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REACTIVE LAMINATION OF PEROVSKITE SOLAR CELLS

By

Lyndie Burns

B.S., University of Louisville, 2017

A Thesis

Submitted to the Faculty of the
J.B. Speed School of Engineering
In Fulfillment of the Requirements
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In Chemical Engineering

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University of Louisville
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B.S., University of Louisville, 2017

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ABSTRACT

Due to the growing demand for energy internationally and the environmental impact of other conventional energy technologies, solar power has been a growing area in the energy landscape. Perovskite research has increased substantially because of the high power conversion efficiencies, up to 22%, with many recent advances in the use of these organic-inorganic hybrid perovskites for photovoltaic cells. However, to bring perovskite solar cells into the industrial world, the overall cost of the manufacturing of the solar cell must be improved to compete with other well-developed photovoltaic technologies. Here is presented an alternative perovskite deposition method for methylammonium lead halide perovskite films that utilizes both two-step liquid phase and gas phase deposition techniques in a reactive lamination method developed by the writer. This new deposition process, while not relying on the use of a vacuum, can allow for the use of transition metal oxides as the hole transport layer, as well as the respective transition metal for the metal contact, which in turn can reduce the overall production cost of the perovskite solar cell. The deposited films were able to achieve highly uniform perovskite crystal formation based on SEM analyses, with around a 90% conversion of the lead iodide to perovskite. Using XRD scans, it was determined that the perovskite crystallization develops in an interesting pattern with a two-step crystallization with a reaction rate ranging from 0.002 and 0.003 mol/L*sec. The results of this study show that perovskite crystals can be developed by laminating two precursor substrates together.

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NOMENCLATURE

Name	Description
CdTe	Cadmium Telluride
CIGS	Copper Indium Gallium Selenide
DI	De-ionized
DMF	Dimethylformamide
DMSO	Dimethyl Sulfoxide
ETL	Electron Transport Layer
eV	Electron Volts
FTO	Fluorine Doped Tin Oxide
HOMO	Highest Occupied Molecular Orbital
HTL	Hole Transport Layer
ITO	Indium Doped Tin Oxide
MAI	Methylammonium Iodide
Ni	Nickel
PCE	Power Conversion Efficiency
PbI ₂	Lead Iodide
PV	Photovoltaics
SEM	Scanning Electron Microscope
Si	Silicon
Spiro-OMeTAD	N ² ,N ² ,N ^{2'} ,N ^{2'} ,N ⁷ ,N ⁷ ,N ^{7'} ,N ^{7'} -octakis(4-methoxyphenyl)-9,9'-spirobi[9H-fluorene]-2,2',7,7'-tetramine
TiO ₂	Titanium Dioxide
TMO	Transition Metal Oxide
UV	Ultraviolet
W _p	Peak Power Under Standard Test Conditions
XRD	X-Ray Diffraction

1. INTRODUCTION

Renewable energy has been a field of interest in recent years due to the environmental impact of conventional energy technologies, which are based in fossil fuels such as coal and natural gas. Approximately 85% of the world's energy needs are covered by these fossil fuels.⁴ However, the fossil fuels can emit harmful gases and are also a finite resource for energy. Solar energy, which is the use of energy from the sun to create thermal or electrical energy, has been established as the cleanest energy source available as well as being the most abundant. Photovoltaics is a way to harness solar power to use for electrical energy. As of 2016, solar energy made up for 0.5% of the total United States Energy Consumption.¹ This low percentage is due largely to the cost, manufacturability, materials, intermittency, and the required space. However, that percentage is increasing steadily as innovative technologies are developed, with the average annual growth rate in photovoltaic cell production being over 40% in the last decade²² due to the improvement in the levelized cost of solar energy production.³⁹ In order to compete with coal or nuclear power generation, industrial solar cells must reach a total system price of less than \$1/W_p.

Currently, silicon dominates the solar industry, with c-Si cells making up for approximately 90% of the solar market share.² This is from its abundance, non-toxicity, understanding of process, and maturity of production.⁴⁷ However, the power conversion efficiencies for silicon have been mostly stagnant, with the highest power conversion efficiencies reported being around 25%²², allowing for newer technologies to emerge in the solar landscape. Standard silicon cells are produced using either monocrystalline or polycrystalline structures.²² The production of these silicon cells is a complex multi-step process involving the reduction and purification to form 100% pure silicon, the doping of the silicon, and the cutting and casting of silicon ingots into wafer discs.⁴⁸ There are then nine more steps in the process of converting the silicon wafers into solar

cells, making for a very complicated process.²³ In order for silicon solar cells to reach the \$1/W_p module cost, they must be produced at less than \$0.7/W_p,²² which is very difficult for silicon cells, despite the many technologies and research throughout the years.

Perovskite solar cell technologies have been a growing area in thin film photovoltaics research due to their potential for high efficiencies and ability to produce low-cost, scalable solar cells, as well as thin films around 500 nm.³⁹ Since 2009, the efficiency of perovskite solar cells has increased drastically from 3.8% to 22.1%^{4,40}, which makes it the fastest growing solar technology to date²⁵, as well as being comparable to other conventional vacuum deposited thin film solar cells such as silicon (21.2% efficient), CIGS (20.8% efficient), and CdTe (20.4% efficient).¹⁴ Moreover, there are also a broad range of device fabrication concepts and new research being conducted to not only increase this efficiency further, but to improve the device and to optimize the performance.²⁴

Perovskite solar cells consist of a hybrid organic-inorganic lead halide-based material for the light absorbing layer. The perovskite materials used in this research were methylammonium lead halides, more specifically methylammonium lead iodide.

However, despite all the advantages of perovskite cells, there are still challenges associated with these cells that must be addressed in order for them to be fully commercialized, such as scaling to large scale manufacturing or degradation of perovskite material, as well as the use of lead in the compounds.²⁵ One of the other major concerns is the overall cost of the perovskite cells. In general, the perovskite material itself is inexpensive, but the electrode material and hole transport layer material are fairly expensive.

Currently, the hole transport layer, HTL, utilizes the material 2,2',7,7'-Tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene (spiro-OMeTAD) in conjunction with the perovskites as the light harvesting layer. Gold is also a very common metal electrode that is used in these types of cells. The purpose of this research and thesis is to show an alternative way of processing the perovskite light absorbing layer to allow for substitutions for both the electrode and hole transport layer materials. This new cell structure would allow for a decrease in the overall cost of the cell itself.

The proposed alternative to aid in this problem is using nickel and nickel oxide as the electrode material and the hole transport layer, respectively. By using these materials instead of the spiro-OMeTad and the gold, it could substantially decrease the overall production cost of the perovskite solar cell. Also, nickel oxide has a wide band gap and a high work function, which are consistent with a p-i-n cell design. Nickel foil could be used for both layers, in which one side is oxidized while the other remains intact, encompassing the necessary layers for the cell in one material. Other transition metal oxides could also be used in the same type of setup and still reduce the cost of the cell, but nickel was the main metal that was the focus of this study based on the band structure of the material, which is demonstrated in Figure 1.1A.

However, the issue with utilizing transition metal oxides is the depositing and manufacturing of the new cell with the nickel layers. The morphology of the perovskite prevents simple deposition of the nickel on top of the perovskite in the same manner that spiro-OMeTAD is usually deposited, especially if foil is used for these layers. To circumvent this issue, it is proposed to deposit the perovskite precursors directly onto the oxidized foil and the pre-fabricated glass substrate with necessary layers. Then, by placing the two separately built substrates together and heating, the perovskite could form from the deposited precursors, forming the new cell structure. Therefore,

instead of building each layer at a time as before, the cell would be built in parts from each end until the perovskite layer, then placed together to form the entirety of the cell. The process proposed in this research is a combination of both solution and gas phase deposition, which combines both the two-step and vapor deposition techniques mentioned previously. This is because the organic and inorganic solutions are processed and deposited separately, then are laminated together. Once the organic solution is sublimated into the gas phase, it reacts with the inorganic solution to form the perovskite film. This method does not have a need for antisolvent or for a vacuum to deposit the materials. More details on this will be discussed in the methods section of this paper. Figure 1.1 shows a schematic of the proposed overall process (A), as well as a diagram of the new cell and its band structures (B), and the diagram of the precursor substrates and their layer orientations to be laminated (C).

Figure 1.1: (A) Schematic of Proposed Process (B) Structure of Cell with (C) Band Diagram and (D) Diagram of Precursor Substrate Layers

Therefore, it was hypothesized that it would be possible to obtain a perovskite crystal structure using this new deposition technique, which combines liquid and vapor phase deposition methods and a lamination of the substrates. By doing so, new materials such as transition metal oxides can be used as the hole transport layer and the metal contact for the perovskite solar cell. The new solar cell structure would thereby decrease the overall production cost of the perovskite cell. The motivation of this research was to determine the formation of these perovskite crystals and to understand the reaction by which they are created. The challenges associated with this new procedure are identifying whether it is possible to form perovskite crystals using this new process, adhesion between the substrates, and controlling the conversion and optimizing the reaction. All of these were addressed in some measure throughout the research.

