



*Master of Science in Organic Electronics & Applications
(OREA)*

***Design, Fabrication and
Characterization of Efficient Solution
Processed Organic–Inorganic Hybrid
Perovskite Solar Cells***

Nikolaos Tzoganakis

Master Thesis

Heraklion 2019

ABSTRACT

Developing countries and emerging markets demands for environmental friendly renewable energy sources continuously increases. Renewable energy technology and especially photovoltaics is an alternative solution that gains ground year after year to replace the established carbon consuming energy production methods. One of the latest and of high potential photovoltaics' generation technology is the so-called perovskite solar cells (PeSCs). A PeSC consists of a laminated structure, which is being developed layer by layer using facile deposition methods onto rigid and flexible substrates. Organic-inorganic hybrid perovskite is a material with the crystal structure AMX_3 , where A is the organic part, M is the metal and X stands for a halide ion. Since 2009 when the first application of organohalide lead perovskite as the light harvester in solar cells was reported¹, tremendous attention has been devoted to these new types of perovskite-based solid-state solar cells and remarkable power conversion efficiency of over 24% has been achieved up to date. With respect to its hybrid nature, the material is endowed with high carrier mobility and absorption coefficient, relatively long diffusion lengths and low temperature processing, that renders it ideal for optoelectronic applications. During the implementation of this thesis, the mixed two perovskites CsMAFA, RbCsMAFA were synthesized and applied as light harvesting material in planar inverted PSCs. In our case the hybrid perovskite semiconductor selected, was deposited using the spin coating deposition technique on top of glass/ITO/PTAA substrate and after that the deposition of an electron transport material followed. To complete the device, thermal evaporation was used to form the silver counter electrode. A variety of factors (annealing temperature of the perovskite, morphology, and additives to perovskite) that play a critical role towards the achievement of high and stable power conversion efficiencies (PCEs) were studied and applied.

Acknowledgments

I would like to thank Prof. Emmanuel Kymakis who has given me the opportunity to join his group and work on such an interesting project, for his encouraging attitude, support and supervision during the implementation of my thesis. I would to thank Prof Costas Petridis who gave me the mental supplies and the logic how to overcome the problems which encountered during the experiments and planning. Also, I am very grateful to my colleague, Kostas Chatzimanolis for his significant contribution in experimental procedure, measurements, his encouragement this last year of my master's program . Moreover ,I would like to give my thanks to Dr. Milos Petrovic for the topography, transient measurements and for fruitful scientific discussions. Moreover, I would like to thank all the lab members , Dr. Minas Stylianakis, Dr. Konstantinos Rogdakis, Dr. Dimitris Tsikritzis, Dr. Maria Bidikoudi, Miron Krassas, Georgios Viskadouros, Georgios Veisakis , Christos Polyzoidis, Anna Orfanoudaki for their support and patience. Last but not least the greatest thank is dedicated to my family for their support , kindness and emotional support all these years.

List of Abbreviations

- AM Air Mass
- AFM Atomic Force Microscope
- a-Si amorphous Silicon • CB Conduction Band
- DMF Dimethylformamide
- DMSO Dimethylsulfoxide
- DSSC Dye Sensitized Solar Cell
- Eg Energy band gap
- EIA Energy Information Administration
- EQE External Quantum Efficiency
- ETL Electron Transport Layer
- FF Fill Factor
- FTO Fluorine doped Tin Oxide
- HTL Hole Transport Layer
- IQE Internal Quantum Efficiency
- Isc & Jsc Short Circuit Current & Short Circuit Current density
- ITO Indium Tin Oxide
- MAI Methylammonium iodide
- MAPbI₃ Methylammonium lead iodide
- OPV Organic Photovoltaic
- MaBr Methylammonium Bromide
- PbI₂ Lead Iodide
- PbBr₂ Lead Bromide
- FAI Formamidinium Iodide
- BCP Bathocuproine
- Cs Cesium
- Rb Rubidium
- PC60BM [6,6]-phenyl-C61-butyric acid methyl ester
- PHJ Planar heterojunction structure • PV Photo Voltaic
- PL Photoluminescence
- PFN Poly [(9,9-bis(3'-(N,N-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)]
- rGO reduced graphene oxide
- SEM Scanning Electron Microscope
- TCO Transparent Conductive Oxide
- UV-Vis Ultraviolet-Visible spectroscopy •
- VB Valence Band
- CB Conduction Band
- Voc Open Circuit Voltage
- XRD X-Ray Diffraction
- CB Chlorobenzene
- EA Ethyl acetate

Figures List

- Figure 1: – Solar cell prototype
- Figure 2 – n type semiconductor
- Figure 3 – p type semiconductor
- Figure 4 – Polycrystalline silicon solar cell
- Figure 5 – Solar cell technologies
- Figure 6 – Lev Perovski , Perovskite mineral
- Figure 7 – Hybrid perovskite structure
- Figure 8 – Hybrid perovskites energy levels
- Figure 9 – Device configurations
- Figure 10 – Cubic perovskite phase
- Figure 11 – Orthorhombic perovskite phase
- Figure 12 – Rhomboedric perovskite phase
- Figure 13 – Goldschmidt tolerance factor
- Figure 14 – MAPbI₃ phases
- Figure 15 – J-V curve explanation
- Figure 16 – P-N junction diffusion , drift mechanism
- Figure 17 – Equivalent circuit
- Figure 18 – Equivalent circuit
- Figure 19 – Carriers motion in solar cells
- Figure 20 – Spin coating technique
- Figure 21 – Spray coating technique
- Figure 22 – Blade coating technique
- Figure 23 – Quantum efficiency setup
- Figure 24 – AFM experimental setup
- Figure 25 – AFM experimental setup
- Figure 26 – XRD operation principle
- Figure 27 – XRD operation principle
- Figure 28 – SEM experimental setup
- Figure 29 – Transient PC operation principle
- Figure 30 – Transient PV operation principle
- Figure 31 – Transient PC operation principle
- Figure 32 – Sonicator device
- Figure 33 – UV ozone cleaner device
- Figure 34 – MBRAUN spincoater
- Figure 35 – MBRAUN glovebox
- Figure 36 – MBRAUN thermal evaporator and operation principle
- Figure 37 – Newport solar simulator
- Figure 38 – Substrates cleaning procedure
- Figure 39 – Solutions after preparation
- Figure 40 – Solutions after preparation

- Figure 41 – Inverted solar device configuration
- Figure 42 – PTAA concentration J-V chart
- Figure 43 – PTAA concentration 2 mg/ml thickness J-V chart
- Figure 44 – PTAA concentration 4 mg/ml thickness J-V chart
- Figure 45 – PTAA concentration 6 mg/ml thickness J-V chart
- Figure 46 – PTAA concentration 6 mg/ml thickness J-V chart
- Figure 47 – AFM topography 2mg/ml
- Figure 48 – Several annealing times J-V chart
- Figure 49 – Several annealing time PCE box plots
- Figure 50 – XRD spectrum 100 C , 60 min
- Figure 51 – XRD spectrum 100 C , 45 min
- Figure 52 – SEM picture 100 C , 45 min
- Figure 53 – EDX spectrum 100 C , 45 min
- Figure 54 – Uv – Vis spectrum
- Figure 55 – Nucleation growth
- Figure 56 – Several antisolvent time dripping J-V chart
- Figure 57 – Several antisolvent time dripping PCE box plot
- Figure 58 – Several antisolvent quantity J-V chart
- Figure 59 – AFM topography 2500 rpm static
- Figure 60 – PCBM rpm comparison J-V charts
- Figure 61 – AFM topography 2500 rpm dynamic
- Figure 62 – J-V w/wo PFN
- Figure 63 – XRD triple cation reference
- Figure 64 – XRD quadrable cation reference
- Figure 65 – XRD triple cation reference
- Figure 66 – XRD quadrable cation reference
- Figure 67- BCP rpm comparison J-V charts
- Figure 68 - BCP vs PFN PCE box plots
- Figure 69- Stabiility measurments for BCP
- Figure 70 - Stabiility measurments for PFN
- Figure 71 - EQE , Integrated Jsc for best device
- Figure 72 - Several perovskite concentrations J-V chart
- Figure 73 – AFM topography 1.24 M
- Figure 74 – AFM topography 1.54 M
- Figure 75 – TPC measurements
- Figure 76 – TPv measurements
- Figure 77 – CELIV measurements
- Figure 78 – Differents Cs percentages J-V chart
- Figure 79 – Differents Rb percentages J-V chart
- Figure 80- MPPT measurement Quadrable (Cs 4%, Rb 4%)
- Figure 81- MPPT measurement Quadrable (Cs 5%, Rb 4%)
- Figure 82 – Energy levels of NiOx based device
- Figure 83 - NiOx based devices PCE box plot

Tables List

- Table 1 – First device characteristics
- Table 2 – PTAA different concentrations Device parameters
- Table 3 – PTAA concentration Thicknesses
- Table 4 – Annealing time Device parameters
- Table 5 - Antisolvent time Device parameters
- Table 6 – Antisolvent Quantity Device parameters
- Table 7- PCBM static Device parameters
- Table 8 – PCBM dynamic Device parameters
- Table 9- With/Wout PFN Device parameters
- Table 10 – BCP rpm Device parameters
- Table 11 – Several different perovskite concentration Device parameters
- Table 12- Differents Cs,Rb percentages Device parameters
- Table 13- Differents Cs,Rb percentages Device parameters

Contents

Chapter 1: Introduction

1.1 Renewable Energy Sources and Categories.....	11
1.2 Advantages of RES.....	12
1.3 Drawbacks of RES.....	12
1.4 Solar energy and significance.....	12
1.5 1.5 Solar energy as RES.....	12

Chapter 2: Background theory

2.1: Photovoltaic effect – Photovoltaic device.....	13
2.2 : Photovoltaic technologies - types of photovoltaic materials.....	16
2.3: Perovskites, applications in photovoltaic technologies.....	18
2.3.1: History of perovskites.....	19
2.3.2 : Perovskite structure	20
2.3.3: Hybrid perovskite solar cells.....	21
2.3.4 : Device architectures.....	22
2.4: Electronic structure of semiconductors.....	.
2.4.1 Atomic orbitals and molecular Orbital bonding.....	24
2.4.2 : Band formations in crystals.....	25
2.4.3 : Perovskite crystal and band structures.....	27
2.4.4 : Perovskite unit cell.....	28
2.5 : PSCs operational principles.....	31
2.5.1 : P-N junctions.....	32
2.5.2: Equivalent circuit.....	36
2.5.3: Charge transport in metal halide perovskites.....	37
2.5.4 : Interfaces and Charge transfer.....	39

Chapter 3: Deposition methods – Characterization techniques

3.1: Deposition methods.....	43
3.1.1: Solar simulator.....	43
3.1.2: Quantum efficiency.....	44
3.1.3: Atomic Force Microscopy.....	45
3.1.4: X- ray Diffraction.....	46
3.1.5: Scanning Electron Microscopy.....	47
3.1.6: Transient response measurements.....	48
3.1.6.1 : Transient photocurrent.....	49
3.1.6.2 : Transient photovoltage.....	51
3.1.6.3 : Charge extraction by linearly increased voltage.....	53
3.2 : Deposition methods	
3.2.1 : Spin coating.....	54
3.2.2 : Spray coating.....	55
3.2.3 : Doctor blading.....	55
3.2.4 : Slot die coating.....	56

Chapter 4: Experimental

4.1 : Equipment.....	57
4.2 : Materials.....	61
4.3 : Experimental procedure.....	63

Chapter 5: Results and discussion

5.1 : Optimization of triple cation Perovskite CsMAFA	69
5.1.1 : PTAA thickness.....	70
5.1.2 : Perovskite.....	74
5.1.2.1 :Annealing time.....	76
5.1.2.2 :Antisolvent quantity.....	79
5.1.2.3 Antisolvent time dripping	82

5.2 : Optimization of PCBM (ETL) : rpm ,static or dynamic.....	83
5.3 : Insert Of PFN below Cathode.....	88
INSERT OF Rb	
5.4: Optimization of quadrable cation Perovskite RbCsMAFA.....	92
5.4.1 :Insert of BCP below Cathode.....	94
5.4.2 :Perovskite Concentration,.....	96
5.4.3 :Cations percentages (Cs %,Rb%): stoichiometry check.....	103
5.5 : Future Work.....	107
 Chapter 6: Conclusion.....	 109
 References.....	 110

Chapter 1 : Introduction

1.1 Renewable Energy Sources and Categories

Renewable energies are forms of exploitable energy of unlimited amounts that come from a variety of natural processes, such as geothermal, wind, water circulation and others. Specifically, renewable non-fossil energy are considered wind, solar, geothermal, hydrothermal, hydroelectric, biomass².

Alternatives to traditional sources of energy (eg oil or coal), such as solar and wind, are generally considered to be 'renewables'. The characterization of renewables is somewhat abusive, since some of these sources, such as geothermal, for example, are not renewed on a millennial scale.

The constant pursuit of human societies is to utilize environmental friendly forms of energy that will not be detrimental to the environment and will be virtually inexhaustible. Various forms of energy have been proposed and utilized in this direction which fall into the category of renewable energy sources.

Wind : is the form of energy derived from the exploitation of the wind. Usually this is done using wind turbines. However, a major disadvantage is the dependence on the particular conditions in each region as well as the deterioration of the natural environment³.

Geothermal: is a form of energy created by the exploitation of natural thermal energy that flows from the interior of the planet to the surface and can be used to generate electricity but also to heat and cool places. It is a form of energy with a small percentage of exploitation as it is confined to specific regions of the planet⁴.

Hydroelectricity is a form of energy generated through the exploitation of floods and followed by the conversion of the stored dynamic energy of water into electricity⁵.

Solar is about the energy radiated to the surface of the planet from the sun. The amount of this energy is practically infinite if we consider that the sun still has 4-5 billion years of life⁶.

1.2 Advantages of RES

1. They are environmentally friendly, with substantially zero waste and waste
2. They are not intended to be used in relation to fossil fuels
3. They can help the energy self-sufficiency of small and developing countries, as well as being an alternative to the oil economy.
4. They could be used on flexible applications, which can generate energy commensurate with the needs of the population on the ground, eliminating the need for huge units of energy production but also energy transfer over long distances.
5. The equipment is simple in construction and maintenance and has a very long life⁷.

1.3 Drawbacks of RES

1. They have a fairly low efficiency factor of 30% ⁸. Consequently, quite large initial application costs are required on a large land surface.
2. The supply and output of wind, hydro and solar energy depend on the time of year, but also on the latitude and climate of the area in which they are installed.
3. For wind machines it is thought that they are not elegant because they cause a lot of noise
4. Due to hydroelectric works it is said that methane is released by the decomposition of plants under water and thus contributes to the greenhouse effect⁷.

1.5 Solar energy as RES

Solar radiation that hits a spot on the surface of the earth for a particular moment is characterized by the direction of impact and the intensity. On the surface of the earth there is only one part of the radiation coming directly from the sun, while the rest is absorbed by the components of the atmosphere or reflected back into space. The

radiation coming to the surface of the earth after successive reflections has no specific direction and is called diffuse radiation.

Chapter 2 : Background Theory

2.1: Photovoltaic effect – Photovoltaic device

The phenomenon was first observed by Adam and Dee when a very small amount of current appeared in the selenium chemical element. The first cell was made in the laboratories of Bell⁹.

The rapid development of this technology began in the late 1970s when the oil crisis essentially gave rise to an alternative source of energy. After many years of experimentation and research in the 1990s, industrial processes for producing highly efficient photovoltaic systems were developed and became widely available for industrial and domestic use¹⁰.

The function of the photovoltaic modules is essentially based on the photovoltaic effect. A photovoltaic system consists of a set of semiconductors, that is, arrays of silicon cells. Of the photons that are impacted, in the cells, some of them are geometrically reflected, some penetrate the surface of the cell and some of them are absorbed by initiating the process of generating loads within the material. The exploitation and movement of

loads leads to the production of electricity and consequently electricity. A prototype of a solar cell is demonstrated in the figure 1.

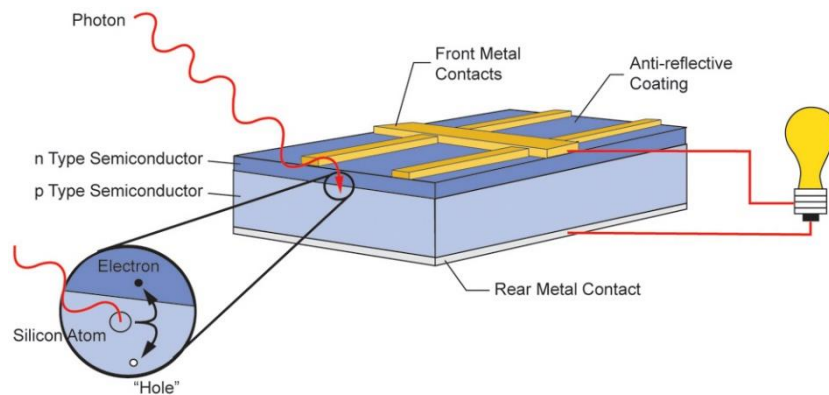


Figure 1 – Solar cell prototype¹¹

Moreover, the photovoltaic cell is made of semiconductor material and in particular silicon. Depending on the type of admixture the type p semiconductor and the type n semiconductor will be used in order to create a p-n junction. For example arsenide, the 4 valence electrons will generate with the corresponding neighboring atoms of the Germanium covalent bonds. With this modifier the fifth atom of the arsenide atom will decrease unbound. Arsenide is called a donor. Increasing the number of donors in a semiconductor increases the number of free electrons resulting in the creation of a small current when the semiconductor is exposed to an electric field. Semiconductors of this type are called semiconductors of type n¹².

If in a trivalent element such as gallium, it is inserted into the semiconductor of silicon then the three electrons create covalent bonds with the three valence electrons of three neighboring silicon atoms.

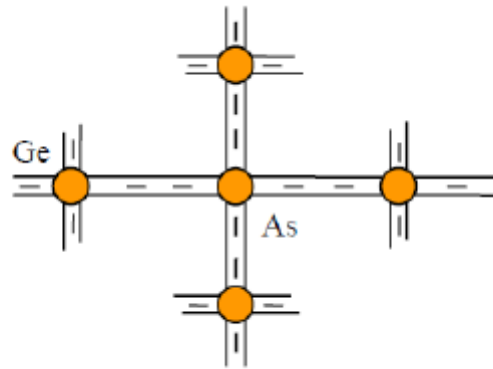


Figure 2 – n type semiconductor¹³

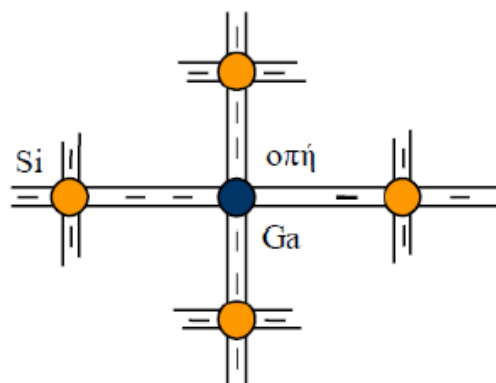


Figure 3 – p type semiconductor¹³

The position of the electron that is essentially missing so that the covalent bond is filled with a hole in the crystal lattice and can thus be covered by a valence electron of a neighboring silicon atom which will jump to that position.

These impurities where the atoms give holes to the crystalline grid and consequently accept electrons are called semiconductors of type II. Immediately after the joining of the two semiconductors the extra electrons from the N-type region diffuse to the P-type. Leaving the N region this leaves behind negative ions. Similarly, the holes leaving the P-type to diffuse towards the N-type region leaves behind negative charged ions. So we have the creation of the depletion region that stops the further diffusion. At this moment we have to apply a forward bias so to keep current flows ¹⁴.

The inverse is extended in the region n that is, the incoming (diffuse) holes are neutralized by the electrons. Thus the atoms emit electrons and are essentially transformed into positive ions.

The photovoltaic cell is regarded as a large diode surface, which is practically created by semiconductor blends of trivalent and pentavalent elements respectively on the two sides. Raw material for the production of the n- type semiconductor is phosphorus, while for the p-type it is boron. Therefore, due to the diffusion occurring in the contact region, with the result that in the diffusion region, the contact energy diagram, the conductivity and vigor zones of the region π , are displaced higher than the corresponding region of the dynamic potential of the contact. When light hits the contact surface, photons that have energy larger than the energy gap, emit electrons from the valance band to the conduction zone, leaving a free hole in the valence band. This creates pairs a carriers (electron-hole), which called excitons. The direction of the electric field created by diffusion in the contact area is such that it directs the electrons to the n-region and the holes in the p-region. This creates the potential of a photovoltaic that can supply a continuous current to an external circuit¹⁵.

2.2 : Photovoltaic technologies - types of photovoltaic materials

- First generation solar cells

a) Monocrystalline silicon

In essence, the monocrystalline silicon solar cells are made by slicing a single crystal from a large single crystal ingot that has been processed at temperatures above 1400 degrees Celsius. The silicon must be of very high purity and have a perfect crystal structure. Practically it is a process with high production costs. Its photovoltaics have the highest efficiency.

b) Polycrystalline silicon

Polycrystalline solar cells are made by the molding process in which the silicon enters a mold and then undergoes appropriate machining. Clearly they have lower manufacturing costs but lag behind in delivering imperfections¹⁶⁻¹⁹.



Figure 4 – Polycrystalline silicon solar cell²⁰

- Second generation solar cells

In this generation four types of solar cells were introduced. Amorphous Silicon cells which can be deposited over large areas with help PECVD. Their band gap was about 1.7 eV and function similar to c-Si. Polycrystalline Silicon are made of pure silicon grains, they work better than previous designs because of their mobility feature. You can easily move them over large magnitude. Cadmium telluride (CdTe) cells are formed with cadmium and tellurium mixed with zinc cubic crystal structure. This material is cheaper than silicon but not as efficient as silicon is. Copper indium gallium diselenide (CIGS) alloy cells are deposited on glass or stainless steel and are complex in model. Their band gap is about 1.38 eV¹⁶⁻¹⁹.



Figure 5 – Solar cell technologies²¹

- Third generation solar cells

This generation was very different from previous generation because innovative semiconductors were used in here. Types of solar cells introduced in this generation includes Nanocrystal solar cells, Photoelectrochemical cells, Dye-sensitized hybrid

solar cells, Polymer solar cells. Nanocrystal solar cells were based on silicon substrate with coating of nano crystals. Thin film of nano crystals is used with it, which was obtained by process named as spin coating. They create higher potential for solar cells. PEC were second on the list, and consisted of a semiconducting photoanode. It works best with electrons and can also separate non salacity of semi conductors. Grätzel cells were dye sensitized cells and use photoelectrons to increase power efficiently. Dyes were made of metal organic complex and its molecules are hit by increasing heat. Polymer solar cells were last invention of this generation, which were lightweight, inexpensive, flexible and disposable on any molecular level. They have little negative impact on environment^{16–19}.

- Fourth generation of solar cells

This generation brings most successful types of solar cells for mankind and those were Hybird- Nanocrystal cells. For generation of these cells polymers and nano particles were mixed to make on layer which can help electrons and protons to move for producing better voltage and good quality of direct current²².

2.3 : Perovskites, applications in photovoltaic technologies

2.3.1: History of perovskites

The origin of perovskite solar cells can be traced back to 1839, when a German scientist, Gustav Rose, during a trip to Russia, discovered a new calcium titanate-based mineral in the Ural Mountains, which was named “perovskite,” in honor of the Russian mineralogist Lev von Perovski²³.



Figure 6 – Lev Perovski , Perovskite mineral²⁴

H.L. Wells et al. at Sheffield Scientific School prepared the first synthetic halide perovskite based on cesium and lead, although its perovskite structure was determined only during the 1950s by C.K. Møller at the Royal Veterinary and Agricultural College in Copenhagen, Denmark. Møller also observed photoconductivity in this material.

Meanwhile, researchers at Philips (Eindhoven, the Netherlands) and Western Electric (New York, N.Y.) introduced oxide perovskites for use in condensers and electromechanical transducers. Starting in the 1950s, research and development related to oxide perovskites flourished, leading to the introduction of these materials in the fabrication of various products, such as fuel cells, glass-ceramic articles, catalysts, gas sensors, heating elements, lasers and superconducting devices, in addition to increasingly popular multilayer capacitors.

In 1978, D. Weber at the University of Stuttgart in Germany developed the first organic-inorganic halide perovskite, in which methylammonium ions replaced the cesium cations in the original halide compound synthesized by Wells et al. in 1892.

However, an additional 16 years would pass before the optoelectronic properties of halide perovskites were exploited for commercial applications. In 1994, researchers at IBM T.J. Watson Research Center (Yorktown Heights, N.Y.) developed light-emitting devices based on luminescent organic-inorganic halide perovskites, and in 1996 Boeing North America (Seal Beach, Calif.) created nonlinear optical crystals based on cesium-germanium halide salts.

In 1999, M. Chikao et al. at the National Institute of Advanced Industrial Science & Technology (Tokyo, Japan) reported the fabrication of an optical absorption layer for a solar cell using a rare-earth-based perovskite compound^{25,26}.

The new millennium began with a sharp increase in research activity related to perovskite solar cells, leading to the introduction of new material formulations and fabrication methods, and the first steps in their commercialization²⁷.

2.3.2 : Perovskite structure

The ideal shape of the grid crystallizes in the cubic system. The crystallization is described as a cube with an octahedral of BO₆ at its corners with an insertion number of ions A, B, C being 12,6,6, respectively. The position of cation A is at the center of the cube and, depending on its atomic radius, distortions are created of the ideal shape with the effect of crystallization elsewhere. Because the ionic radius of cation A is smaller than that required to maintain the cubic structure, different structures have been determined based on the geometry. These limits are set by the Goldsmith factor.

The perovskite structure is stable in the range $1 < \tau < 0.75$ while the cubic structure is maintained for values close to value 1. When the deformation is large enough, other crystalline symmetries, such as rhomboid and orthorhombic, appear below.

Obviously, it is the stability of the structure that allows for sufficiently large deviations from the ideal stoichiometry, with this modification in the substitution at the A or B position of the same class of ions or by the reductive reactions associated with the present metal^{28–33}.

2.3.3: Hybrid perovskite solar cells

Hybrid perovskite combines the advantages of the inorganic and organic materials. It is the same chemical formula ABX₃, but with different ions, A is an organic cation, B is a metal cation and X is a halide anion. Perovskites were first used in photovoltaics by Miyasaka et al in 2009. They made photocells with a liquid phase electrolyte based on mesoporous TiO₂ photocathodes sensitized with CH₃NH₃PbX₃ (X=I, Br). They achieved an average PCE of 3.8%, which in comparison with other fields at the time

was not very impressive. In terms of structure such a system suffers from fast degradation due to the dissolution of perovskite absorber into the organic electrolyte. Three years later in 2012 Grätzel et al³⁴ used methylammonium lead triiodide perovskite (MAPbI₃) as a light harvester in combination with the solid hole conductor on mesoporous TiO₂ reporting a PCE of 9,7% 11. This solid-state cell managed to spark new interest in the field of perovskite photovoltaics.^{33,35–38}

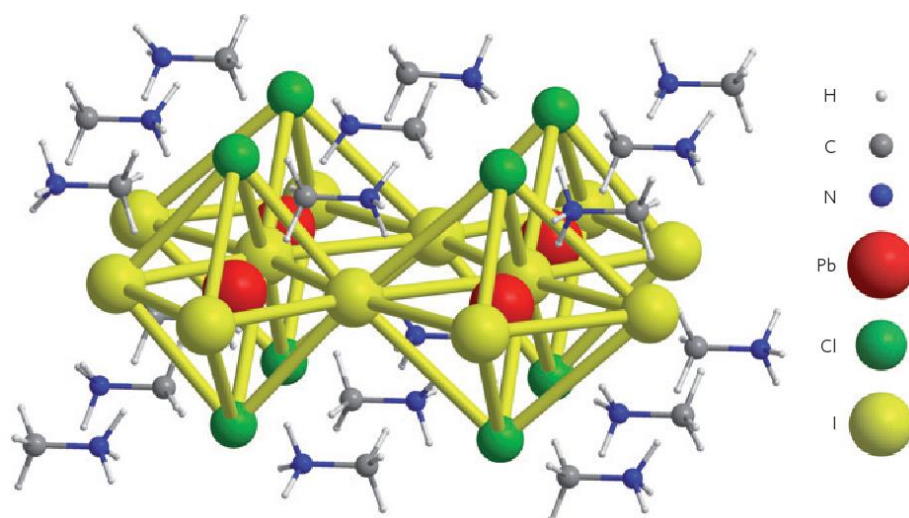


Figure 7 – Hybrid perovskite structure³⁹

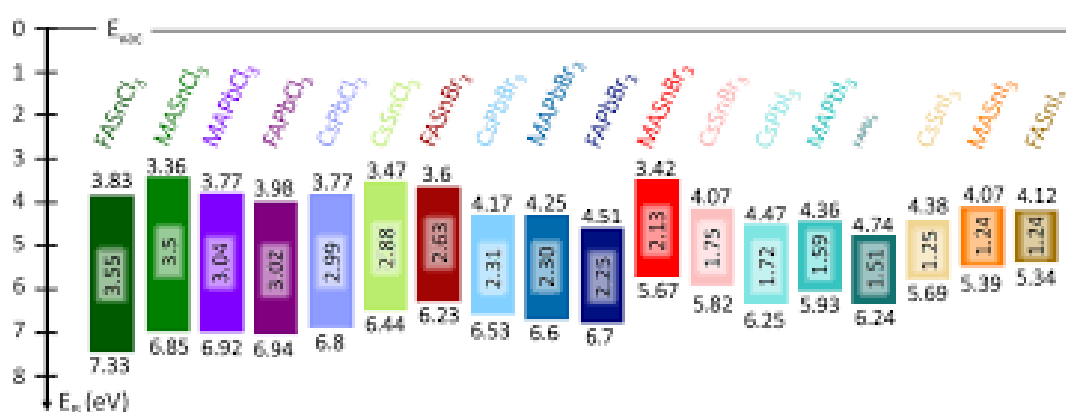


Figure 8 – Hybrid perovskites energy levels²⁵

2.3.4 : Device architectures

The device configuration is one of the most crucial factors for evaluating the overall performance of perovskite solar cells. PSCs can be classified as regular (n-i-p) and inverted (p-i-n) structures depending on which transport (electron/hole) material is present on the exterior portion of the cell/encountered by incident light first. These two structures can be further divided into two categories: mesoscopic and planar structures.

The mesoscopic structure incorporates a mesoporous layer whereas the planar structure consists of all planar layers. Perovskite solar cells without electron and hole-transporting layers have also been tested. In summary, six types of perovskite solar cell architectures have been studied by various researchers thus far: the mesoscopic n-i-p configuration, the planar n-i-p configuration, the planar p-i-n configuration, the mesoscopic p-i-n configuration, the ETL-free configuration, and the HTL-free configuration.^{31,35,36,40,41}

- Normal n-i-p structure

The conventional n-i-p mesoscopic structure was the first arrangement of perovskite photovoltaics to be tested, in which the light-harvesting dye was replaced with lead halide perovskite semiconductors in a traditional DSSC-type architecture . The interest in perovskite solar cells increased more when so-called mesoscopic device structures were formed by substituting the liquid electrolyte with a solid-state hole conducting material . The assembly begins with a transparent glass cathode followed by the electron transportation material (ETM). The structure is then layered with a mesoporous metal oxide containing the perovskite, followed by the hole transport material (HTM), and capped with a metallic anode . This initial advancement in PSCs created an important field of interest for photovoltaic researchers and consequently led to the development of other PSC device configurations.

