Calculated IS parameters from fitted curves.

OCVD measurement was also performed to investigate effect of plasma on lifetime of carriers. Measured voltage decay and calculated lifetime are shown in Figure 4.12. Three

portions could be distinguished from lifetime curve: close to open circuit condition with lifetime in range of 1-10 ms, middle portion for voltages 0.4-0.9 V with almost steady lifetime value, and a low-voltage part with extraordinary high values on the order of 1-2 s. Snaith et al. reported that some cells exhibit a persistent photovoltage that extends the decay time into the region of seconds when the voltage falls below 0.4 V.¹⁶ This behavior could be attributed to slow recombination dynamic as Frost et al. predicted the formation of small polarized domains within the perovskite film that may act as small pn-junctions.¹⁷ Such small polarized domains are believed to help separate the electrons and holes and also depress charge carrier recombination.¹⁸ In PSC cells or sDSCs using a TiO₂ scaffold as an ETM, a long carrier lifetime is also found and was explained in terms of segregation of the electrons into the TiO₂.^{19, 20}

The carrier lifetime in the voltage range near the open-circuit voltage reduced slightly with upon plasma treatment. Lifetime in the lower voltage range was nearly unaffected by the treatment. The reduction of life time at higher voltages can be correlated with the impedance results discussed in earlier. Results from both impedance spectroscopy and OCVD measurements showed that to some extent the spiro-OMeTAD/perovskite interface was affected by oxygen plasma treatment. Nevertheless, we demonstrated that the damage could be minimized and performance could be maximized by appropriately choosing the plasma conditions.

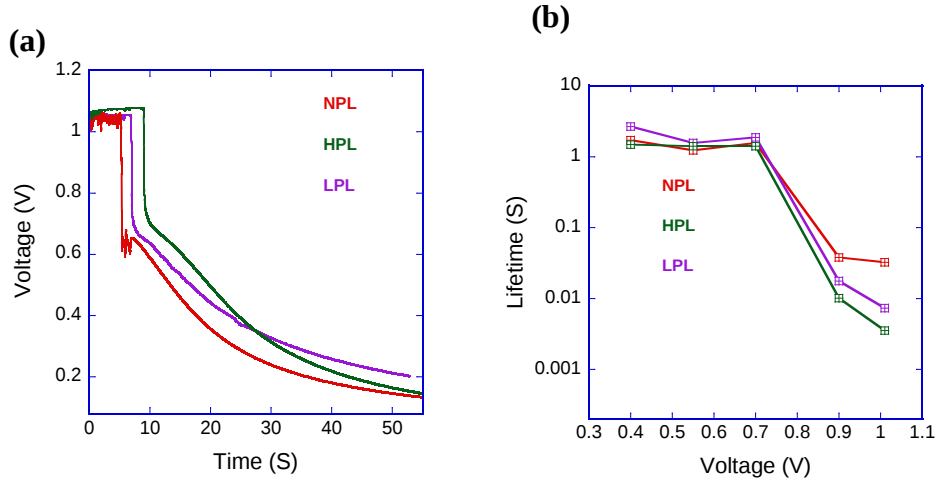


Figure 4.12. (a) Measured OCVD curves

(b) Calculated lifetime for non-plasma and plasma treated devices.

4.3. Conclusion

In this chapter we showed our study on the effect of measurement atmosphere and plasma treatment on electrical elements. With IS study we notice humidity during measurement could change capacitance values while oxygen only didn't show significant change in circuit though it showed an enhancement in FF. In plasma treated increase in capacitance value mainly with high power could be correlated with observed increase in hysteresis.

4.4. References

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5. Summary and outlook

5.1. Conclusions

The primary aim of this dissertation work was to study systematically the factors influencing the performance of PSCs and their nature of interaction. We used impedance spectroscopy as a diagnostic tool for mechanistic understanding. In the course of this dissertation work, we developed a plasma based treatment strategy to improve the conductivity of the hole transport layer, spiro-OMeTAD, in a few seconds and hence, the performance of the PSCs. Major outcomes of the work are summarized below.

We prepared mixed halide perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_2\text{Cl}$) films by the sequential deposition method in a controlled humidity environment. The stack consisted of a sol-gel titania layer on FTO glass, the perovskite layer, hole transport layer (spiro-OMeTAD) and silver electrode. In our mixed halide cells we found that Cl doping enhanced PCE and improved device tolerance to measurement ambient humidity. Although it was reported to be hard to detect Cl in film using XPS, we could find Cl in the stack and study the distribution with depth. Our study showed the distribution of Cl within the perovskite layer is an important factor determining the superior performance of the PSCs.

We noticed that not only the performance, but also the crystal structure was effected by annealing temperature of the perovskite layer. At higher temperatures, perovskite started decomposing, which was confirmed by deteriorated performance of the device and

increased peak intensity of PbI_2 in XRD pattern. Furthermore, we found that the high thickness of the HTM could diminish the device performance.

Spiro-OMeTAD is known to show high conductivity by using additives like Li-TFSI and TBP. A common method to further improve the conductivity is the use of FK dopant. In our study, we discovered that conductivity of spiro-OMeTAD could be improved by using a short oxygen plasma post fabrication treatment without using FK dopant. Although voltage was not affected significantly, the FF changed dramatically. The short circuit current also showed some increase. Nevertheless, a high power plasma power was found to deteriorate the device performance. The treatment using plasma power in the range of a few watts for a few seconds was found to be the optimum. This method is expected to reduce the fabrication cost and time of the cell, which is relevant for the commercialization of the technology.

We demonstrated that not only the RH level during fabrication but also that present in the testing environment could determine the performance of PSCs. A certain level of RH during fabrication was needed in order to get working PSCs. At the same time device could only tolerate a certain amount of water molecules and increasing RH and hence the amount of water molecules in perovskite could deteriorate device.

From investigations on the nature of interaction of parameters such as humidity and oxygen in the fabrication and testing environment and plasma treatment conditions using impedance spectroscopy, we found that devices require a certain amount of water molecules and oxygen in spiro-OMeTAD and perovskite layer to have the maximum fill factor. Nevertheless, excess of oxygen and water in the perovskite layer could degrade it.

Upon plasma treatment oxygen oxidized spiro-OMeTAD and increased the conductivity of the spiro-OMeTAD layer. Oxygen reached the spiro-OMeTAD/perovskite interface even in low power plasma. Oxygen driven to the perovskite layer at high power plasma made the cell to suffer degradation. In short, low power oxygen plasma treatment is a quick and cost effective way to improve the conductivity of the spiro-OMeTAD layer and hence, the performance of PSCs.

5.2. Recommendations for future work

The information gathered through this research is expected to help understand the fundamentals of PSC working. Following are the suggestions for future efforts.

1. Stability is a concern in present day PSCs. We found that stability was affected by both oxygen and humidity in the fabrication as well as device testing conditions. A spectroscopical approach, if used in a very controlled environment, would throw more light into the molecular interaction causing degradation.
2. Extend the plasma treatment strategies to cells in other PSC geometries and compositions.
3. Explore cheaper ways to fabricate PSCs.
4. Test buffer layers at the perovskite/spiro-OMeTAD interface to prevent the oxygen diffusion into the perovskite layer.
5. Understand the cause of the hysteresis and eliminate it.