In order to prove this, experiments were first run to test the development of the perovskite crystals through the use of XRD, or x-ray diffraction. Then, calculations and tests were run to identify the necessary composition of the precursor solutions as well as the different deposition methods for each solution. Next, an experiment and resulting calculations were conducted to determine the temperature at which the reaction would run. Once the compositions and optimum reaction temperature were determined, the conversion of the perovskite was addressed through the enclosure of the substrates during the reaction to further push the reaction mechanism. Some other experiments were run using flexible glass substrates and the nickel foil to test if it was possible to get the conversion to the perovskite using these new substrate materials. After running more reactions at varying time intervals, a graph was developed to show how the conversion of the perovskite material changed over time, allowing for a reaction rate and maximum conversion to be determined. Finally, SEM, or scanning electron microscope, scans were performed to determine the crystal formation of the films.

This paper will elaborate on this new perovskite deposition method and the implications for future technology associated with perovskite photovoltaics. Chapter 1 will show the need for renewable solar energy, while touching on the challenges associated with silicon solar cells and elaborating on the potential for next generation solar cells, specifically perovskite. It will also detail the need for the development of a new process to allow for new hole transport layer materials and the proposed method for accomplishing this to decrease the overall production cost of perovskite solar cells. Chapter 2 is a comprehensive background on the history of perovskite solar cells, their operating principles, the state-of-the-art manufacturing processes to deposit the material, the reactions associated with perovskite formation, and the layers of the perovskite solar cell. Chapter 3 details the experimental procedure of this newly proposed deposition process, as well as details associated with the equipment used for analyses in this research. Chapter 4 will show the results of the experiments performed, as well as discuss these results and deliver the proof of concept. Chapter 5 will conclude the findings of this research, with Chapter 6 discussing the recommendations for future work associated with these findings.

2. BACKGROUND

In 1991, O'Regan and Gratzel found inspiration for solar cells in the principle of photosynthesis, which led them to constructing a solar cell that could convert more of the sun light energy into electrical energy.⁴ They called these cells dye-sensitized solar cells and reported an efficiency of about 7%.⁵ They quickly took off due to their numerous advantages compared to other solar technologies at the time. Some of these include abundant raw materials, simplistic processing, and low material cost.

The emergence of perovskite solar cells came from the concept of dye-sensitized solar cells that utilize perovskite compounds. Perovskite structured compounds were first used to make a solar cell in 2009 by Miyasaka and colleagues.⁴ Instead of the usual dye pigment used in most dye-sensitized solar cells at that time, they replaced it with organic-inorganic hybrid halide-based perovskites, $\text{CH}_3\text{NH}_3\text{PbBr}_3$ and $\text{CH}_3\text{NH}_3\text{PbI}_3$. These new perovskite-based solar cells achieved power conversion efficiencies of 3.13% and 3.81%.^{6,41} This low efficiency resulted from the use of a liquid electrolyte as the hole transport layer.

Perovskites made a much larger jump into the photovoltaics realm in 2012 when Kim, Gratzel, and Park used them as the light absorbing layer when fabricating meso-superstructured perovskite solar cells.⁴ With the use of spiro-MeOTAD and mp-TiO₂ as the hole transport and electron transport materials, respectively, they were able to achieve a power conversion efficiency of 9.7%.⁷ This was the first reported perovskite-based solid-state mesoscopic heterojunction solar cell.⁴ After this breakthrough, perovskite solar cell research grew substantially over the years, now reaching efficiencies of 22.1% in early 2016⁸ with the ability to achieve even better efficiencies with further research and by tuning bandgaps using mixed halides. Figure 2.1 shows a graph of the power

conversion efficiency improvements of perovskite solar cells in comparison of other well developed solar cells.

Figure 2.1: Perovskite Solar Cell Power Conversion Efficiencies Vs. Other Solar Cell Technologies²⁵

The term perovskite refers to a type of ceramic oxide molecule with the formula ABX_3 , which was discovered by a German mineralogist named Gustav Rose in 1839.⁴ Perovskite refers to any material that has an identical crystal structure as calcium titanium oxide. The crystal structure of a perovskite is shown in Figure 2.2. The A and B represent two cations of varying size, most commonly organic and inorganic cations when referring to perovskite solar cells, making them a hybrid organic-inorganic material. For most perovskite solar cells, the organic cation is an ammonium ion and the inorganic cation is a lead cation. The X refers to the halogen atom, usually iodine, bromine, chlorine, or some combination.

Figure 2.2: Crystal Structure of Perovskite Compound²⁸

Perovskite solar cells use these types of materials as the light absorbing layer, also known as the light harvesting or photoactive layer, of the cell. This layer absorbs the incident light, which in turn generates an electron and hole. The electron transport layer (n) and hole transport layer (p) then extract and transport their respective charge carriers. These charge carriers are collected by the electrodes and therefore, convert the light energy to electrical energy.⁴ A perovskite solar cell therefore acts as a p-i-n device, where the perovskite acts as an intrinsic semiconductor (i) because it can transfer both holes and electrons.²⁷ Figure 2.3 shows a diagram of a p-i-n device.

Figure 2.3: Diagram of Typical P-I-N Junction Solar Device²⁷

Perovskite solar cells have many benefits leading to their potential use in the photovoltaic industry, such as their high efficiency which is constantly improving. Also, perovskites are direct gap semiconductors, meaning that a much thinner layer of material, ~400-nm-thick layer,²⁶ can be used to achieve the same efficiencies as an indirect gap semiconductor such as silicon. The optical bandgap of these materials ranges from 1.5 to 2.3 eV depending on the selected structure. Another reason that perovskites have been growing in photovoltaic technologies is their high absorption coefficient of 10^5 /cm and their ability to absorb light across most visible wavelengths, allowing them to be able to absorb and convert more sunlight into electricity.²⁶ These compounds can also be processed at low temperatures between 80-150°C and can basically self-assemble from the solution phase.²⁰ Perovskites can also offer flexible, semi-transparent, and light-weight cells, giving them many potential applications in the solar industry.

The most significant benefit of perovskite cells is the simplicity of their processing. Silicon cells have a very expensive, multistep manufacturing process which must be conducted at high temperatures and in a high vacuum. However, perovskite solar cells can be manufactured with multiple techniques, all of which can be made much simpler than the silicon process and have the potential to be scaled up to a larger scale manufacturing level.

Despite all the advantages of perovskite solar cells, there are still issues that are currently being researched and addressed, such as the overall cell production cost, process scaling, and degradation of the cell,⁴² as mentioned previously, as well as the low long-term stability of the cells.⁴⁶

The three main processes currently researched in perovskite photovoltaics are two-step deposition, single-step deposition, and gas phase deposition. In order to form high quality films, there are many factors that must be controlled, such as a uniform thickness, well-crystallized

grains, and surface morphology.¹¹ Also, the performance of the cell is strongly influenced by the size of the perovskite crystals, which affects the photocurrent density and the fill factor of the film, leading to a difference in the power conversion efficiencies.¹²

Two-step deposition is a form of solution processing which consists of depositing the inorganic film, lead iodide in most cases, directly onto the TiO₂ and FTO coated glass substrate. This can be deposited in several ways, such as vapor deposition, dip coating, or spin coating. Once the inorganic film has been deposited to the desired thickness, it is dipped into the organic solution, forming the perovskite crystals when heat is added.¹¹ The organic solution can also be spin coated directly onto the inorganic substrate as shown in Figure 2.4. This method is extremely convenient because of the stepwise nature, with easily controllable variables to produce good-quality films with fairly high power conversion efficiencies (average PCE of 13.9%) due to the improved morphology of the films.¹² However, this method has some issues in photovoltaic performance due to phase transitions when using certain compounds in the inorganic films. It is also harder to regulate the organic film thickness and surface roughness due to the user error involved in dip coating techniques,¹² as well as controlling the molar ratios of the organic and inorganic solutions.

Single-step deposition, another form of solution processing, involves mixing both the inorganic and organic components into a single solution, as they are often soluble within most conventional organic solvents. The solution is then spin coated onto the substrate where the perovskite crystals can form. This method allows the formation of the perovskite crystals while also evaporating the solvent. The spinning rate, drying process, and temperature all affect the morphology of the perovskite film.¹² Using this method can produce high-quality, highly oriented layered perovskite films, and is most widely used today for its ease in processing. However, it is more difficult to control the film thickness, uniformity, and surface morphology of the perovskite

film when using spin coating, making it a less consistent method of deposition.¹¹ It is also not suitable for cases where the organic and inorganic materials have incompatible solubility characteristics. This usually gives it a lower power conversion efficiency when compared to two-step deposition techniques, with an average power conversion efficiency of only 7.5%¹², due to the simplicity of the solution processing causing voids, platelets, and other defects in the perovskite layer. Figure 2.4B and 2.4C shows a comparison of two-step versus single-step deposition.

