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Fabricating Perovskite Solar Cells: Fabrication Guide for Limited Lab Capabilities

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Fabricating Perovskite Solar Cells: Fabrication Guide for Limited Lab Capabilities

Abstract

Within the realm of emerging photovoltaics, Perovskite cells are one of the most intriguing technologies. Within a little over a decade, Perovskite solar cells have rivaled the efficiencies of traditional silicon solar cells and strongly outpaced other emerging photovoltaic technologies. This paper aims to show a fabrication guide for creating Perovskite solar cells in a limited lab setting. The fabrication guide created structures with strong physical reliability, but limited electrical reliability. More research is needed to ensure greater reliability and proper electrical function.

1. Introduction

Within the realm of emerging photovoltaics, Perovskite cells are one of the most intriguing technologies. They are made of an organic-inorganic hybrid material that shows the potential for significant efficiencies due to its tunable band gap (Ansari et. al., 2018) which would allow for greater capture of solar energy. Within a little over a decade, Perovskite solar cells have reached lab efficiencies of up to 25.7%, rivaling the efficiencies of traditional silicon solar cells – which are nearing their theoretical efficiency limit – and strongly outpacing other emerging photovoltaic technologies like dye-sensitized solar cells and other thin film technologies (NREL, 2022). Along with this promise for strong returns within solar energy, they have shown promise for being simple to manufacture (Ansari et. al., 2018). Since they are produced using low-temperature wet lab techniques at close-to-environmental conditions rather than metallurgically processed as traditional silicon solar cells are (Ansari et. al., 2018), they have the potential to be suitable for research in small labs with limited equipment capabilities. While they have been manufactured with great success across the literature in this field, lab efforts at Macalester have struggled with reliability, ease of fabrication, and electrical quality. This research was intended to create a reliable fabrication process for Perovskite cells that would be suitable for these small labs.

2. Methodology

I primarily followed a procedure from the company Ossila (Ossila), but changed the structure slightly so that it would be a planar structure with a planar titanium oxide layer rather than a structure that included a mesoporous titanium oxide layer – a layer

that creates a rigid structure that the Perovskite then forms inside, providing a sort of scaffold – due to the equipment constraints of the lab I was working in. This component of the method was following a paper by Huang et. al (2020). The complete fabrication process can be found in Appendix 1. Note that this fabrication guide has been written for the Macalester College lab capabilities and may not be specific or applicable to other labs.