The planar architecture is an evolution of the mesoscopic structure, where the perovskite light harvesting layer is sandwiched between the ETM and HTM. The absence of a mesoporous metal oxide layer leads to an overall simpler structure. It is

possible to achieve a high efficiency without the mesoporous layer by carefully controlling the interfaces between the different layers that make up the PSC (the perovskite light absorber layer, the electron transporting layer, the hole-transporting layer, the electrodes as well as the perovskite layer itself. With the same materials and approach, a planar n-i-p PSC shows increased V_{oc} (open-circuit voltage) and J_{sc} (short-circuit current density) relative to a mesoscopic PSC device; however, the planar configuration also had more severe J-V hysteresis which calls into question the accuracy of the reported efficiencies. The grain and thickness of this buffer layer influence the J-V hysteresis behavior. It's been also observed that J-V hysteresis problem is significantly dependent on the p-type hole-transporting materials and found that the hysteresis behavior can become negligible with a reduced capacitance, which can be done by replacing Spiro-OMeTAD with poly(3,4-ethylene dioxythiophene)-poly(styrene sulfonate) (PEDOT:PSS) or any other inorganic hole-transporting materials. However, the J-V hysteresis behavior is also dependent on voltage scan direction, scan rate, and range. To counter this problem, a thin mesoporous buffer layer was incorporated within the planar n-i-p PSC structure. To date the best mesoscopic n-i-p device has exhibited a PCE 24.3%.^{31,35,36,40,41}

- Inverted p-i-n structure

The p-i-n PSC structured is derived from the organic solar cell. In the case of the p-i-n planar perovskite architecture, the HTM layer is deposited first followed by the ETM layer. It was discovered that perovskites are capable of transporting the holes themselves, which led to Jeng et al¹. developing the first planar hetero-junction PSC with an inverted structural design. With this advancement, the inverted p-i-n configuration has expanded the options to explore more for selective layer from organic to inorganic materials and the use of oxide HTM allow for constructing mesoscopic pi-n device architecture. Planar p-i-n PSC offers low-temperature processing, negligible hysteresis behavior with high efficiency of above 18%. The device configuration of the inverted p-i-n planar and mesoscopic PSC is shown in Figure 9.^{31,35,36,40,41}

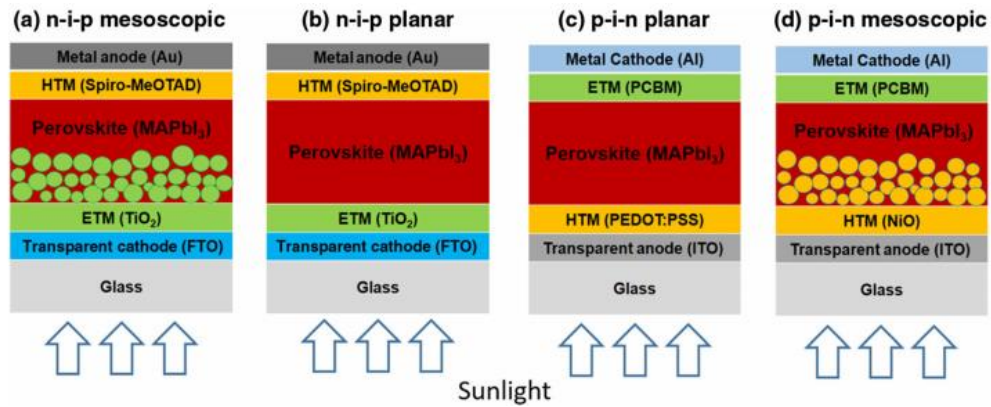


Figure 9 – Device configurations⁴²

2.4 : *Electronic structure of semiconductors*

2.4.1 *Atomic orbitals and molecular Orbital bonding*

The origin of the energy band gap, conduction bands, valence bands, highest occupied molecular orbitals, and lowest unoccupied molecular orbitals in inorganic and organic semiconductors comes from the nature of molecular orbital bonding, hybridisation, and band formation in repeating crystal structures and in organic materials. The nature of crystalline solids is discussed here, whereas atomic orbital hybridisation and the formation of band-like structure of organic polymers are outside the relevant scope of this thesis. As such, such processes are briefly described, with citations indicating where they are discussed with clarity and detail.⁴³

Atoms have a nucleus surrounded by electrons orbitals of different energies where the positions of electrons can only be described as probably distributions. The shape, occupation and properties of electrical orbitals define the properties of the atom and how it interacts with other atoms. Because of the fundamental uncertainty in the exact position of electrons these orbitals are described as electron density clouds. Electronic orbitals are described by four quantum numbers. To satisfy the Schrödinger equation, ensure quantization, and obey conservation of observable quantities, these properties may only take a set of discrete values. Pauli's Exclusion Principle states that no two electrons can have the same value for all four quantum numbers^{43,44}.

As two atoms are brought close together, their atomic orbitals will overlap. The occupancy, direction and relative energies of the electronic orbitals defines how an

atom will bond with other atoms when forming a bond. As two atoms orbitals overlap, their electron wavefunctions may combine (constructively) in-phase, become a bonding orbital, or (destructively) out of phase. Then an antibonding orbital is created where, the lack of electron density between the atoms causes a reduction in Coulomb shielding, which increases the relative energy of the bond. Due to Pauli's Exclusions Principle. If there are available additional electrons will be unable to join the already occupied stable bonding orbital and will instead occupy an antibonding orbital.⁴⁵⁻⁵⁰

2.4.2 : Band formation in crystals

Crystals are structures of tightly ordered atoms arranged in a periodic pattern. This periodicity can be simplified to a unit cell. Crystal structures can be identified or 'indexed' by using crystallography to find lattice planes. Planes are named after their Miller indices, which are the smallest possible ratio of integers of the reciprocal values at the intercepts for the plane at the edge of the unit cell.

When multiple atoms are brought together to form a molecule, their electronic orbitals overlap. In the process of covalent bonding, hybridisation of p and s states occurs, allowing more bonds to be formed between adjacent atoms. The resultant bonding and antibonding that occurs leads to multiple allowed bonding and antibonding energy levels, which electrons can occupy..

Due to Pauli's Exclusion Principle, none of these orbitals can have the same energy, and every resultant orbital forms at a slightly different energy. The larger the number of atoms, the more orbitals are formed, a process that continues until the high density of energy states can be said to form a band of potential energy states.

Here, the four valence electrons located in the s and p bonding orbitals, make up the valence band, with the top of the valence band determined by the energy level of the p bonding orbitals. The base of the conduction band arises due to the s antibonding orbitals.

The energy of all bands is typically given as an energy value away from vacuum

energy. For example, when an energy level of band is given, or a work function value is stated (typically in eV) that is the energy it would take to promote an electron from that level to escape to infinity with no remaining energy. Electron affinity refers to the energy difference between the bottom of a conduction band and infinity (vacuum energy) whilst hole affinity refers to the energy difference between the top of the valence band and vacuum energy.

An incoming photon can excite a valence electron to the conduction band if it satisfies the condition $E\lambda > EG$.^{51,52}

Theoretical solid-state physics describes these bands through Bloch theory and Brillouin zones, where the Schrödinger equation is solved with wavefunctions of allowed eigenstates for electrons in a periodic lattice. This leads to bands (with index n) that are characterised by their energy, crystal momentum k vector and a dispersion relation $E_n(k)$. Since there are a set of bands within a semiconductor, then there are also many available energy levels for any given value of k . Semiconductors will either have direct or indirect band gaps between their conduction and valence bands, where the closest proximity of the band structures will either be aligned or displaced by a k vector. Modelling the band structure of a density of states can then lead to semiconductor optoelectronic properties being extracted from band structure..⁵³⁻⁵⁷

2.4.3 : Perovskite crystal and band structures

Perovskites are crystalline materials with a chemical structure of the form ABX_3 , where A and B cations with X anions form a crystal structure demonstrated in. PSCs typically utilize organic-metal halide hybrid perovskite active layers in which A is a large organic cation MA (CH_3NH_3), FA ($HC(NH_2)_2$), inorganic cesium (Cs), or potassium (K). The B cation atom in most high PCE devices is lead (Pb), but research increasingly focusses on perovskite with tin (Sn) B site cations. The halides iodine (I), chloride (Cl), and bromide (Br) are all implemented individually or as halide blends. Perovskite blends that result in high efficiency devices include: $MAPbI_{3-x}Cl_x$, $MAPb(I_{1-x}Br_x)_3$, $FAPbI_yBr_{3-y}$, $FAPbI_{3-x}Cl_x$, $(FAPbI_3)_{0.85-0.87}(MAPbBr_3)_{0.15-}$

0.13, fully inorganic cation perovskites $\text{Cs}_{0.925}\text{K}_{0.075}\text{PbI}_2\text{Br}$, with the most recent high PCE PSCs using triple cation compositions $\text{CsI}_{0.05}((\text{FAPbI}_3)_{0.85-0.83}(\text{MAPbBr}_3)_{0.15-0.17})_{0.95}$, sometimes with additional 0-10 %M of potassium or rubidium⁵⁸⁻⁶⁰.

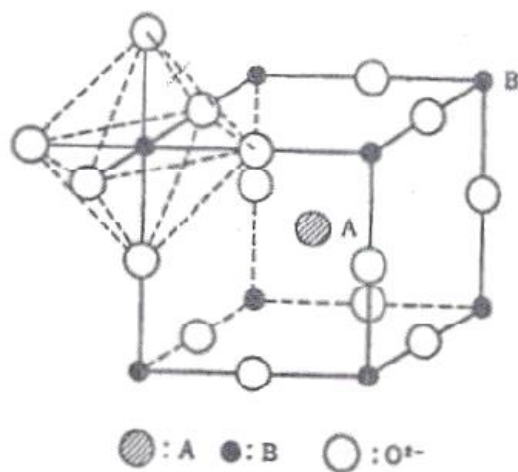


Figure 10 – Cubic perovskite phase⁶¹

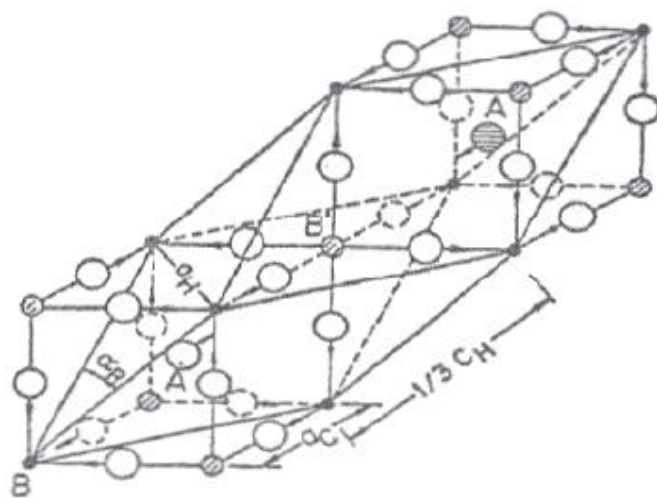


Figure 11 – Orthorhombic perovskite phase⁶¹

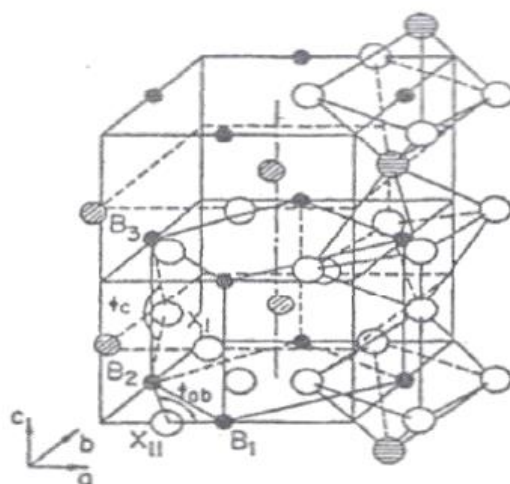


Figure 12 – Rhomboedric perovskite phase⁶¹

2.4.4: Perovskite Unit Cell

The perovskite unit cell can be represented as a cage of organic A cations enclosing an octahedral structure of halide anions X with the metal cation B in the center.

There are several phases of the extended perovskite crystal structure with differing unit cells. Phase changes are influenced by changes in temperature, pressure and the composition of the perovskite. Modelling of MA⁺ cations has predicted that they are rotating rapidly at room temperature. Larger organic A site molecules may cause the tilting of the internal octahedra and the shifting of the halide-Pb bond angles^{62–64}.

The stability of a crystal structure can be described with a Goldschmidt tolerance factor (t), calculated from Figure 13 below. This uses the ionic radii R of constituent atoms to determine whether the crystal is stable, distorted, or unstable.

In order for the perovskite cubic crystal structure to form, the relative size of the anions and cations must have a Goldschmidt tolerance factor between $0.8 \rightarrow 1$ ^{29,65–67}.

$$t = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)} \quad (2.1)$$

Figure 13 – Goldschmidt tolerance factor

- **Methylammonium Lead Iodide Perovskite Band Structure**

Metal-organic methylammonium lead iodide perovskite, MAPbI₃, has an electronic band structure that is primarily determined by the electronic bonding orbitals of the lead and iodide. Lead and iodide are Pb²⁺ cations and I⁻ anions when in the perovskite crystal, and have electronic configurations of 5d¹⁰, 6s², 6p⁰ and 4d¹⁰, 5s², 5p⁶ respectively. The highest energy orbital is therefore the empty 6p Pb²⁺ ion, which forms the conduction band. Hybridisation of the I 5p and Pb 6s states (with such orbitals shielding each other) leads to an antibonding orbital, forming the valence band.^{25,68}

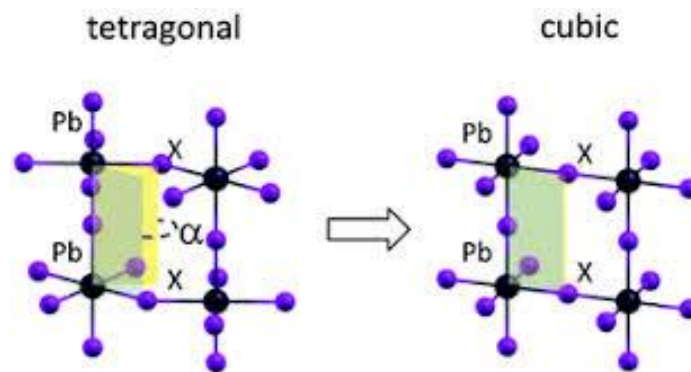


Figure 14 – MAPbI₃ phases⁶¹

2.5 : PSCs operational principles

2.5.0 : Solar cell parameters

- **Short-Circuit Current (*J_{sc}*)**

The short-circuit current is the current through the solar cell when the voltage across the solar cell is zero (i.e., when the solar cell is short circuited).

The short-circuit current is due to the generation and collection of light-generated carriers. For an ideal solar cell at most moderate resistive loss mechanisms, the short-

circuit current and the light-generated current are identical. Therefore, the short-circuit current is the largest current which may be drawn from the solar cell.

The short-circuit current depends on a number of factors which are described below:

- the area of the solar cell. To remove the dependence of the solar cell area, it is more common to list the short-circuit current density (J_{sc} in mA/cm^2) rather than the short-circuit current.
- the number of photons (i.e., the power of the incident light source). I_{sc} from a solar cell is directly dependant on the light intensity as discussed in Effect of Light Intensity.
- the spectrum of the incident light. For most solar cell measurement, the spectrum is standardised to the AM1.5 spectrum.
- the optical properties (absorption and reflection) of the solar cell.
- the collection probability of the solar cell, which depends chiefly on the surface passivation and the minority carrier lifetime in the absorber⁶⁹.

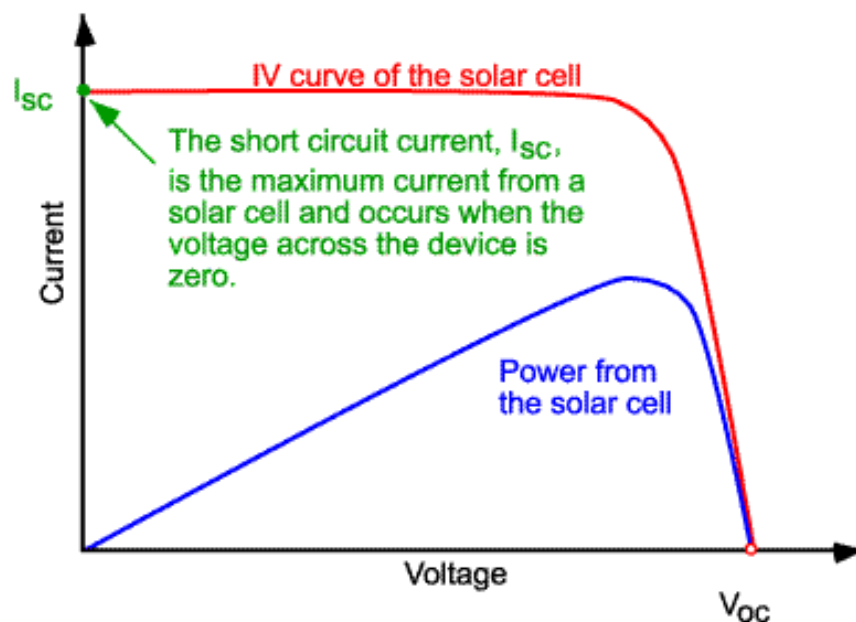


Figure 15 – J-V curve explanation⁷⁰

- ***Open-Circuit Voltage***

The open-circuit voltage, V_{oc} , is the maximum voltage available from a solar cell, and this occurs at zero current. The open-circuit voltage corresponds to the amount of forward bias on the solar cell due to the bias of the solar cell junction with the light-generated current. The open-circuit voltage is shown on the IV curve below.

An equation for V_{oc} is found by setting the net current equal to zero in the solar cell equation to give:

$$V_{oc} = \frac{nKT}{q} \ln\left(\frac{I_L}{I_0} + 1\right) \quad (2.2)$$

A casual inspection of the above equation might indicate that V_{oc} goes up linearly with temperature. However, this is not the case as I_0 increases rapidly with temperature primarily due to changes in the intrinsic carrier concentration n_i . The effect of temperature is complicated and varies with cell technology.⁷⁰

- ***Fill Factor***

The short-circuit current and the open-circuit voltage are the maximum current and voltage respectively from a solar cell. However, at both of these operating points, the power from the solar cell is zero. The "fill factor", more commonly known by its abbreviation "FF", is a parameter which, in conjunction with V_{oc} and I_{sc} , determines the maximum power from a solar cell. The FF is defined as the ratio of the maximum power from the solar cell to the product of V_{oc} and I_{sc} .

$$FF = P_{mp}/(V_{oc} * I_{sc}) \quad (2.3)$$

- ***Solar Cell Efficiency***

The efficiency is the most commonly used parameter to compare the performance of one solar cell to another. Efficiency is defined as the ratio of energy output from the solar cell to input energy from the sun. Efficiency depends on the spectrum and

intensity of the incident sunlight and the temperature of the solar cell. Therefore, conditions under which efficiency is measured must be carefully controlled in order to compare the performance of one device to another. Terrestrial solar cells are measured under AM1.5 conditions and at a temperature of 25°C. Solar cells intended for space use are measured under AM0 conditions. Recent top efficiency solar cell results are given in the page Solar Cell Efficiency Results.

The efficiency of a solar cell is determined as the fraction of incident power which is converted to electricity.

$$PCE = Voc * Isc * FF / Pin \quad (2.4)$$

2.5.1 : P-N junctions

The Fermi level of a material is the electrochemical potential which is the thermodynamic work required to add one electron to that material. Electrochemical potential must be defined relative to an energy state, here, the electrochemical potential of a semiconductor can be defined as the energy relative to the top of the valance band of that semiconductor. The Fermi level of a material can also be defined as the energy level at which there is a 50% probability of an electronic state being occupied.

For conductors with no bandgap, the Fermi level lies within a single band (the overlapping valence and conduction band), close to the work function of the conductor¹³.

In an intrinsic semiconductor the Fermi level is located in the middle of the band gap. In an n-type semiconductor there is an increased statistical change of electrons being in the conduction band (relative to holes being in the valence band) and the Fermi level lies closer to the conduction band. Conversely, in a p-type semiconductor there is an increased statistical chance of holes being found in the valence band (relative to electrons being in the conduction band) and the Fermi level lies closer to the valence band.¹³

As mentioned above when a p-type semiconductor and an n-type semiconductor are brought in contact with each other, there is an induced diffusion of intrinsic charge carriers (with electrons moving to the material with the lower chemical potential) which allow the system to approach equilibrium. Holes from the p-type material migrate to the n-type semiconductor and electrons from the n-type material migrate to the p-type material. This leaves behind positive ions in the n-type material, and negative ions in the p-type material. Carriers from one side of the p-n junction are referred to as majority carriers when they are on the side they originate from and minority carriers if they diffuse into the opposite side. As this process continues a region depleted of intrinsic carriers known as the depletion region is formed. The ions either side of the depletion region generate a built-in electric field, which creates an electronic barrier preventing further diffusion of carriers until the equilibrium is perturbed. At equilibrium a p-n junction can be said to have a total chemical potential that is constant across the whole diode.^{11,21}

An applied bias can then be applied to the p-n junction. In forward bias the external field opposes the built-in electric field. As the forward bias is increased the net field is increased, leading to a reduction in barrier height. Now the minority carriers recombine with carriers from the other side of the junction, leading to a dark recombination current. This is the origin of diode like response in p-n junctions, where a large current is observed in forward bias. The opposite case (of applying reverse bias), decreases the probability of carriers diffusing across the depleted region, as the external electric field increases the net field across the depleted region. For large reverse bias conditions, the depleted region also increases in size. Practical operation of solar cells is performed under illumination at a forward applied bias that does not exceed the open circuit voltage of the solar cell.

Characterization of solar cells is usually performed under steady state conditions, with different illumination intensities or applied biases. These external parameters can also be changed rapidly to investigate solar cell response under transient changes in voltage or illumination intensities. p-i-n junctions generally have a large (relatively) undoped intrinsic semiconductor (i) between the p-type and n-type semiconductors that acts as a large depletion region. Both p-i-n or n-i-p junctions are commonly used semiconductor models for PSCs. In fact, p-i-n PSCs are known as inverted PSCs. Here

the cell architecture typically has a hole transport layer below the perovskite layer and an electron transporting layer above the perovskite layer. n-i-p PSCs, more commonly known as standard architecture devices have the charge transport layers the opposite way around. The development of early PSC architectures is detailed later in this chapter. As described above, the perovskite band structure enables it to act as an absorbing layer, with incoming photons exciting charges across a band gap. However, the simplistic picture of a strong electric field across the depleted region, driving photogenerated charges towards the n and p type contacts, is not an accurate model for the functionality of a PSC because is very complex system , where not only electron and holes are free to move but also anions and cations^{14,71,72} .

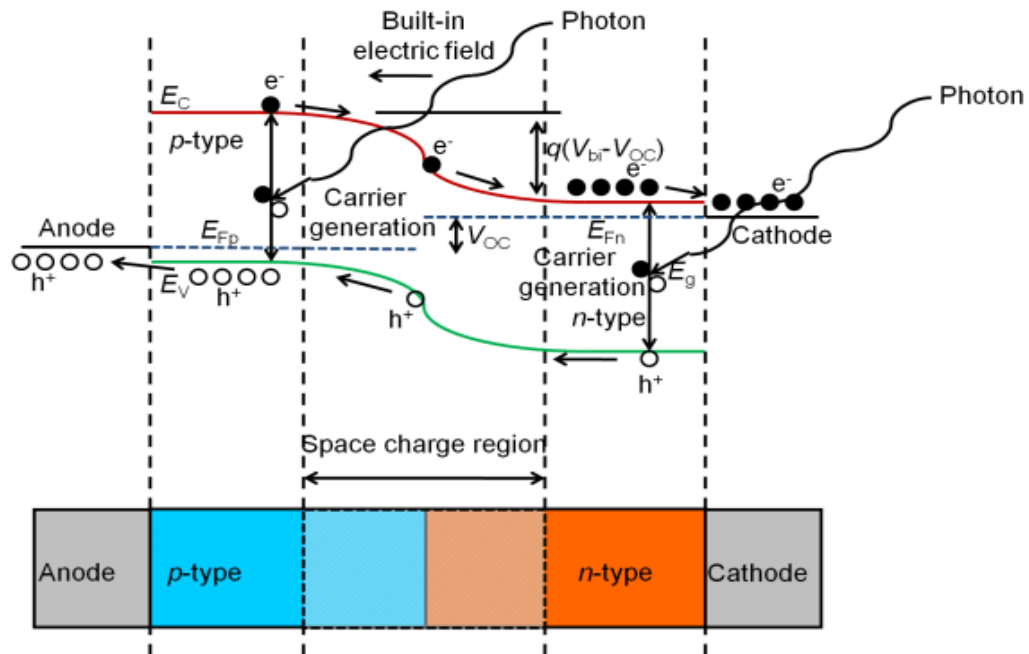


Figure 16 – P-N junction diffusion , drift mechanism

2.5.2: Equivalent circuit

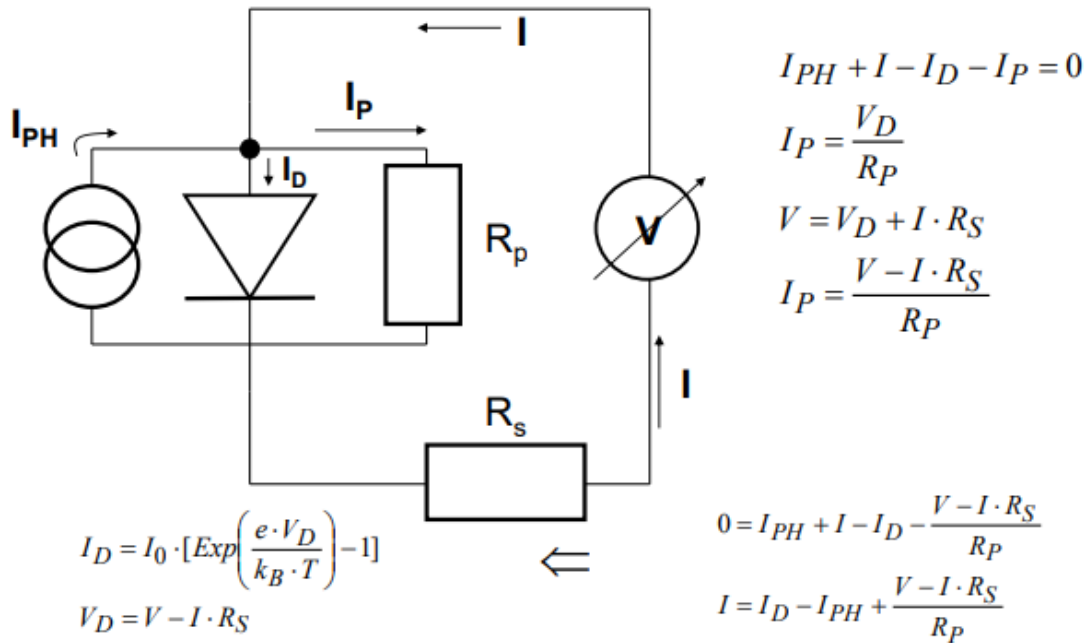
The nature of a simple PV device is best modelled by the Shockley ideal photodiode equation .Here J_{ph} is the photocurrent provided by the photoactive absorbing layer, the J_D diode current (also known as dark diode current) and J_0 the diode reverse saturation current. As the applied voltage (V) increases, the diode current (which opposes the photocurrent) exponentially increases as represented in the following equation:

$$(V) = Jph - JD = Jph - J0 [\exp (eV/KBT) - 1] \quad (1)$$

When solar cell parasitic losses and a non-ideal diode are considered, the model transforms into Equation 2. R_S is the series resistance that considers all processes that oppose the photocurrent generation and extraction, R_{SH} is the shunt resistance against all of the parallel circuit pathways that bypass one or more of that layers that generate or select charges, K_B is the Boltzmann constant, and T is the temperature (in kelvin). The ideality factor n is mostly a measure of the type recombination occurring in solar cell. For an ideal diode with $n=1$, all recombination must occur outside the depletion region of the photoactive absorbing layer. For absorbing layers with charge recombination or diodes with energetic barriers (for example poorly aligned metal-semiconductor Schottky diodes, described later in this chapter) the ideality factor can exceed $n = 2$.

$$(V) = Jph - J0 [\exp ((V + JRs nKBT) - 1) - V + JRsRsh] \quad (2)$$

It is widely agreed that this simple circuit model is not able to fully characterize a perovskite solar cell (Due to ion migration and charge transport modulations at charge extraction interfaces).



$$I = I_0 \cdot \left[\exp\left(\frac{e \cdot (V - I \cdot R_S)}{n \cdot k_B \cdot T}\right) - 1 \right] + \frac{V - I \cdot R_S}{R_P} - I_{PH} \quad (2.5)$$

Figure 17 – Equivalent circuit

2.5.3: Charge transport in metal halide perovskites

On irradiating a semiconductor with a photon, the excitation of an electron from the valence to the conduction band causes the formation of an exciton. Depending on the semiconductor material the exciton can either be a large. A weakly-bound Wannier-Mott exciton with a binding energy on the order of ~ 10 meV or a small tightly bound Frenkel exciton with a binding energy typically between 0.1 and 1 eV. c-Si semiconductors support Wannier-Mott excitons, with the electron and holes having diffusion lengths that are large enough such that they can be extracted to the electrodes as free charges. Exciton binding energy is inversely correlated to the coulombic charge screening within that material, defined as the dielectric constant ϵ_r of the semiconductor. An increase in temperature will lead to increasingly likelihood for bound excitons to dissociate.

Most lead-halide perovskites generate weakly bound Wannier-Mott excitons, resulting in the generation of free charges. However the value of binding energy (EB) as determined by experiment and theory vary from 1 to 50 meV. If excitons did indeed have a binding energy of 50 meV, then it is possible that excitons would remain bound at room temperature, and thus reduce the quantum efficiency of a perovskite device. However, the large PCEs of perovskite devices suggest that the generated excitons are unlikely to be tightly bound.

The calculation of exciton binding energy values usually involves determination of the dielectric constant of the perovskite. There some discussion in how to best define proper the value of the dielectric constant through the use of simulations .

Common techniques suggests that MAPbI₃ films at room temperature (in the

tetragonal phase) may have a binding energy as low as 5 meV, caused by dielectric screening from the MA cations. Mixed halide perovskites have also been found to have reduced excitonic screening due to collective reorientations of MA cations. Because of the low exciton binding energy, electrons and holes quickly dissociate much like charges in a fully inorganic semiconductor⁷³.

There is some debate as to whether the typical model of a depletion region with charges being swept out by a built-in field is appropriate for a PSC. A built-in field should be generated by well aligned hole and electron transporting levels respective to the perovskite band structure. However, experimental evidence suggests that PSCs still function with badly aligned charge transporting layers, or without charge transport layers at all. These results generate a myriad of potential theoretical issues regarding device junction models⁷⁴.

It has been suggested that perovskites do not require a built-in field, and that either Fermi level pinning in the perovskite leads to charge selectivity, or that charge diffusion in the perovskite is so efficient that charges always reach the charge transporting layer interfaces. In the latter case, efficient generation of photocurrent would be entirely reliant on the charge blocking capabilities of the charge selective layers either side of the perovskite. Given that there is evidence of a significant number of free ions present in the perovskite (discussed later in context of perovskite hysteresis), it is likely that photogenerated charges are effectively screened from external electric fields.

It is generally accepted that perovskites have remarkable charge transport capabilities. Electron and holes have impressive mobilities. In the case of MAPbI₃ perovskites, experimentally determined charge carrier mobilities are around 10-20 cm²/Vs with hole mobility often reported as higher than electron mobility.

Electron and hole mobilities can be theoretically calculated through the density of states, which takes into account disorder parameters that broaden the density of transport states.

Perovskite single crystals have been shown to have charge diffusion lengths longer than a millimeter. There is not a great difference from crystalline silicon which has charge mobilities of around 10²-10³ cm²/Vs, with diffusion lengths about 100 micrometers. As previously discussed the electronic properties of perovskites are likely enhanced due to photon recycling, meaning that charges generated deep in the bulk of the perovskite can

radiatively recombine and yet still contribute to photocurrent by generating new charges that eventually reach the charge transport interfaces⁷⁵.

The success of the metal lead halide perovskite in PV devices is due to its remarkable optoelectronic properties. Its large absorption coefficients allow photons to be efficiently absorbed even if the perovskite layer is only a few 100 nm thick. For most perovskite active layers the diffusion length is of the order of the typical film thickness ($\sim 0.5 \mu\text{m}$), with FA based multi-cation mixed halide perovskites having the advantage of diffusion lengths greatly exceeding film thickness. Taken together, a high charge carrier mobility, low bi-molecular charge recombination, and photon recycling allow perovskite PV to function even if the active layer has a thicknesses exceeding a micron. Charge generation occurs on the order of picoseconds whilst most recombination is on the order of microseconds. The low non-radiative recombination rate results in a small difference of under 400 meV between V_{OC} and E_g/q ; a value better than many alternative PV semiconductors^{68,75–78}.

2.5.4 : Charge transportation in organic layer

The properties of organic charge transporting layers stem from atomic orbital hybridisation and charge delocalisation processes which are well described elsewhere.

Put simply, the highest energy π bonding orbital that is normally occupied in an organic charge transport layer is known as the highest occupied molecular orbital (HOMO). The next highest orbital (π^*) is known as the lowest unoccupied molecular orbital (LUMO). These orbitals are analogous to the valence and conduction bands as found in inorganic semiconductor materials. As with inorganics, photons can excite electrons from the HOMO to the LUMO level. When organics have an electron excited into the LUMO band level, a strongly bound exciton is formed (Frenkel exciton). Although this exciton is neutral, and its constituent electron and hole are bound, the electron and hole distort the local atomic structure of the polymer⁷⁹.

These charges, which cause local energy distortions, are better known as hole and electron polarons. Since excitons are neutral they can only diffuse within the polymer - this is typically through a hopping process along the polymer backbone or from polymer chain to polymer chain. This diffusion occurs as either a short range electron exchange (Dexter transfer) or a dipole-dipole energy exchange (Förster resonant energy transfer).

In the case of PSCs, organic materials are often used to transport delocalised charge. Since acceptor or donor (hole or electron transporting) polymer layers and acceptor fullerenes (eg PCBM, C₆₀) are significantly disordered, delocalized charges can only travel along and across polymer chains via a short range 'hopping' process. Whilst the majority of PV research will refer to band structures in polymers, it is not correct to describe charges in polymers as moving through a conduction band. Firstly, photoexcited charges remain in strongly bound excitonic states that can only diffuse through the polymer. Secondly, delocalised charges moving along charge conjugated polymers have limited delocalisation and hence low charge mobilities⁸⁰.