Gas phase deposition, also known as vapor deposition or vacuum evaporation technique, is another process that can be used to form perovskite solar cells. It is considered another two-step coating process due to its two chemical sources.¹² This method is performed by first depositing the inorganic material, which can be done in numerous methods such as the ones done in typical two-step deposition methods. Next, the organic material is evaporated and deposited onto the inorganic film in the form of a vapor, therefore forming the perovskite film. The benefits of this technique are that the thickness and morphology of the surface can be easily controlled. However, the organic salt used in the evaporation could potentially be thermally unstable at the temperatures needed to evaporate the material.⁴³ It is also more difficult to control the balance of the organic and inorganic rates, which is extremely important when producing perovskite solar films.¹¹ Figure 2.4A shows a diagram of the typical gas phase deposition method.

Delamination is a fairly uncommon method of perovskite deposition. It involves the deposition of the precursor organic and inorganic materials onto separate substrates. The substrates are then brought together, and the reaction to form the perovskite occurs between the substrates through the use of applied heat. After the reaction takes place, the substrates are taken apart, leaving the perovskite formed on the single substrate. The remaining layers of the cell are then

built atop the perovskite like the previous deposition methods. A diagram showing this method is outlined in Figure 2.4D.

Figure 2.4: (A) Gas Phase Deposition (B) Two-Step Deposition (C) Single-Step Deposition (D) Delamination Method³⁰

Reactive lamination is the process of bringing two films or substrates together in which adhesion caused from the reaction between the films causes them to remain attached to each other. This process occurs because the compounds create chemical bonds to both films which leads to adhesion between the two.¹³ Much like the delamination deposition method, this process utilizes the deposition of the precursor solutions onto separate substrates, but instead of separating the

substrates after the reaction, they remain together due to the adhesion. This is a similar process that is being performed in these experiments using the two deposition techniques, as the two films are being brought together, allowing for reaction to occur between the two, ideally adhering them together. Reactive lamination is most commonly used to fabricate multilayer foils or thermoplastics, although a similar lamination method was used to produce a perovskite solar cell in ambient conditions.¹⁸ This method, however, involved a single complex amine precursor solution deposited on a substrate and then a polyamide film was laminated on top of the solution to form the perovskite, in which the film was then removed, making it a delamination style method.¹⁸ During the reactive lamination process for solar cells, the mechanism that the reaction goes through is that of a sublimation reaction. The organic MAI crystals are sublimated at the reaction temperature. Since the reaction is contained between the substrates, all the sublimated gas can react with the inorganic lead iodide crystals on the other substrate. The reaction between the two form the perovskite crystals.

As stated previously, the perovskite material is the light harvesting layer of the solar cell with the chemical formula of $\text{CH}_3\text{NH}_3\text{PbI}_3$ for this research. It absorbs the light energy from the sun and generates the light-generated carriers.

The chemical reaction of the two precursors is shown below:

This shows that the reaction operates on a 1:1 molar ratio.⁷ This reaction tends to generate different morphologies than other perovskite reactions that are not 1:1 molar ratio, with branchlike crystals on the planar substrate.¹⁵ This reaction was found to develop a better crystal product when compared to other reactions with different mechanisms and molar ratios, as well as a faster reaction

speed.¹⁵ This fast reaction speed is based on the “collision” probability. The high degree of collisions of this reaction cause it to have a fast reaction speed.¹⁵

Degradation of the perovskite material is a big concern with the future of perovskite solar cells, as they can usually only maintain their power conversion efficiencies for thousands of hours at most, which is not close to being comparable to other well-developed technologies.¹⁹ Several extrinsic factors such as light, temperature, humidity, or oxygen can contribute to the degradation of the perovskite solar cell. The cause of the lack of chemical and structural stability is the low energetic barrier for the perovskite crystal formation.²⁰ The thermal decomposition of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskites involves the breakdown of the molecule into gases, which are methyl-iodide (CH_3I) and ammonia (NH_3) formed from the decomposition of the methylammonium iodide.¹⁹ It first degrades back into the lead iodide due to the loss of the MAI over time, with the release of the gases being simple sublimation or assisted chemical reaction.²⁰ During the degradation of the perovskite, there are two mass loss steps, the first being the loss of the MAI precursor of about a quarter of the total mass, then the loss of the lead iodide component. During the mass loss of the MAI component, there are two gases emitted, the methyl iodide and ammonia, with this degradation being energetically favored.¹⁹ The degradation reaction is therefore (after the MAI has also decomposed):

Eq. 2

Therefore, the methylammonium iodide degrades through a reverse Menshutkin reaction.¹⁹ However, the ammonia undergoes even further decomposition and rearrangement to ammonium ion, nitrogen, and hydrogen, since the ammonia can reaction with the remaining methylammonium ions that have not decomposed yet.¹⁹

Perovskite materials, as well as their precursors, are soluble in many solutions. For single step deposition, both precursors are soluble in many solvents, although due to the non-homogenous layers that can occur with the spin coating in this method, other antisolvent chemicals such as DMSO must be added. Perovskite crystals are formed from the addition of the antisolvent into the system or cooling of the saturated solution which causes a loss of the solubility of the crystals.²⁰

HTL materials extract the photo-generated carrier or the hole from the light harvesting layer and carry it to the metal electrode. The HTL for perovskite solar cells performs several roles. The first is that it acts as a layer between the metal electrode and the perovskite layer, avoiding direct contact between the two and therefore increasing the selectivity of the contact. This helps to reduce the recombination effects, adding to an overall better efficiency. The HTL also increases the internal quantum efficiency by reducing the diffusion loss of charges.¹⁶ There are four factors that are considered when choosing a hole transport material: cost, stability, charge transfer, and overall photovoltaic performance.¹⁶ The goal is to enhance hole-collection ability, while also reducing the charge recombination, increasing built-in voltage, and thereby improving the performance and stability of the solar cell.¹⁶

Spiro-OMeTAD is the most commonly used material for the HTL in perovskite solar cells. It was first used in 2012 to replace the liquid electrolyte previously used as the HTL.⁷ When it was discovered that this could dramatically improve the efficiencies of the perovskite cells, it became widely used and considered to be the best solid-state hole transporting material for these types of solar cells. The compound is a very complex organic material with two major ring systems. Despite its role as a great HTL material, spiro-OMeTAD is also extremely expensive, therefore increasing the cost of the cell manufacturing. It also has a low charge-carrier mobility since it is an organic material and can cause poor stability of the perovskite solar cell.¹⁷

The alternative HTL material is metal oxides, more commonly transition metal oxides, or TMOs. These include nickel, chromium, molybdenum, copper, vanadium, and tungsten. These have been used as HTL materials because of their wide band gap, good chemical stability, and good hole-transport properties ¹⁷, with some of the TMOs being significantly cheaper than spiro-OMeTAD. TMOs have very good semiconducting properties due to their bands, shells, and orbitals, and have band gaps that fit well within a perovskite p-i-n structure.¹⁷ Table 2.1 shows the band gaps of common transition metal oxides.

Table 2.1: Experimental Band Gaps³² with the calculated minimum (E_g) and direct gaps ($E_{g,d}$) in eV³¹

	E_g^{expt}	E_g	$E_{g,d}$
TiO ₂ (rutile)	3.0	2.97	3.03
TiO ₂ (anatase)	3.3	3.45	3.77
V ₂ O ₃	0.6	1.16	1.18
V ₂ O ₅	2.3	1.97	2.33
Cr ₂ O ₃	2.3	3.19	3.21
MnO (rs)	3.5	3.46	4.14
MnO (zb)	-	2.18	2.30
FeO	2.1	2.18	2.77
Fe ₂ O ₃	2.1	2.14	2.19
CoO (rs)	2.8	2.95	3.47
CoO (zb)	-	2.07	2.19
Co ₃ O ₄	1.5	1.61	1.61
NiO	3.5	3.48	3.80
Cu ₂ O	2.2	2.04	2.04
CuO	1.6	1.24	1.46

As can be seen, nickel oxide is an ideal hole transport layer in perovskite solar cells due to its wide band gap, therefore making it one of the more common TMOs to research for these types of cells.⁴⁴ It is a p-type transition metal oxide and was the focus of the research in this paper due to its cost, availability, and current interest in other studies compared to the other TMOs. It has a

wide band gap of 3.7 eV¹⁷ with a high transmittance and low work function, as well as having a valence band edge that is well-aligned to the HOMO (highest occupied molecular orbital) of most light harvesting materials used in solar cells, including perovskites. Not only does nickel oxide have good hole-transporting properties, but it also has solid electron-blocking properties.¹⁷ Therefore, due to all these factors, nickel oxide can act as a good HTL material to replace spiro-OMeTAD in perovskite solar cells, while still maintaining high efficiency cells.⁴⁵ However, the main obstacle that has occurred in using nickel oxide for the HTL is finding a way to deposit the material.