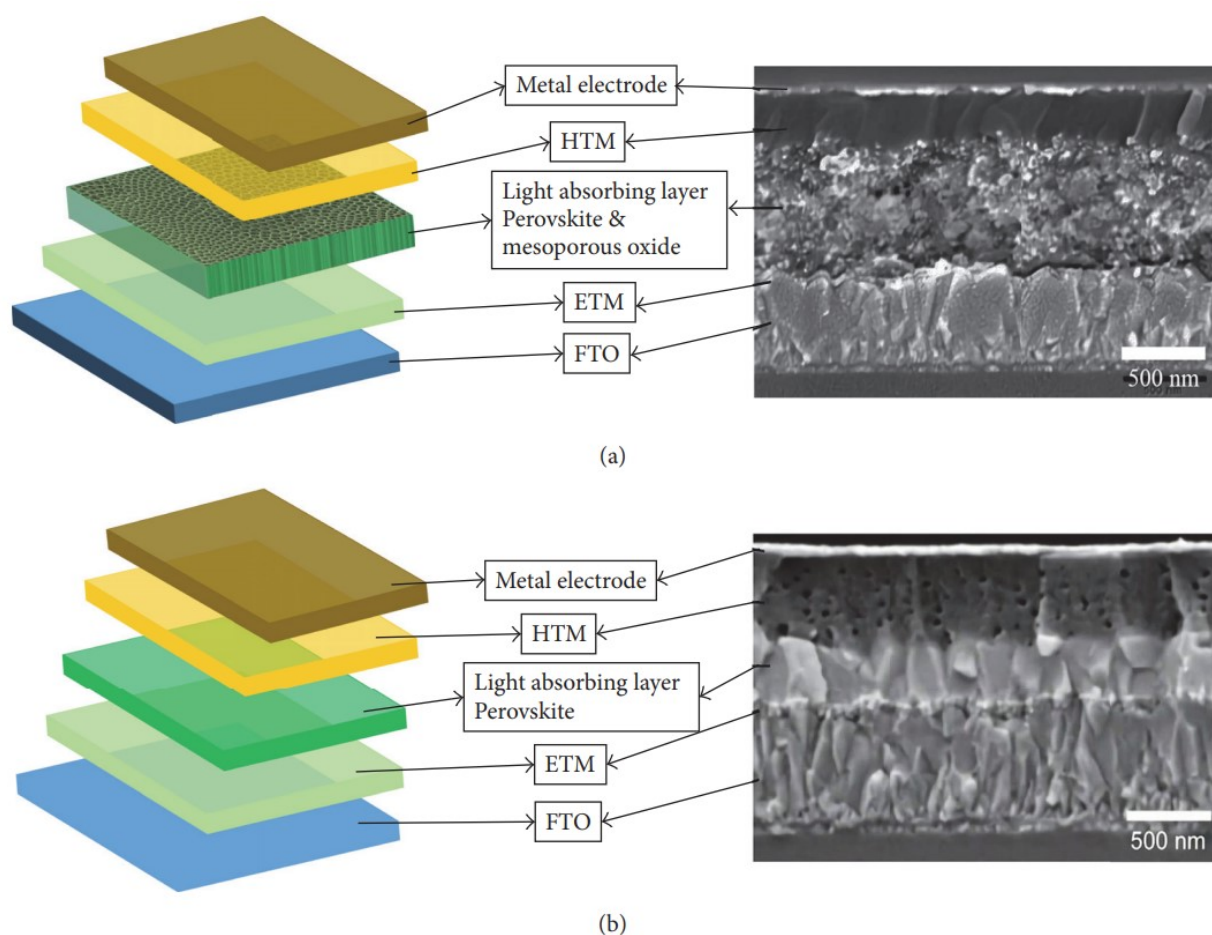


Figure 1: Diagrams and SEM images showing a planar structure (a) and a mesoporous structure (b) Perovskite cell. Image from Zhou et. al., 2018.

The completed cell was a p-i-n (positive-intrinsic-negative) planar junction structure consisting of a glass substrate pre-printed with indium-doped tin oxide (ITO) anodes, titanium oxide electron transport medium, a mixed methylammonium (MA) lead iodide and MA lead chloride Perovskite layer, Spiro-OMeTAD hole transport layer, and gold cathode.

I started the process by cleaning the substrates in an ultrasonic cleaner (this process is called sonication) in a heated Hellmanex solution and isopropyl alcohol and dump rinsing in deionized (DI) water in between sonications. Once the substrates were dry, I then spin coated the substrates in a titanium isopropoxide solution which, when annealed in a tube furnace, created the titanium oxide layer. Once this layer was complete, I put the substrates into a nitrogen-filled glove box with very low humidity to create the Perovskite layer. I spin-coated the substrates with a multi-cation Perovskite ink from Ossila. This layer was annealed in the glove box. I then spin-coated the substrates with the Spiro-OMeTAD layer and left the layer to oxidize overnight. Finally, I took the cells out of the glove box and put them into a deposition mask and used a sputtering machine to evaporate a thin layer of gold onto the structure, creating the anode. Throughout the entire process, I made sure to wipe part of the cathode clean to allow for proper electrical conduction in the completed cell. After the anode deposition, I used a razor to make sure the individual cells in the structure were electrically disconnected from one another.

To characterize the cells, I used a scanning electron microscope and an atomic force microscope to analyze the physical and surface characteristics of the layers. To

measure the electrical and photovoltaic properties of the cells, I used an apparatus that would use a LabView program to measure the current-voltage curve of the structure both in darkness and under simulated sunlight. The program would also calculate the fill factor, efficiency, open-circuit voltage, and closed-circuit current of the structure.

3. Results and Discussion

a. Physical Results and Discussion

The physical results of this fabrication process were generally favorable. Most completed structures showed uniform layer structures with few to no physical defects. However, there were defects that were relatively common to each layer.

I found the quality of the titanium oxide layer to be most dependent on the layer thickness. If the layer was too thick, the layer would crack and flake off of the substrate. I observed this behavior around thicknesses of 150 nm. At the desired thicknesses of between 50 and 100 nm, as dictated by the Ossila guide (Ossila), there were fewer defects of this nature. The only defects I observed at this thickness were short, curved cracks. Based on AFM imaging, these cracks did not extend through the entire layer. However, even these defects were very rare when the titanium oxide layer was prepared with the proper solution filtration and layer thickness.

