Perovskite Solar Cell: A Simple Hot Casting Method to Formulate High-quality, Lead-free, Sn-based Perovskite Films with Reduced Pinholes

Abstract

Hybrid organic-inorganic lead halide perovskite solar cells, PVSCs, have emerged in the past decade as a promising, low cost, thin film photovoltaic device with the power conversion efficiency (PCE) increasing from 3.8% to 22.7%. However, poor long-term stability of PVSCs and toxic nature of lead limits future commercial applications. Fabrication of uniform perovskite films with full coverage and fewer pinholes are the prerequisites for achieving a high-performance perovskite. To achieve a good morphology, one-step solution processing and anti-solvent engineering were used. All precursors (Formamidinium Iodide and Tin Iodide) were dissolved in DMSO and GBL. Before put in the spin coater, the precursor solution and the glass substrates were heated to 60 oC, 70 oC, 80 oC, 90 oC, and 100 oC. During spin coating, the anti-solvent wash with toluene was performed to removed excess DMSO. After spin-coating, the perovskite glass substrates were annealed at 100 degrees Celsius. Perovskite layers were characterized by X-Ray Diffraction (XRD) and its surface morphology was investigated by a Scanning Electron Microscope (SEM). From the SEM pictures, it was concluded that 70 oC was the optimal temperature for the precursor to create a pinhole free perovskite layer. Through the XRD peak analysis, the morphology and crystallinity of the perovskite structure were analyzed and confirmed to have a stable and simple cubic structure with a lattice constant of 4.09A. Thus, 70 oC had the optimal temperature to construct a perovskite film.

Objective:

➨The objective of the project is to improve the morphology and crystallinity of the perovskite layer and to create a uniform, pinhole free, high quality perovskite films

➨The goal is to create lead free perovskite using one step processing technique, anti-solvent wash and simple hot casting method.

➨The goal is also to fabricate a device and measure the power conversion efficiency of the perovskite.

Question:

How does the temperature of the precursor solution affect the morphology and crystallinity of the Perovskite layer created?
How does the temperature of the precursor solution affect the Power Conversion Efficiency (PCE) of the perovskite device

Materials

Tin(II) iodide (SnI2, 99.99%), lead(II) bromide (PbBr2, 99.999%), cesium iodide (CsI, 99.999%), tin(II) Fluoride (SnF2 99%), toluene (anhydrous, 99.8%), g-butyrolactone (GBL, $99%), N,N-dimethyl sulfoxide (DMSO, anhydrous, $99.9%), and bathocuproine (BCP, 96%) were purchased from Sigma-Aldrich (St. Louis, Missouri) and used without further purification. Formamidinium iodide (FAI) was purchased from Greatcell Solar (Queanbeyan, Australia) without further purification. The PC60BM (>99.5%) was purchased from American Dye Source (Quebec, Canada).

Experimental: Perovskite thin film fabrication

The perovskite precursor solutions were prepared by dissolving FAI and SnI2 the corresponding molar ratios in GBL and DMSO (volume ratio 7 : 3) with a total concentration of 1M. A 10% SnF2 per molar weight of SnI2 was added to the precursor solution as a reducing agent. Plain glass was cut into 1.5 cm by 1.5 cm substrates which were then cleaned via ultrasonication for 15 min in detergent in Millipore deionized water, acetone, and isopropanol in sequence. The substrates were treated with oxygen plasma under 100 W for 10 min. Both the precursor solution and the substrate was heated to 60°C. A 70 mL drop of precursor solution was spin-coated on a cleaned glass substrate at 500 rpm for 5 s, 1000 rpm for 15 s, and 4000 rpm for 40 s in a nitrogen glove box. A toluene anti-solvent was in situ dripped onto the substrate during the last 15 s of the third spin-coating step. The perovskite films were then thermally annealed at 100 °C for 10 min. The same was repeated by heating the precursor solution for 70°C, 80°C, 90°C, 100°C.