Therefore, a new procedure for not only depositing the HTL, but also depositing the perovskite layer could lead to new possibilities in materials used in the cell construction. The current structure of typical perovskite solar cells begins with FTO (fluorine doped tin oxide) coated glass substrates, with the FTO acting as one of the electrodes. Next, a layer of titanium di-oxide, or TiO₂, is added to act as an inhibitor of the recombination processes at the interface and also used as the electron transport material/layer, or ETL. The perovskite material is added as the light absorbing layer with the structure of CH₃NH₃PbX₃, with the X representing a halogen atom. Iodine is commonly used as this halogen atom. The HTL is the next layer, most commonly spiro-OMeTAD, as mentioned before. This is the first hurdle needed to overcome in order to decrease the overall cost to produce a cell, as this material is extremely expensive, therefore making the alternative suggested per this proposal nickel oxide or some other TMO. The final layer is the other electrode material, most commonly gold, which is also an expensive material used in the setup of these cells. The overall setup for a normal perovskite solar cell using spiro-OMeTAD and gold can be seen in Figure 2.5, as well as the band diagram for this cell setup.

Figure 2.5: (A) Traditional Setup of Perovskite Solar Cell Using Spiro and Gold (B) Band Diagram of This Cell Setup

However, there are some issues associated with a perovskite cell design such as this. Some of these include the cost of the hole transport layer and metal contact, the need for a vacuum during the process, and the complications with deposition of the perovskite. Therefore, a procedure in which to fabricate a perovskite solar cell that can optimize this process and decrease the cost of the materials is necessary to move forward in industrializing perovskite solar cells.

3. METHODS

Materials: The materials used for these experiments were purchased from either Sigma-Aldrich, Dyesol, or Alfa Aesar. 1inx1in square glass substrates coated in FTO were used in the two glass substrate experiments. 2inx2in square willow glass (thin flexible glass) and nickel foil with a thickness of 0.0254 mm cut into 2inx2in square to match the willow glass were used for the remaining experiments. Methylammonium iodide crystals and 98.5% lead iodide powder were used when preparing the organic and inorganic solutions, with isopropanol and DMF (dimethylformamide) as the solvents. For the even application of the weighted pressure, aluminum blocks were used, either 1.5inx1.5in or 2inx2in, with a thickness of 0.75 cm each and smoothed to achieve as flat a surface as possible.

Substrate Preparation: The glass substrates were cleaned using a sonicator. Substrates were placed first in a beaker of 1:10 ratio of Hellmanox soap detergent to water and sonicated for 10 minutes. This was repeated but in a beaker of fresh DI water, then ethanol, then fresh DI water again. Glass substrates were then dried with nitrogen. All samples, including glass and willow glass substrates, were plasma cleaned for 50 cycles at 20 mm/sec. Then samples were placed in UV oven for treatment for 30 minutes.

Solution Preparation: For the preparation of the MAI solution, 0.514 g of MAI was weighed on a scale and added to a vial. Next, 6 mL of isopropanol was added via pipette to the vial and then a stir bar was added, and the vial was placed on a hot plate to stir for 1 hour. For the preparation of the lead iodide solution, 0.757 g of lead iodide powder was weighed and added to a vial with 1.5 mL of DMF. The solution was mixed with stir bar and heated on hot plate at 80°C for ~30 minutes.

Two Glass Substrates Deposition: The MAI solution was deposited on the glass side, the side without the FTO coating. It was dip coated fully into the solution and then placed on a hot plate at 70°C for ~10 minutes, at which time the isopropanol evaporated, and the MAI crystals could be easily seen. For the lead iodide substrate, the solution was spin coated onto the FTO coated side of the glass substrate. The solution was preheated to 80°C and the slides were preheated to ~60°C. The warm slides were then placed on the spin coater and the hot solution was deposited. The slides were spin coated at 4000 rpm for 20 seconds and at an acceleration of 4000 rpm. The slides were then heated on a hot plate at 100°C for 5 minutes. The substrates were then placed together, solution side facing each other, and taped using high temperature tape all around the outside of the glass substrates. Figure 3.1 shows the cell setup after taping. The substrates were then placed on a hot plate with flat metal plate on top, then a weight was added atop the metal plate to be sure the pressure added was uniform across the surface of the cells. The cells were then heated at 150°C for the desired time length, usually 1.5 hours for most experiments. Once the heating was complete, the cells were taken off the hot plate and the tape was removed.

Figure 3.1: Two Glass Substrate Cell Setup After Enclosure

Flexible Glass and Nickel Foil Substrates Deposition: The MAI solution was deposited onto the nickel foil squares after they had been flattened. This was done using a dip coating method similar to that for the glass substrates. The foil was then heated on hot plate at 70°C for ~10 minutes after the solution was deposited. The lead iodide solution was added to the willow glass. The solution was preheated to 80°C. The willow glass was placed on spin coater with special puck that would distribute the vacuum evenly to prevent the shattering of the thin glass. The warm solution was pipetted onto the glass and then spin coated at 4000 rpm for 20 seconds, with an acceleration of 4000 rpm. The substrate was then placed on a hot plate and heated at 100°C for 5 minutes. The two substrates were then placed together with the solution sides facing each other. There were two methods that could be used to enclose the substrates, both utilizing aluminum metal blocks. The first is to simply tape around the substrates as it was done with the two glass substrates using high temperature tape. The 1.5inx1.5in aluminum blocks were then placed on either side of the taped substrates and they were placed on the hot plate. The other method was to use the 2inx2in aluminum blocks and place them on either side of the substrates. Next, the tape was applied along the edge of the aluminum blocks, enclosing the substrates inside, and placed on hot plate. Figure 3.2 shows the two different cell setups after taping. Next, the substrates were heated on hot plate at 150°C for 1.5 hours. The substrates were then removed from the hot plate and the tape was removed from either configuration.

Figure 3.2: (A) Flexible Glass and Nickel Foil Cell Setup with Taping Cells (Left) and Taping Aluminum Blocks (Right) (B) Diagram of Structure with Aluminum Blocks

Characterization:

After the experiment is complete, the cell is taken to the XRD and SEM for further analysis.

XRD, or x-ray diffraction/x-ray crystallography, is primarily used as a nondestructive analysis technique to characterize crystalline materials. It can be used to identify/quantify crystalline phases, measure structural parameters such as average crystalline size, strain, or micro-strain effects in bulk and thin film materials, quantify preferred orientations, and determine the ratio of crystalline to amorphous materials.⁹ The x-ray diffraction pattern of a material is basically the fingerprint of atomic arrangements of said material. The process works by the crystalline atoms diffracting a beam of incident x-rays into varying directions. These angles and intensities of the diffracted beams are what are measured. One way of understanding the method of XRD is from the Bragg model of diffraction, which mathematically explains why certain faces of crystals reflect x-ray beams at particular angles of incidence. Therefore, it is very useful for this research in analyzing perovskite crystals and their structure, as well as conversion rates of the lead iodide to

the perovskite material through comparison of peak ratios. The XRD for these analyses was run from 10 degrees to either 20, 35, or 80 degrees depending on what was being looked at, and a scanspeed of 0.25 sec/step. A typical XRD pattern for this particular perovskite chemical reaction features the (110) perovskite peak at 14.1 degrees¹⁵ and the lead iodide peak at 12.6 degrees.

SEM, or scanning electron microscope, produces detailed images of a particular sample. This is done by scanning the sample surface with a focused electron beam, which then interacts with the atoms in the sample at varying depths and produces signals. These signals contain the information about the sample's surface topography and composition. An SEM can achieve resolutions better than one nanometer, with magnifications from 10 to 500,000 times.¹⁰ SEM is primarily used in this research to investigate the size of the perovskite crystals but can also be used to identify the thickness of layers of the solar cell. The SEM for these experiments was between either 1 μm to 100 nm to analyze the crystal structure.

4. RESULTS AND DISCUSSION

The purpose of this research is to first prove the formation of perovskite material through the proposed deposition method. The first experiment was conducted per the two glass substrate deposition method in an enclosed glove box, and data was collected via XRD to prove the formation of these perovskite crystals. This first experiment was performed without any enclosure of the substrates and was run for an hour and a half. The reaction temperature was also tested during this experiment to determine the minimum temperature possible to evoke the color change to the perovskite. It was first tested at 100°C on the hot plate with a weight applied to the top of the substrates, and increased until it reached 150°C. The temperature was not tested above this temperature because perovskites can start to decompose at temperatures higher than 150°C. At 150°C, the color change occurred from the yellow of the lead iodide to the brown of the perovskite. After an hour of heating at 150°C, the substrates had full coverage of the color change across the glass, with even better color conversion after an hour and a half. As can be seen in Figure 4.1, there is some formation of perovskite crystals in the (110) plane at 14.1 degrees. It also features a significant lead iodide peak at 12.6 degrees, indicating that although there is perovskite formation using this method, the conversion of the lead iodide to perovskite is only 47.05%. It was also noted that the perovskite only formed on the lead iodide substrate, with the MAI substrate only containing remnant MAI crystals and no color change. This was due to the fact that there was no adhesion between the substrates, allowing them to be separated with ease. The MAI crystals sublimated into the lead iodide crystal structure, forming the perovskites on the lead iodide surface of the substrates, which is why the color change was only observed on the lead iodide substrate.