Typical donor and acceptor organic polymers (and fullerenes) have mobilities not exceeding $10^{-3} \text{ cm}^2/\text{V}\cdot\text{s}$, which is several orders of magnitude lower than metalhalide perovskites. As such, when organics are employed as transport layers they either need to be thin (to reduce the length charges travel) or be doped (to increase the conductivity). Whilst inorganic semiconductors are p-type or n-type doped by introducing inorganic impurities, doping of organic semiconductors is typically achieved by the addition of other organic species. These dopants should ideally have band-like structures that either have LUMO levels close to the HOMO level of the material being doped, resulting in p doping, or HOMO levels next to the LUMO level of the organic being doped, resulting in n doping. In p doping, the host organic's HOMO level is moved down and in n doping, the host organic's LUMO level is moved up relative to its original position from vacuum energy⁸⁰.

The low coulombic screening in organic semi-conductors (low dielectric constant ϵ_r), means that dopants can easily disturb the original structure of the organic, breaking down ordered bond lengths, generating sub band gap states, and widening the original band gap of the material. Significant doping causes sub-bands to appear inside the band

gap. Therefore, dopants can make a significant contribution to the density of states of the host organic. It has been observed that p doping can lead to exciton quenching in donor polymers, leading to a reduced rate of damaging reactions between incident photons and excited states, and hence leading to reduced degradation of the polymers^{81–85}.

2.5.5: Interfaces and Charge Transfer

When two materials are brought into contact with each other, the interface that is formed will always have material specific chemical interactions, surface oxides, or other surface defects and traps. When two metals or a metal and a semiconductor are brought together their Fermi levels will tend to align. In the case of a metal-semiconductor, the large number of free charges in the metal relative to the semiconductor means that the band structure of the metal will stay the same whilst the band structure of the semiconductor will accommodate the alignment. as a Schottky barrier), making the interface rectifying in nature. It has been found that Schottky barrier height is mostly independent to the metal work function as the semiconductor Fermi level is usually pinned to the metals Fermi level²⁴.

For transfer of holes between two semiconductors, alignment of the valence (or HOMO) levels of both is required, and for efficient extraction of electrons alignment of the conduction (or LUMO) levels is required. Charge blocking can be achieved by ensuring a significant energy barrier is present between the conduction levels at the hole extraction interface and the valence levels at the electron extraction interface.

Charge transport will be significantly reduced if a step up is present on either extraction interface, instead of a step down. Perfect semiconductor charge transfer at interfaces having an ideal alignment are characterized by limited band bending, limited surface depletion region, small barriers to charge transfer, and a small number of surface trap states^{86–89}.

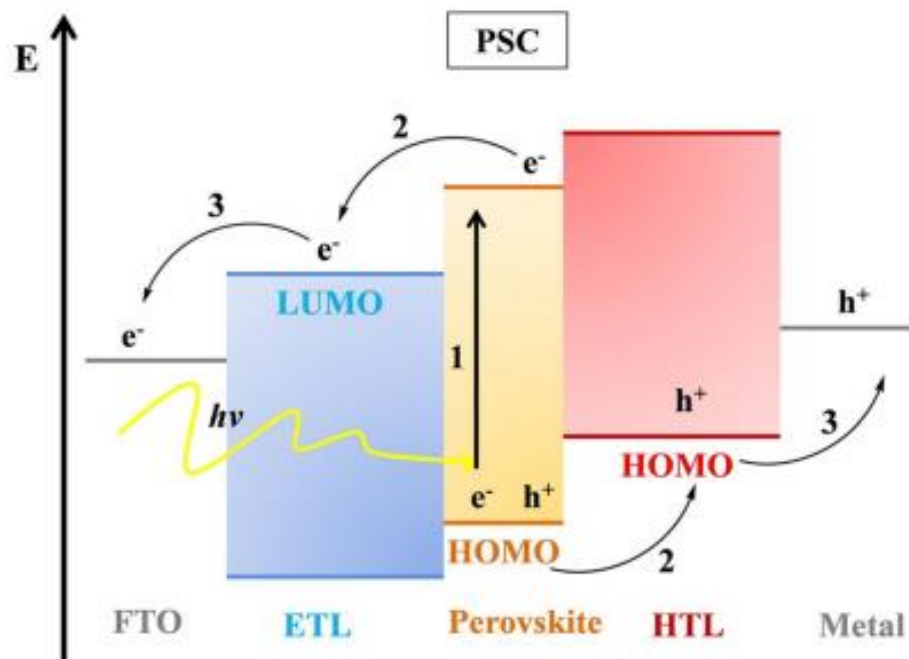


Figure 19 – Carriers motion in perovskite solar cells⁴³

Chapter 3: Deposition methods – Characterization techniques

3.2.1 : Spin coating

Spin coating is widely used to deposit small-area thin films in research laboratories. Although this technique might not be suitable for large-area, high-throughput film deposition, it can be conveniently used to optimize ink formulations in fundamental studies in which cell area is not major objective. Typically, in spin coating, a small amount of solution is first dropped onto a substrate to fully wet the substrate surface (Fig. 20). Subsequently, the substrate is fully covered with a layer of solution and spun to accelerate evaporation of the solvent. The film thickness is controlled by the

concentration of the solution and rotational velocity. Even though all processing conditions (annealing temperature, solution concentration and spinning speed) have been considered, spin-coated perovskite film quality is often poor, with a high density of pinholes and small grain sizes. These pinholes cause shunt pathways that degrade solar cell performance. With additives engineering the crystallization of perovskite could be finely tuned and perovskite films with significantly improved quality can be prepared for high performance solar cells. There are two aspects for the spin coating deposition, static and dynamic. In static deposition, the liquid simply is spreaded on the substrate without rotation being initiated. In dynamic deposition, the solution is deposited on the substrate when it has reached its maximum speed, which it has been set^{90–92}.

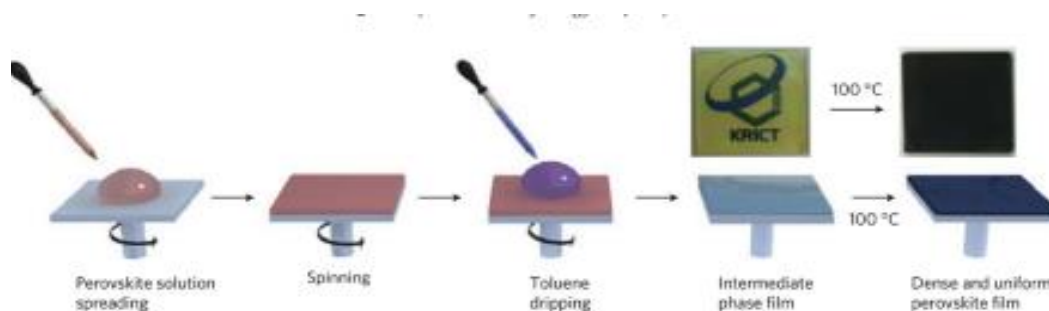


Figure 20 – Spin coating technique⁹²

3.2.2 : *Spray coating*

Spray coating has been widely employed to deposit perovskite films and compact TiO₂ films and is compatible with large-scale, high-throughput fabrication (Fig. 21). The first

attempt to prepare perovskite films using spray coating borrowed the method from polymer solar cell fabrication^{93–95}.

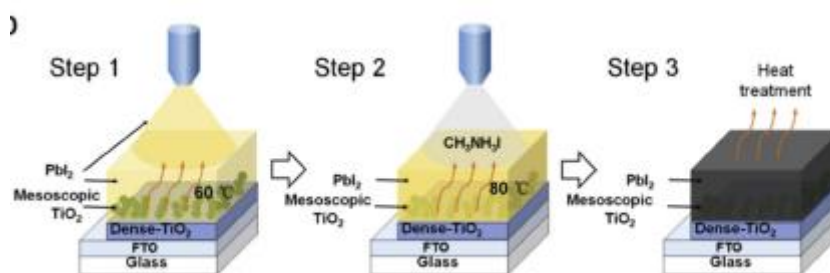
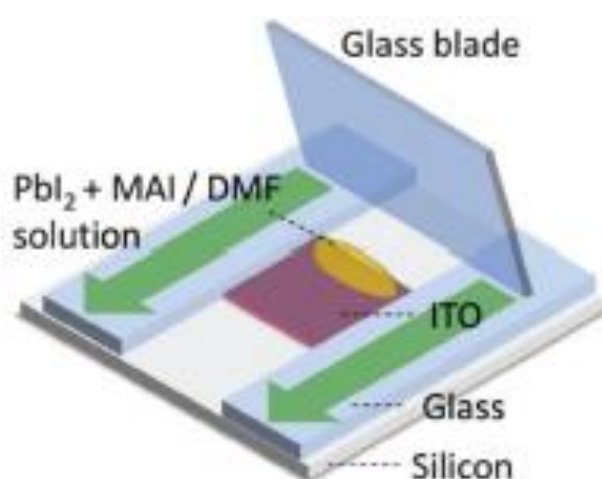


Figure 21 – Spray coating technique⁹¹

3.2.4 : Doctor blading

Film deposition by doctor blading is simple and low-cost, and can be integrated into roll-to-roll processes for optoelectronic device fabrication (Fig. 22). Compared with spin coating, there is almost no solution waste when doctor blading is employed. In addition, doctor blading can be operated under ambient conditions.

The solution readily wets the substrate with blade movement. Slower solvent evaporation time leads to slower nucleation and crystal growth, resulting in perovskite films with higher coverage and better quality compared to those prepared by spin coating^{96–98}.



3.2.4 : Slot die coating

This is a solution-processed, roll-to-roll compatible, highly scalable process and is almost similar to blade-coating technique with the advantage of less or no material wastage which is seen in the case of blade-coating technique. Among other techniques, this technique has achieved large success in the production of PVs. This process produces uniform and controlled thickness film in the material and is called as premetered coating process. By controlling the amount of the material feeding, thickness of the film can be controlled. It is a laboratory to fab transition technique, i.e., having high potential to be used at industrial scale for PSC manufacturing. This process is advantageous over the spin-coating technique in terms of scalability over a large-scale and less material wastage. The basic schematic of the slot die coater using mini roll coater unit is as shown in Figure 23.

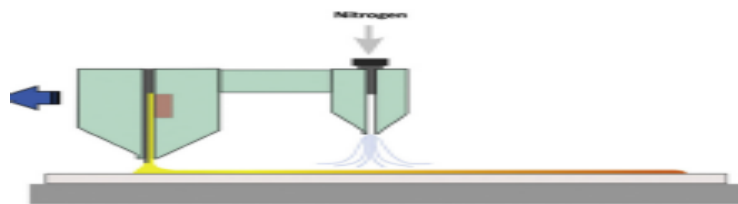


Figure 23 – Blade coating technique⁹²

3.1.1 : Solar simulator

A solar simulator is an apparatus that provides illumination approximating natural sunlight. The purpose of the solar simulator is to provide a controllable indoor test facility under laboratory conditions, used for testing solar cells, sun screens and other types of materials and devices. A solar simulator attached to the bottom of the glove box was used.

3.1.2 : Quantum efficiency

Quantum efficiency represents the ratio of numbers of carriers that are extracted from the solar cell to the number of photons of a given energy incident on the solar cell. The quantum efficiency can be given as a function of wavelength or energy. That kind of measurement indicates the amount of current that the solar cell will produce illuminated by photons of a particular wavelength. While quantum efficiency ideally has the square shape shown above, the quantum efficiency for most solar cells is reduced due to recombination effects. The same mechanisms which affect the collection probability also affect the quantum efficiency. For example, front surface passivation affects carriers generated near the surface, and since blue light is absorbed very close to the surface, high front surface recombination will affect the "blue" portion of the quantum efficiency. Similarly, green light is absorbed in the bulk of a solar cell and a low diffusion length will affect the collection probability from the solar cell bulk and reduce the quantum efficiency in the green portion of the spectrum. The quantum efficiency can be viewed as the collection probability due the generation profile of a single wavelength, integrated over the device thickness and normalized to the incident number of photons⁹⁹.

The "external" quantum efficiency of a silicon solar cell includes the effect of optical losses such as transmission and reflection. However, it is often useful to look at the quantum efficiency of the light left after the reflected and transmitted light has been lost. "Internal" quantum efficiency refers to the efficiency with which photons that are not reflected or transmitted out of the cell can generate collectable carriers. By measuring the reflection and transmission of a device, the external quantum efficiency curve can be corrected to obtain the internal quantum efficiency curve. As a result, one can evaluate the amount of current density (J_{sc}) that the cell will produce. For characterizing the solar cells, QE-T quantum efficiency setup by EnliTech was used (Figure 23).

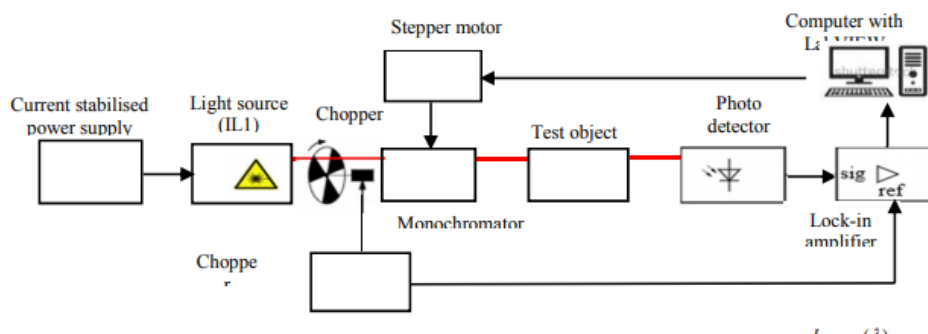
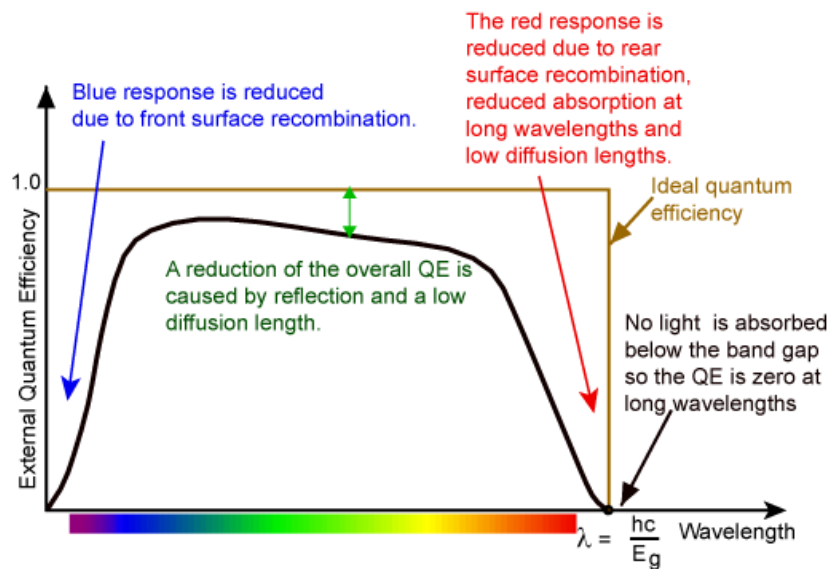
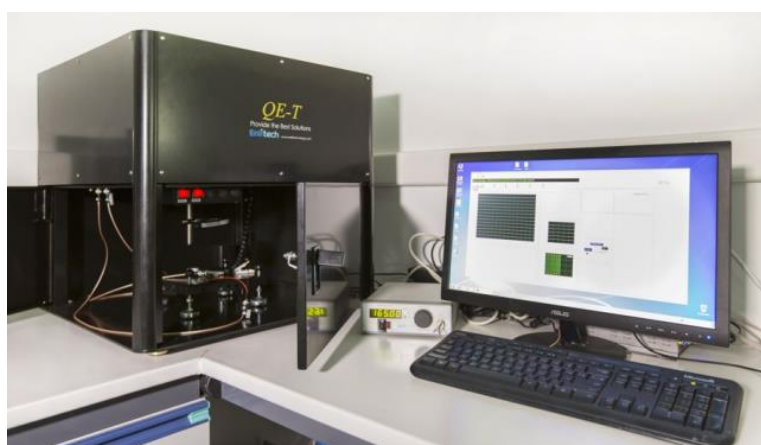


Figure 23 – Quantum efficiency setup⁹⁵



3.1.3 : Atomic Force Microscopy

An AFM uses a cantilever with a very sharp tip to scan over a sample surface. As the tip approaches the surface, the close-range, attractive force between the surface and the tip cause the cantilever to deflect towards the surface. However, as the cantilever is brought even closer to the surface, such that the tip makes contact with it, increasingly repulsive force takes over and causes the cantilever to deflect away from the surface.

A laser beam is used to detect cantilever deflections towards or away from the surface. By reflecting an incident beam off the flat top of the cantilever, any cantilever deflection will cause slight changes in the direction of the reflected beam. A position-sensitive photo diode (PSPD) can be used to track these changes. Thus, if an AFM tip passes over a raised surface feature, the resulting cantilever deflection (and the subsequent change in direction of reflected beam) is recorded by the PSPD.

An AFM images the topography of a sample surface by scanning the cantilever over a region of interest. The raised and lowered features on the sample surface influence the deflection of the cantilever, which is monitored by the PSPD. By using a feedback loop to control the height of the tip above the surface—thus maintaining constant laser position—the AFM can generate an accurate topographic map of the surface features^{100–104}.

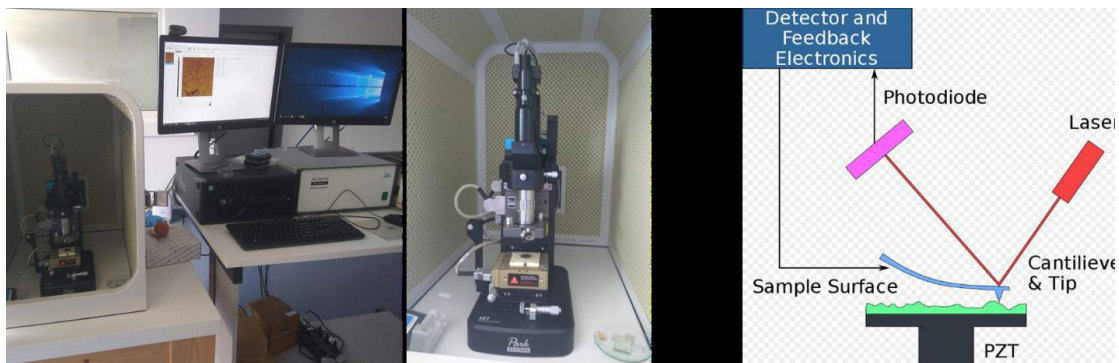
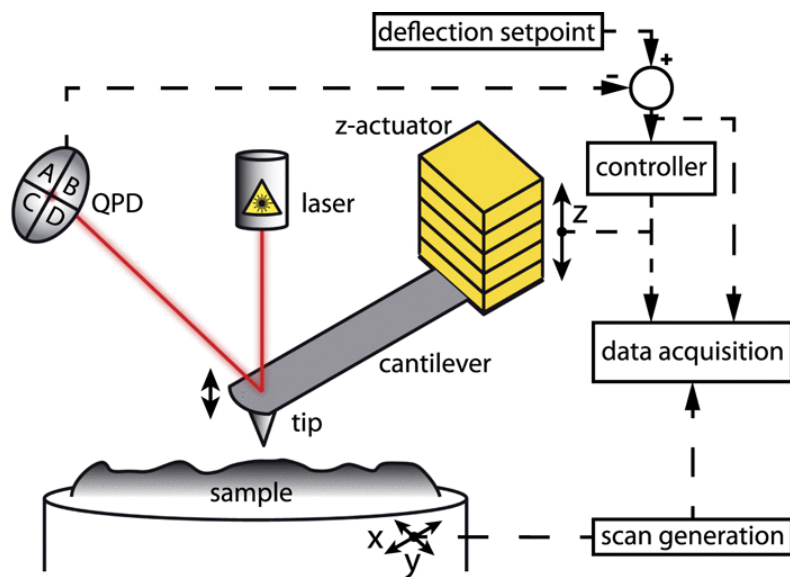


Figure 24 – AFM experimental setup¹⁰⁰

3.1.4 : X- ray Diffraction

X-rays are electromagnetic waves with wavelength ranging from 0,01nm to 10nm. When X-ray photons hit a crystal, the atomic and molecular structure of that crystal can be identified. The atoms of the crystal will scatter X-ray waves and constructive interference from multiple scattering signals will be occurred in specific directions. The whole phenomenon is described by Bragg's law.

$$2 d \sin\theta = n \lambda$$

Where d is the spacing between diffracting planes, θ is the incident angle, n is an integer number and λ is the wavelength. The distance is inverse proportional to the scattering angle. In other words, small repeating distances will refract to larger angles. By that the distance between ordered molecules can be determined. Figure 26 shows an illustration of X-ray diffraction by a crystal.

X-ray diffractometers consist of three basic elements: an X-ray tube, a sample holder, and an X-ray detector. X-rays are generated in a cathode ray tube by heating a filament to produce electrons, accelerating the electrons toward a target by applying a voltage, and bombarding the target material with electrons. When electrons have sufficient energy to dislodge inner shell electrons of the target material, characteristic X-ray spectra are produced. These spectra consist of several components, the most common being $K\alpha$ and $K\beta$. $K\alpha$ consists, in part, of $K\alpha_1$ and $K\alpha_2$. $K\alpha_1$ has a slightly shorter wavelength and twice the intensity as $K\alpha_2$. The specific wavelengths are characteristic of the target material (Cu, Fe, Mo, Cr). Filtering, by foils or crystal monochrometers, is required to produce monochromatic X-rays needed for diffraction. $K\alpha_1$ and $K\alpha_2$ are sufficiently close in wavelength such that a weighted average of the two is used. Copper is the most common target material for single-crystal diffraction, with $\text{Cu}K\alpha$ radiation = 1.5418 Å. These X-rays are collimated and directed onto the sample. As the sample and detector are rotated, the intensity of the reflected X-rays is recorded. When the geometry of the incident X-rays impinging the sample satisfies the Bragg Equation, constructive interference occurs and a peak in intensity occurs. A detector records and processes this X-ray signal and converts the signal to a count rate which is then output to a device such as a printer or computer monitor.

The geometry of an X-ray diffractometer is such that the sample rotates in the path of the collimated X-ray beam at an angle θ while the X-ray detector is mounted on an arm to collect the diffracted X-rays and rotates at an angle of 2θ . The instrument used to maintain the angle and rotate the sample is termed a goniometer. For typical powder patterns, data is collected at 2θ from $\sim 5^\circ$ to 70° , angles that are preset in the X-ray scan^{105–109}.

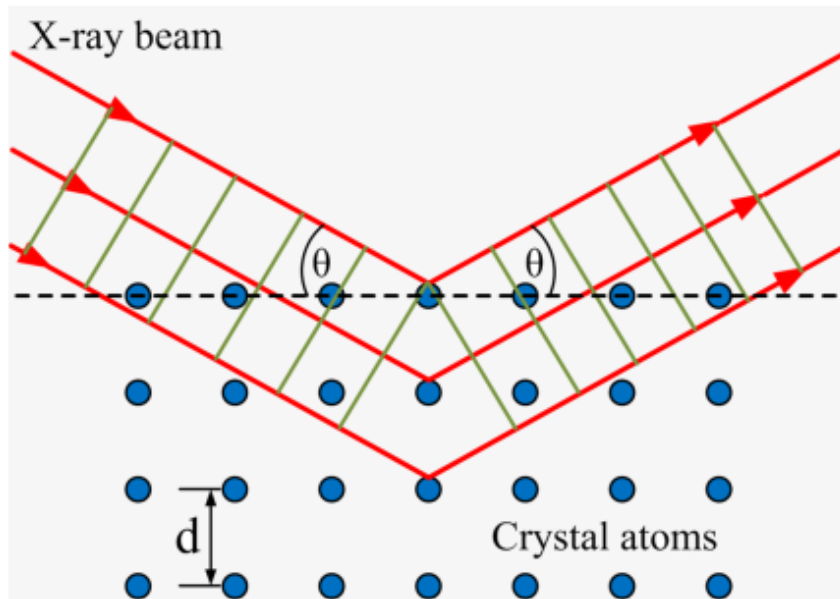
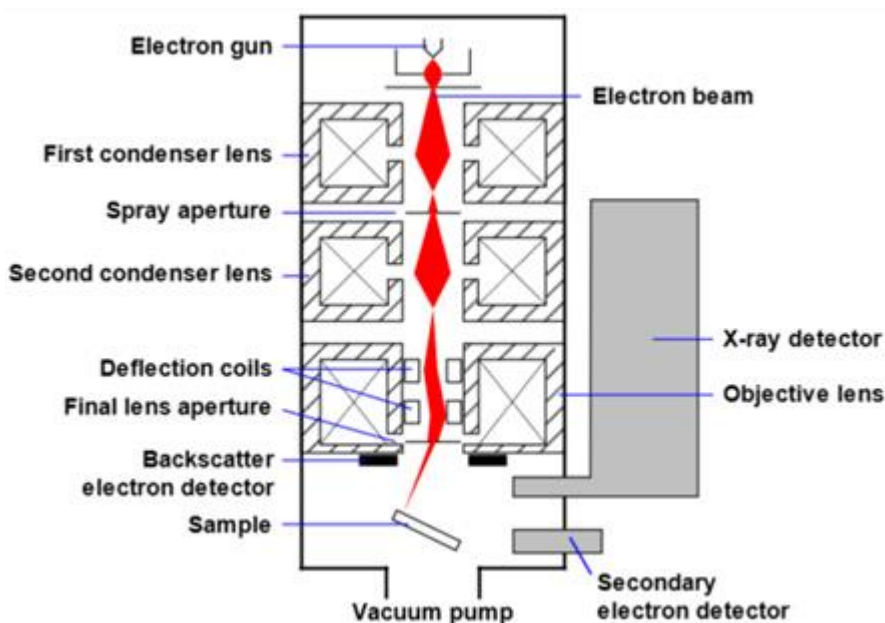


Figure 26 – XRD operation principle¹¹⁰

3.1.5 : Scanning Electron Microscopy

Scanning electron microscope (SEM) uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive from electron-sample interactions reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample. In most applications, data are collected over a selected area of the surface of the sample, and a 2-dimensional image is generated that displays spatial variations in these properties. Areas ranging from approximately 1 cm to 5 microns in width can be imaged in a scanning mode using conventional SEM techniques (magnification ranging from 20X to approximately 30,000X, spatial resolution of 50 to 100 nm). The SEM is also capable of performing analyses of selected point locations on the sample; this approach is especially useful in qualitatively or semi-quantitatively determining chemical compositions (using EDS), crystalline structure, and crystal orientations (using EBSD). The design and function of the SEM is very similar to the EPMA and considerable overlap in capabilities exists between the two instruments.

Accelerated electrons in an SEM carry significant amounts of kinetic energy, and this energy is dissipated as a variety of signals produced by electron-sample interactions when the incident electrons are decelerated in the solid sample. These signals include secondary electrons (that produce SEM images), backscattered electrons (BSE), diffracted backscattered electrons (EBSD that are used to determine crystal structures and orientations of minerals), photons (characteristic X-rays that are used for elemental analysis and continuum X-rays), visible light (cathodoluminescence--CL), and heat. Secondary electrons and backscattered electrons are commonly used for imaging samples: secondary electrons are most valuable for showing morphology and topography on samples and backscattered electrons are most valuable for illustrating contrasts in composition in multiphase samples (i.e. for rapid phase discrimination). X-ray generation is produced by inelastic collisions of the incident electrons with electrons in discrete orbitals (shells) of atoms in the sample. As the excited electrons return to lower energy states, they yield X-rays that are of a fixed wavelength (that is related to the difference in energy levels of electrons in different shells for a given element). Thus, characteristic X-rays are produced for each element in a mineral that is "excited" by the electron beam. SEM analysis is considered to be "non-destructive"; that is, x-rays generated by electron interactions do not lead to volume loss of the sample, so it is possible to analyze the same materials repeatedly¹¹¹⁻¹¹⁴.



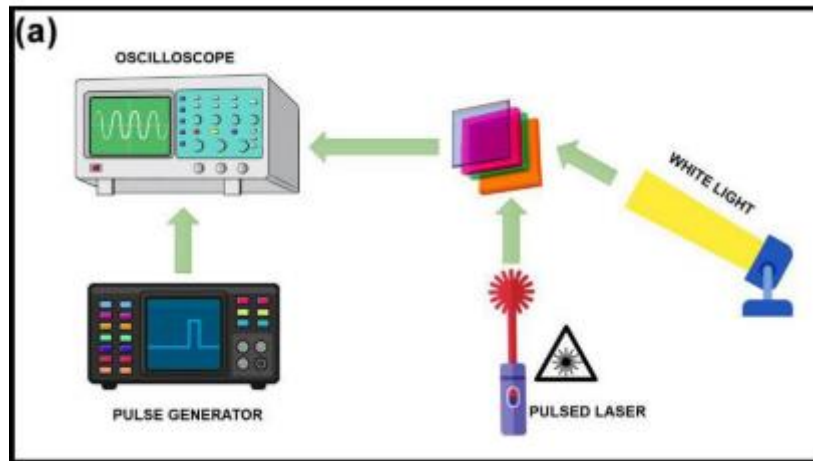
3.1.6 : Transient response measurements

Transient lifetime measurements rely on the decay of carriers over time. Carriers are generated by a very short pulse of light and the decay of the carrier density with time is measured. The longer the minority carrier lifetime the more slowly the carriers decay.

3.1.6.1 : Transient photocurrent

Transient photocurrent (TPC) is a measurement technique, typically employed in the physics of thin film semiconductors. TPC allows to study the time-dependent (on a microsecond time scale) extraction of charges generated by photovoltaic effect in semiconductor devices, such as solar cells^{115–117}.

A semiconductor is sandwiched between two extracting electrodes. When it is excited with a short pulse of light (as short as 100 femtoseconds), the photogenerated charges are extracted on the electrodes, resulting in a current, which is detected by an oscilloscope in form of voltage across a resistor. Since the excitation pulse is square, there are two ways to measure TPC: in a “light on” and a “light off” positions. In a “Light on”, the signal is recorded as soon as the excitation pulse is switched on, allowing to observe the build-up of charges on the electrode after the start of excitation. “Light off” measurements show how the charges decay after the pulse is switched off. PC measurements are conducted under short circuit condition and yield information about extractable charges, charge recombination and density of states. Quite often, TPC measurements help to build “drift-diffusion” model which reflects trapping and detrapping of the photogenerated charges and the quality of contact between different layers. TPC allows varying different measurement parameters, such as intensity or length of the light pulse, applied voltage.



3.1.6.2 : Transient photovoltage

Under open-circuit condition the external current is zero and hence charge generation is equal to charge recombination. Techniques probing the device under open-circuit are generally suited to study recombination. Open-circuit voltage decay (OCVD, sometimes also called large-signal TPV) measurements reveal information about recombination and the shunt resistance. In OCVD measurements, the device is first illuminated by an LED or a laser to create charge carriers. Then the light is turned-off and the decay of the voltage is measured over time^{118,119}.

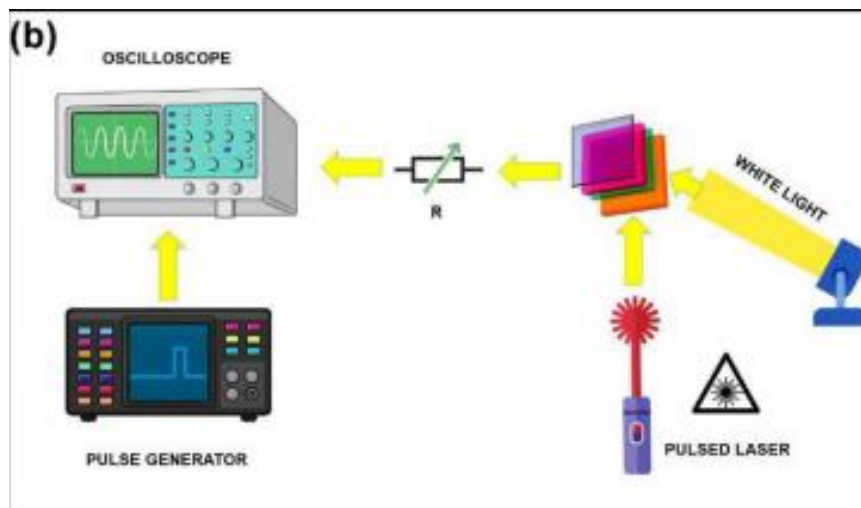
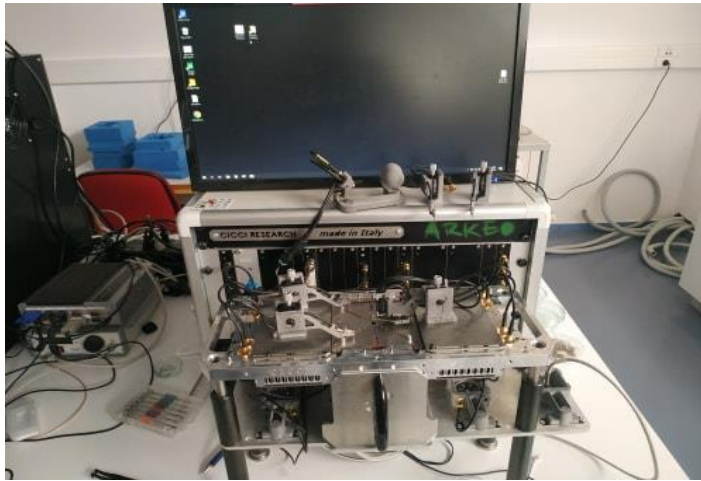


Figure 30 – Transient PV operation principle¹²⁰



3.1.6.3 : Charge extraction by linearly increasing voltage (CELIV)

CELIV is a popular technique to estimate charge carrier mobilities in thin-film solar cells. It was introduced by Juška in 2000 and many adaptations or extensions were proposed. If charge carriers are present in the device, they are extracted and lead to a peak in the transient current. According to the time of the current-peak (t_{max}) the charge carrier mobility can be estimated.