The Perovskite layer seemed to primarily depend on the conditions of the glove box, but this layer was the most enigmatic in its behavior. If the glove box had a higher humidity level (>6%), the Perovskite layers would tend to have poor structures but this behavior was inconsistent. Most of the structures had the desired plate-like crystal structures to minimize defects in the final electrical behavior. This minimizes the risk for

major physical - and therefore electrical - defects in the final structure. The plate-like crystal structure creates a more uniform layer than other crystal formations, such as a “pine needle”-like crystal formation that the lab previously struggled with when the layers were processed in air and under non-humidity controlled conditions. Using this process, the major issue with the final cells were pinholes in the Perovskite layer. These are small holes, typically 0.5 to 1 μm in diameter, in the Perovskite layer that extend down to lower layers. This would create electrical short circuits between the layers, creating poor electrical quality in the completed structures. I tried to minimize the presence of the pinholes through various methods, including decreasing the humidity in the glove box, increasing the time spent annealing, and ensuring that the substrate was fully wetted while spin-coating. The prevalence seemed minimally affected by all of these efforts.

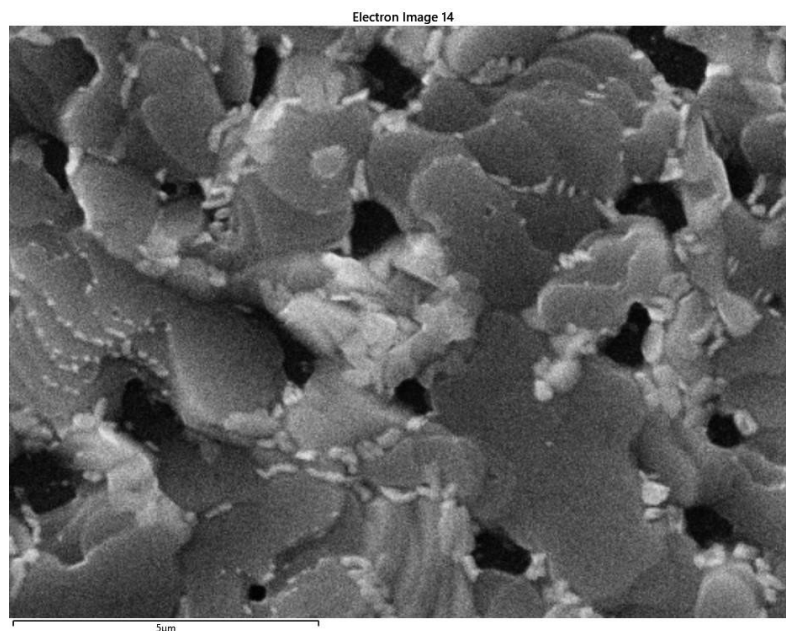


Figure 2: SEM image showing ideal plate-like crystal formations and non-ideal pinhole defects in a layer of Perovskite.

The quality of the Spiro-OMeTAD layer was primarily dependent on if it was deposited on a glass slide or on a Perovskite layer. When the Spiro-OMeTAD layer was deposited on a glass slide, it would not properly adhere to the surface and the complete layer would have almost no coverage in the middle of the slide. It would be filled with holes and appear “lacy” or like Swiss cheese. When deposited on a Perovskite layer, it would fully adhere to the layer and create a mostly defect-free surface. The only other defect would occur if, due to human error during spin coating, too thick of a layer was deposited. The layer would appear cracked and would flake, much in the same way that the titanium oxide layer behaved.

The cathode layer had major effects on the rest of the structure. I had originally attempted to use an aluminum cathode that was deposited using vacuum evaporation. However, I found that both the aluminum and the vacuum evaporation process were too harsh for the structure. The aluminum appeared to corrode the layers of the structure, destroying its electrical capabilities. The heat from the vacuum evaporation process appeared to degrade the Spiro-OMeTAD layer, creating an appearance of a “shadow” under visual microscopes. While it did degrade the layer, when the cathode was made of gold, it was not especially noticeable. If equipment capabilities required it, vacuum evaporation could be a viable alternative to sputtering. When I replaced the cathode with gold that was deposited using sputtering, there were no visible defects in the structure.

b. Electrical Results and Discussion

The electrical results of this process were unfavorable. Many cells had negligible fill factors and efficiencies, displaying only diode-like behavior. 41.1% of the complete cells showed diode-like behavior and only 24.4% of the completed cells showed a photocurrent. While this is more reliable than previous results from this lab, this is not an especially reliable result. A major issue with the electrical characterization occurred while completing the current-voltage scan. If the parameters for the voltage were set too high, a scan down through the voltage would show linear Ohmic behavior, even if the scan up would show diode-like behavior. While hysteresis is expected with Perovskite materials, this behavior suggests that the cells can short circuit if a voltage that is too high is applied.