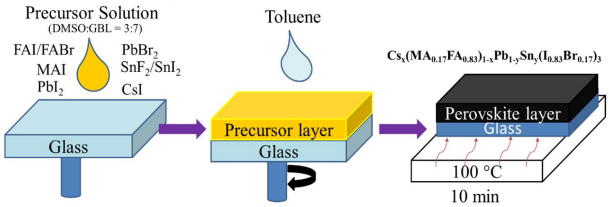
Device fabrication

ITO coated glass were cut and cleaned as described above. The PEDOT:PSS solution was filtered with a 0.45 mm nylon filter. A 70 mL drop of PEDOT:PSS was spin-coated on a cleaned ITO coated glass substrate at 5000 rpm for 60 s and annealed at 150 _C for 10 min in air. The substrates were transferred to a glove box and the perovskite thin lms were fabricated as described above. A PC60BM solution (15 mg ml_1 in chloroform) was then spin coated on the perovskite films at 4000 rpm for 60 s and dried without annealing. The substrates were loaded into a thermal evaporation chamber to thermally 8nm of BCP. Finally, a mask with 3.14 _ 10_6 m2 area holes was placed on devices to evaporate 150 nm of silver for electrodes in a high vacuum evaporator .The resulting device structure is ITO/PEDOT:PSS/perovskite/PC60BM/BCP/Ag.

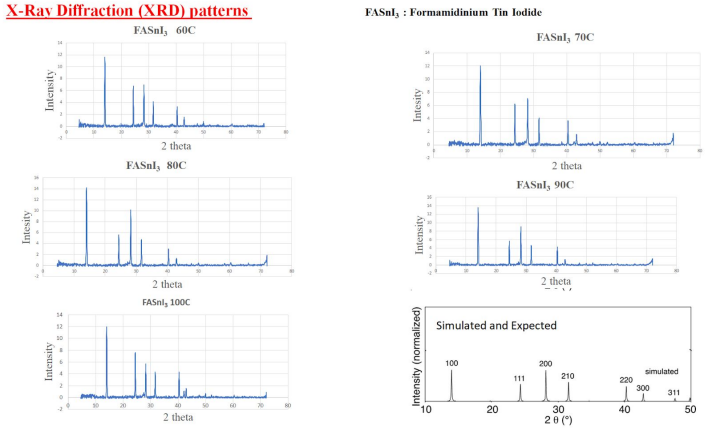
Device characterization

The photocurrent density–voltage (J–V) curve measurements were conducted in a N2 glovebox with a Keithley 2400 Source Meter and a Solar Light Co. Xenon lamp (16S-300 W) and an AM 1.5 filter. Before measurements, the light intensity was calibrated to 100 mW cm_2 using a standardized National Renewable Energy Laboratory calibrated silicon solar cell.

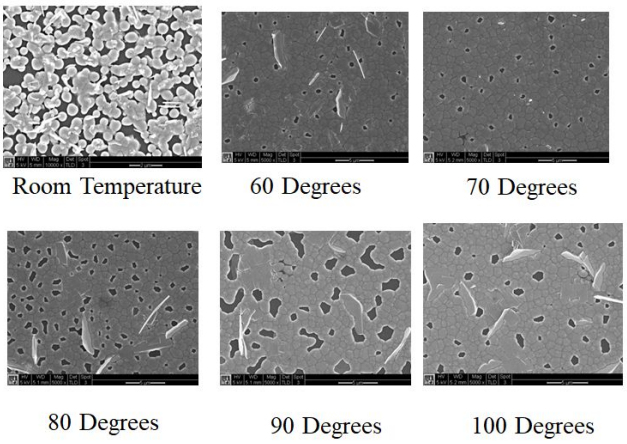
Perovskite Thin Film via One-Step Anti-Solvent Method



X-Ray Diffraction (XRD) patterns

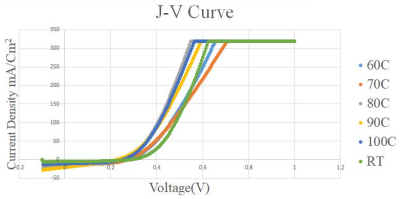


SEM(Scanning Electron Microscope)