The charges that are extracted by the voltage ramp can be intrinsic (dark-CELIV), be generated by illumination prior to extraction (photo-CELIV) or be injected by a positive voltage prior to extraction (injection-CELIV)^{121–123}.

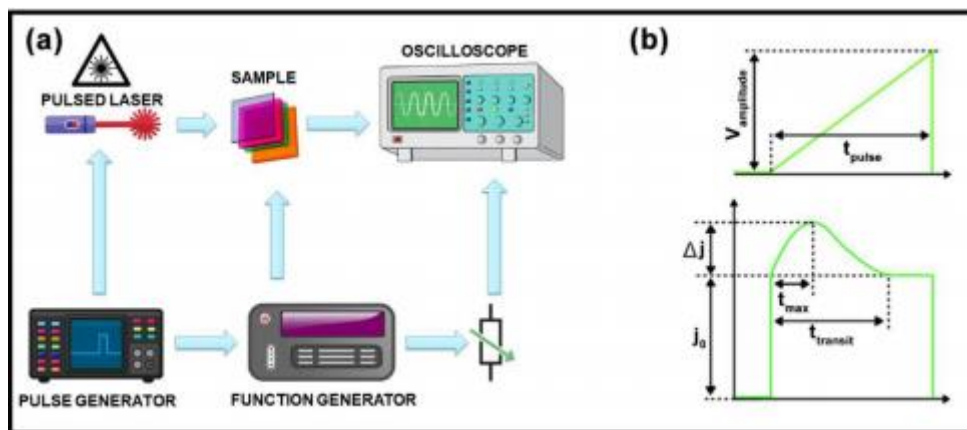


Figure 31 – CELIV operation principle

Chapter 4: Experimental

4.1: Experimental equipment

- **Sonicator**

Ultra-sonication is required for the cleaning of substrates. In this process sound energy (acoustic waves) is applied (200-400 kHz) to a container where a solvent and the substrates are placed. The solvent is usually water. This phenomenon creates rapid vibrations around the substrates that remove most of the contaminants such as dust, dirt (etc)³⁹. In this work Elma Sonicator by Elmasonic was used



Figure 32 – Sonicator device

- **UV ozone**

Ultraviolet ozone treatment is a subsequent method of cleaning the substrates. The specific method aims to remove the organic contamination and increase the surface hydrophilicity to deposit a uniform layer afterwards. This effect is caused by irradiating the surface of a substrate with suitable lamps that emit ultraviolet light at wavelengths of 185 nm and 254 nm⁴⁰. It is a photo-sensitized oxidation process by atomized oxygen

and high reactive ozone. The UV ozone cleaner that was used is a MB-UV-O3-Cleaner by MBRAUN.

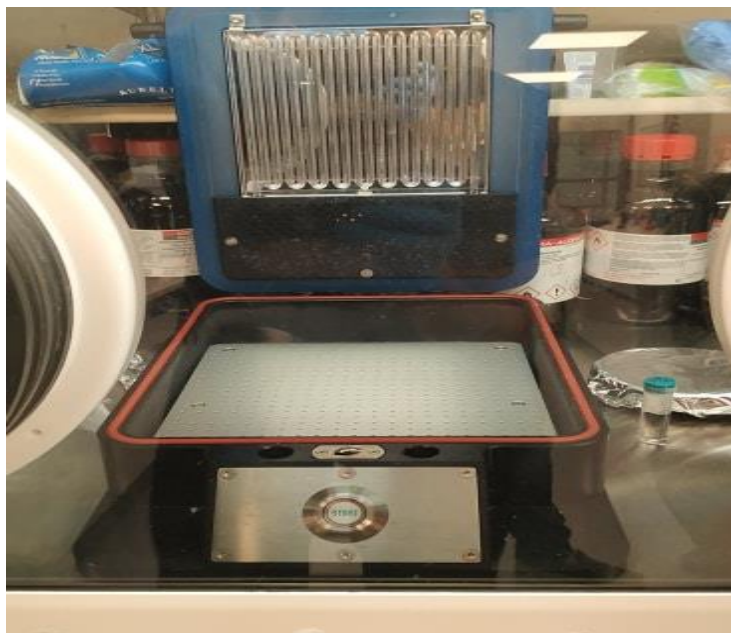


Figure 33 – UV ozone cleaner device

- ***Spin coater***

Spin coating is the process where a uniform thin film is deposited on a flat substrate by coating a solution of the desired material in a solvent while it is rotating. The rotation of the substrate at high speed ($>600\text{rpm}$) means that the centripetal force combined with the surface tension of the solutions of the solution pulls the liquid coating into an even covering (Figure 34). During this time the solvent then evaporates to leave the desired material on the substrate

in an even coverage. Two spin coaters were used, the MB-SC-200 by Ossila (in glove box) and the WS-650-23 by Laurell (Figure 34).

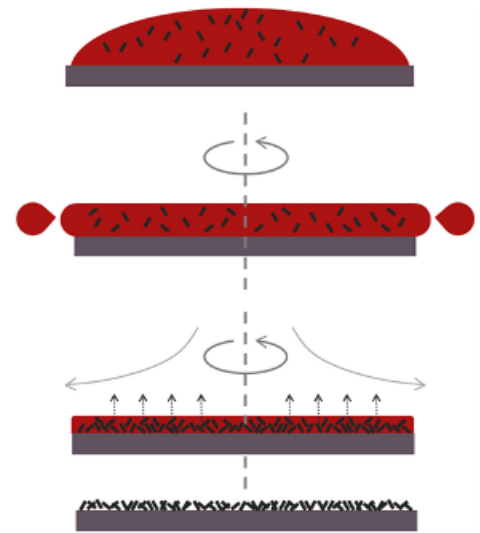


Figure 34 – MBRAUN spincoater

- ***Glove box***

Glove box is a sealed container designed to allow one to manipulate objects where an inert atmosphere is desired. Typically, a glove box is filled with nitrogen, an inert gas which is used to avoid unwanted chemical reactions degrading a sample. Furthermore, the inert gas in a glove box is pumped through a series of devices which remove vapors of solvents, water and oxygen from the gas. All above make the glove box a high purity inert atmosphere container, suitable for manipulating materials which are sensitive to oxygen and water molecules⁴³. A MB-200B Modular glove box work station was used by MBRAUN (Figure 35).



Figure 35 – MBRAUN glovebox

- ***Evaporator***

Thermal evaporation is a method of thin film deposition. The solid material is heated in a high vacuum chamber, reaching a melting point temperature where it produces some vapor pressure. The vapor stream of the evaporated material traverses the chamber to reach the substrate and make a coating. The high vacuum is required so that the evaporated particles can travel directly to the substrate without colliding with the background gas. Once the particles reach the substrate, they condense back to solid state forming a compact thin film (Figure 36) .The MB-EcoVap by MBRAUN evaporator system was used.

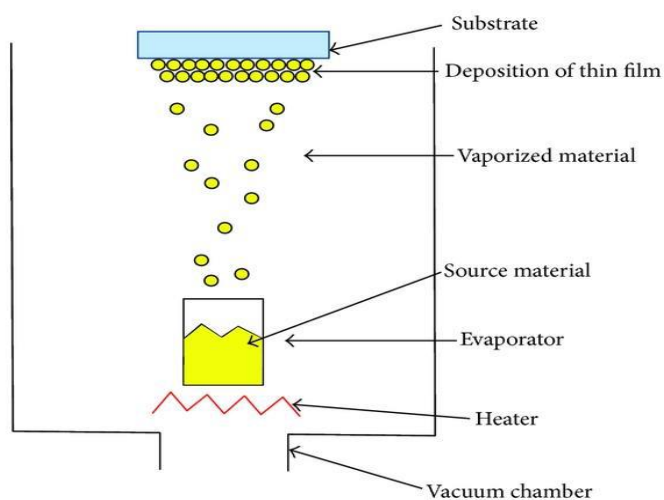


Figure 36 – MBRAUN thermal evaporator and operation principle

- ***Solar simulator***

A solar simulator is an apparatus that provides illumination approximating natural sunlight. The purpose of the solar simulator is to provide a controllable indoor test facility under laboratory conditions, used for testing solar cells, sun screens and other types of materials and devices. A solar simulator attached to the bottom of the glove box was used

In this section, the deposition techniques that took place are described. Different conditions and additives were tested to achieve the optimum morphology and the best PCE . All methods are described in detail below.

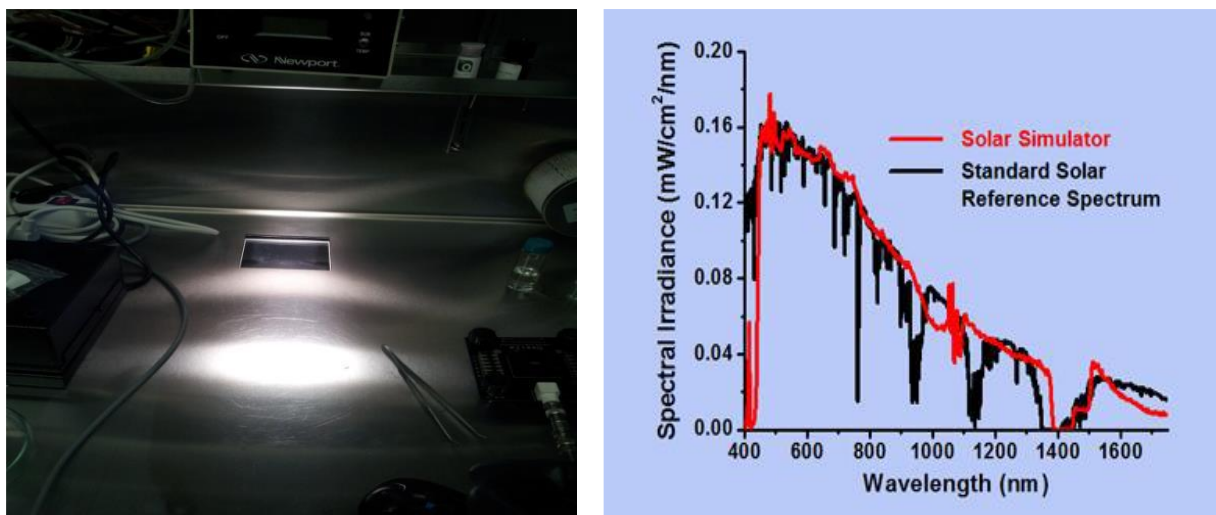


Figure 37 – Newport solar simulator

4.2 Materials

All the materials that were used to fabricate a perovskite solar cell are listed below.

- PbI_2 precursor with molecular weight of 4561 g/mol 99.999 trace metal basis was purchased from TCI
- PbBr_2 precursor with molecular weight of 367.01 g/mol was purchased from Sigma Aldrich
- Methylammonium iodide (MABr) precursor with molecular weight of 111.97 g/mol was purchased from Greatcellsolar
- Formamidinium iodide (FAI) precursor with molecular weight of 171.97g/mol was purchased from Greatcellsolar
- PTAA polymer with polydispersity of 2,53 was purchased from Ossila
- Rubidium Iodide precursor with molecular weight of 212.37 g/mol was purchased from Alfa Aesar
- Cesium Iodide precursor with molecular weight of 259.81 g/mol was purchased from Sigma Aldrich
- Glass substrates with Indium Tin Oxide electrode with resistance of 20 Ω/sq were purchased from Naranjo Substrates

- Bathocuproine (BCP) 99.99% trace metal basis precursor with molecular weight of 360.45 g/mol was purchased from Sigma Aldrich
- PC₆₀BM [6,6]-phenyl-C₆₁-butyric acid methyl ester (>99.9%) with molecular weight of 910,88 g/mol was purchased from Solenne BV.
- Dimethylformamide (DMF) (>99.8) with molecular weight of 73,09 g/mol was purchased from Sigma-Aldrich
- Dimethylsulfoxide (DMSO) (>99.99) with molecular weight of 73,09 g/mol was purchased from Sigma-Aldrich
- Isopropanol 99.5% Extra Dry with molecular weight of 85.17 g/mol was purchased from Acros
- Ethylacetate 99.9 % Extra Dry with molecular weight of 86.12 g/mol was purchased from Acros
- Chlorobenzene 99.8 Extra Dry with molecular weight of 76.12 g/mol was purchased from Acros
- Methanol 99.9% Anhydrous
- PFN with molecular weight Mw= 50-250kD was purchased from Solaris Chem
- Ag pellets were purchased from Kurt J. Lesker

Experimental process

Preparation methods

• Cleaning the substrates

To fabricate a solar cell, first the glass/ITO substrates must be cleaned. This was achieved using ultrasonic bath with deionized water, acetone and isopropanol for 10 minutes each. After sonication the substrates were taken to a drying oven at 120°C for 20 minutes. The next step of cleaning is the ultraviolet ozone treatment. The substrates were taken into the ultraviolet ozone cleaner for 15 minutes (Figure 38).

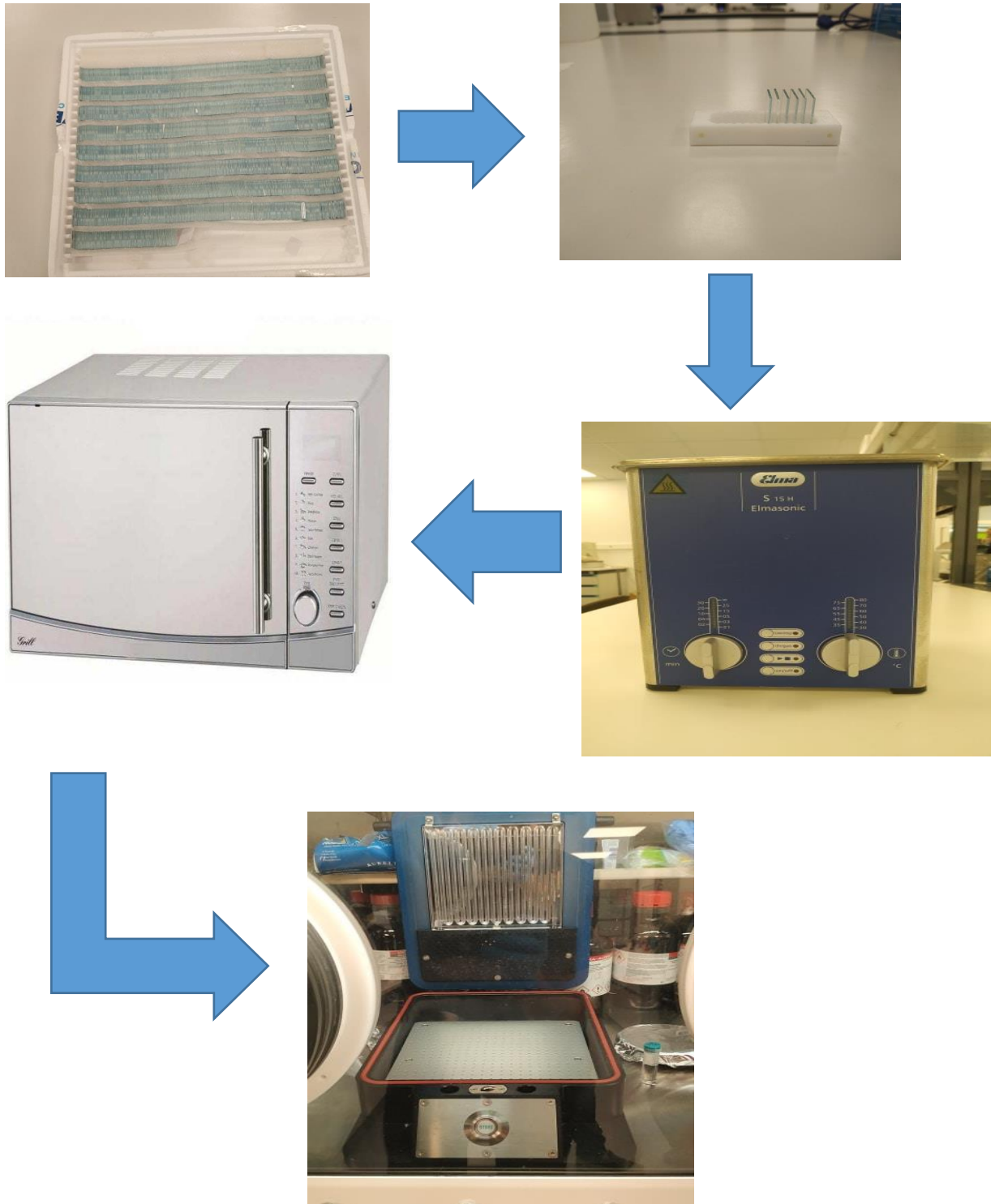


Figure 38 – Substrates cleaning procedure

- ***Preparation of RbCsMAFA perovskite***

To synthesize the triple cation perovskite with stoichiometry $(\text{RbPbI}_3)_{0.05}(\text{CsPbI}_3)_{0.05}[(\text{FAPbI}_3)_{0.85}(\text{MAPbBr}_3)_{0.15}]_{0.95}$, the precursors must be mixed in a glove box under nitrogen atmosphere. More specifically for 1ml solution 181,3 mg of FAI, 529.7 mg PbI_2 , 68.28mg of PbBr_2 , and 20.83 mg of MaBr are mixed in 1ml DMF:DMSO solution (molar ratio 4 :1) until a clear solution is obtained under vigorous stirring. Subsequently 309.5 mg of RbI are mixed in 1 ml DMF:DMSO (4:1) and 389.7 mg of CsI in 1 ml DMSO . Finally 52.6 μL of CsI and 55.4 μL RbI of stock solutions were added in pristine MAFA solution in order to obtain final optimum concentration (1.54M)

Preparation of PTAA

For the HTL solution, 2 mg of PTAA were dissolved in 1ml of toluene. The solution was stirred at room temperature for 12 hours.

Preparation of PC₆₀BM

To prepare the ETL solution, 20 mg of PC₆₀BM were dissolved in 1ml of anhydrous chlorobenzene and stirred at 70°C for 12 hours

Preparation of PFN

To prepare the solution, 0,5 mg of PFN were dissolved in 1ml of anhydrous methanol and stirred at room temperature for half an hour.

Preparation of BCP

To prepare the solution, 0,5 mg of BCP were dissolved in 1ml of anhydrous isopropanol and stirred at 50°C for 12 hours

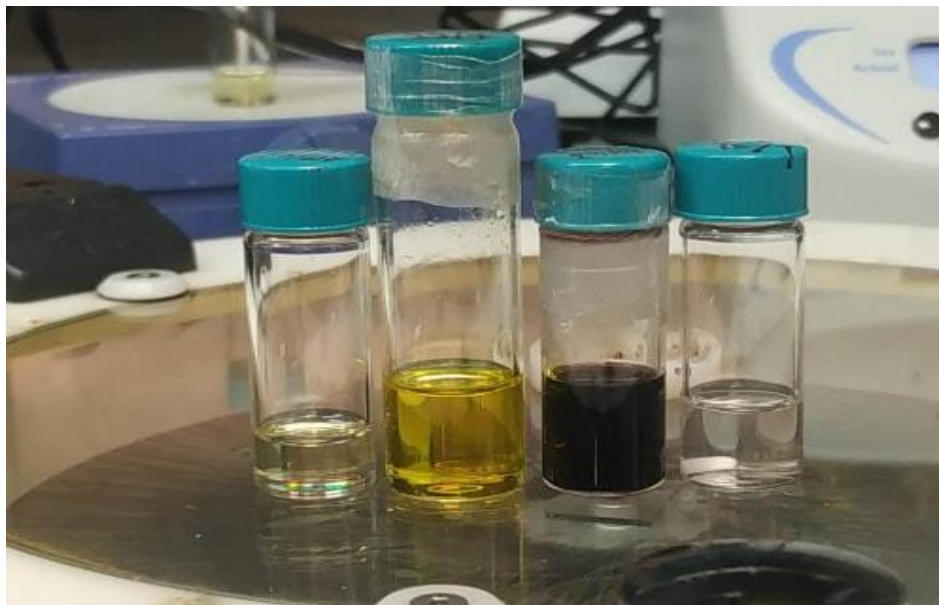


Figure 39 – Solutions after preparation (left PTAA, Perovskite, PCBM,BCP)

Deposition of HTL, perovskite, ETL and counter electrode

- ***PTAA deposition***

The PTAA solution was spin-coated onto the ITO substrates at 6000 rpm for 30 seconds. The thickness of PTAA was about 10 nm. The substrates were then annealed on a hotplate at 110°C for 10 minutes.

- ***Perovskite deposition***

The RbCsMAFA precursor solution was spin-coated at 6000 rpm for 45s with dynamic technique and 20s before the end of the program different quantities of CB or EA were dripped in the middle of the substrate .Then the substrates were placed on a hot plate at various temperatures and annealing times. The annealing temperature and time was ranging from 10min to 90min and 70°C to 120°C respectively as stated in the literature.

Subsequently , a little area was cleaned using a swab dipped into DMF. The cleaning process took place during the thermal annealing of the perovskite.

- ***PC₆₀BM deposition***

PCBM solution with concentration of 20mg/ml in chlorobenzene was spin coated at different rpm and statically or dynamically on top of the perovskite layer. This time the area was cleaned using a swab dipped into chloroform. The substrates dried at room temperature for 30 minutes inside a petri-dish with open lid.

- ***PFN deposition***

After the deposition of the ETL, PFN solution was spin coated on the substrates at 2000 rpm for 45s dynamically . A final step of cleaning with chloroform was performed before the deposition of Ag electrode.

- ***BCP deposition***

After the deposition of the ETL, BCP solution was spin coated on the substrates at 4000 rpm for 45s dynamically . A final step of cleaning with chloroform was performed before the deposition of Al electrode.

- ***Ag electrode deposition***

Finally, to complete the device, the cathode electrode must be deposited on top of all layers. The deposition of silver was performed by thermal evaporation under vacuum (1×10^{-6} mbar) with rate of 1,2 Å per second. A shadow mask was used to define an active area of 0,4 cm².

Cleaning process for each of the layers took place exactly after coating to keep an open area on the ITO pattern for electrical measurements. This way the ITO electrode would not be affected by any residual. Figure 41 shows the schematic representation of device fabrication and the cleaning process and Figure 41 shows the cross section of the complete device.

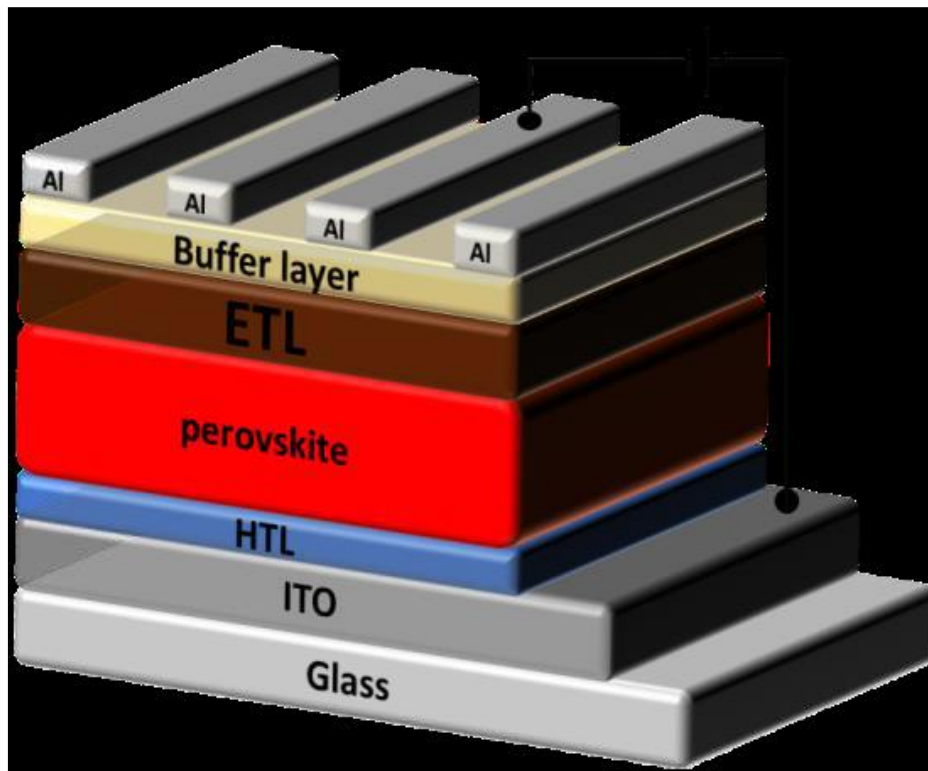
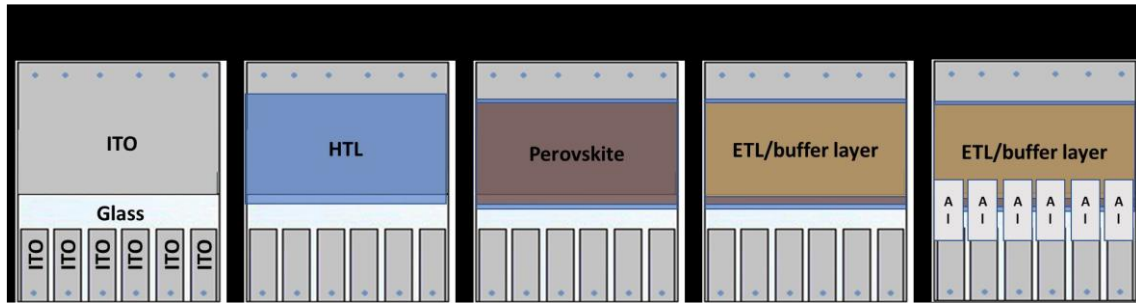


Figure 41 – Inverted solar device configuration¹¹⁰

Chapter 5: Results and discussion

In this section, the experimental results which obtained with the methods described in section three are presented and analyzed. The parameters that affected the morphology and the total performance of the cells are discussed. Prior to extensive step-by-step analysis, a small overview of the steps taken during the photovoltaic optimization effort is provided.

Optimization of triple cation Perovskite CsMAFA

- A) PTAA thickness
- B) Perovskite
 1. Annealing time
 2. Antisolvent quantity
 3. Antisolvent time dripping
- C) Optimization of PCBM (ETL) : rpm ,static or dynamic
- D) Insertion Of PFN below Cathode

INTRODUCTION OF Rb

Optimization of quadrable cation Perovskite RbCsMAFA

- A) Insertion of BCP below Cathode
- B) Perovskite Concentration
- C) Cations percentages (Cs %,Rb%): stoichiometry check

5.1 Optimization of triple cation perovskite CsMAFA

To optimize a device based on the triple cation perovskite, previously reported method based on Saliba's publication¹²⁴ was followed. However, due to the fact that in the inverted structure a simplified and low temperature process can be used, this work was focused on the planar inverted architecture. A 10nm thin layer of PTAA was deposited on top of the ITO substrate as a hole transport layer. On top of that about ~500nm of perovskite layer was spin coated at by centrally dropping 45 μL of the perovskite solution on a $2.5 \times 2.5 \text{ cm}^2$ ITO/PTAA substrate and spincoating at 6000 rpm with 700 rpm/s acceleration for 45 s. After 10 s, 300 μL of ethyl acetate (CB) is dispensed on the sample. The annealing time for the perovskite layer was 60 minutes at 100°C. On top of the perovskite about ~50nm layer of PCBM (solution) was deposited. On the top of PCBM a very thin interlayer was deposited PFN, in order to achieve better interface with silver and 100nm of Ag was deposited to complete the device as described in the previous section. However, in the inverted structure the specific method of did not provide the expected results. The respective photovoltaic characteristics are summarized in Table 1 below.

Scan Direction	PCE (%)	FF (%)	Jsc (mA.cm^2)	Voc (V)	MP (W)	Rshunt (Ohm.cm^2)	Rseries (Ohm.cm^2)
Forward	6.22004	56.86178	10.66069	0.95427	-5.78464	311.4869	15.61203
Reverse	6.239916	57.39494	10.39731	0.97245	-5.80312	442.0426	14.82977

Table 1

As mentioned in the first part of this Msc thesis, a major problem of perovskite PV is their instability in time as well as the repeatability in the manufacturing process. Therefore, because the correct creation of photovoltaic depends largely on the

experimental conditions prevailing in each lab so in any case is necessary to develop the optimization process step by step from the beginning.

Different polymers have been used for hole transporting layers such as poly [N, N0-bis(4-butylphenyl)-N, N0-bis (phenyl)benzidine] (poly-TPD) which resulted in a Voc value of 1 V because of a better CB and VB alignment and a better crystallization of the perovskite^{125–127}. Furthermore, through the plethora of HTL materials, a careful selection must be done in terms of solvent orthogonality. For example, the hole transporting layer should not be affected by the solvent of the perovskite precursor which in this case is DMF:DMSO. For this case Poly[bis(4-phenyl) (2,4,6-trimethylphenyl) amine Poly(triarylamine) PTAA was used as the HTL which is sustainable to DMF wash.

5.1.1 : PTAA thickness

Keeping constant the previous parameters, the purpose of this section is to investigate how photovoltaic parameters were affected by thickness of the first layer. Based on this logic investigated different concentrations of the HTL solution. The results are summarized in the table below.