Figure 4.1: XRD Data Before Enclosure of Substrates

After this experiment was conducted, it was noted that there was some vapor deposition on the underside of the weighted beaker that was on top of the substrates. In order to improve the conversion to the perovskite material, it was proposed to enclose the reaction between the substrates, which could encapsulate the vapors being formed from the sublimation of the MAI and aid in pushing the reaction forward. High temperature tape was used around the edge of the substrates that were deposited with the same procedure as the original experiment and was heated at 150°C for 1.5 hours. Figure 4.2 shows that the encapsulation of the reaction between the substrates did in fact increase the conversion to the perovskite material from 47.05% to that closer to 75%, indicating the importance of the vapor formed from the reaction and showing that the reaction is in fact acting in a similar manner as a gas phase deposition.

Figure 4.2: XRD Data After Enclosure of Substrates

The thicknesses of these films from the second experiment were also tested via profilometer, namely the thickness of the lead iodide layer before running the experiment, which would be used in later calculations involving the conversion of the lead iodide to the perovskite. Table 4.1 lists these thicknesses.

Table 4.1: Film Thickness Before and After Reaction Via Profilometer

Film	Thickness (nm)
MAI Film Before Reaction	380
MAI Film After Reaction	283
Lead Iodide Film Before Reaction	250
Perovskite Film After Reaction	500

Moles of Lead Iodide Before Reaction

$$\text{Area} * \text{Layer Thickness} = \text{Volume of Layer}$$

$$6.4514 \text{ cm}^2 * (2.5 * 10^{-5} \text{ cm}) = 1.61285 * 10^{-4} \text{ cm}^3 = 1.61285 * 10^{-4} \text{ mL}$$

$$\frac{\text{Volume of Layer} * \text{Density}}{\text{Molecular Weight}} = \text{Number of Moles}$$

$$\frac{(1.61285 * 10^{-4} \text{ mL}) * (6.16 \frac{\text{g}}{\text{mL}})}{461.01 \frac{\text{g}}{\text{mol}}} = 2.28445 * 10^{-6} \text{ mol of Lead Iodide}$$

Next, several time trials were conducted to evaluate the conversion over time. The same method was used for the two glass substrates with tape enclosure. After the MAI was dip coated, some large white crystals, which appeared to be almost like a powder, were observed along with the usual clear crystals. The experiments were conducted at 15-minute intervals with a substrate used as a constant that was not heated at all. The reactions were conducted for two hours in order to allow as much conversion as possible and to show the peak conversion time. Figure 4.3 shows the XRDs for all the substrates, as well as a single XRD of all the graphs for a direct comparison. Figure 4.3 also shows the conversion over time curve and photos of the color change over time. Based on the conversion graph, this reaction is a zeroth order reaction, which means that the reaction is not based on the concentration of the reactants. The reaction rates of each of the peaks were then calculated, and the overall reaction rate was calculated based on these. The value obtained for the rate of the reaction until the first peak height at 30 minutes, when the conversion was 38.29%, was $\text{Rate} = 0.00301 \text{ mol/L} * \text{sec}$. The reaction rate for the second peak height at 90 minutes, considering the start to be from 60 minutes when the conversion was 20.83%, was $\text{Rate} = 0.00546 \text{ mol/L} * \text{sec}$. The overall reaction rate, based on the highest conversion after 90 minutes, was $\text{Rate} = 0.00237 \text{ mol/L} * \text{sec}$. Below are the calculations to reach these rates:

Conversion

$$\frac{\text{Intensity of Perovskite Peaks}}{\text{Total Intensity of Lead Iodide and Perovskite Peaks}} * 100\% = \text{Percent Conversion} \quad \text{Eq. 3}$$

Reaction Rate

$$\frac{\frac{(\text{Fraction of Conversion Final}) * (\text{Number of Moles})}{\text{Volume}} - \frac{(\text{Fraction of Conversion Initial}) * (\text{Number of Moles})}{\text{Volume}}}{\text{Final Time} - \text{Initial Time}} = \text{RXN Rate} \quad \text{Eq. 4}$$

Reaction Rate of First Peak

$$\frac{\frac{(0.382887) * (2.28445 * 10^{-6} \text{mol})}{1.61285 * 10^{-7} \text{L}} - \frac{(0) * (2.28445 * 10^{-6} \text{mol})}{1.61285 * 10^{-7} \text{L}}}{1800 \text{sec} - 0 \text{sec}} = 0.0030129 \text{ mol/L} * \text{sec}$$

Reaction Rate of Second Peak

$$\frac{\frac{(0.9024322) * (2.28445 * 10^{-6} \text{mol})}{1.61285 * 10^{-7} \text{L}} - \frac{(0.2082945) * (2.28445 * 10^{-6} \text{mol})}{1.61285 * 10^{-7} \text{L}}}{5400 \text{sec} - 3600 \text{sec}} = 0.0054621 \text{ mol/L} * \text{sec}$$

Overall Reaction Rate

$$\frac{\frac{(0.9024322) * (2.28445 * 10^{-6} \text{mol})}{1.61285 * 10^{-7} \text{L}} - \frac{(0) * (2.28445 * 10^{-6} \text{mol})}{1.61285 * 10^{-7} \text{L}}}{5400 \text{sec} - 0 \text{sec}} = 0.002367 \text{ mol/L} * \text{sec}$$

Figure 4.3: (A) XRD Scans for Each Time Interval (B) XRD Scan For All Time Intervals Together (C) Conversion Over Time Graph (D) Pictures of Color Change Over Time

Based on the above data, it can be seen that the conversion increases steadily until around 30 minutes, at which it starts to decline. Between 1 and 1.25 hours, the conversion increases again, with an overall higher conversion at 1.5 hours. This indicates that the highest conversion of 90.24% was first achieved at 1.5 hours. This type of conversion curve with two separate peaks led to a test to determine the cause of this type of graph. One hypothesis was that the perovskite starts degrading at the 30-minute interval due to the reaction temperature being right at the lower end of the perovskite degradation temperatures. Since it is at the very low end of this degradation temperature range, it is not believed that the degradation reaction goes further than breaking into its precursors, therefore not producing the ammonia and the methyl iodide. Also, since the MAI is produced first in the degradation reaction, then it is believed that much of the crystal structure of the lead iodide is maintained. This decreasing conversion or degradation continues for another 30

minutes until it starts to increase again at a time of one hour. The increase is caused by the degradation reaction producing the precursor MAI vapor as well as the forward reaction continuing to produce MAI vapor. The degradation produces MAI vapor in which it is still held within the lead iodide crystal lattice. The combination of an overabundance of MAI vapor eventually reaches a saturation point of sorts, at which time the reaction starts to produce more perovskite than is degrading, leading to the continuous increase until it reaches its overall peak conversion of the lead iodide to perovskite.

Another hypothesis was that of the different perovskite crystal orientations. The different indices of the crystal orientations give different XRD patterns, so this hypothesis was tested via XRD analyses. After doing so, it was determined that there were intense peaks at 12.6, 14.1, and ~19.7 degrees. It was determined that these peaks corresponded to lead iodide, (110) tetragonal perovskite, and (112) tetragonal perovskite.²¹ The (112) orientation has been reported in epitaxially grown films³⁶ and single crystal perovskites.³⁷ The main difference in these experiments versus previous time trials was that the lead iodide was deposited directly onto glass instead of the FTO coating. As can be seen in previous graphs, this 19.7 peak did not appear as intense in the other experiments as it did here. Therefore, the (112) crystal formation only was prevalent when the perovskite was formed directly onto glass. This plane is directly parallel to the substrate³², with the crystallographic plane shown in Figure 4.4, and is a parallelogram natural crystallographic facet.³⁴ This indicates that there is a preferential orientation so that the edges of the structure are in direct contact with the substrate.³³ It is structurally confined in the direction of the crystal growth.³⁵ Some studies indicated that the (112) is based on the intermediates and precursor solutions used to form the perovskites.³³ However, since the precursor solutions for this trial did not change from previous trials, this most likely was not the cause of this formation. It was also

found in previous studies that the formation of the (112) perovskite is preferentially formed based on the early stage of the crystallization process.³⁸ Therefore, this orientation could be formed based on the initial crystal structure of the lead iodide film framework. Due to the fact that glass and FTO have different surface energies, the lead iodide crystals could have developed differently than when they were spin coated onto the FTO coated glass substrates. If this is the case, this could be the cause of the (112) perovskite crystal formation in this experiment. However, further tests would need to be conducted to confirm this.