4. Summary and Conclusions

The success of the physical characteristics of this process shows that this is a promising start for a lab with limited equipment capabilities. The process was simple to execute and gave reliable results in the physical properties of the structure. However, more experimentation is necessary to ensure better reliability and improved electrical results. This is a promising field of photovoltaic research, especially for small research labs, and this fabrication guide should be a strong start for any lab trying to begin research into Perovskite technology.

References

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APPENDIX 1

Cleaning Substrates

20 minutes

1. Put DI water in a beaker
2. Put 1% by volume Hellmanex solution in a beaker
3. Place both on a hot plate set to maximum temperature
4. Monitor Hellmanex solution until it gets to 70°C
5. Use that solution to sonicate the ITO coated substrates for 5 minutes
6. At this point, the DI water should be boiling. Use that water to dump rinse the substrates to remove the Hellmanex solution
7. Sonicate the substrates again in isopropyl alcohol for 5 minutes
8. Dump rinse the substrates again in the boiling DI water
9. Shake excess water off the substrate and dry using a compressed nitrogen gun
10. Store cleaned substrates in a case. Substrates stay clean for a few hours, so I recommend completing this process right before you need to use them.

TiO₂ Solution, Deposition, and Annealing

3 hours total, 30-45 minutes of active work Should be completed in the fume hood

1. Measure 2.5 mL of isopropyl alcohol using a graduated cylinder. Put into a small (30 mL) beaker with a magnetic stir bar.
2. Measure 2.5 mL of isopropyl alcohol using a graduated cylinder. Dispense 35 μ L of 2M hydrochloric acid (HCl) into the graduated cylinder and set aside.
3. Measure 738 μ L titanium (IV) isopropoxide using a micropipette and dispense into the beaker with only isopropyl alcohol. The titanium isopropoxide is very, very hygroscopic and will gel up if it absorbs too much water, so I try to do this step last.
4. Dispense the HCl/isopropyl alcohol solution into the titanium solution dropwise. This can be done either by slowly pouring the graduated cylinder or using a glass pipette.
5. Turn on stirring to ~level 3 (this is a relatively arbitrary number because the paper I took this process from said 300 rpm, but there are no rpm values on the hot plate in the fume hood). Cover the beaker well with parafilm. Stir for at least 2 hours.
6. Near the end of the stirring, turn on the tube furnace set to 550°C.
7. Cover another small, empty (30 mL) beaker with parafilm. This is done so that you expose the solution to as little atmospheric humidity as possible.

8. Take the solution off stirring. Use a syringe with a needle on the tip to take out <2 mL of the solution.
9. Replace the needle with a 0.2 μm filter and attach the needle to the tip of the filter. Dispense into the new, clean beaker.
10. Repeat steps 8 and 9 until all of the material is filtered. The filter tends to get clogged if this is done all in one step, so it works better to work in multiple steps and potentially use multiple filters. I have 2-3 filters set up before this step for this purpose.
11. Use a glass pipette or a micropipette to dispense at least 50 μL of the solution onto a clean substrate. Dynamically spin coat at 3000 rpm for 15 seconds.
12. Immediately after spin coating, use a cotton swab soaked in isopropyl alcohol to wipe off the cathode strips on the substrate. You may need to scrub to get all of the material off. This layer gets very tough very quickly, so perform this step as quickly as possible.
13. Place coated substrate on a 180°C hotplate to dry for at least 5 minutes.
14. Spin coat as many substrates as you'd like. This quantity of solution can make at least 4 3x1" microscope slides for testing the layers. The furnace can fit a maximum of 6 ITO substrates, so I recommend making up to 6.
15. Once all substrates are coated and dried, put them in the tube furnace set to 550°C for 30 minutes. This can be done in air. I start my timer when the internal thermometer reaches 550°C.
16. Let the substrates cool until the internal temperature is <200°C and remove from the furnace.