PTAA concentration	PCE (%)	FF (%)	Jsc (mA/cm ²)	Voc (V)
2 mg /ml	11.03	73	14.8	0.95
4mg/ml	8.38	66	12.7	0.93
6 mg/ml	2.67	48	6.1	0.85
12 mg/ml	1.27	40	5.8	0.55

Table 2

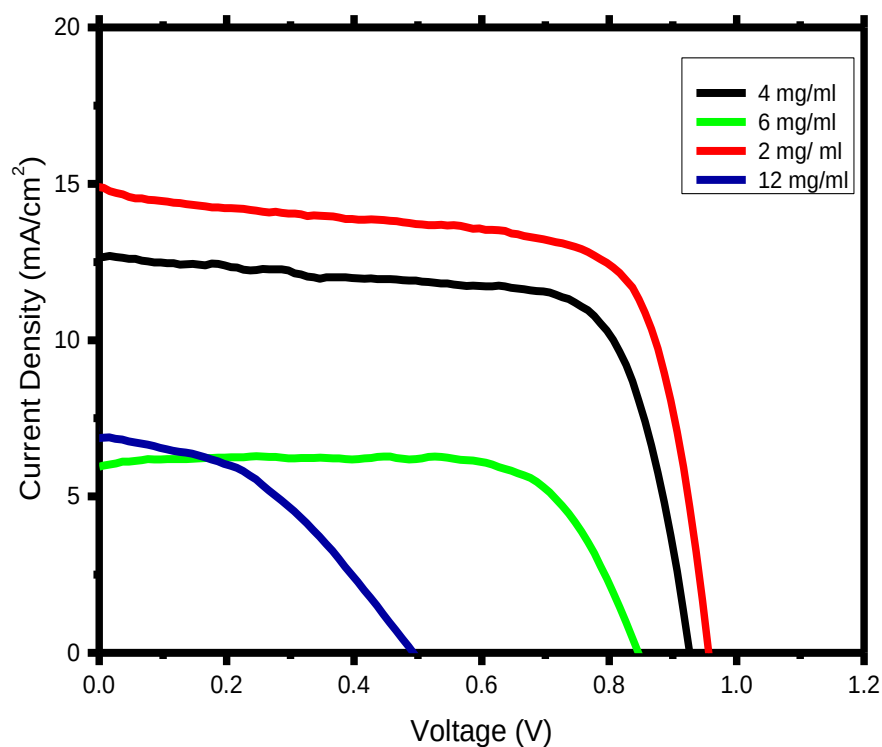


Figure 42 – PTAA concentration J-V chart

It is easy to be observed a significant improvement compared with the first attempt which took place, with the use of minimum elevated concentration 2mg/ml compared to the initial 1.5 mg/ml, fill factor was increased dramatically and this promises a better interface with the perovskite. Which makes favorable the transport of holes to anode, with the result current enhancement. With the use of the atomic scanning microscopy were measured thicknesses for each different concentrations. For both edges of the scale were made also topographic surveys, which are listed below (Figures 43-46). The difference in the axis of the y provide us the measurement for the thickness

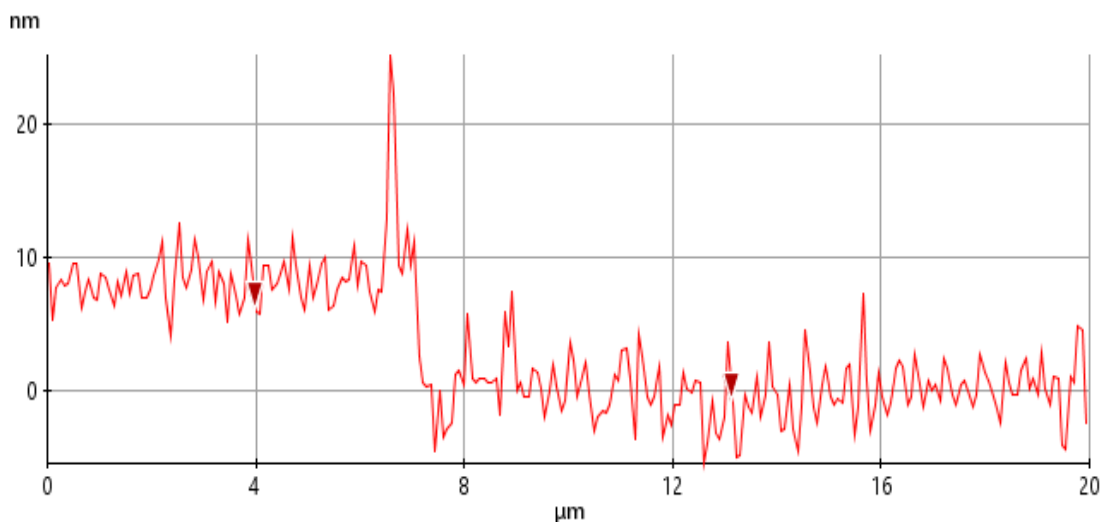


Figure 43 – PTAA concentration 2 mg/ml thickness J-V chart

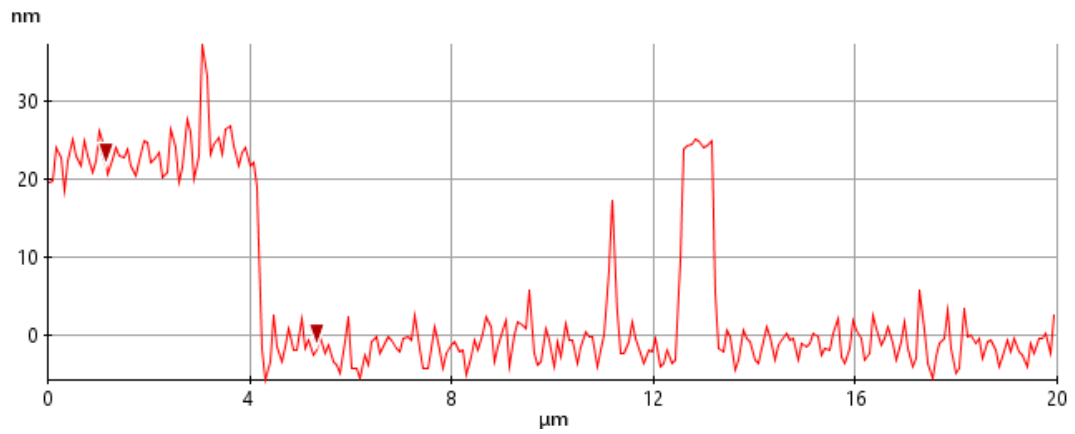


Figure 44 – PTAA concentration 4 mg/ml thickness J-V chart

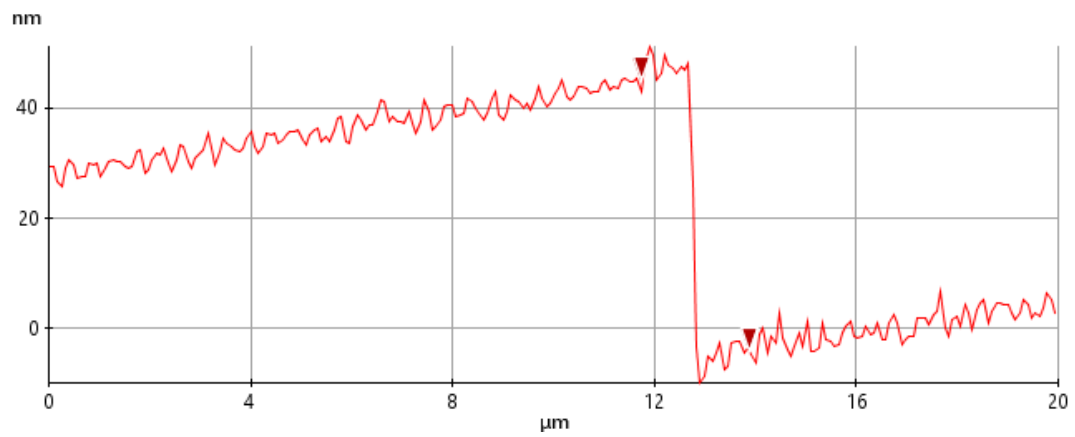


Figure 45 – PTAA concentration 2 mg/ml thickness J-V chart

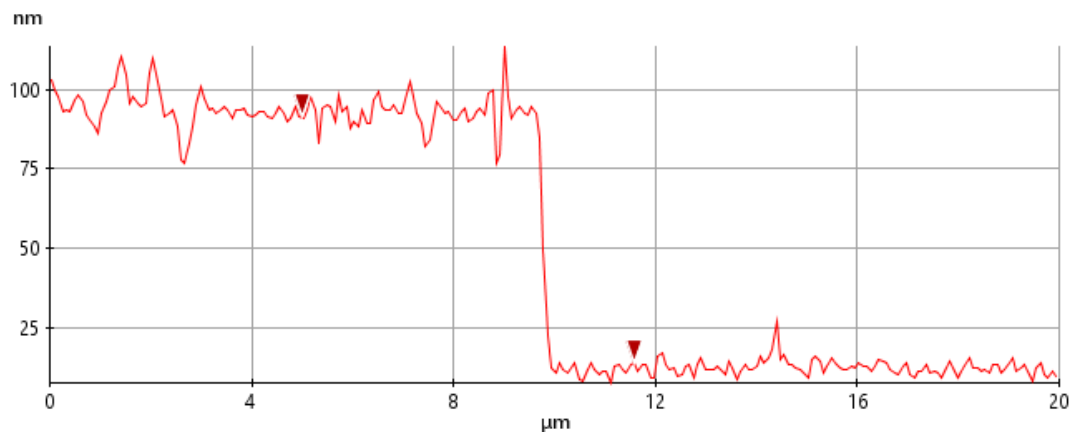
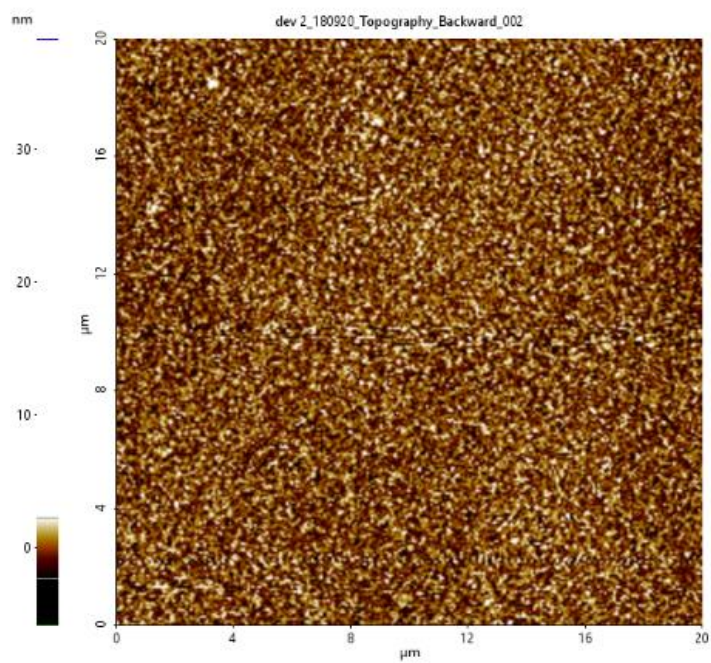


Figure 46 – PTAA concentration 12 mg/ml thickness J-V chart

Concentration (mg/ml)	Thickness (nm)
2	6
4	20
6	40
12	85

Table 3



Statistics										
Region	Min(nm)	Max(nm)	Mid(nm)	Mean(nm)	Rpv(nm)	Rq(nm)	Ra(nm)	Rz(nm)	Rsk	Rku
Whole	-5.816	38.248	16.216	0.000	44.064	1.180	0.898	31.319	-1.877	38.218

Figure 47 – AFM topography 2mg/ml

5.1.2 : Perovskite

5.1.2.1 :Annealing optimization

A polar solvent such as dimethylformamide (DMF), g-butyrolactone (GBL) and dimethyl sulfoxide (DMSO)^{128–130} in perovskite precursor solution. During the deposition on a substrate, solvent is removed by thermal annealing on a hot plate or drying in an air or inert atmosphere after the spinning process. Causing super saturation in the film for nucleation and crystal growth of the perovskites^{38,62,131,132}. This method is a facile and simple approach to evaporate solvent for perovskite deposition.

To enhance the photovoltaic characteristics of the device the fabrication process should be optimized.

Thus, an annealing optimization was carried out to improve the crystallization of the perovskite layer and the performance of the perovskite solar cell. Different annealing times were tested by keeping the same spinning conditions (6000 rpm) and annealing temperature set at 100°C. More specifically the annealing time was varied from 10 min to 90 min. Table 4 below shows the results of the temperature optimization where the best annealing time was found to be at 45 min. All the characteristics at the specific time were significantly enhanced compared to the previous experimental conditions. Figure 48 shows the J-V curves that were recorded for each of the annealing temperatures. Also, the curve that corresponds to the optimized annealing temperature is better and has the appropriate shape approaching a square.

<i>Time (min)</i>	<i>PCE (%)</i>	<i>Jsc ma/cm²</i>	<i>Voc (V)</i>	<i>FF (%)</i>	<i>Rshunt (Ohm.cm²)</i>	<i>Rseries (Ohm.cm²)</i>
10	7.56	11.59	0.93	64.38	1426.55	10.91
45	14.11	17.34	0.94	75.48	3270.45	3.85
60	11.22	16.22	0.97	64.96	1539.18	9.01
90	8.92	13.98	1.00	59.17	812.54	16.85

Table 4

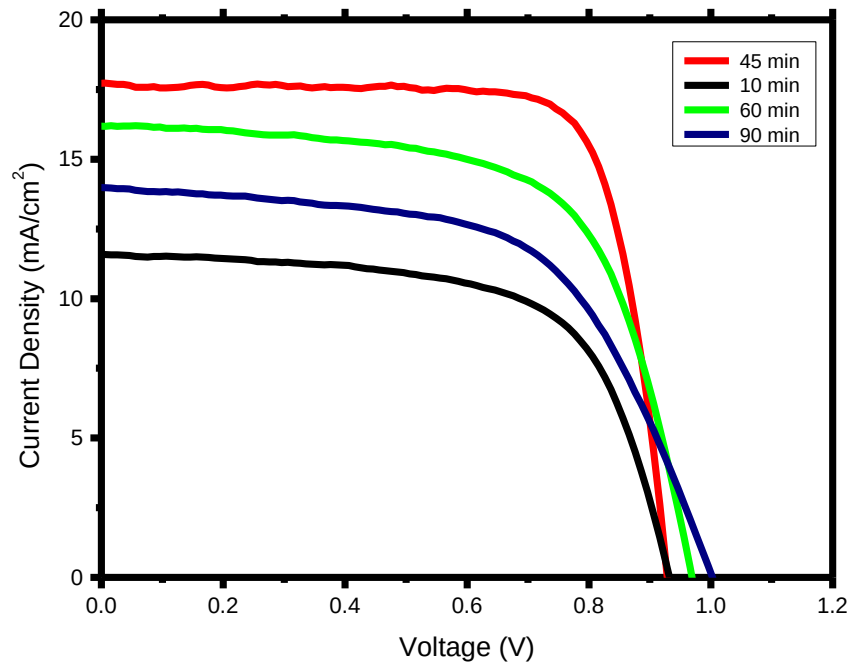


Figure 48 – Several annealing times J-V chart

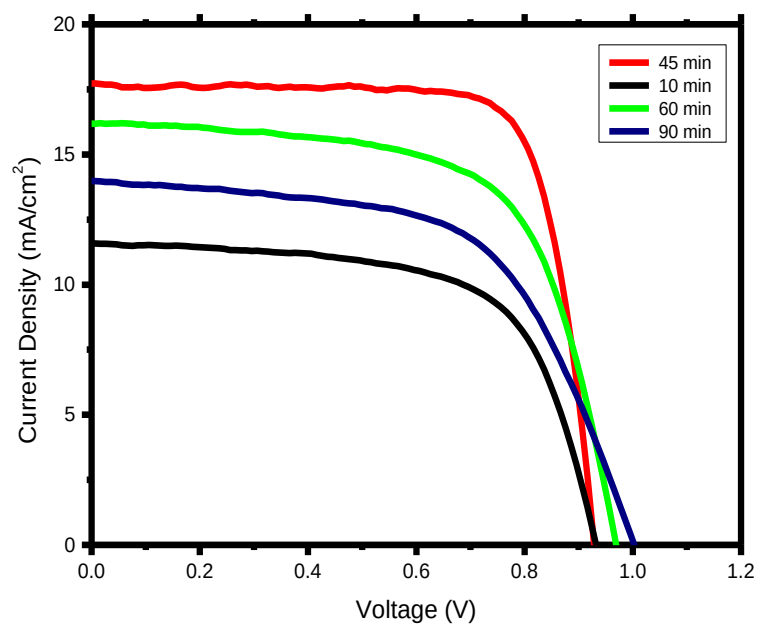


Figure 49 – Several annealing time PCE box plots

In order to confirm the correct crystallinity of perovskite XRD measurements were carried out also with the help of microscope scans measured the thickness of the absorber(Figures 50,51).

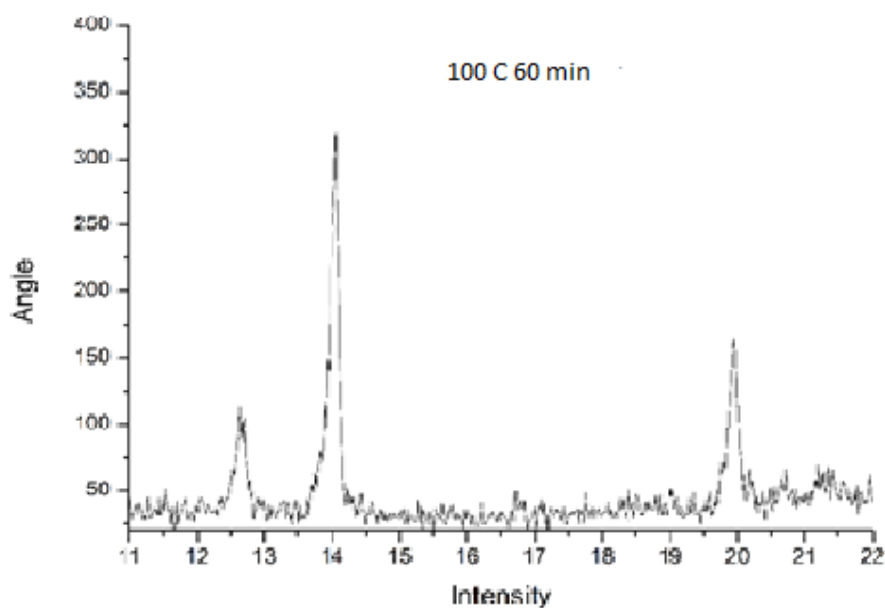


Figure 50 – XRD spectrum 100 C, 60 min

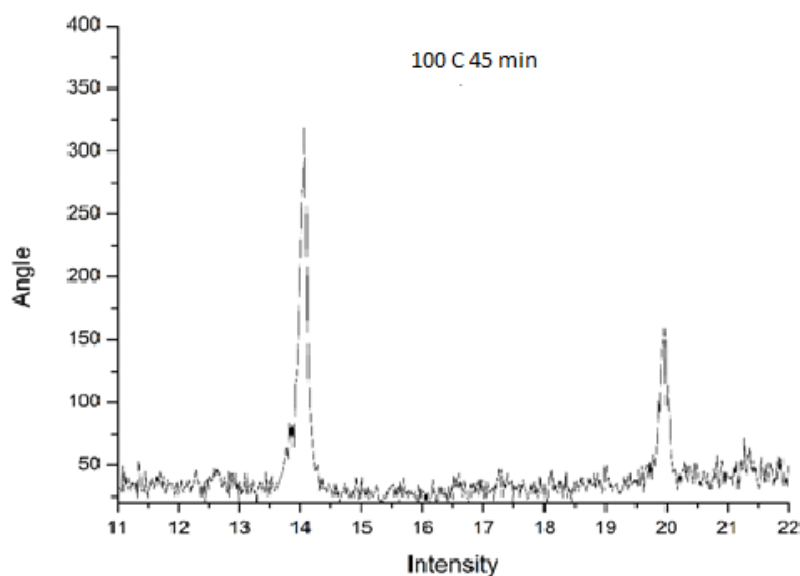


Figure 51 – XRD spectrum 100 C, 45 min

XRD pattern in Figure 51 shows a fully crystalline perovskite phase and no other picks from the residual precursors were identified. Specifically at 45 min , PbI₂ peak at 12.8 degrees is totally suppressed. Furthermore main perovskite plane [001] at 14.3 deg is enhanced ,indication for the proper crystallization of the provskite^{63,133}. By using SEM measurments grains of around 300 nm were observed , fact that fits very well with bibliography^{133,134}. UV-vis absorption and EDX spectra show in Figures 53,54 confirm the formation of triple cation perovskite with an optical band gap of 1,6 eV¹³⁵ and the existence of all elements .

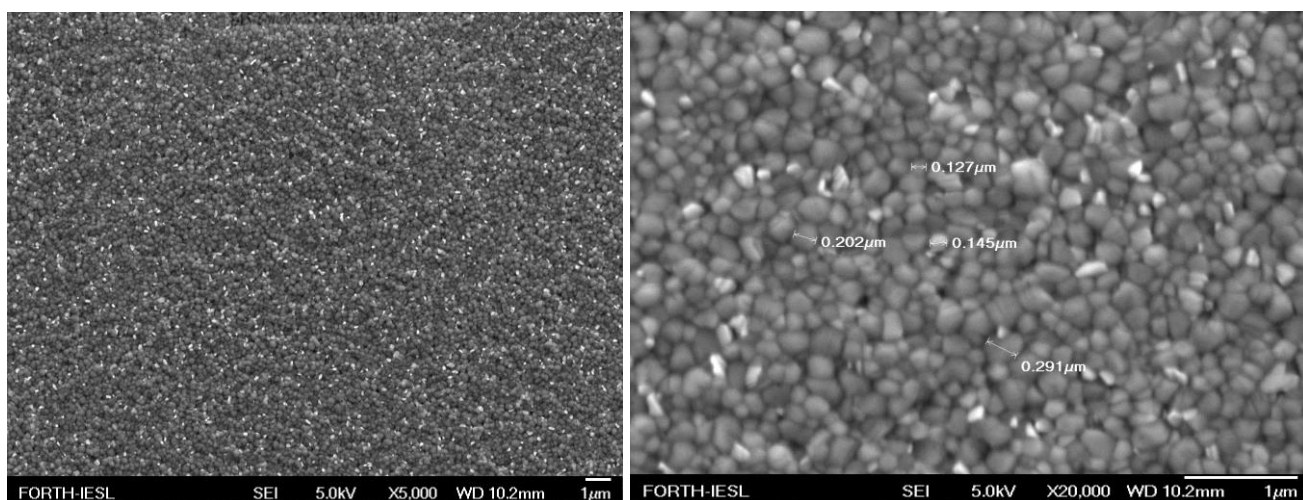


Figure 52 – SEM picture 100 C, 45 min

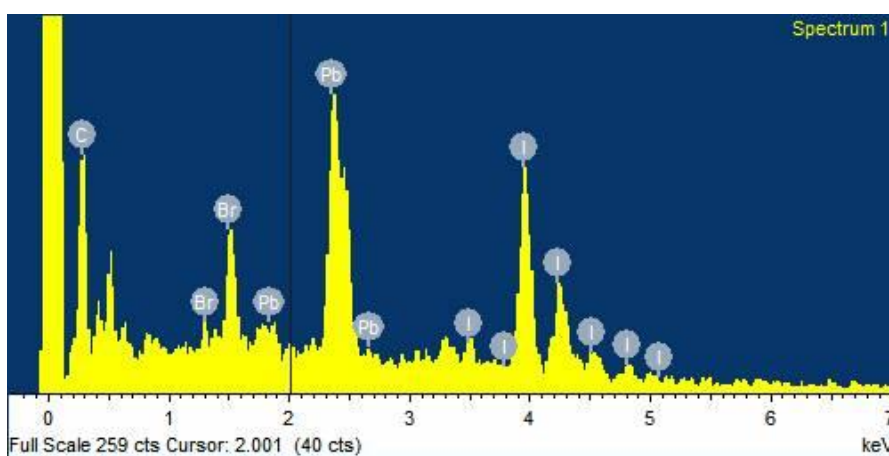


Figure 53 – EDX spectrum 100 C , 45 min

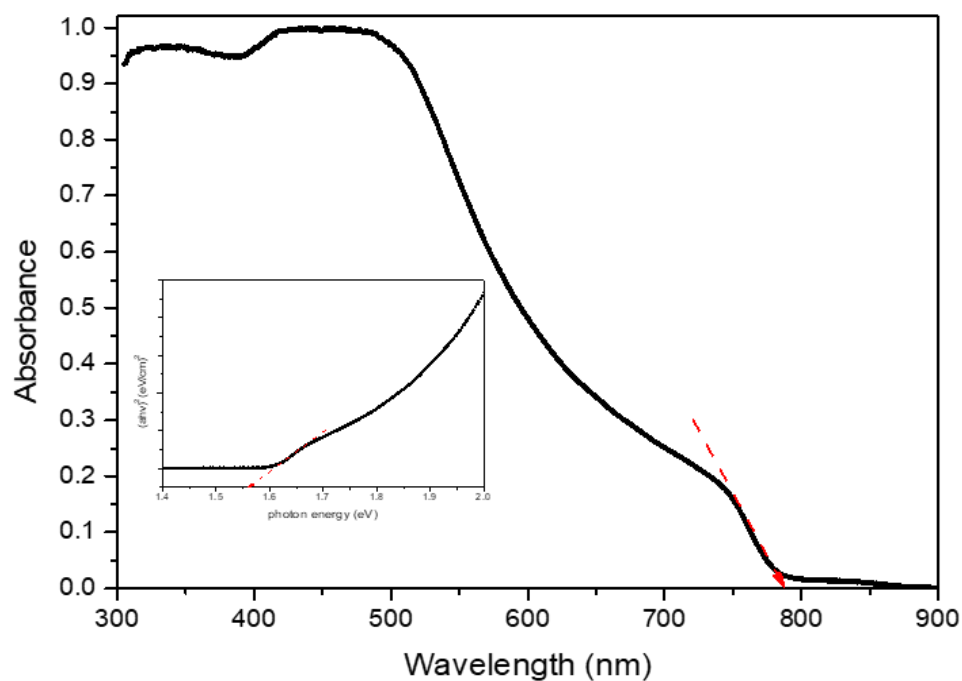


Figure 54 – Uv – Vis spectrum

5.1.2.2: Antisolvent time Dripping

The selection of an anti-solvent and its dropping volume has become a significant issue when fabricating high-performance perovskite photovoltaic devices.

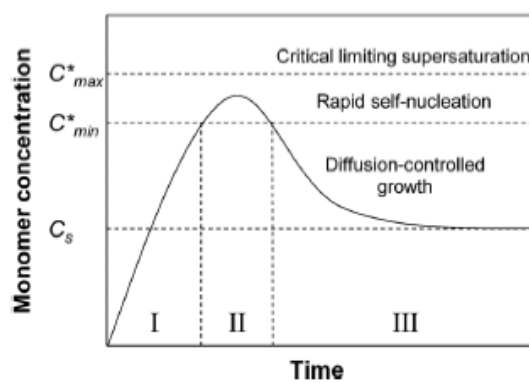


Figure 55 – Nucleation growth

Further to the importance of the perovskite precursor–solvent interaction to understand the nature of an intermediate phase in the solvent engineering process, an anti-solvent also plays a significant role in the surface morphology and crystalline properties of the perovskite films. In this section, the role of the anti-solvent in the solvent engineering process will be described. The requirement of the anti-solvent (non-polar solvent) is the miscibility with the deposition solvents in perovskite precursor solution, and insolubility of perovskites in the anti-solvent. The introduction of the anti-solvent onto the precursor solution films deposited on a substrate can induce fast supersaturation and precipitation of the perovskite precursor film by removing solvents from the precursor solution^{62,136,137}. Several studies reported that dropping chlorobenzene on a perovskite precursor film during the spinning process induces a uniform perovskite film with good reproducibility and enhanced efficiency^{136,138–140}. In the following two sub sections optimization of the time dripping and quantity of antisolvent was carried out.

<i>Anti-solvent Time (s)</i>	<i>PCE (%)</i>	<i>Jsc (mA/cm²)</i>	<i>Voc (V)</i>	<i>FF (%)</i>	<i>Rshunt (Ohm.cm²)</i>	<i>Rseries (Ohm.cm²)</i>
10	3.58	16.53	0.75	25.88	38.52	36.28
17	13.78	17.72	1.01	69.32	342.55	4.5
20	14.51	17.55	0.989	76.92	569.67	4.2
25	15.47	18.01	1.01	62.50	879.82	3.94

Table 5

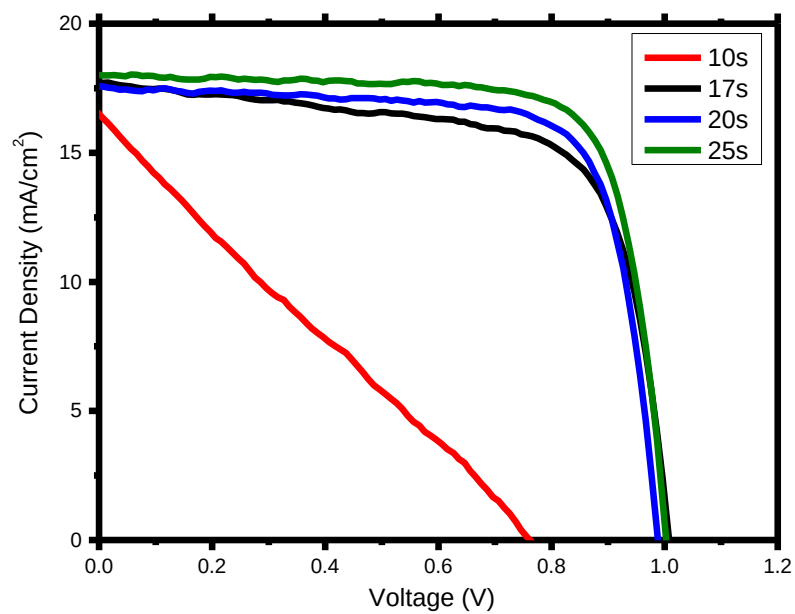


Figure 56 – Several antisolvent time dripping J-V chart

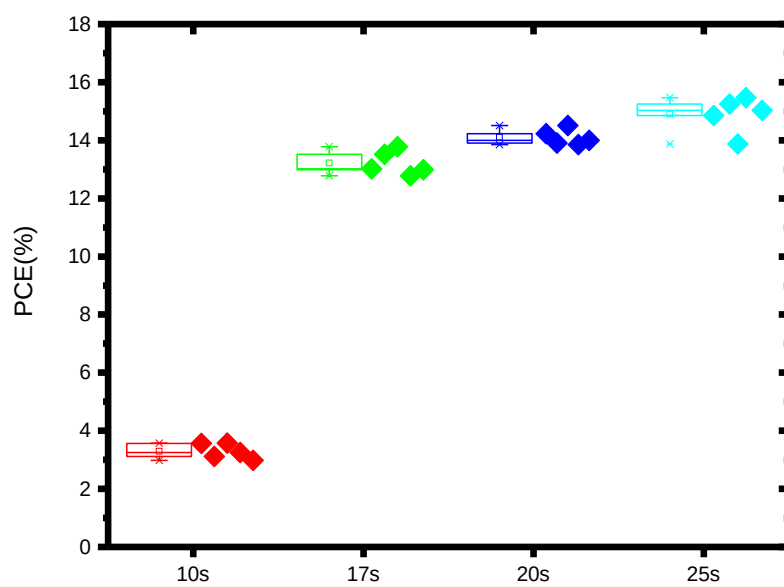


Figure 57 – Antisolvent time dripping PCE box plot

5.1.2.3: Antisolvent Quantity optimization

In order to further optimize this architecture, it has to be done a comprehensive research also in the quantity of antisolvent. Thus, the best program according to the previous section was kept constant (dripping antisolvent 25s prior end of program).

<i>Anti-solvent Quantity</i>	<i>PCE (%)</i>	<i>Jsc mA/cm²</i>	<i>Voc (V)</i>	<i>FF (%)</i>	<i>Rshunt (Ohm.cm²)</i>	<i>Rseries (Ohm.cm²)</i>
100	13.99	16.34	0.98	77.22	490.52	4.28
200	16.09	17.97	1.01	79.03	580.55	3.91
300	15.38	18.01	0.99	76.92	418.45	3.85
400	11.32	17.28	0.94	62.50	405.18	9.01
500	11.77	18.06	0.97	60.13	229.55	5.35

Table 6

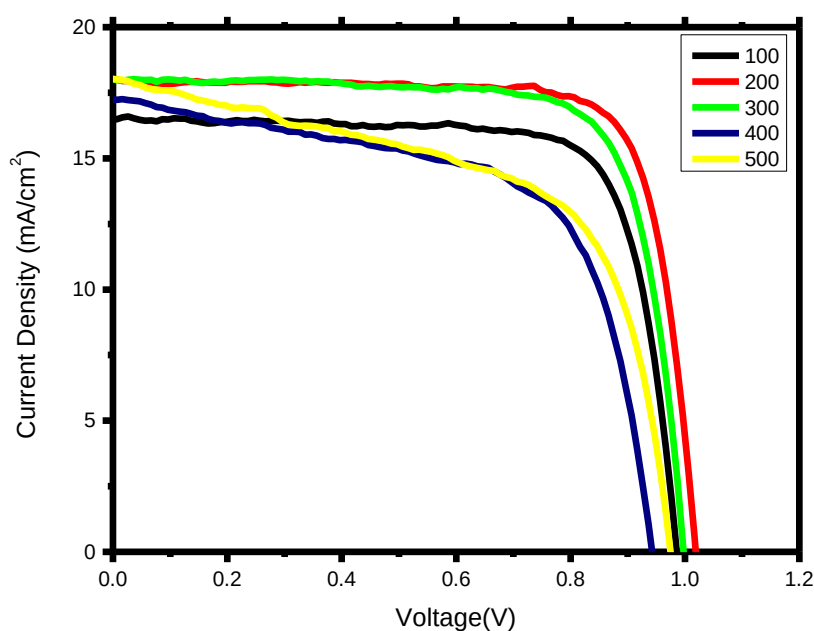


Figure 58 – Several antisolvent quantity J-V chart

5.2 : PCBM(ETL) OPTIMIZATION- RPM STATIC, DYNAMIC

Continuing further design and optimization, order has the electron transport layer PCBM. In order to properly design shall be taken into account two factors.

The Space charge effect : When the ETL thickness decreased, the unabsorbed light would be reflected from the metal electrode. Some of it would pass through the ETL again, the light would be absorbed by the perovskite film to generate more electron hole pairs.

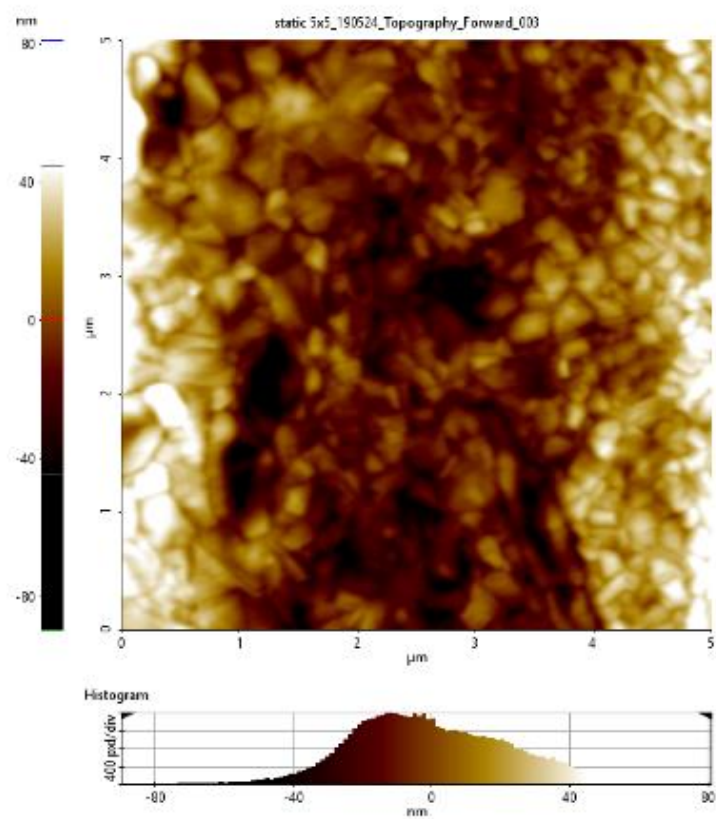
The morphology of the perovskite film The perovskite film surface is not flat. The ETL layer should be thick enough to cover the rough surface of perovskite layer to decrease the shunting of the devices. When the PCBM layer thickness decreases, the leakage of the devices would increase. This would lead to the decrease of the FF. A better perovskite film would improve all three parameters of the device^{31,141–143}. Thus, by keeping constant the concentration of solution, attempted to be found the optimum layer thickness by testing dynamic and static deposition of solution at various rpms. In case

of best efficiency, which achieved with dynamic deposition, thickness is estimated around 50 nm.