Figure 4.5: (112) Perovskite Crystal Orientation and Comparison of the Planes

Based on these findings, the conversions for the perovskite calculations were recalculated to include the total perovskite crystal formation. By including this other crystal formation in the calculations for the conversion, the shape of the graph more closely fits a typical conversion graph with a single conversion peak for this particular experiment, but still having a plateau area around

the same point as there was a peak previously. However, it is important to note that this was based off one set of data, so further experimentation to prove this would be necessary. Also, in this new experiment, the rate based on the conversion of 89.08% at 75 minutes was $Rate = 0.002804 \text{ mol/L} \cdot \text{sec}$. Figure 4.5 shows the new conversions including both perovskite crystal formations, as well as the XRD scans from this experiment to show the (112) perovskite peak. The calculations for this experiment are below, while using Equations 3 and 4.

$$Rate = \frac{\frac{(0.890844333) * (2.28445 * 10^{-6} \text{mol})}{1.61285 * 10^{-7} \text{L}} - \frac{(0) * (2.28445 * 10^{-6} \text{mol})}{1.61285 * 10^{-7} \text{L}}}{4500 \text{sec} - 0 \text{sec}}$$

$$= 0.002804 \text{ mol/L} \cdot \text{sec}$$

Figure 4.5: (A) Graph of Conversion Including Both Perovskite Formations (B) XRD Scans Including New Perovskite Peaks

An SEM scan was performed on these cells as well to look at the perovskite crystals and to compare them to the pure lead iodide crystals. Figure 4.6 shows the results of the SEM scans for the perovskite crystals at both conversion peak heights, as well as the crystals of the lead iodide before the reaction to act as a comparison of the crystal development from the reaction. However,

it is important to note that the crystal structure of the lead iodide does not show the tendril-like crystals that are typically seen. Based on these results, the perovskite crystals formed were dense with a large grain size. The large grain size indicates that this deposition method is helpful in the growth of the perovskite crystals, which would reduce trap states and thereby improve the performance of the cell.¹⁸ The film was also determined to be highly uniform through the SEM analysis. There were also few defects in the films at the higher conversion rate, leading to a good defect density that aids in suppressing charge recombination and increasing diffusion lengths of the charge carriers.³³

Figure 4.6: SEM Analyses of (A) Lead Iodide Crystals at 10 μm and 4 μm (B) Perovskite Crystals at 20.8% Conversion at 4 μm , 2 μm , and 500 nm (C) Perovskite Crystals at 100% Conversion at 4 μm , 1 μm , and 500 nm

Throughout all the experiments conducted with the two glass substrates, adhesion became a consistent issue that was encountered. The earlier experiments saw no adhesion whatsoever, with no color change on the MAI substrate and no sticking between the substrates. The time trial saw some adhesion between substrates when the MAI substrate had some larger white crystals with the smaller clear crystals. When these larger white crystals were present, there would be some adhesion only at the sites of these crystals, with some of the white MAI “powder” transferring to

the lead iodide/perovskite substrate. In these instances, there was adhesion in those areas with the larger crystals and some MAI was leftover, as it was in most of the reactions. This, therefore, is a defect in the reactive lamination as they did not fully adhere to each other.

Since it was determined that perovskites could be formed using this new method of deposition, the next step was to test whether the method could be used with new substrates and to move towards creating a full cell. Once all these experiments with the two glass substrates were completed, further experiments were conducted using the willow glass and nickel foil substrates. Several samples were prepared using the method detailed above and heated at 150°C for 1.5 hours without the metal blocks. Instead, a simple weighted beaker was used. The main purpose of this experiment was to determine the method for deposition on these new substrates, as well as test the adhesion between them. Figure 4.7 shows the pictures taken of the substrates at the end of the reaction. It was observed that there was not an even coverage of the perovskite color change, and it was determined this was caused from an uneven pressure application of the applied weight.

Figure 4.7: Pictures of Substrates Without Even Color Change Distribution

Once this was noticed, the metal blocks were created to ensure an even distribution of the applied pressure. Several experiments were conducted to determine the affects of using such blocks. The same deposition process was used as the previous experiment, and the two metal blocks were put on either side of the substrates with a weight applied on top. Figure 4.8 shows a picture of the results of these experiments.

Figure 4.8: Picture of Substrates After Use of Aluminum Blocks

It was observed that the color change was, although more even than before, not as dark as what was seen in the two glass substrate experiments. Several tests and calculations were conducted to determine the cause of this. Since previous experiments involved the substrates having direct contact with the hot plate, they were able to have direct heat transfer from the hot plate to the substrates. However, with the new procedure involving a metal block beneath the substrates, the rate of heat transfer changes due to the slight heat resistance of the aluminum. Therefore, the reaction temperature must be adjusted to account for this, or the reaction could be placed in an oven for an even heating of all surfaces. Figure 4.9 shows a working diagram of the

process involving the flexible glass and nickel foil substrates using lab pictures taken throughout.

Figure 4.9: Process Diagram with Lab Photos

5. CONCLUSIONS

Perovskite solar cells are an emerging thin film, third generation photovoltaic technology with ever growing power conversion efficiencies, some reaching above 20%.⁸ However, due to the materials used as the HTL and the metal contact, the overall cost of cell production is fairly high. In order to move from using materials such as spiro-OMeTAD and gold for the HTL and metal contact, respectively, this research proposes a new method of perovskite deposition to allow for the use of transition metal oxides and their respective metals as these cell layers.

The proposed method entails a combination of liquid phase two-step deposition and vapor phase deposition of the perovskite material. This is accomplished by depositing the organic and inorganic precursor solutions separately onto different substrates, then bringing them together and heating them, thereby forming the perovskite crystals between the substrates. By doing so, the MAI crystals, or organic precursor, is heated into its gas phase where it can then react with the lead iodide, or inorganic precursor, to produce the perovskite light absorbing layer of the cell. This method not only allows for the use of different substrates, namely the transition metal oxide as one substrate to act as the HTL, but also simplifies the deposition of the material by allowing it to be produced outside an enclosed glove box environment. It can also be deposited on flexible substrates, allowing for an option that can be beneficial in many applications and for roll-to-roll production.

To test the ability of this process to form the desired perovskite layer, several experiments were conducted to determine if perovskite was formed, the conversion of the lead iodide to perovskite, the layer thickness, the adhesion of the substrates, and the reaction parameters such as temperature and time of reaction. Based on the results of these experiments, it was concluded that perovskite material can be formed using this method, with a conversion of 90.24% of the lead

iodide to perovskite and an overall reaction rate of $Rate = 0.00237 \text{ mol/L} * \text{sec.}$ after 90 minutes. It was also determined that the method developed a good crystal layer with uniformity throughout.

It was also found that the conversion over time graph developed some interesting results with two separate conversion peaks during the reaction time. After running experiments and tests to determine the cause of this shape in the graph, it was found that this process develops two configurations of perovskite crystals, (110) and (112), when deposited directly onto glass substrates. When including both configurations, the conversion of the new experiment was 89.08% and a reaction rate of $Rate = 0.002804 \text{ mol/L} * \text{sec}$ after 75 minutes. However, this did result in a conversion over time graph that had only one conversion peak, which was at the 75 minutes, and only occurred when the lead iodide was deposited directly onto glass.

6. RECOMMENDATIONS

One of the main issues that must be addressed is the lack of adhesion, causing a delamination of the substrates. This must be corrected in further studies as it is important to improve this adhesion to be able to use transition metal oxides as the HTL in future perovskite solar cell developments.

For future work associated with this study, along with improvement of the adhesion forces between the precursors when forming the perovskite, several other steps must be taken to further enhance the potential for this process. Research into the formation of the oxide layer from the nickel foil or other transition metal is important to be able to achieve the desired layer thickness for the HTL. Another step is to delve further into the cause of the double peaked conversion graph shown by this process, as this can help to understand the reaction and its rate that are occurring to form the perovskite. Also, more trials would be necessary to further optimize the process to improve perovskite film thickness, decrease the degradation, and to enhance the overall process and procedures. It is also important to look further into the cause of the (112) perovskite formation and to have a better understanding of how the different crystal facets can be grown. Finally, once these other steps are researched and improved, the development of a working cell and improvement of the power conversion efficiency through optimization of the process is the last step towards achieving a cheaper alternative for perovskite photovoltaic cells.

RESOURCES

1. Institute for Energy Research. “Solar.” Institute for Energy Research, instituteforenergyresearch.org/topics/encyclopedia/solar/.
2. Perovskite Info. “Perovskite Solar.” Perovskite Solar Panels: Introduction and Market Status - Page 2 | Perovskite-Info, 8 Jan. 2018, www.perovskite-info.com/perovskite-solar?page=2.
3. Lavery, Brandon W., et al. (2016) “Intense Pulsed Light Sintering of CH₃NH₃PbI₃ Solar Cells.” ACS Applied Materials & Interfaces 8(13): 8419-8426.
4. Tang, He. (2017) “A Short Progress Report on High-Efficiency Perovskite Solar Cells.” Nanoscale Research Letters. 12 (410): 1-8.
5. O’Regan B, Gratzel M (1991) “A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO₂ films”. Nature 353(6346):737–740.
6. Kojima A, Teshima K, Shirai Y, Miyasaka T (2009) “Organometal halide perovskites as visible-light sensitizers for photovoltaic cells”. Journal American Chem Society 131(17):6050–6051.
7. Kim HS, Lee CR, Im JH, Lee KB, Moehl T (2012) “Lead iodide perovskite sensitized all-solid-state submicron thin film mesoscopic solar cell with efficiency exceeding 9%.” Scientific Report 2(591): 1-7.
8. Nazeeruddin MK (2016) “In retrospect: twenty-five years of low-cost solar cells.” Nature 538(7626):463–464.
9. EAG Laboratories. “X-Ray Diffraction Analysis | XRD | Phase Identification.” EAG Laboratories, www.eag.com/techniques/spectroscopy/x-ray-diffraction-xrd/.