Photovoltaic performances of PVSCs fabricated under AM1.5G

Temp	V_{oc} (V)	J_{sc} (mA/ cm²)	Fill Factor	PCE(%)
Room Temp	0.28	4.79	0.45	0.60
60ºC	0.26	6.44	0.52	0.87
70ºC	0.27	13.75	0.48	1.78
80ºC	0.24	18.41	0.35	1.57
90ºC	0.22	20.00	0.30	1.31
100ºC	0.25	10.88	0.45	1.20



Observations

Images of the Scanning Electron Microscope shows the perovskite film prepared with a precursor solution

•At 70 C has less number of pin holes

•At room temperature is loosely packed and is opened to degradation

•At 60 C has less number of pin holes but also unformed perovskite that shows as white lines and it has a potential to regroup

•Above 70 C has more pinholes. The size of the pinholes increase with temperature

•The white lines above 70 C shows segregation and hence not stable

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Crystallinity of the perovskite was analyzed using the XRD.

- Miller Indices :
  - -Used to specify directions and planes.
  - -These directions and planes could be in lattices or in crystals
  - - The number of indices will match with the dimension of the lattice or the crystal.

- Miller Indices plane was calculated using Braggs law and calculated 1/d2 and then applied the common ratio.
- XRD shows peaks at 100, 111,200, 210,220, 300, 221 planes. The peaks confirms the cubic structure of the lattice.

Goldschmidt tolerance factor :

Goldschmidt tolerance factor (*t*) is an empirical index for predicting stable crystal structures of perovskite materials. A *t* value between 0.8 and 1.0 is favorable for cubic perovskite structure, and larger (>1) or smaller (<0.8) values of tolerance factor usually result in non-perovskite structures.

r_A is the radius of the A-cation. FA+ (2.53 °A),

r_B is the radius of the B-cation. Sn2+ (1.15 °A)

r_x is the radius of the X-anion. I -(2.20 °A),

Tolerance factor for FaSnI3 is 0.9985A which confirms its cubic nature.

Power Conversion Efficiency(PCE):

The maximum power conversion efficiency(PCE) of 1.78% was found at 70ºC. This is much less than the maximum PCE(10%) reached with pure tin halide so far. Since we have found the good temperature of precursor, future research is needed to improve the efficiency. This can be achieved by using different composition of cations and anions.

Conclusion

My hypothesis was partially correct. From the Scanning Electron Microscope images, it was found that 70 ℃ was the optimal temperature for a perovskite to form, at which it is uniform and has minimum pinholes. As the temperature get higher, number of pinholes created decreased but only until a certain point. After 70℃, the pinholes started being bigger. Below 70 ℃, there were areas where the perovskite did not form. This was due to the perovskite not having enough activation energy. Above 70 ℃, the white lines indicated segregation because there was too much energy. Also the maximum power conversion efficiency of 1.78% was reached at 70 ℃.

The crystallinity of the perovskite layer was studied using X-ray Diffraction. The FASnI3 film shows six dominant diffraction peaks at angles of 14.0°, 24.4°, 28.22°, 31.65°, 40.36° ,42.94 °assigned to the crystallographic planes (100), (111), (200), (220), (221/300), respectively. This diffraction pattern is in agreement with the cubic structure of the FaSnI3. The cubic structure of the perovskite makes it a more stable structure. The lattice constant of 4.09 Å guarantees a more stable, lead-free silicon based solar cell. If the lattice constant grows or shrinks, the solar cell performance will go down as well.

Future Research

As the first phase of the research, 70ºC was found be the optimum temperature of the precursor solution to created PVSC with minimum pinholes. In the summer of 2019 the following will be tried to increase the PCE of the Perovskite Solar Cell.

- Different cations – Combination of formamidinium and methylammonium as the monovalent cations. Also add inorganic cesium resulting triple cation perovskite compositions.
- Annealing the perovskite structure at 110C and 120C
- Different anti-solvent
- chlorobenzene,
- Diethyl ether
- Different rpm of the spin coater
- 500, 1000,3000 rpm in 5 sec, 15 secs and 40 sec
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