- ***Static Deposition***

<i>Rpm</i>	<i>PCE (%)</i>	<i>Jsc mA/cm²</i>	<i>Voc (V)</i>	<i>FF (%)</i>	<i>Rshunt (Ohm.cm²)</i>	<i>Rseries (Ohm.cm²)</i>
1000	8.93	15.76	0.93	57.14	383.52	6.28
1500	11.84	14.43	1.01	78.27	430.10	4.69
2000	13.30	16.52	0.98	76.78	1467.18	4.34
2500	13.58	16.99	1.01	69.56	378.73	4.89
3000	11.29	13.88	0.99	77.2	3168.06	5.24
4000	14.59	16.89	1.01	75.16	639.58	4.63

Table 7



Statistics

Region	Min(nm)	Max(nm)	Mid(nm)	Mean(nm)	Rpv(nm)	Rq(nm)	Ra(nm)	Rz(nm)	Rsk	Rku
Whole	-89.782	80.965	-4.408	0.000	170.746	22.743	18.379	164.354	-0.238	2.956

Figure 59 – AFM topography 2500 rpm static

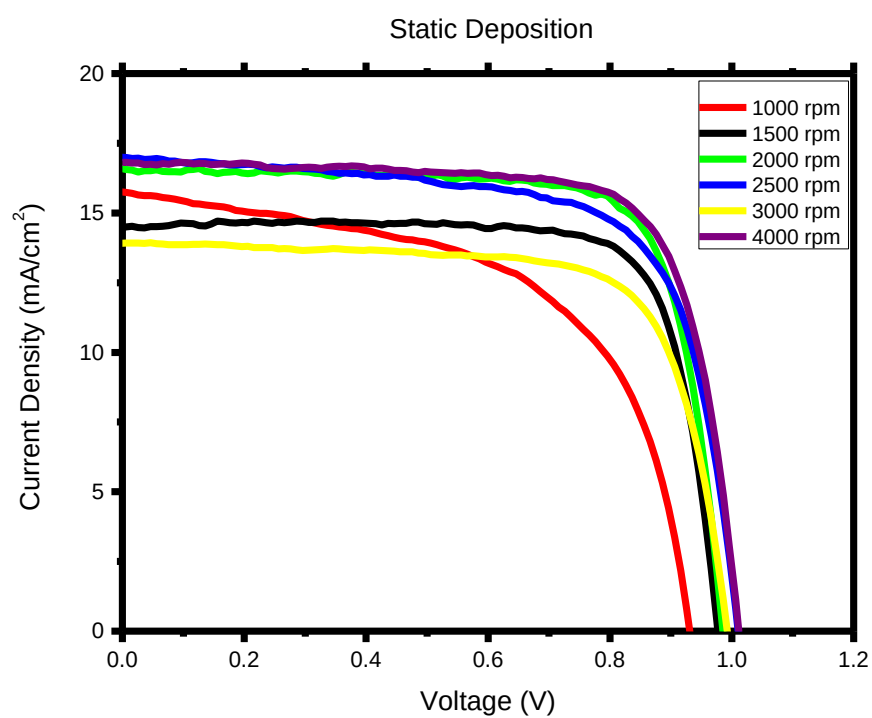


Figure 60 – PCBM static rpm comparison J-V charts

- **Dynamic deposition**

<i>Rpm</i>	<i>PCE</i> (%)	<i>Jsc</i> (mA/cm²)	<i>Voc</i> (V)	<i>FF</i> (%)	<i>Rshunt</i> (Ohm.cm²)	<i>Rseries</i> (Ohm.cm²)
1000	12.72	16.15	0.98	72.91	4057.56	4.34
1500	13.47	16.55	0.99	77.47	2651.23	4.17
2000	13.85	16.42	1.01	73.37	478.18	4.76
2500	15.80	18.00	0.99	79.77	256.05	4.06

3000	10.42	13.88	0.97	77.92	1148.06	5.82
4000	13.30	16.52	0.98	76.78	1467.18	4.34

Table 8

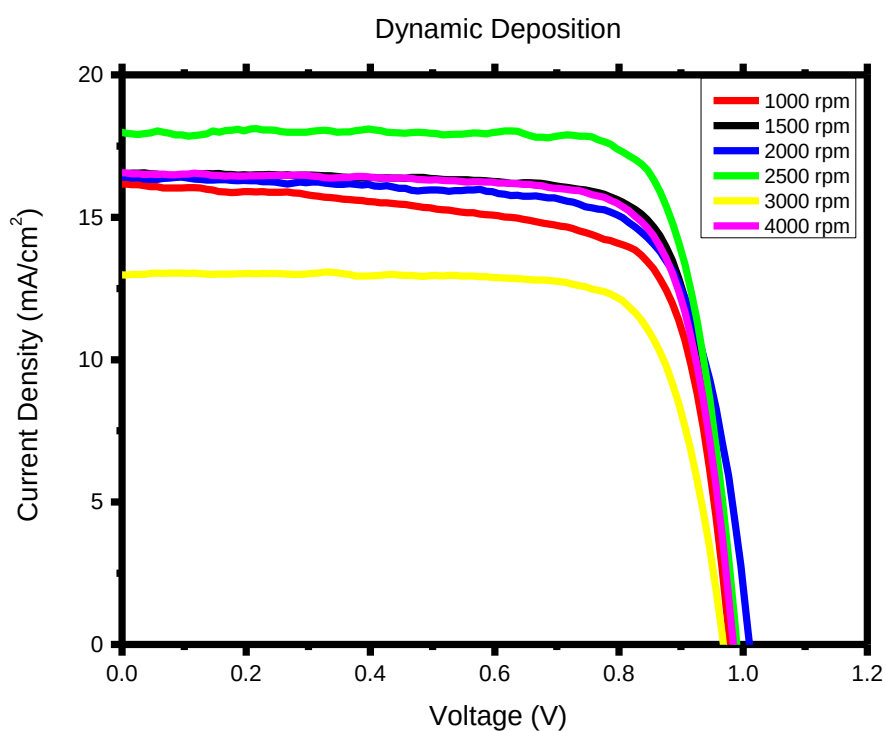
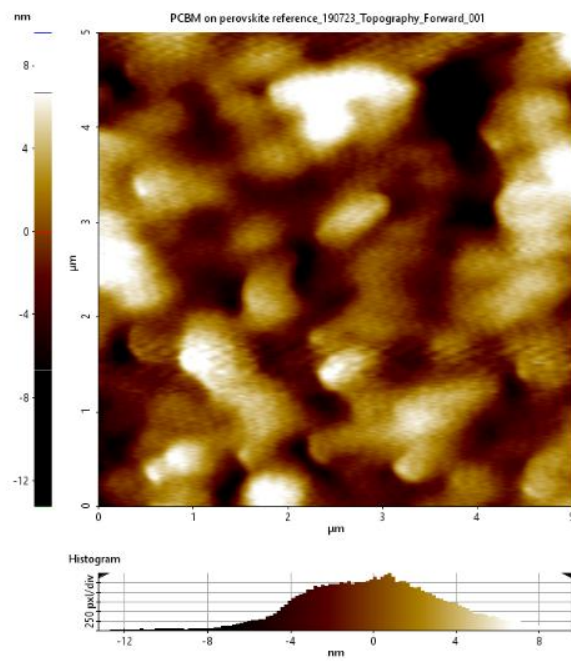
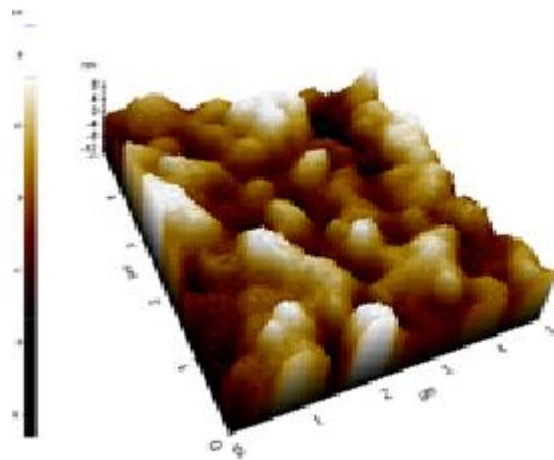


Figure 60 – PCBM dynamic rpm comparison J-V charts



Statistics

Region	Min(nm)	Max(nm)	Mid(nm)	Mean(nm)	Rpv(nm)	Rq(nm)	Ra(nm)	Rz(nm)	Rsk	Rku
Whole	-13.261	9.585	-1.838	0.000	22.845	3.408	2.714	22.453	0.088	3.177

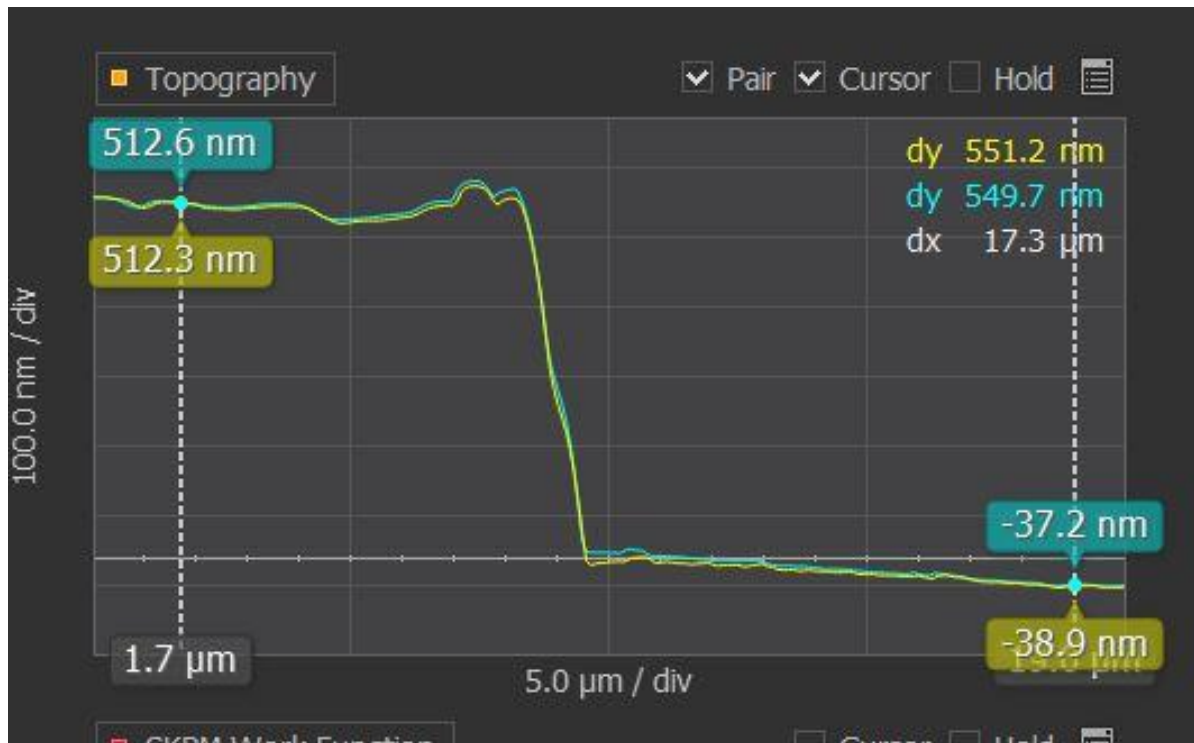


Figure 60 – AFM topography 2500 rpm dynamic

5.3 :Introduction of PFN

As it was shown by previous studies, the PC60BM layer might not form a compact film thus failing to form an ideal ohmic contact with the silver electrode. Hence, direct contact between perovskite and the metal counter electrode might occur forming a Schottky barrier which reduces the device performance.

Different studies have investigated the PCBM/metal interface reporting inclusion of additional layers such as Ca, LiF, TiO_x, ZnO.^{81,86,144} To improve even further the reproducibility and performance of the devices, a Poly [(9,9-bis(3'-(N,N-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)] (PFN) which is a hole-blocking layer was introduced. The solution processing of the PFN layer is simple, economical and proceeds at room temperature. The introduction of PFN on top of PCBM60 would reduce the energetic barrier between the valence band of PCBM and

the work function of Ag . Furthermore, the PFN layer could act as a capping layer which uniformly covers the underlying perovskite and PCBM. This can result in a limit to possible shunt paths, where the perovskite is not covered by the PCBM and avoid the contact of perovskite and Al electrode. Table below shows the results with the incorporation of a thin (~5nm) PFN layer. This improvement attributed mainly to the better ohmic contact of PCBM and Al, and the effective hole blocking. Figure 63 shows the EQE curves that were recorded for the samples with PFN and without. A difference of about 7% can be observed in the quantum efficiency in the range of 300- 750nm for the sample with PFN. This enhancement is an indication of the improved electrical contact between PCBM and Ag.^{145,146}

<i>Material</i>	<i>PCE</i> <i>(%)</i>	<i>Jsc</i> <i>(mA/cm²)</i>	<i>Voc</i> <i>(V)</i>	<i>FF</i> <i>(%)</i>	<i>Rshunt</i> <i>(Ohm.cm²)</i>	<i>Rseries</i> <i>(Ohm.cm²)</i>
With PFN	15.67	17.91	0.98	80.33	2557.56	3.34
Without PFN	11.6	16.04	0.96	65.7	586.23	15.17

Table 9

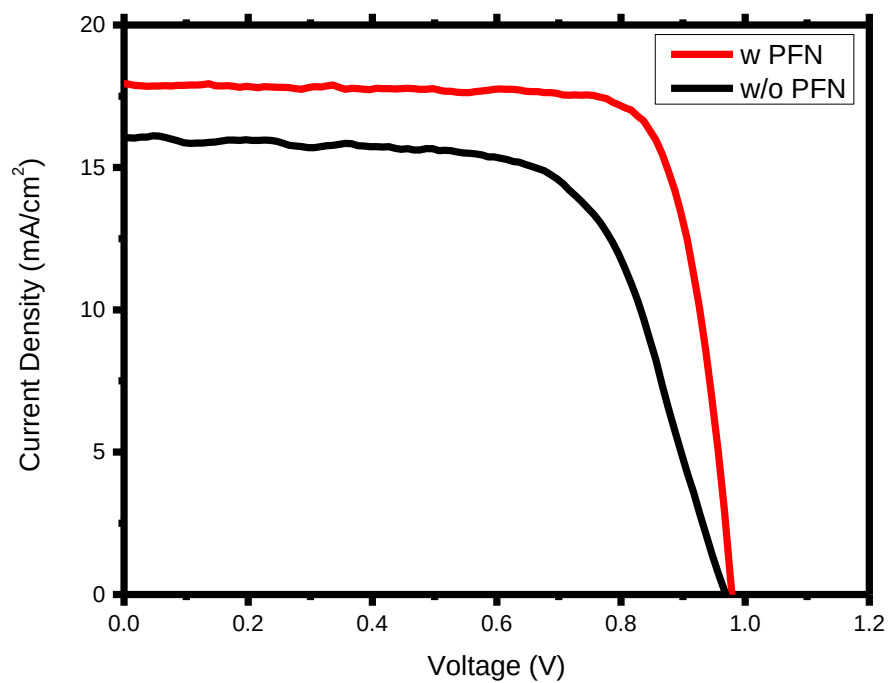


Figure 62 – J-V w/wo PFN

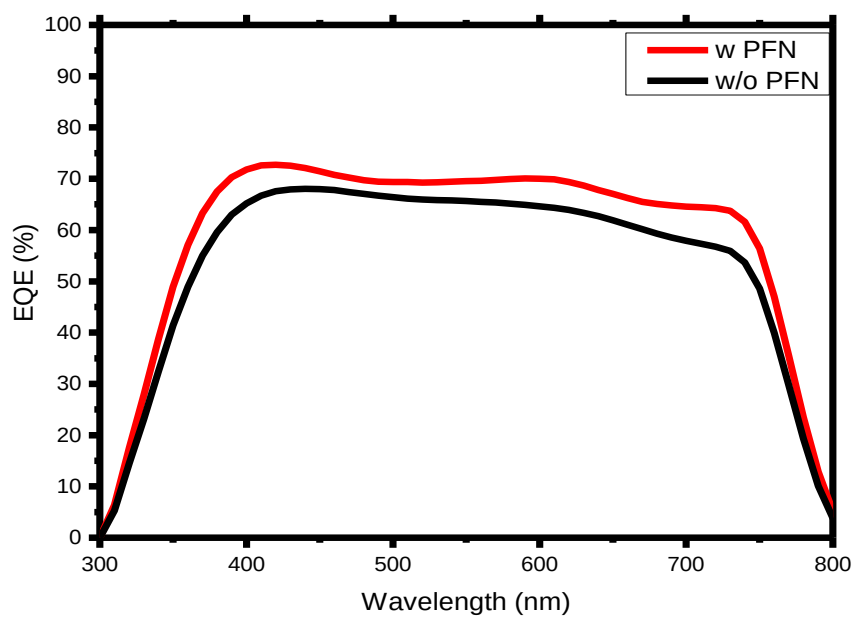


Figure 63 – EQE spectrum w/wo PFN

Incorporation of Rubidium

In general, increasing the perovskite complexity is motivated by the need to improve stability by adding more inorganic elements and increasing the entropy of mixing. Which can be stabilized ordinarily unstable materials (such as the “yellow,” non photoactive phase of FAPbI₃ that can be avoided by using small amounts of the otherwise unstable perovskite phase. In this work, is demonstrated embedding Rb⁺, only slightly smaller than Cs⁺, into a photoactive perovskite phase using multiple A-cation formulations. Formamidinium is retained as the majority cation because of the beneficial, red-shifted band gap^{147–150}. With purpose to examine how the amount of rubidium cations contribute to the crystallinity of the active layer, XRD measurements were made from those its obvious that better crystallinity was achieved because perovskite’s main plane [001] was increased.

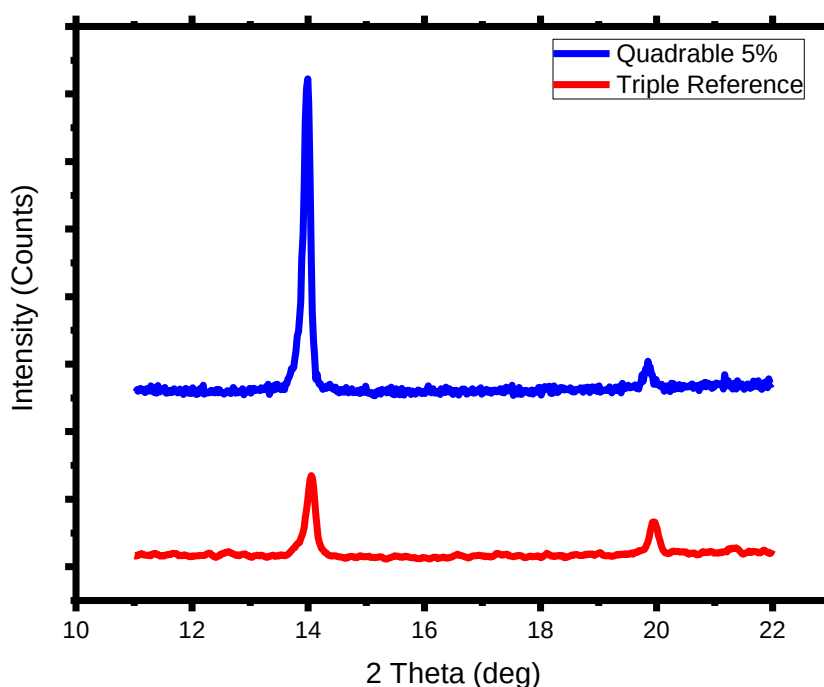


Figure 64 – XRD triple-quadrable cation reference

5.4.1: Introduction of BCP instead of PFN optimization

Introducing the BCP as the buffer layer between the PCBM and Ag layers was mainly to change the contact mode between the electron transport layer and the metal layer as mentioned before in case of PFN. According to literature, inverted perovskite solar cells with BCP interlayer instead of PFN below Ag, demonstrate better stability and reproducibility^{151–153}. So a brief research was made in order to replace PFN.

<i>Rpm</i>	<i>PCE (%)</i>	<i>Jsc mA/cm²</i>	<i>Voc (V)</i>	<i>FF (%)</i>	<i>Rshunt (Ohm.cm²)</i>	<i>Rseries (Ohm.cm²)</i>
2000	15.07	16.55	1.02	79.46	383.52	6.28
3000	15.42	17.23	1.01	78.37	430.10	4.69
4000	16.16	17.57	1.02	80.29	1467.18	4.34
5000	15.41	17.47	1.01	77.38	378.73	4.89

Table 10

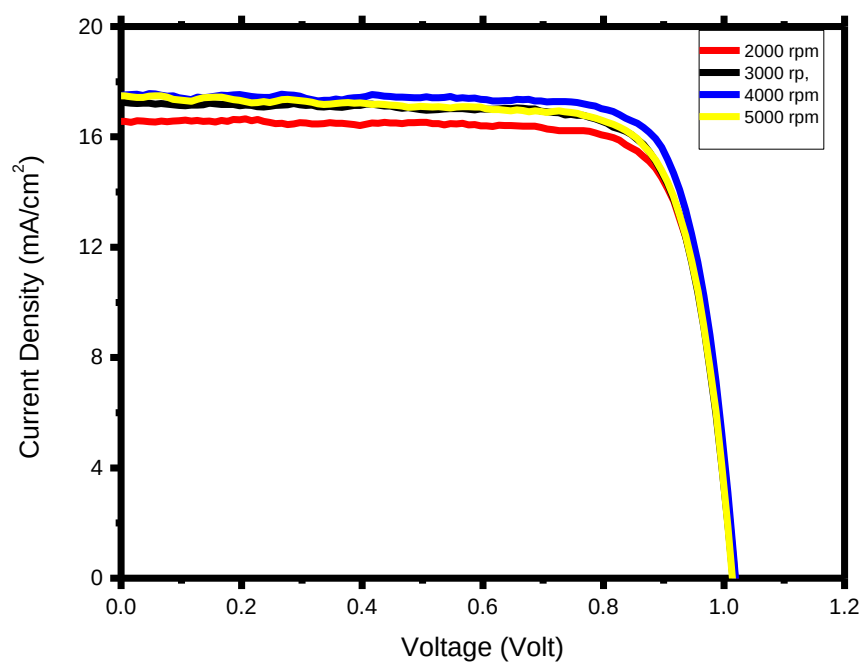


Figure 67- BCP rpm comparison J-V charts

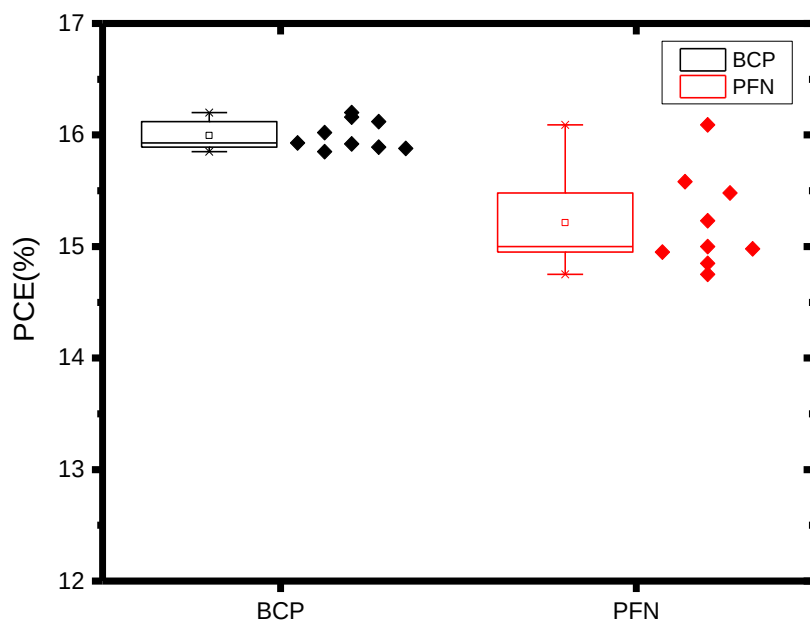


Figure 68- BCP vs PFN PCE box plots

By adopting the above program of 4000 rpm, which gave the best results, reproducibility was examined. The results are summarized below, which is clear that devices with BCP instead of PFN are more reproducible and gave better results in terms of efficiency. In the end, stability studies were realized at 50°C and relative humidity 47%. From those, it is obvious that reference sample with BCP is more stable than this with PFN. Specifically sample with PFN, efficiency halved in about 0.9 hour in comparison with BCP which halved in 1.5 hour.

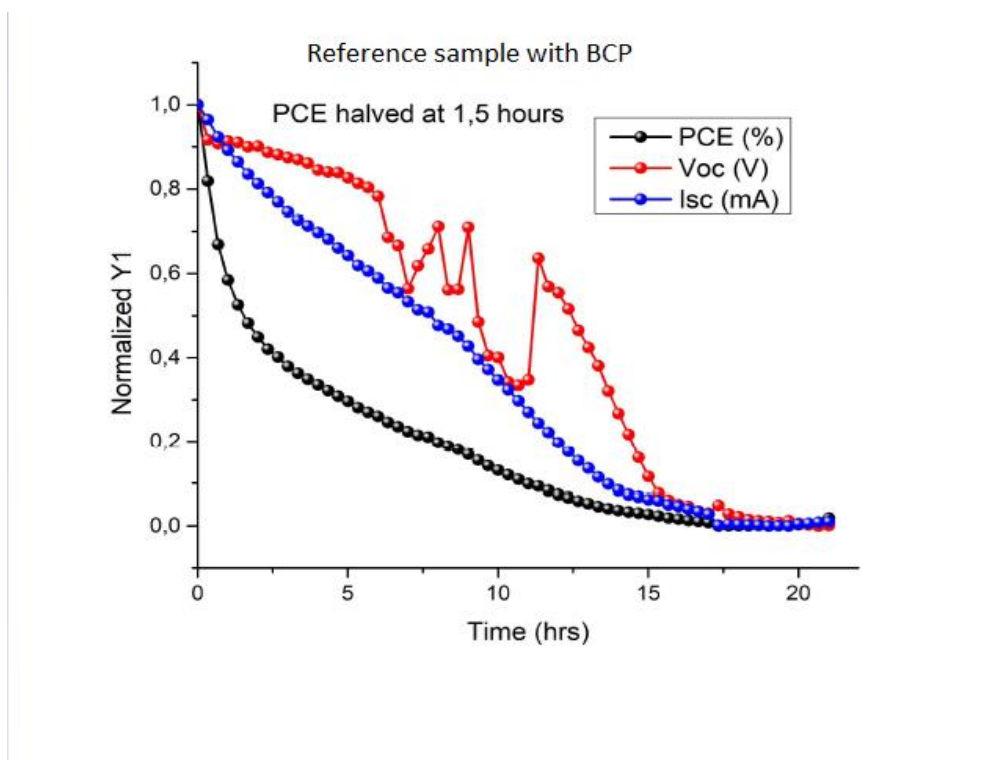


Figure 69 - Stability measurements for BCP based device

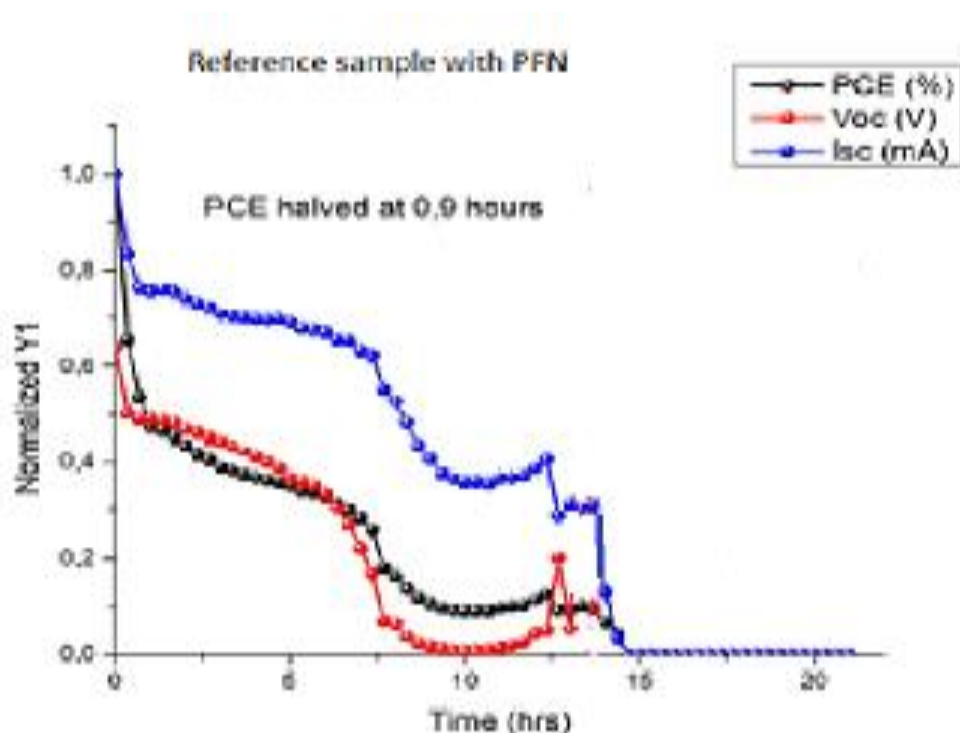


Figure 70 - Stability measurements for PFN based device

5.4.2: Quadruple perovskite thickness development

Perovskite thickness is one of the most crucial parameter of PSCs. It has to be noted that there have been a few recent reports on loss analysis of perovskite solar cells – although with some limitations^{154–157}. . On the other hand, thickness optimization reported in the literature, lacks in quantification of losses due to the different mechanisms. Further, it is mentioned that the efficiency is invariant with active layer thickness beyond a certain value for p-i-n structures while, on the other side, there are experimental results which indicate that efficiency peaks for certain active layer thickness. Minemoto et al.¹¹⁰ performed thickness optimization calculations considering only SRH, Radiative, Auger recombination in the active layer. In this section , different concentrations of perovskite were tested in order to find optimum thickness.