10. “Scanning Electron Microscope.” Wikipedia, Wikimedia Foundation, 1 Apr. 2018, en.wikipedia.org/wiki/Scanning_electron_microscope.
11. Liang, Kangning, et al. (1998) “Synthesis and Characterization of Organic-Inorganic Perovskite Films Prepared Using a Versatile Two-Step Dipping Technique.” *Chemistry of Materials*. 10 (1): 403-411.
12. Lee, Jin-Wook, and Nam-Gyu Park. (2015) “Two-Step Deposition Method For High-Efficiency Perovskite Solar Cells.” *Perovskite Photovoltaics*. 40 (8): 654-659.
13. Schuler, Anne-Katrin, et al.(2014) “A Novel Reactive Lamination Process for the Generation of Functional Multilayer Foils for Optical Applications.” *Procedia Technology* pp. 147–155.
14. Green, M.A., Emery, K., Hishikawa, Y., Warta, W. & Dunlop, E. D. (2015) “Solar cell efficiency tables” (version 45). *Progress in Photovoltaics Research and Applications*. 23, 1–9.
15. Wang, Baohua, et al.(2015) “Elucidating the Reaction Pathways in the Synthesis of Organolead Trihalide Perovskite for High-Performance Solar Cells.” *Scientific Reports*. 5(10557): 1-11.
16. Tress, Wolfgang, et al.(2014) “The Role of the Hole-Transport Layer in Perovskite Solar Cells Reducing Recombination and Increasing Absorption.” *At Photovoltaics Specialties Conference*. 8-13 June. Denver, Colorado.
17. Pingli, Qin, et al. (2017). “Transition Metal Oxides as Hole-Transporting Materials in Organic Semiconductor and Hybrid Perovskite Based Solar Cells.” *Science China Chemistry*. 60(4): 472-489.

18. H, Chen, et al. (2017) “A Solvent- and Vacuum-Free Route to Large-Area Perovskite Films for Efficient Solar Modules.” *Nature*. 550(7674): 92-95.
19. Juarez-Perez, Emilio, and Zafar Hawash.(2016). “Thermal Degradation of CH₃NH₃PbI₃ Perovskite into NH₃ and CH₃I Gases Observed by Coupled Thermogravimetry-Mass Spectrometry Analysis.” *Energy & Environmental Science*. 9: 3406-3410.
20. Manser, Joseph, and Makhsud Saidaminov. (2016). “Making and Breaking of Lead Halide Perovskites”. *Accounts of Chemical Research*. 49 (2): 33-38.
21. Takeo Oku (October 22nd 2015). “Crystal Structures of CH₃NH₃PbI₃ and Related Perovskite Compounds Used for Solar Cells”, *Solar Cells* Leonid A. Kosyachenko, IntechOpen. Available from: <https://www.intechopen.com/books/solar-cells-new-approaches-and-reviews/crystal-structures-of-ch3nh3pbi3-and-related-perovskite-compounds-used-for-solar-cells>.
22. Saga, Tatsuo. (2010) “Advances in Crystalline Silicon Solar Cell Technology for Industrial Mass Production.” *NPG Asia Materials*. 96-102.
23. “Solar Cell Production: from Silicon Wafer to Cell.” (2015) “Sinovoltaics - Your Solar Supply Network.” sinovoltaics.com/solar-basics/solar-cell-production-from-silicon-wafer-to-cell/.
24. Green, Martin A., et al. (2014). “The Emergence of Perovskite Solar Cells”. *Nature Photonics*. vol. 8, 506–514.
25. “Perovskites and Perovskite Solar Cells: An Introduction.” “Ossila,” www.ossila.com/pages/perovskites-and-perovskite-solar-cells-an-introduction.

26. Hossain, M. I., and B. Aissa. (2017) “Effect of Structure, Temperature, and Metal Work Function on Performance of Organometallic Perovskite Solar Cells.” *Journal of Electronic Materials*. 46 (3): 1806-1810.
27. Lavery, Brandon. (2016) “Methods for Forming a Perovskite Solar Cell.” USPTO, 62/299, 593.
28. Tome Lopez, Cesar. “Effects of Defects and Water on Perovskite Solar Cells.” *Mapping Ignorance*, 8 Oct. 2015, mappingignorance.org/2015/10/08/effects-of-defects-and-water-on-perovskite-solar-cells/.
29. Yang Yang Laboratory (UCLA). (2014)/ “Vapor Assisted Solution Process (VASP).” *Perovskite Solar Cells via VASP, UCLA*, www.ngsf.org/2014/02/10/perovskite-solar-cells-via-vasp-yang-yang-laboratory-ucla/.
30. Zhao, Yixin, and Kai Zhu. (2016). “Organic-Inorganic Hybrid Lead Halide Perovskites for Optoelectronic and Electronic Applications”. *Chemical Society Review* 45: 655-689.
31. Lany, Stephan. (2015). “Semiconducting Transition Metal Oxides.” *Journal of Physics: Condensed Matter*. 27 283203.
32. M. Shishkin, G. Kresse (2006). “Implementation and performance of the frequency-dependent GW method within the PAW framework.” *Physical Review B* 74, 035101.
33. Cho, Namchul, et al. (2016). “Pure Crystal Orientation and Anisotropic Charge Transport in Large-Area Hybrid Perovskite Films.” *Nature Communications*. 7 13407.
34. Lian, Zhipeng, and Qingfeng Yan. (2015) “High-Performance Planar-Type Photodetector on (100) Facet of MAPbI₃ Single Crystal.” *Scientific Reports*. 5 16563.

35. Niu, Guangda, et al. (2016) “Controlled Orientation of Perovskite Films through Mixed Cations toward High Performance Perovskite Solar Cells.” *Nano Energy*, vol. 27, 2016, pp. 87–94.
36. Koza, J. A., Hill, J. C., Demster, A. C. & Switzer, J. A. (2016). “Epitaxial electrodeposition of methylammonium lead iodide perovskites.” *Chemistry Materials* **28**, 399–405.
37. Peng, W. et al. (2016). “Solution-grown monocrystalline hybrid perovskite films for hole-transporter-free solar cells”. *Advance Materials* **28**, 3383–3390.
38. Miyadera, T. et al. (2015) “Crystallization dynamics of organolead halide perovskite by real-time X-ray diffraction.” *Nano Letters*. **15**, 5630–5634.
39. Huang, Jinsong, et al. (2017). “Understanding the Physical Properties of Hybrid Perovskites for Photovoltaic Applications.” *Nature Reviews*. 2 17042.
40. Yang, Shida, et al. (2017). “Recent Advances in Perovskite Solar Cells: Efficiency, Stability and Lead-Free Perovskite.” *Journal of Materials Chemistry A*. 5, 11462-11482.
41. Nam-Gyu, Park. (2015). “Perovskite Solar Cells: an Emerging Photovoltaic Technology.” *Materials Today*. 18 (2): 65-72.
42. Petrus, Michiel L., et al. (2017). “Perovskite Solar Cells: Capturing the Sun: A Review of the Challenges and Perspectives of Perovskite Solar Cells. *Advanced Energy Materials*, Wiley-Blackwell. 7 (16): 1700264.
43. Avila, Jorge, et al. (2017). “Vapor-Deposited Perovskites: The Route to High-Performance Solar Cell Production.” *Joule*. 1 (3): 431-442.

44. Lampande, Raju, et al. (2013). "A Highly Efficient Transition Metal Oxide Layer for Hole Extraction and Transport in Inverted Polymer Bulk Heterojunction Solar Cells." *Journal of Materials Chemistry A*. 1. 6895-6900.
45. Chang, Sehoon, et al. (2016). "Transition Metal-Oxide Free Perovskite Solar Cells Enabled by a New Organic Charge Transport Layer." *ACS Applied Materials and Interfaces*. 8 (13): 8511-8519.
46. Sanchez, Rafael, and Elena Mas-Marza. (2016) "Light-Induced Effects on Spiro-OMeTAD Films and Hybrid Lead Halide Perovskite Solar Cells." *Solar Energy Materials and Solar Cells*. 158 (2): 189-194.
47. Blakers, Andrew, et al. (2013) "High Efficiency Silicon Solar Cells." *Energy Procedia*. 33. 1-10.
48. Green, M A. (1993) "Silicon Solar Cells: Evolution, High-Efficiency Design and Efficiency Enhancements." *Semiconductor Science and Technology*. 8 (1): 1-12.