NOTE: 2M HCl is a ratio of 1 mL of 12M HCl to 6 mL of DI water

Perovskite Deposition

~4 hours total, 30 minutes of active work Should be completed in the glove box

1. Remove the label from the bottle of ink. Heat the ink at ~70°C in the sand bath on the hot plate for at least 2 hours
2. Take the bottle out of the sand bath and place it on the metal floor of the glove box to cool to room temperature.
3. Set the temperature of the hotplate to 80°C
4. Place the ITO coated substrate (at room temperature) onto the spin-coater and spin the substrate at 4000 rpm (for 30s)
5. Dynamically dispense 30-50 μL of perovskite ink
6. Place substrate back onto the hotplate at 80°C
7. Once all substrates have been coated, anneal for 90 mins

8. To clean the cathode, remove the perovskite layer by using a scalpel to scrape off the material. Blow or dust off the perovskite residue to prevent contamination on the final two layers.

NOTE: The bottles of perovskite ink have large labels on them that I took off before heating them so there was no risk of the label melting or catching on fire.

Spiro-OMeTAD Solution and Deposition

30 minutes active work + 12 hour oxidation Should be done in glove box and desiccator

1. Prepare the following solutions; Spiro-OMeTAD at a concentration of 97 mg/ml in chlorobenzene, Li-TFSI at a concentration of 175 mg/ml in acetonitrile, and TBP at a volumetric percentage of 46.6% in acetonitrile. The Spiro-OMeTAD and Li-TFSI materials are both powders so they are challenging to measure out. I used the scale in the Keck lab to measure out the powders. The Li-TFSI solution is stable for long periods of time, so that solution can be made in large quantities. Spiro-OMeTAD oxidises, which makes bad layers, so it should be made the day of making the layer (if storing the total solution in air) or it can be made within 3-4 days of making the layer (if storing the solution in nitrogen).
2. Combine 1000 μ l Spiro-OMeTAD, 30.2 μ l Li-TFSI, and 9.7 μ l TBP solutions
3. Dispense 50 μ l of the combined solution onto the perovskite, allowing it to spread across the substrate
4. Spin at 2000 rpm for 30 seconds
5. Use a cotton swab soaked in chlorobenzene to wipe off the cathode
6. Move the completed substrates into a desiccator in air and leave in the dark for 12 hours for total oxidation of the spiro layer

Metal Sputtering

45 minutes

1. Place the samples into the cathode mask. You should use the smaller backplate (the thick metal backplate). I find it most effective to place the devices upside down in the top plate of the mask in the divots and then slide the back plate on top. To hold the devices in place, you can put a small dot of rubber cement on the backplate using the wooden part of a cotton swab. You should leave the devices in place for <5 minutes to let the rubber cement dry.
2. Use the "Auto" function of the sputtering machine to complete a 200 second gold sputtering of the devices.

3. Use a scalpel/razor blade/precision screwdriver to scrape away the borders between the devices so that they are not electrically connected.

Completed Devices and Characterization

After the metal evaporation, the devices are complete and can be tested. I test the resistance of each device using a multimeter to make sure that the device is properly positioned and to do an initial check of the device. Typically, the devices that don't exhibit diode-like behavior and appear more like resistors have stable resistances $<1\text{ k}\Omega$ and devices that do exhibit diode-like behavior have resistances $>10\text{ k}\Omega$, even going as high as $10\text{ M}\Omega$, and the resistance is rapidly changing. I measured these resistances with a DVM. Try to avoid moving the device on the pins of the reader because this can scratch and remove the metal electrodes.

This entire process, aside from the metal evaporation because that must be completed after the spiro oxidation which takes 12 hours, can be completed in a 9 to 5 workday. The schedule that I have used is attached below. Shaded time periods indicate passive processes, while boxed time periods indicate active work. I marked off time periods relatively broadly, so this may be completed more quickly than I have indicated.

9:00 AM			
9:15 AM			
9:30 AM	prep TiISO soln		
9:45 AM	TiISO stirring		
10:00 AM			
10:15 AM		Set glove box	
10:30 AM		hot plate temp	
10:45 AM		Heat perov	Clean
11:00 AM			substrates
11:15 AM	Set fume hood		
11:30 AM	hot plate temp	Set furnace	
11:45 AM	TiO ₂ spin coat		
12:00 PM			
12:15 PM	TiO ₂ anneal		
12:30 PM			
12:45 PM	cool down		
1:00 PM	Perov spin		
1:15 PM	coat		

1:30 PM	Perov anneal		
1:45 PM			
2:00 PM			
2:15 PM			
2:30 PM		Make spiro soln	
2:45 PM			
3:00 PM	Spin coat spiro		
3:15 PM			
3:30 PM			