Concentration	PCE (%)	Jsc mA/cm²	Voc (V)	FF (%)	Rshunt (Ohm.cm²)	Rseries (Ohm.cm²)
1.24 M (ref)	16.01	19.48	1.03	77.11	1438.79	4.28
1.44 M	16.08	19.64	1.03	76.99	595.71	4.88
1.54 M	17.27	20.00	1.09	76.27	2174.76	4.88
1.64 M	15.14	19.09	1.00	75.75	1023.56	4.89

Table 11

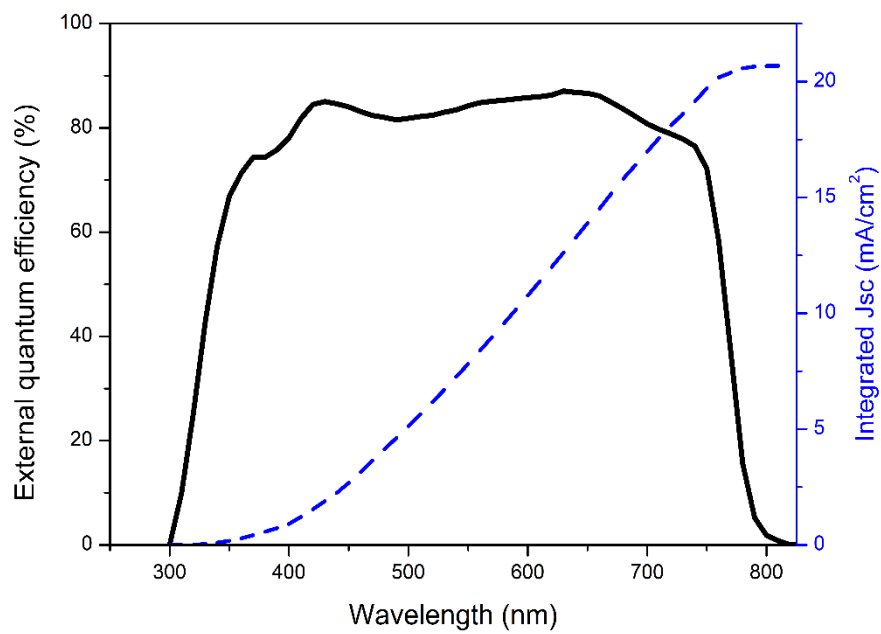


Figure 71 - EQE , Integrated Jsc for best device

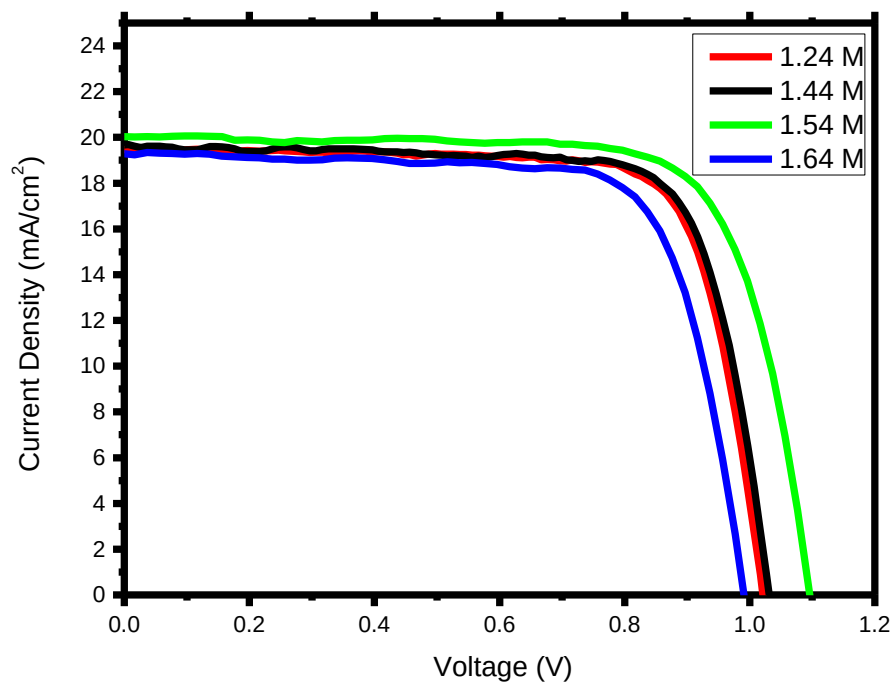


Figure 72 - Several perovskite concentrations J-V chart



Statistics

Region	Min(nm)	Max(nm)	Mid(nm)	Mean(nm)	Rpv(nm)	Rq(nm)	Ra(nm)	Rz(nm)	Rsk	Rku
Whole	-73.681	133.028	29.674	0.000	206.709	19.597	14.937	193.604	-0.927	4.755

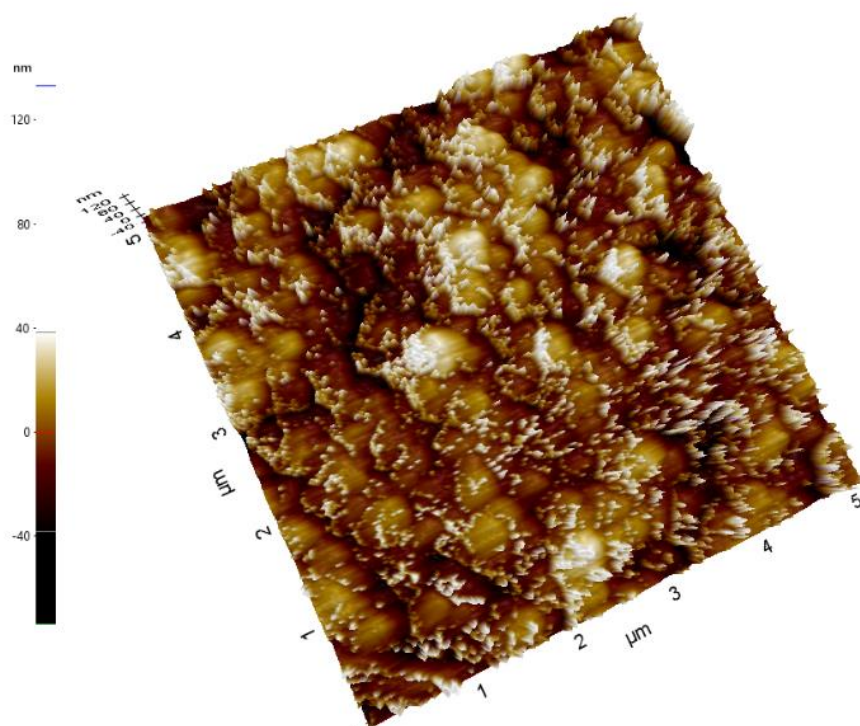
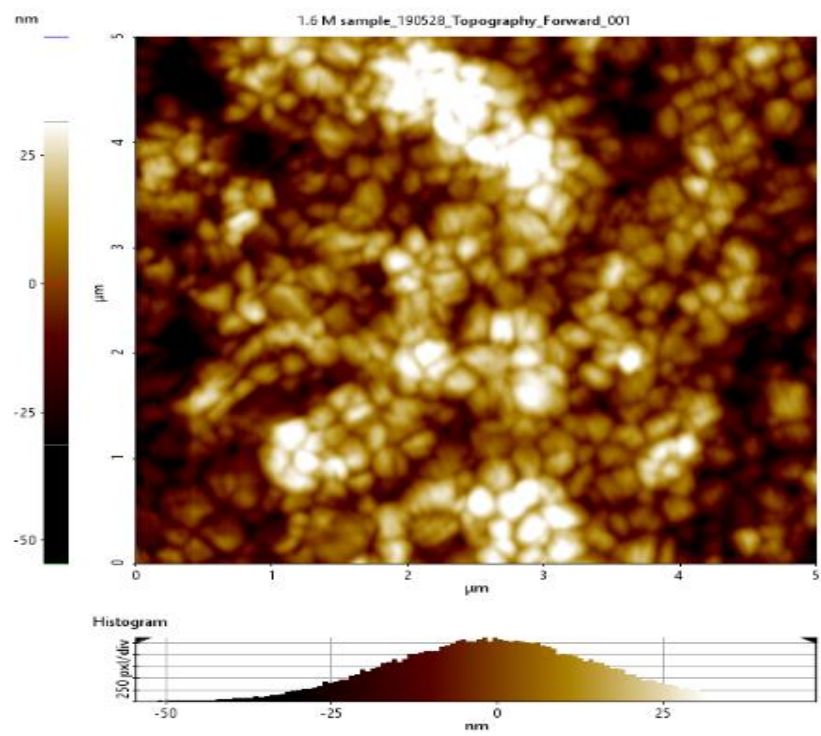


Figure 73 – AFM topography 1.24 M



Statistics

Region	Min(nm)	Max(nm)	Mid(nm)	Mean(nm)	Rpv(nm)	Rq(nm)	Ra(nm)	Rz(nm)	Rsk	Rku
Whole	-54.517	48.092	-3.212	0.000	102.609	16.016	12.811	100.510	-0.100	2.854

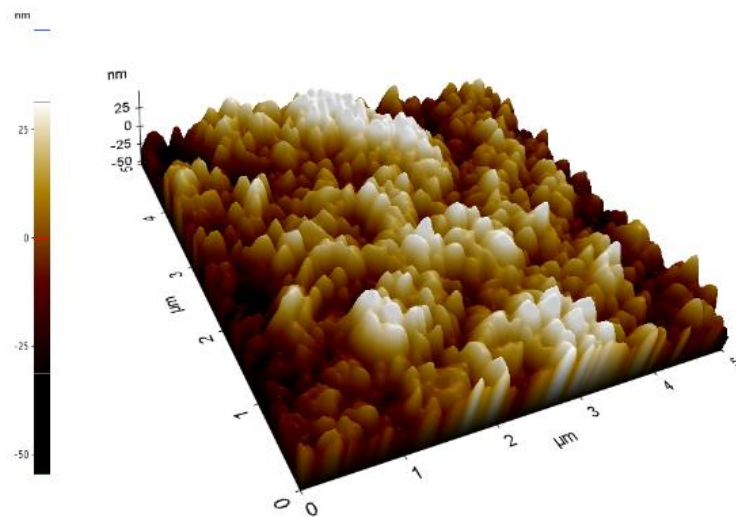


Figure 74 – AFM topography 1.54 M

Topography measurements shown slightly less rough surface in case of 1.54 M perovskite with average roughness 16.07 nm, in comparison with 1.24 M (20 nm) and much more uniformity. Obviously, significant difference exists in terms of thickness around 404 nm for 1.24 M and 503 nm for 1.54 M.

Further optimization of such hybrid perovskite devices now needs to be supported by better understanding of how light is converted into electrical currents. In order to assess

the lifetime of carriers, charge collection capability as well as the mobility of the carriers, various time resolved transient spectroscopy techniques were employed .

Charge carrier lifetime extracted from TPV response fitted to a single exponential decay shows expected dependency on open circuit voltage as in Figure 75. Increase of the light bias leads towards larger exposure to incident light, resulting in improved generation of charge carriers and providing more prospective recombination centers, which in turn drastically shortens their lifetime.

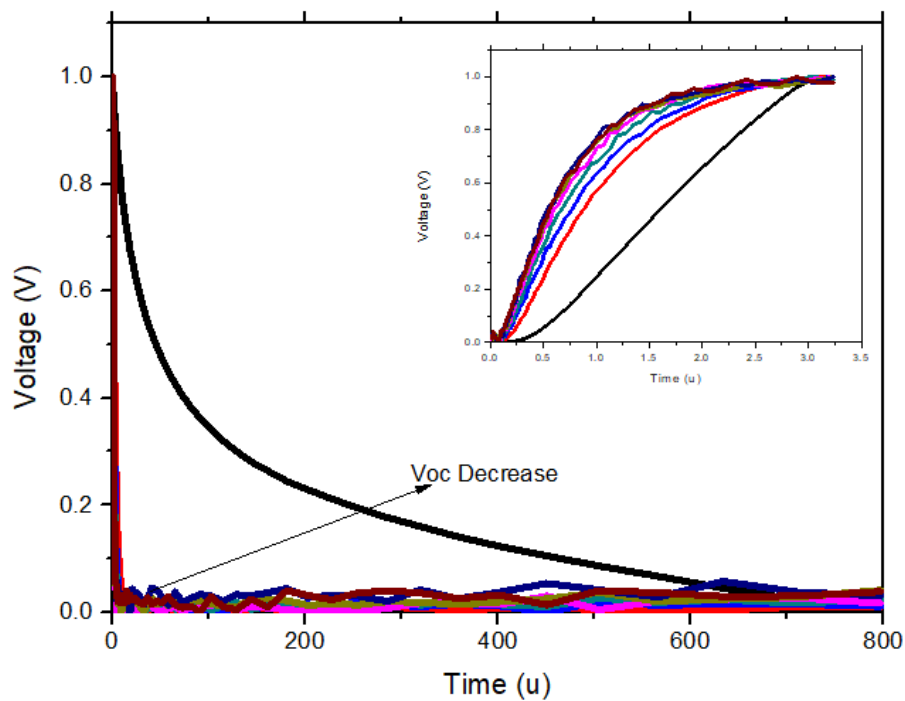


Figure 76 – TPV measurements

In the large-perturbation TPC mode, variation of duty cycle maps charge collection capabilities of measured devices and serves as reliable indicator of trap population. Combination of voltage, light pulse intensity and acquisition window, yields information about charge carrier concentration, trap emission from the DOS. In figure 77 is demonstrated the response for 4 different duty cycles 0.005, 0.3, 0.5, 0.8, in which there is no apparent difference in the shape of the curves for the different perturbations, which is an indication that no deep traps are established.

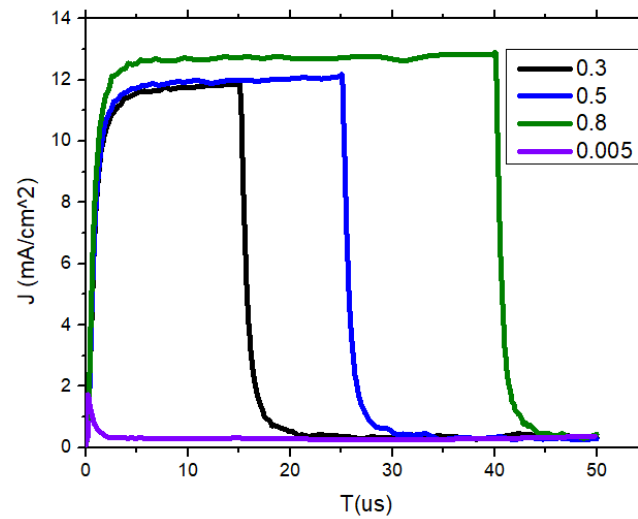
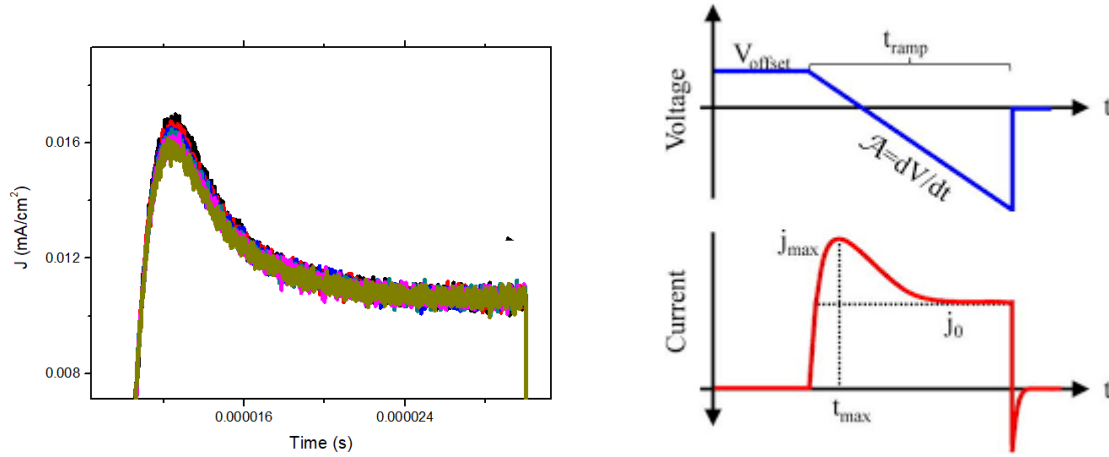


Figure 77 Large Current perturbations for TPC measurements

In order to verify the validity of measurement, should be calculated the time constant discharge of the capacitor τRC and be compared with the time taken by carriers to be transferred from the moment of their generation towards the electrodes (transit time). It should be at least orders of magnitude lower than transit time, with this way it is ensured that, no parasitic losses exist due to the external circuit. Capacitance can be calculated by using the following equation.

$$RC = J_0 / (V_{max} / T_{pulse}) = 2.1 \text{ E-}09 \text{ s}$$

Displacement charging current was calculated by using the technique Photo-CELIV technique. The highest resistance in the circuit was set to 50 Ω in order to create conditions equivalent to TPC measurements applied voltage amplitude of triangle pulse was 1V and signal width was set to 20 μs .



In case of small disturbances, injected concentration of carriers Δn is sufficiently small to avoid disturbing the field distribution and technique provides small amplitude response. With the added charge (Δn), semiconductor continuity equation can be written as:¹²⁰

$$\frac{\partial(n + \Delta n)}{\partial t} = N + \frac{\partial}{\partial x} \cdot \left(D \cdot \frac{\partial(n + \Delta n)}{\partial t} \right) - \frac{(n + \Delta n)}{\tau} \quad (5.6)$$

where N is carrier generation rate, D is diffusion coefficient and τ is a lifetime. Since optical bias provides steady-state conditions and we are interested in changes caused by small perturbation, linearization of equation to give¹²⁰s:

$$\frac{\partial \Delta n}{\partial t} = D \cdot \frac{\partial^2 \Delta n}{\partial x^2} - \frac{\Delta n}{\tau} \quad (5.7)$$

Because voltage decay is mirroring variation in charge concentration between electrodes following initial redistribution, for $x = 0$ we can further simplify the above relation to :

$$\frac{\partial \Delta n}{\partial t} = -\frac{\Delta n}{\tau} \quad (5.7)$$

Since small perturbation of voltage caused by laser pulse is proportional to the change of charge ($\Delta V \propto \Delta n$) and under assumption that capacitance remains constant during perturbation¹²⁰:

$$\Delta V(t) = \frac{q \cdot \left| \frac{x=t}{x=0} \right| \cdot \text{thickness}}{C} = \frac{q \cdot \Delta n_{\text{initial}} \cdot \text{thickness}}{C} \cdot e^{-\frac{t}{\tau}} \quad (5.7)$$

A mono-exponential decay was fitted, from the slope of the curve, transit time can be estimated with value 1.31E-06 as represented in Figure 78

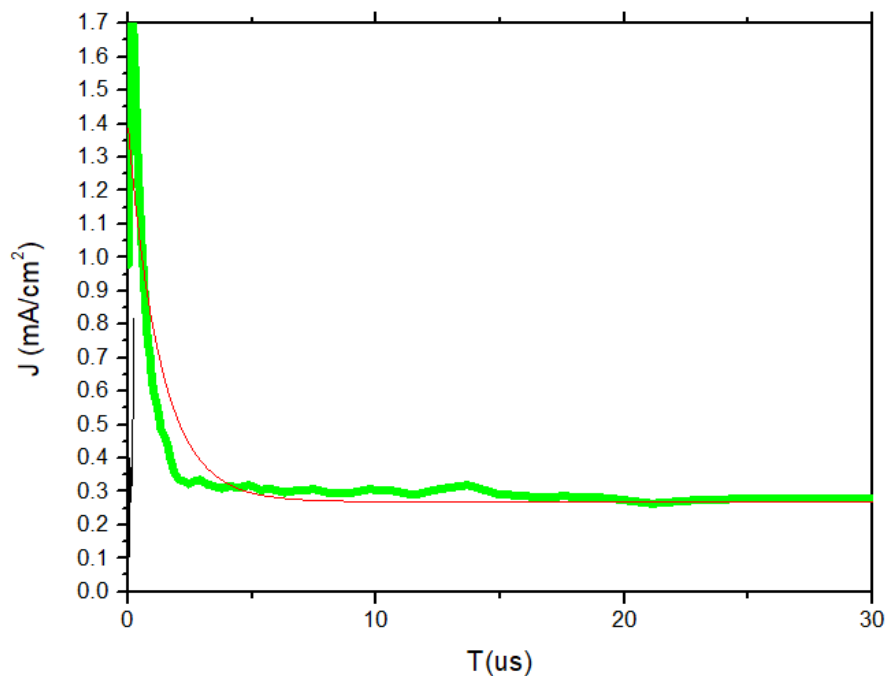


Figure 77 Exponential mono decay fit in small perturbation (0.005)

Additionally charge carrier mobility was estimated, by using photo- CELIV technique. The charge carrier mobility is estimated from the time necessary for transient to reach its maximum value (t_{max}) and quotient of extracted current density at the maxima. The formula ,which was used is represented below. Mobility was estimated as $\mu = 11\text{E-}04 \text{ cm}^2/(\text{V}\cdot\text{s})$

$$\mu = \frac{d^2}{2 \cdot A \cdot t_{max}^2} \cdot \left[\frac{1}{6.2 \cdot \left(1 + 0.002 \cdot \frac{\Delta j}{j_0}\right)} + \frac{1}{1 + 0.12 \cdot \frac{\Delta j}{j_0}} \right]^2 \quad (5.8)$$

5.4.3 : Perovskite stoichiometry check – Optimum percentages of Cs ,Rb

Besides improving the perovskite crystallization mechanism, the actual incorporation of the inorganic cations into the perovskite lattice probably plays a critical role in affecting the charge transport and trap landscape of the metal halide perovskite. At the addition of Cs barely affects the charge carrier mobility, but considerably reduces the trap density and the effective second-order recombination rate in the metal halide perovskite, which likely leads to the higher Voc and therefore higher performance found in Cs-containing devices. According to the literature the addition of Cs barely affects the charge carrier mobility, but considerably reduces the trap density and the effective second-order recombination rate in the metal halide perovskite, which likely leads to the higher Voc and therefore higher performance found in Cs-containing devices^{148,149,158}. In addition In the literature, the icorporation of rubidium leads to reduction of hysteresis in quadruple cation mixtures , to a lower defect density and thus a lower trap density within the perovskite crystals compared to triple cation mixtures without Rb.^{1,147–149,159} So a brief research took place, in order to confirm how different

percentages of inorganic cations affect the photovoltaic parameters and stability of PSCs.

(Cs , Rb) %	PCE (%)	Jsc <i>mA/cm²</i>	Voc (V)	FF (%)	Rshunt (<i>Ohm.cm²</i>)	Rseries (<i>Ohm.cm²</i>)
Cs,Rb (3,4)	10.42	16.02	0.95	65.99	301.79	4.88
Cs,Rb (4,4)	16.27	19.48	1.02	78.52	1743.99	3.79
Cs,Rb (5,4) ref	15.85	19.65	1.02	75.82	1925.84	4.65
Cs,Rb (6,4) ref	12.46	17.83	0.97	68.93	1374.56	7.13

Table 12

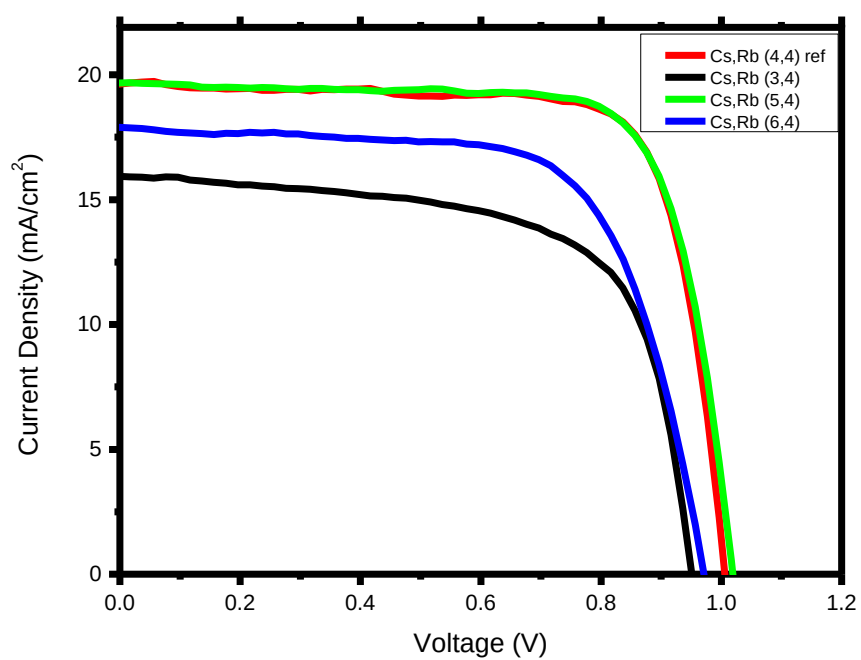


Figure 78 – Different Cs percentages J-V chart

<i>(Cs , Rb)</i> %	<i>PCE</i> (%)	<i>Jsc</i> <i>mA/cm²</i>	<i>Voc</i> (V)	<i>FF</i> (%)	<i>Rshunt</i> <i>(Ohm.cm²)</i>	<i>Rseries</i> <i>(Ohm.cm²)</i>
Cs,Rb (4,2)	11.87	18.19	0.88	71.42	623.51	4.53
Cs,Rb (4,3)	13.56	18.71	0.93	75.46	1187.99	4.76
Cs,Rb (4,4)	16.54	19.74	1.1	73.48	2199.84	5.24
Cs,Rb (4,5) ref	15.84	19.35	1.09	72.85	1438.86	5.65
Cs,Rb (4,7)	13.63	17.60	1.01	73.71	1270.01	4.18

Table 13

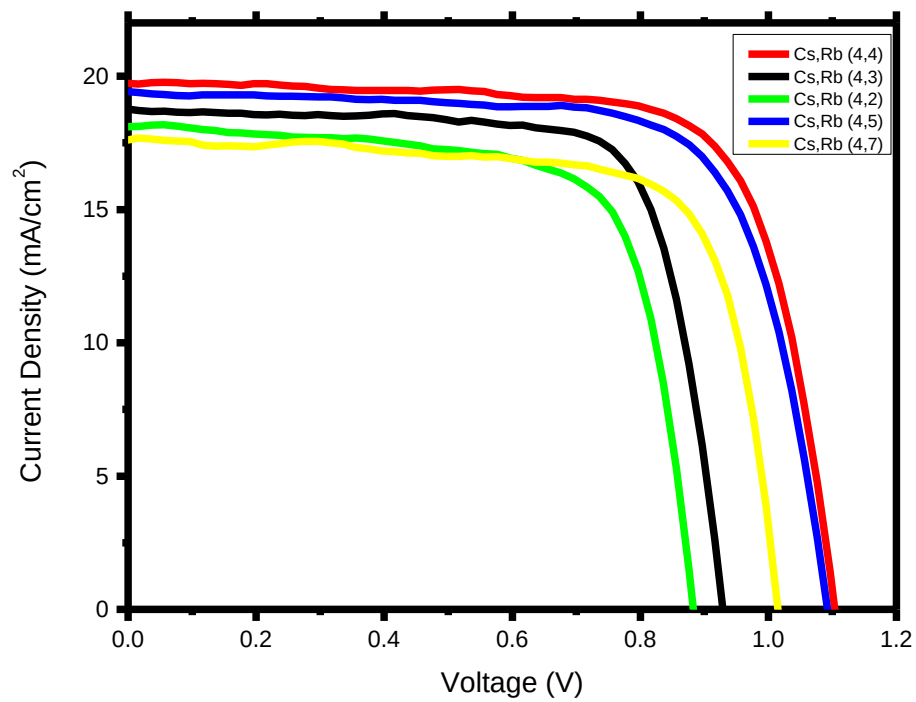


Figure 79 – Different Rb percentages J-V chart

A significant range of varying percentages were tested. First, we found that the segregation of cations and halides during the growth of mixed-halide lead perovskite films is influenced by the formation of two competing phases: an MA-I-rich solvated phase and FA-Br-rich hexagonal phases. the roles of Cs⁺ and Rb⁺ addition, individually and collectively, on the crystallization pathways of the perovskite thin films. These components, when added together, enable the uniform distribution of halides, which in turn prevents the formation of isolated halide- and cation-rich phases. An optimal combination of Cs⁺ and Rb⁺ additions into the perovskite precursor (5% Cs⁺, 4% Rb⁺) results in well-defined quadrable cation perovskite crystals correlating with slightly worse efficiency than the reference, but obviously better in terms of stability. The enhanced stability is attributed to the synergistic effect of Cs⁺ and Rb⁺ on suppressing the inherent segregation of halides by promoting the singular formation of the desired photoactive “black” phase of perovskite and also the limitation of grain boundaries which are recombination centers¹⁶⁰. The stability measurements are summarized in the Figures 80,81 . The lifespan of Reference cell (Cs 4%, Rb 4%) was 4 hours and in the case of In the case of enriched perovskite with more cesium (Cs 5%, Rb 4%), it was still operative after 25 hours.

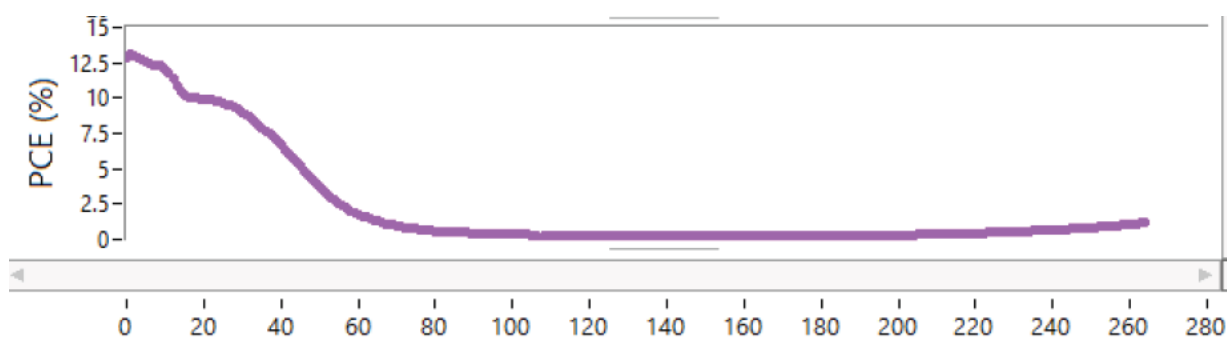


Figure 80- MPPT measurement Quadrable (Cs 4%, Rb 4%)

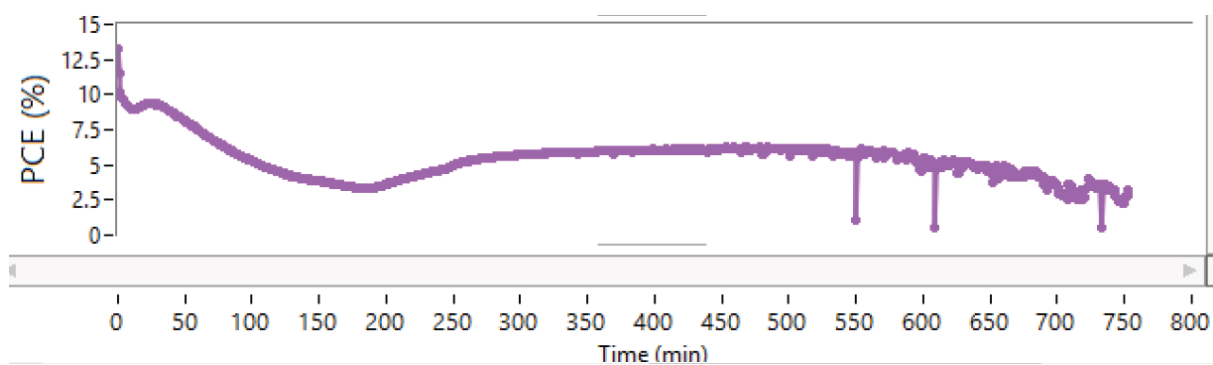


Figure 81- MPPT measurement Quadrable (Cs 5%, Rb 4%)

5.5 :Future Work

The optimized device was used in another project , which is under progress where the stability of such devices was studied. Briefly, an introduction of solution metallic flakes Bis2Te3, Bis2Se3 below silver electrode took place enhancing slightly the device stability .The improved device stability is attributed to better alignment between flakes and silver avoiding the accumulation dipoles, which are created in the interface of the organic layer (BCP) and the electrode. Another part of this project is doping ETL with these kind of materials in order to enhance charge transport and create more conductive paths. In addition, due to the fact that PTAA is quite expensive, so necessity of replacement has risen. One of the promising candidates is Nickel Oxide (NiOx) , that can be used for larger scale photovoltaics. For the preparation of nickel oxide solution , the following recipe was followed. For the sol–gel-processed NiOx, 248.8 mg $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (1.0 mmol) with 60 μL (0.001 mmol) ethanolamine was dissolved in 2-methoxyethanol (10 mL). Then, the solution was stirred at 70 °C for 4 h. In the following figures are presented the energy levels of each material and a box plot of PCE.

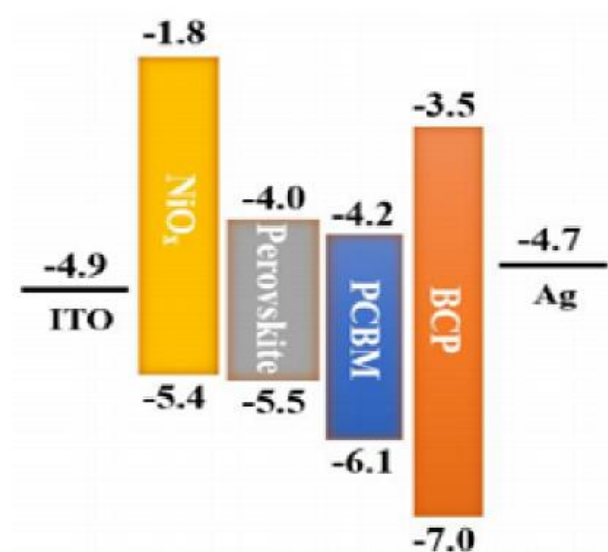


Figure 82 – Energy levels of NiOx based device

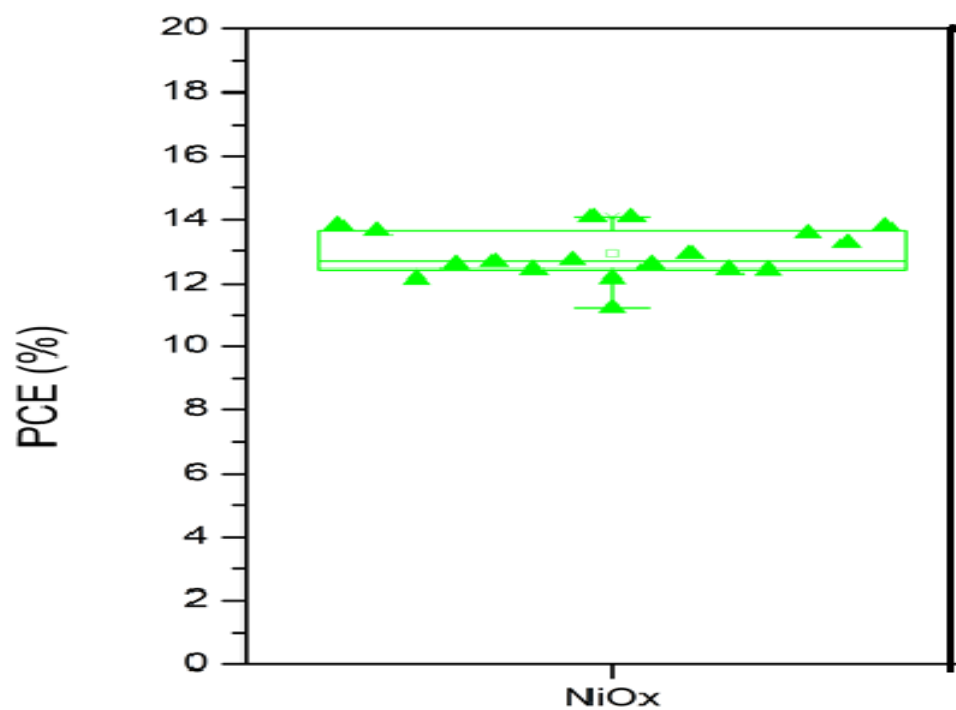


Figure 83 - NiOx based devices PCE box plot

Chapter 6: Conclusion

In conclusion, one of the most promising perovskites for scalable applications was optimized. First was examined the thickness of HTL in order to achieve the best possible transportation of holes to anode and in addition the proper substrate for deposition of perovskite. One of the critical points was found to be the thickness and annealing time of the active layer. A thinner layer resulted in fewer pinholes and more compact film as shown from SEM images. Moreover, antisolvent was examined from the aspect of time dripping and quantity in order to obtain a full crystalline perovskite with no residual precursors which improved the reproducibility of the devices. Furthermore, an introduction of a small cation, in this case rubidium gave a better crystallinity of perovskite according to XRD measurements. With replacement of PFN and introducing another organic material, BCP quite better stability was achieved. Finally optimizing concentration of absorber gave the optimum thickness (490 nm) which gave best efficiency 17.2 %.