APPENDICES

Appendix I: Data Tables

a). First Time Trial XRD Peaks and Resulting Conversion

Time (min)	PbI2 Degrees	Perovskite Degrees	Conversion (%)
0	96	0	0
30	122	74	37.755102
60	480	60	11.1111111
90	0	95	100
120	45	91	66.9117647

b) Second Time Trial XRD Peaks and Resulting Conversion

Time (min)	PbI2 Degrees	Perovskite Degrees	Conversion (%)
0	28500	0	0
15	16250	500	2.98507463
30	1200	2300	65.7142857
45	2800	2650	48.6238532
60	9200	4700	33.8129496
75	0	2850	100
90	0	7450	100
105	0	6150	100
120	0	6550	100

c) Third Time Trial XRD Peaks and Resulting Conversion

Time (min)	PbI2 Degrees	Perovskite Degrees	Conversion (%)
0	9134	0	0
15	16522	743	4.3035042
30	15891	2044	11.3967103
45	7444	1382	15.6582823
60	11250	2397	17.5642998
75	521	3102	85.6196522
90	2094	5060	70.7296617
105	4508	2908	39.2125135
120	2853	5689	66.6003278

d) All Time Trial Conversions with Average and Standard Deviation

Time (Min)	Conversion 1 (%)	Conversion 2 (%)	Conversion 3 (%)	Average (%)	SD
0	0	0	0	0	0
15	2.98507463	4.3035042		2.429526	0.93227
30	65.7142857	11.3967103	37.755102	38.2887	27.16272
45	48.6238532	15.6582823		21.42738	23.31018
60	33.8129496	17.5642998	11.1111111	20.82945	11.69783
75	100	85.6196522		61.87322	10.16844
90	100	70.7296617	100	90.24322	16.89924
105	100	39.2125135		46.40417	42.98324
120	100	66.6003278	66.9117647	77.83736	19.19404

e) Final Time Trial XRD Peaks Including Both Perovskite Peaks and Resulting Conversion

Time (min)	Lead Iodide	Perovskite 1 Degrees	Perovskite 2 Degrees	Conversion (%)
0	9134	0	0	0
15	16522	743	4100	22.6679148
30	15891	2044	5700	32.7649672
45	7444	1382	2250	32.7916215
60	11250	2397	3100	32.8237893
75	521	3102	1150	89.0844333
90	2094	5060	3950	81.1419308
105	4508	2908	5200	64.2675967
120	2853	5689	9350	84.054326

Appendix II: Calculations

a) Moles of Lead Iodide Before Reaction

$$\text{Area} * \text{Layer Thickness} = \text{Volume of Layer}$$

$$6.4514 \text{ cm}^2 * (2.5 * 10^{-5} \text{ cm}) = 1.61285 * 10^{-4} \text{ cm}^3 = 1.61285 * 10^{-4} \text{ mL}$$

$$\frac{\text{Volume of Layer} * \text{Density}}{\text{Molecular Weight}} = \text{Number of Moles}$$

$$\frac{(1.61285 * 10^{-4} \text{ mL}) * (6.16 \frac{\text{g}}{\text{mL}})}{461.01 \frac{\text{g}}{\text{mol}}} = 2.28445 * 10^{-6} \text{ mol of Lead Iodide}$$

b) Conversion

$$\frac{\text{Intensity of Perovskite Peaks}}{\text{Total Intensity of Lead Iodide and Perovskite Peaks}} * 100\% \\ = \text{Percent Conversion}$$

c) Reaction Rate

$$\frac{\frac{(\text{Fraction of Conversion Final}) * (\text{Number of Moles})}{\text{Volume}} - \frac{(\text{Fraction of Conversion Initial}) * (\text{Number of Moles})}{\text{Volume}}}{\text{Final Time} - \text{Initial Time}} \\ = \text{Reaction Rate}$$

a. First Set with Single Perovskite Peak

i. Reaction Rate of First Peak

$$\frac{\frac{(0.382887) * (2.28445 * 10^{-6} \text{ mol})}{1.61285 * 10^{-7} \text{ L}} - \frac{(0) * (2.28445 * 10^{-6} \text{ mol})}{1.61285 * 10^{-7} \text{ L}}}{1800 \text{ sec} - 0 \text{ sec}} = 0.0030129 \text{ mol/L} * \text{sec}$$

ii. Reaction Rate of Second Peak

$$\frac{\frac{(0.9024322) * (2.28445 * 10^{-6} mol)}{1.61285 * 10^{-7} L} - \frac{(0.2082945) * (2.28445 * 10^{-6} mol)}{1.61285 * 10^{-7} L}}{5400sec - 3600sec}$$

$$= 0.0054621 \text{ mol/L} * sec$$

iii. Overall Reaction Rate

$$\frac{\frac{(0.9024322) * (2.28445 * 10^{-6} mol)}{1.61285 * 10^{-7} L} - \frac{(0) * (2.28445 * 10^{-6} mol)}{1.61285 * 10^{-7} L}}{5400sec - 0sec} = 0.002367 \text{ mol/L} * sec$$

b. Second Set with Both Perovskite Peaks

$$\frac{\frac{(0.890844333) * (2.28445 * 10^{-6} mol)}{1.61285 * 10^{-7} L} - \frac{(0) * (2.28445 * 10^{-6} mol)}{1.61285 * 10^{-7} L}}{4500sec - 0sec}$$

$$= 0.002804 \text{ mol/L} * sec$$

Appendix III: XRDs

a. September 12th Trial with Two Glass Substrates Testing for Perovskite Formation

(Coupled TwoTheta/Theta)

(Coupled TwoTheta/Theta)

b. October 5th Trial with Two Glass Substrates and Enclosing Substrates

- c. March 7th Time Trial in 30-minute Intervals
a. 0 minutes

b. 30 minutes

c. 60 minutes

d. 90 minutes

e. 120 minutes

- d. March 29th Time Trial with 15-minute Intervals
a. 0 minutes

- b. 15 minutes

c. 30 minutes

d. 45 minutes

e. 60 minutes

f. 75 minutes

g. 90 minutes

h. 105 minutes

i. 120 minutes

j. All

- e. April 5th Time Trial with 15-minute Intervals Testing for Other Perovskite Crystal Formations
- a. 0 minutes

- b. 15 minutes

c. 30 minutes

d. 45 minutes

e. 60 minutes

f. 75 minutes

g. 90 minutes

h. 105 minutes

i. 120 minutes

j. All

Appendix IV: SEMs

a. Lead Iodide Film

HV	spot	WD	mag	det	7/18/2017	HFW	curr	← 4 μm →
	10.00 kV	3.0	15.3 mm	6 080 x	ETD	5:31:31 PM	24.5 μm	80 pA

b. Perovskite Film at 30 Minutes

HV	spot	WD	mag	det	7/18/2017	HFW	curr	500 nm
	10.00 kV	3.0	15.2 mm	25 142 x	ETD	5:39:22 PM	5.93 μ m	80 pA

c. Perovskite Film at 1.5 Hours

HV	spot	WD	mag	det	7/18/2017	HFW	curr	← 300 nm →
	10.00 kV	4.0	6.4 mm	64 950 x	TLD	5:08:11 PM	2.30 μ m	0.32 nA

HV	spot	WD	mag	det	7/18/2017	HFW	curr	← 300 nm →
	10.00 kV	4.0	6.4 mm	64 937 x	TLD	5:10:40 PM	2.30 μ m	0.32 nA

HV	spot	WD	mag	det	7/18/2017	HFW	curr	← 300 nm →
10.00 kV	4.0	6.4 mm	64 935 x	TLD	5:12:01 PM	2.30 μ m	0.32 nA

HV	spot	WD	mag	det	7/18/2017	HFW	curr	▸ 200 nm ▸
	10.00 kV	4.0	6.4 mm	84 236 x	TLD	5:12:50 PM	1.77 μ m	0.32 nA

HV	spot	WD	mag	det	7/18/2017	HFW	↔ 100 nm ↔
	10.00 kV	4.0	6.4 mm	175 889 x	TLD	5:15:31 PM	848 nm

HV	spot	WD	mag	det	7/18/2017	HFW	curr	← 300 nm →
	10.00 kV	4.0	6.4 mm	64 950 x	TLD	5:17:15 PM	2.30 μ m	0.32 nA

HV	spot	WD	mag	det	7/18/2017	HFW	curr	↔ 300 nm ↔
	10.00 kV	4.0	6.4 mm	59 468 x	TLD	5:20:51 PM	2.51 μ m	0.32 nA

HV	spot	WD	mag	det	7/18/2017	HFW	curr	↔ 300 nm ↔
	10.00 kV	4.0	6.4 mm	59 468 x	TLD	5:21:38 PM	2.51 μm	0.32 nA

HV	spot	WD	mag	det	7/18/2017	HFW	curr	↔ 300 nm ↔
	10.00 kV	4.0	6.4 mm	59 468 x	TLD	5:22:09 PM	2.51 μ m	0.32 nA	

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