REFERENCES

1. Matsui, T. *et al.* Effect of rubidium for thermal stability of triple-cation perovskite solar cells. *Chem. Lett.* (2018). doi:10.1246/cl.180211
2. Ketsetzi, A. & Capraro, M. M. Renewable energy sources. in *A Companion to Interdisciplinary Stem Project-Based Learning: For Educators by Educators (Second Edition)* (2016). doi:10.1007/978-94-6300-485-5_17
3. Blaabjerg, F. & Ma, K. Wind Energy Systems. *Proc. IEEE* (2017). doi:10.1109/JPROC.2017.2695485
4. Toth, A. & Bobok, E. What Is Geothermal Energy? in *Flow and Heat Transfer in Geothermal Systems* (2017). doi:10.1016/b978-0-12-800277-3.00001-3
5. Maehlum, M. Hydroelectric Energy Pros and Cons. *Energy Inf.* (2018).
6. Lewis, N. S. Solar Energy Use. *Science* (80-.). (2007). doi:10.1126/science.1137014
7. fatih Uyar. The Advantages and Disadvantages of Renewable Energy. *Atilim Univ.* (2014).
8. Bush, K. A. *et al.* Minimizing Current and Voltage Losses to Reach 25% Efficient Monolithic Two-Terminal Perovskite-Silicon Tandem Solar Cells. *ACS Energy Lett.* (2018). doi:10.1021/acsenergylett.8b01201
9. Lamont, L. A. History of photovoltaics. in *Comprehensive Renewable Energy* (2012). doi:10.1016/B978-0-08-087872-0.00102-5
10. Green, M. A. Photovoltaic solar energy conversion. *Brazilian J. Phys.* (1996).
11. Lutz, J. *et al.* pn-Junctions. in *Semiconductor Power Devices* (2010). doi:10.1007/978-3-642-11125-9_3

12. Bube, R. H. & Fahrenbruch, A. L. Photovoltaic Effect. *Adv. Electron. Electron Phys.* (1981). doi:10.1016/S0065-2539(08)60424-2
13. Soclof, S. Semiconductors. in *Microelectronics, Second Edition* (2005).
14. Shockley, W. The Theory of p-n Junctions in Semiconductors and p-n Junction Transistors. *Bell Syst. Tech. J.* (1949). doi:10.1002/j.1538-7305.1949.tb03645.x
15. Anthony, J. E., Facchetti, A., Heeney, M., Marder, S. R. & Zhan, X. N-Type organic semiconductors in organic electronics. *Adv. Mater.* (2010). doi:10.1002/adma.200903628
16. Kazici, M. *et al.* Solar Cells. in *Comprehensive Energy Systems* (2018). doi:10.1016/B978-0-12-809597-3.00426-0
17. Green, M. A. Photovoltaics: Coming of age. in *Conference Record of the IEEE Photovoltaic Specialists Conference* (1990).
18. Ikhmayies, S. *Advances in silicon solar cells. Advances in Silicon Solar Cells* (2018). doi:10.1007/978-3-319-69703-1
19. Choubey, P. C., Oudhia, A., Dewangan, R. & Autonomous, V. Y. T. P. G. A review : Solar cell current scenario and future trends. *Recent Res. Sci. Technol.* 2012 (2012).
20. Yu, P. Y. & Cardona, M. *Fundamentals of Semiconductors. Computer Engineering* (2010). doi:10.1007/978-3-642-00710-1
21. Razeghi, M. Semiconductor p-n and Metal-Semiconductor Junctions. in *Fundamentals of Solid State Engineering* (2009). doi:10.1007/978-0-387-92168-6_9
22. Auf Der Maur, M., Albes, T. & Gagliardi, A. Thin-film solar cells. in *Handbook of Optoelectronic Device Modeling and Simulation: Lasers, Modulators, Photodetectors, Solar Cells, and Numerical Methods* (2017). doi:10.4324/9781315152318
23. Green, M. A. & Ho-Baillie, A. Perovskite Solar Cells: The Birth of a New Era in Photovoltaics. *ACS Energy Letters* (2017). doi:10.1021/acsenergylett.7b00137

24. Pepper, M. Metal-semiconductor contacts. *Phys. Technol.* (1974).
doi:10.1088/0305-4624/5/4/405
25. Docampo, P. & Bein, T. A Long-Term View on Perovskite Optoelectronics. *Acc. Chem. Res.* (2016). doi:10.1021/acs.accounts.5b00465
26. Fang, R., Zhang, W. J., Zhang, S. S. & Chen, W. The rising star in photovoltaics-perovskite solar cells: The past, present and future. *Sci. China Technol. Sci.* (2016). doi:10.1007/s11431-016-6056-8
27. Fang, X., Pan, X. & Chen, W. Advances and prospects in research on organometal halide perovskites solar cells. *Cailiao Daobao* (2015).
doi:10.11896/j.issn.1005-023X.2015.09.002
28. Park, N. G. Perovskite solar cells: An emerging photovoltaic technology. *Materials Today* (2015). doi:10.1016/j.mattod.2014.07.007
29. Li, C. *et al.* Formability of ABX₃ (X = F, Cl, Br, I) halide perovskites. *Acta Crystallogr. Sect. B Struct. Sci.* (2008). doi:10.1107/S0108768108032734
30. Levy, M. R. Chapter 3: Perovskite Perfect Lattice. *Cryst. Struct. Defect Prop. Predict. Ceram. Mater.* (2005).
31. Meng, L., You, J., Guo, T. F. & Yang, Y. Recent Advances in the Inverted Planar Structure of Perovskite Solar Cells. *Acc. Chem. Res.* (2016).
doi:10.1021/acs.accounts.5b00404
32. Hassan, Y. *et al.* Structure-Tuned Lead Halide Perovskite Nanocrystals. *Adv. Mater.* (2016). doi:10.1002/adma.201503461
33. Yusoff, A. R. B. M. & Nazeeruddin, M. K. Organohalide Lead Perovskites for Photovoltaic Applications. *J. Phys. Chem. Lett.* (2016).
doi:10.1021/acs.jpcllett.5b02893
34. Baikie, T. *et al.* Synthesis and crystal chemistry of the hybrid perovskite (CH₃NH₃)PbI₃ for solid-state sensitised solar cell applications. *J. Mater. Chem. A* (2013). doi:10.1039/c3ta10518k
35. Hu, Y. *et al.* Hybrid Perovskite/Perovskite Heterojunction Solar Cells. *ACS Nano* (2016). doi:10.1021/acs.nano.6b01535

36. Jung, H. S. & Park, N. G. Perovskite solar cells: From materials to devices. *Small* (2015). doi:10.1002/sml.201402767
37. Liang, J. *et al.* All-Inorganic Perovskite Solar Cells. *J. Am. Chem. Soc.* (2016). doi:10.1021/jacs.6b10227
38. Frost, J. M. *et al.* Atomistic origins of high-performance in hybrid halide perovskite solar cells. *Nano Lett.* (2014). doi:10.1021/nl500390f
39. Tiep, N. H., Ku, Z. & Fan, H. J. Recent Advances in Improving the Stability of Perovskite Solar Cells. *Adv. Energy Mater.* (2016). doi:10.1002/aenm.201501420
40. Lin, Q., Armin, A., Nagiri, R. C. R., Burn, P. L. & Meredith, P. Electro-optics of perovskite solar cells. *Nat. Photonics* (2015). doi:10.1038/nphoton.2014.284
41. Lee, M. M., Teuscher, J., Miyasaka, T., Murakami, T. N. & Snaith, H. J. Efficient hybrid solar cells based on meso-superstructured organometal halide perovskites. *Science* (80-.). (2012). doi:10.1126/science.1228604
42. Wojciechowski, K. *et al.* Heterojunction modification for highly efficient organic-inorganic perovskite solar cells. *ACS Nano* (2014). doi:10.1021/nn505723h
43. Köhler, A. & Bäessler, H. *Electronic processes in organic semiconductors: An introduction. Electronic Processes in Organic Semiconductors: An Introduction* (2015). doi:10.1002/9783527685172
44. Ishii, H., Kudo, K., Nakayama, T. & Ueno, N. *Electronic processes in organic electronics: Bridging nanostructure, electronic states and device properties. Electronic Processes in Organic Electronics: Bridging Nanostructure, Electronic States and Device Properties* (2015). doi:10.1007/978-4-431-55206-2
45. Fleming, I. *Molecular Orbitals and Organic Chemical Reactions, Student Edition. Molecular Orbitals and Organic Chemical Reactions, Student Edition* (2009). doi:10.1002/9780470684306
46. McWEENY, R. Molecular Orbitals. *Nature* (1966). doi:10.1038/2121014c0

47. Berry, R. S. Atomic orbitals. *J. Chem. Educ.* (1966).
48. Foster, J. P. & Weinhold, F. Natural Hybrid Orbitals. *J. Am. Chem. Soc.* (1980). doi:10.1021/ja00544a007
49. Harrison, N. & Cornelius, A. Electronic structure. *Phys. Rev. B - Condens. Matter Mater. Phys.* (2000). doi:10.1103/PhysRevB.61.1779
50. Gill, G. B., Willis, M. R., Gill, G. B. & Willis, M. R. Atomic and molecular orbitals. in *Pericyclic Reactions* (1974). doi:10.1007/978-94-009-5718-3_1
51. Dünkel, L. Photoelectronic Properties of Semiconductors. *Zeitschrift für Phys. Chemie* (1994). doi:10.1524/zpch.1994.184.part_1_2.296
52. Alonso, M. I. & Garriga, M. Optical properties of semiconductors. in *Springer Series in Optical Sciences* (2018). doi:10.1007/978-3-319-75377-5_4
53. Busch, K. & John, S. Photonic band gap formation in certain self-organizing systems. *Phys. Rev. E - Stat. Physics, Plasmas, Fluids, Relat. Interdiscip. Top.* (1998). doi:10.1103/PhysRevE.58.3896
54. Slater, J. C. Band theory. *J. Phys. Chem. Solids* (1959). doi:10.1016/0022-3697(59)90265-3
55. Bayer, M. *et al.* Optical demonstration of a crystal band structure formation. *Phys. Rev. Lett.* (1999). doi:10.1103/PhysRevLett.83.5374
56. Peirce, D., Asaro, R. J. & Needleman, A. Material rate dependence and localized deformation in crystalline solids. *Acta Metall.* (1983). doi:10.1016/0001-6160(83)90014-7
57. Zhu, H. *et al.* Screening in crystalline liquids protects energetic carriers in hybrid perovskites. *Science* (80-.). (2016). doi:10.1126/science.aaf9570
58. Ohmann, R. *et al.* Real-Space Imaging of the Atomic Structure of Organic-Inorganic Perovskite. *J. Am. Chem. Soc.* (2015). doi:10.1021/jacs.5b08227
59. Schouwink, P. *et al.* Structure and properties of complex hydride perovskite materials. *Nat. Commun.* (2014). doi:10.1038/ncomms6706
60. Islam, M. A., Rondinelli, J. M. & Spanier, J. E. Normal mode determination of perovskite crystal structures with octahedral rotations: Theory and applications.

- J. Phys. Condens. Matter* (2013). doi:10.1088/0953-8984/25/17/175902
61. Terpstra, P; Westenbrink, H. G. On the Crystal-structure of Lead-Iodide. *Proc. K. Ned. Acad. van Wet.* (1926).
 62. Gao, H. *et al.* Nucleation and crystal growth of organic-inorganic lead halide perovskites under different relative humidity. *ACS Appl. Mater. Interfaces* (2015). doi:10.1021/acsami.5b00895
 63. Salado, M. *et al.* Identifying the charge generation dynamics in Cs⁺-based triple cation mixed perovskite solar cells. *Phys. Chem. Chem. Phys.* (2017). doi:10.1039/c7cp03760k
 64. Rolston, N. *et al.* Effect of Cation Composition on the Mechanical Stability of Perovskite Solar Cells. *Adv. Energy Mater.* (2018). doi:10.1002/aenm.201702116
 65. Tsui, K. Y., Onishi, N. & Berger, R. F. Tolerance Factors Revisited: Geometrically Designing the Ideal Environment for Perovskite Dopants. *J. Phys. Chem. C* (2016). doi:10.1021/acs.jpcc.6b09277
 66. Maughan, A. E., Ganose, A. M., Almaker, M. A., Scanlon, D. O. & Neilson, J. R. Tolerance Factor and Cooperative Tilting Effects in Vacancy-Ordered Double Perovskite Halides. *Chem. Mater.* (2018). doi:10.1021/acs.chemmater.8b01549
 67. Johansson, M. & Lemmens, P. Perovskites and thin films - Crystallography and chemistry. *J. Phys. Condens. Matter* (2008). doi:10.1088/0953-8984/20/26/264001
 68. Manser, J. S., Saidaminov, M. I., Christians, J. A., Bakr, O. M. & Kamat, P. V. Making and Breaking of Lead Halide Perovskites. *Acc. Chem. Res.* (2016). doi:10.1021/acs.accounts.5b00455
 69. Christians, J. A., Manser, J. S. & Kamat, P. V. Best practices in perovskite solar cell efficiency measurements. Avoiding the error of Making Bad Cells Look Good. *Journal of Physical Chemistry Letters* (2015). doi:10.1021/acs.jpcllett.5b00289
 70. Tao, M. Physics of solar cells. in *SpringerBriefs in Applied Sciences and*

- Technology* (2014). doi:10.1007/978-1-4471-5643-7_3
71. Sah, C. T., Noyce, R. N. & Shockley, W. Carrier Generation and Recombination in P-N Junctions and P-N Junction Characteristics. *Proc. IRE* (1957). doi:10.1109/JRPROC.1957.278528
 72. de Cogan, D. & de Cogan, D. p-n Junctions. in *Solid State Devices* (1987). doi:10.1007/978-1-349-18658-7_6
 73. Liu, M., Johnston, M. B. & Snaith, H. J. Efficient planar heterojunction perovskite solar cells by vapour deposition. *Nature* (2013). doi:10.1038/nature12509
 74. Kim, H. S., Im, S. H. & Park, N. G. Organolead halide perovskite: New horizons in solar cell research. *J. Phys. Chem. C* (2014). doi:10.1021/jp409025w
 75. Motta, C., El-Mellouhi, F. & Sanvito, S. Charge carrier mobility in hybrid halide perovskites. *Sci. Rep.* (2015). doi:10.1038/srep12746
 76. Herz, L. M. Charge-Carrier Dynamics in Organic-Inorganic Metal Halide Perovskites. *Annu. Rev. Phys. Chem.* (2016). doi:10.1146/annurev-physchem-040215-112222
 77. Malinkiewicz, O. *et al.* Perovskite solar cells employing organic charge-transport layers. *Nat. Photonics* (2014). doi:10.1038/nphoton.2013.341
 78. Wehrenfennig, C., Eperon, G. E., Johnston, M. B., Snaith, H. J. & Herz, L. M. High charge carrier mobilities and lifetimes in organolead trihalide perovskites. *Adv. Mater.* (2014). doi:10.1002/adma.201305172
 79. Kolobov, A. V. & Tominaga, J. Excitons. in *Springer Series in Materials Science* (2016). doi:10.1007/978-3-319-31450-1_9
 80. Roncali, J., Leriche, P. & Blanchard, P. Molecular materials for organic photovoltaics: Small is beautiful. *Advanced Materials* (2014). doi:10.1002/adma.201305999
 81. Zhang, Y. *et al.* Charge selective contacts, mobile ions and anomalous hysteresis in organic-inorganic perovskite solar cells. *Mater. Horizons* (2015).

doi:10.1039/c4mh00238e

82. Zhao, W. & Kahn, A. Charge transfer at n-doped organic-organic heterojunctions. in *Journal of Applied Physics* (2009). doi:10.1063/1.3153962
83. Matsushima, T. *et al.* Interfacial charge transfer and charge generation in organic electronic devices. *Org. Electron. physics, Mater. Appl.* (2011). doi:10.1016/j.orgel.2011.01.001
84. Ogomi, Y. *et al.* Control of charge dynamics through a charge-separation interface for all-solid perovskite-sensitized solar cells. in *ChemPhysChem* (2014). doi:10.1002/cphc.201301153
85. Kumar, A. *et al.* Interface limited charge extraction and recombination in organic photovoltaics. *Energy Environ. Sci.* (2014). doi:10.1039/c4ee00665h
86. Shi, J., Xu, X., Li, D. & Meng, Q. Interfaces in perovskite solar cells. *Small* (2015). doi:10.1002/sml.201403534
87. Vandewal, K. *et al.* Efficient charge generation by relaxed charge-transfer states at organic interfaces. *Nat. Mater.* (2014). doi:10.1038/nmat3807
88. Zhu, X. Y., Yang, Q. & Muntwiler, M. Charge-transfer excitons at organic semiconductor surfaces and interfaces. *Acc. Chem. Res.* (2009). doi:10.1021/ar800269u
89. Yang, D. *et al.* Surface optimization to eliminate hysteresis for record efficiency planar perovskite solar cells. *Energy Environ. Sci.* (2016). doi:10.1039/c6ee02139e
90. Norrman, K., Ghanbari-Siahkali, A. & Larsen, N. B. Studies of spin-coated polymer films. *Annual Reports on the Progress of Chemistry - Section C* (2005). doi:10.1039/b408857n
91. Sukanek, P. C. SPIN COATING. *J. imaging Technol.* (1985).
92. University of Louisville. Spin Coating Theory. <https://louisville.edu/micronano/files/documents/standard-operating-procedures/SpinCoatingInfo.pdf/view> (2013).
93. Kang, Y. J. *et al.* Fully spray-coated inverted organic solar cells. in *Conference*

- Record of the IEEE Photovoltaic Specialists Conference* (2011).
doi:10.1109/PVSC.2011.6186161
94. Dorfman, M. R. Thermal spray coatings. in *Handbook of Environmental Degradation of Materials* (2005). doi:10.1016/B978-081551500-5.50022-7
 95. Aziz, F. & Ismail, A. F. Spray coating methods for polymer solar cells fabrication: A review. *Materials Science in Semiconductor Processing* (2015). doi:10.1016/j.mssp.2015.05.019
 96. Allison, T. Doctor blades. *Gravure* (2007).
 97. Krebs, F. C. Fabrication and processing of polymer solar cells: A review of printing and coating techniques. *Solar Energy Materials and Solar Cells* (2009). doi:10.1016/j.solmat.2008.10.004
 98. Tang, S. *et al.* Composition Engineering in Doctor-Blading of Perovskite Solar Cells. *Adv. Energy Mater.* (2017). doi:10.1002/aenm.201700302
 99. Shang, Y., Hao, S., Yang, C. & Chen, G. Enhancing solar cell efficiency using photon upconversion materials. *Nanomaterials* (2015). doi:10.3390/nano5041782
 100. Hiesgen, R. & Friedrich, K. A. Atomic force microscopy. in *PEM Fuel Cell Diagnostic Tools* (2011).
 101. Hölscher, H. Atomic force microscopy and spectroscopy. in *Dynamic Force Spectroscopy and Biomolecular Recognition* (2012).
 102. Johnson, D., Oatley-Radcliffe, D. L. & Hilal, N. Atomic Force Microscopy (AFM). in *Membrane Characterization* (2017). doi:10.1016/B978-0-444-63776-5.00007-3
 103. Morita, S. & Sugawara, Y. Noncontact Atomic Force Microscopy. in *Optical and Electronic Process of Nano-Matters* (2001). doi:10.1007/978-94-017-2482-1_9
 104. BLANCHARD, C. R. Atomic Force Microscopy. *Chem. Educ.* (1996). doi:10.1007/s00897960059a
 105. Dorset, D. L. X-ray Diffraction: A Practical Approach. *Microsc. Microanal.*

- (1998). doi:10.1017/S143192769800049X
106. Roller, J. X-ray diffraction. in *PEM Fuel Cell Diagnostic Tools* (2011).
 107. Huxford, T. X-Ray Crystallography. in *Brenner's Encyclopedia of Genetics: Second Edition* (2013). doi:10.1016/B978-0-12-374984-0.01657-0
 108. Waseda, Y., Matsubara, E. & Shinoda, K. *X-Ray Diffraction Crystallography*. *X-Ray Diffraction Crystallography* (2011). doi:10.1007/978-3-642-16635-8
 109. Stanjek, H. & Häusler, W. Basics of X-ray diffraction. *Hyperfine Interact.* (2004). doi:10.1023/B:HYPE.0000032028.60546.38
 110. Yadav, P. *et al.* Exploring the performance limiting parameters of perovskite solar cell through experimental analysis and device simulation. *Sol. Energy* (2015). doi:10.1016/j.solener.2015.09.046
 111. Pendry, J. B., Pretre, A. B. & Krutzen, B. C. H. Theory of the scanning tunnelling microscope. *J. Phys. Condens. Matter* (1991). doi:10.1088/0953-8984/3/24/001
 112. McMullan, D. Scanning electron microscopy 1928–1965. *Scanning* (1995). doi:10.1002/sca.4950170309
 113. Joy, D. C. Introduction to the Scanning Electron Microscope. *Microsc. Microanal.* (2003). doi:10.1017/s1431927603447788
 114. Everhart, T. E. & Hayes, T. L. The scanning electron microscope. *Sci. Am.* (1972).
 115. McNeill, C. R., Hwang, I. & Greenham, N. C. Photocurrent transients in all-polymer solar cells: Trapping and detrapping effects. *J. Appl. Phys.* (2009). doi:10.1063/1.3177337
 116. Hwang, I., McNeill, C. R. & Greenham, N. C. Drift-diffusion modeling of photocurrent transients in bulk heterojunction solar cells. *J. Appl. Phys.* (2009). doi:10.1063/1.3247547
 117. Hwang, I. & Greenham, N. C. Modeling photocurrent transients in organic solar cells. *Nanotechnology* (2008). doi:10.1088/0957-4484/19/42/424012
 118. Alsari, M. *et al.* Degradation Kinetics of Inverted Perovskite Solar Cells. *Sci.*

- Rep. (2018). doi:10.1038/s41598-018-24436-6
119. Lin, W. M. M., Bozyigit, D., Yarema, O. & Wood, V. Transient Photovoltage Measurements in Nanocrystal-Based Solar Cells. *J. Phys. Chem. C* (2016). doi:10.1021/acs.jpcc.6b03695
 120. Gerhard, A. PROBING CHARGE TRANSPORT AND INTERFACE PROPERTIES OF PLANAR AND MESOPOROUS PEROVSKITE BASED SOLAR CELLS A THESIS SUBMITTED FOR THE DEGREE OF DOCTOR OF PHILOSOPHY DEPARTMENT OF MECHANICAL ENGINEERING Supervisors : Professor Seeram Ramakrishna Dr . Vijila C. (2018).
 121. Lorrmann, J., Badada, B. H., Inganäs, O., Dyakonov, V. & Deibel, C. Charge carrier extraction by linearly increasing voltage: Analytic framework and ambipolar transients. *J. Appl. Phys.* (2010). doi:10.1063/1.3516392
 122. Neukom, M. T., Reinke, N. A. & Ruhstaller, B. Charge extraction with linearly increasing voltage: A numerical model for parameter extraction. *Sol. Energy* (2011). doi:10.1016/j.solener.2011.02.028
 123. Kokil, A., Yang, K. & Kumar, J. Techniques for characterization of charge carrier mobility in organic semiconductors. *Journal of Polymer Science, Part B: Polymer Physics* (2012). doi:10.1002/polb.23103
 124. Saliba, M. *et al.* How to Make over 20% Efficient Perovskite Solar Cells in Regular (n-i-p) and Inverted (p-i-n) Architectures. *Chem. Mater.* (2018). doi:10.1021/acs.chemmater.8b00136
 125. Liu, F., Li, Q. & Li, Z. Hole-Transporting Materials for Perovskite Solar Cells. *Asian Journal of Organic Chemistry* (2018). doi:10.1002/ajoc.201800398
 126. Caliό, L., Kazim, S., Grätzel, M. & Ahmad, S. Hole-Transport Materials for Perovskite Solar Cells. *Angewandte Chemie - International Edition* (2016). doi:10.1002/anie.201601757
 127. Bi, D. *et al.* Effect of Different Hole Transport Materials on Recombination in. *J. Phys. Chem. Lett.* (2013). doi:10.1021/jz400638x
 128. Cai, B., Zhang, W. H. & Qiu, J. Solvent engineering of spin-coating solutions for planar-structured high-efficiency perovskite solar cells. *Cuihua*

- Xuebao/Chinese J. Catal.* (2015). doi:10.1016/S1872-2067(15)60929-9
129. Seo, Y. H., Kim, E. C., Cho, S. P., Kim, S. S. & Na, S. I. Hysteresis data of planar perovskite solar cells fabricated with different solvents. *Data Br.* (2018). doi:10.1016/j.dib.2017.11.064
 130. Lin, S. *et al.* Effects of Different Solvents on the Planar Hetero-junction Perovskite Solar Cells. in *MATEC Web of Conferences* (2015). doi:10.1051/mateconf/20152205002
 131. Tidhar, Y. *et al.* Crystallization of methyl ammonium lead halide perovskites: Implications for photovoltaic applications. *J. Am. Chem. Soc.* (2014). doi:10.1021/ja505556s
 132. Jeon, N. J. *et al.* Compositional engineering of perovskite materials for high-performance solar cells. *Nature* (2015). doi:10.1038/nature14133
 133. Saliba, M. *et al.* Cesium-containing triple cation perovskite solar cells: Improved stability, reproducibility and high efficiency. *Energy Environ. Sci.* (2016). doi:10.1039/c5ee03874j
 134. Stolterfoht, M. *et al.* Approaching the fill factor Shockley-Queisser limit in stable, dopant-free triple cation perovskite solar cells. *Energy Environ. Sci.* (2017). doi:10.1039/c7ee00899f
 135. Zhang, R. *et al.* Theoretical lifetime extraction and experimental demonstration of stable cesium-containing tri-cation perovskite solar cells with high efficiency. *Electrochim. Acta* (2018). doi:10.1016/j.electacta.2017.11.182
 136. Paek, S. *et al.* From Nano- to Micrometer Scale: The Role of Antisolvent Treatment on High Performance Perovskite Solar Cells. *Chem. Mater.* (2017). doi:10.1021/acs.chemmater.6b05353
 137. Zhao, P. *et al.* Antisolvent with an Ultrawide Processing Window for the One-Step Fabrication of Efficient and Large-Area Perovskite Solar Cells. *Adv. Mater.* (2018). doi:10.1002/adma.201802763
 138. Yi, J. *et al.* Regulated perovskite crystallinity via green mixed antisolvent for efficient perovskite solar cells. *Org. Electron. physics, Mater. Appl.* (2019). doi:10.1016/j.orgel.2019.03.021

139. Zhang, X. *et al.* Antisolvent-Derived Intermediate Phases for Low-Temperature Flexible Perovskite Solar Cells. *ACS Appl. Energy Mater.* (2018). doi:10.1021/acsaem.8b01413
140. Wang, M. *et al.* Improving the Performance and Reproducibility of Inverted Planar Perovskite Solar Cells Using Tetraethyl Orthosilicate as the Antisolvent. *ACS Appl. Mater. Interfaces* (2019). doi:10.1021/acsami.8b18402
141. Fang, Y., Bi, C., Wang, D. & Huang, J. The Functions of Fullerenes in Hybrid Perovskite Solar Cells. *ACS Energy Letters* (2017). doi:10.1021/acsenenergylett.6b00657
142. Yang, G., Tao, H., Qin, P., Ke, W. & Fang, G. Recent progress in electron transport layers for efficient perovskite solar cells. *Journal of Materials Chemistry A* (2016). doi:10.1039/c5ta09011c
143. Xu, J. *et al.* Perovskite-fullerene hybrid materials suppress hysteresis in planar diodes. *Nat. Commun.* (2015). doi:10.1038/ncomms8081
144. Steim, R., Kogler, F. R. & Brabec, C. J. Interface materials for organic solar cells. *J. Mater. Chem.* (2010). doi:10.1039/b921624c
145. Hu, Q. *et al.* Efficient and low-temperature processed perovskite solar cells based on a cross-linkable hybrid interlayer. *J. Mater. Chem. A* (2015). doi:10.1039/c5ta04695e
146. Tripathi, N., Shirai, Y., Yanagida, M., Karen, A. & Miyano, K. Novel Surface Passivation Technique for Low-Temperature Solution-Processed Perovskite PV Cells. *ACS Appl. Mater. Interfaces* (2016). doi:10.1021/acsami.5b11286
147. Saliba, M. *et al.* Incorporation of rubidium cations into perovskite solar cells improves photovoltaic performance. *Science* (80-.). (2016). doi:10.1126/science.aah5557
148. Hu, Y. *et al.* Understanding the Role of Cesium and Rubidium Additives in Perovskite Solar Cells: Trap States, Charge Transport, and Recombination. *Adv. Energy Mater.* (2018). doi:10.1002/aenm.201703057
149. Yadav, P. *et al.* The Role of Rubidium in Multiple-Cation-Based High-Efficiency Perovskite Solar Cells. *Adv. Mater.* (2017).

doi:10.1002/adma.201701077

150. Park, N.-G. Methodologies for high efficiency perovskite solar cells. *Nano Conver.* (2016). doi:10.1186/s40580-016-0074-x
151. Liao, H. C. *et al.* Dopant-Free Hole Transporting Polymers for High Efficiency, Environmentally Stable Perovskite Solar Cells. *Adv. Energy Mater.* (2016). doi:10.1002/aenm.201600502
152. Liu, J. *et al.* Understanding the Role of the Electron-Transport Layer in Highly Efficient Planar Perovskite Solar Cells. *ChemPhysChem* (2017). doi:10.1002/cphc.201601245
153. Zhou, H. *et al.* Interface engineering of highly efficient perovskite solar cells. *Science* (80-.). (2014). doi:10.1126/science.1254050
154. Da, Y., Xuan, Y. & Li, Q. Quantifying energy losses in planar perovskite solar cells. *Sol. Energy Mater. Sol. Cells* (2018). doi:10.1016/j.solmat.2017.09.002
155. Wei, J. *et al.* Hysteresis analysis based on the ferroelectric effect in hybrid perovskite solar cells. *J. Phys. Chem. Lett.* (2014). doi:10.1021/jz502111u
156. Minemoto, T. & Murata, M. Theoretical analysis on effect of band offsets in perovskite solar cells. *Sol. Energy Mater. Sol. Cells* (2015). doi:10.1016/j.solmat.2014.10.036
157. Lee, Y. H. *et al.* Unraveling the Reasons for Efficiency Loss in Perovskite Solar Cells. *Adv. Funct. Mater.* (2015). doi:10.1002/adfm.201501024
158. Philippe, B. *et al.* Chemical Distribution of Multiple Cation (Rb⁺, Cs⁺, MA⁺, and FA⁺) Perovskite Materials by Photoelectron Spectroscopy. *Chem. Mater.* (2017). doi:10.1021/acs.chemmater.7b00126
159. Saliba, M. *et al.* Incorporation of rubidium cations into perovskite solar cells improves photovoltaic performance Incorporation of rubidium cations into perovskite solar cells improves photovoltaic performance. *Science* (80-.). (2016). doi:10.1126/science.aah5557
160. Dang, H. X. *et al.* Multi-cation Synergy Suppresses Phase Segregation in Mixed-Halide Perovskites. *Joule* (2019). doi:10.1016/j.joule.2019.05.016

54.<https://www.pveducation.org/pvcdrom/solar-cell-operation/short-circuit-current>

55.<https://www.pveducation.org/pvcdrom/solar-cell-operation/fill-factor>

56.<https://www.pveducation.org/pvcdrom/solar-cell-operation/solar-cell-efficiency>

57.<https://www.pveducation.org/pvcdrom/solar-cell-operation/short-circuit-current>