

Development of Low-cost Hybrid Perovskite Solar Cells

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Abstract

Development of efficient and economically affordable photovoltaic (PV) technology is important to realize solar power as the primary source of renewable energy. Solar cells are electronic devices that directly convert sunlight into electrical energy using a photo-absorber material. Organic-inorganic lead halide-based hybrid perovskites have recently emerged as a promising photo-absorber material for efficient and low-cost solar cells. In this work, we report on the fabrication and characterization of hybrid perovskite solar cells employing methyl ammonium lead iodide ($\text{CH}_3\text{NH}_3\text{PbI}_3$) nanocrystalline thin film as the light harvesting material. An inexpensive one-step spin-coating technique was used for the absorber film deposition. Surface morphology of the absorber layer was investigated using scanning electron microscopy (SEM). Solar cells were fabricated on FTO-coated soda-lime glass (SLG) substrates with RF magnetron sputtered ZnO as the electron transport layer. Spin-coated Spiro-MeOTAD was used as the organic hole transport layer. Current-voltage (I-V) characteristics of the fabricated solar cells were measured under simulated AM1.5 solar spectrum and under dark conditions. Electrical parameters, such as open-circuit voltage (V_{oc}), short-circuit current (I_{sc}), fill factor (FF), and efficiency were calculated from the measured I-V characteristics. A power conversion efficiency of 1.14% was achieved under an irradiance of 1000 W/m^2 . Detailed solar cell fabrication, characterization, and photovoltaic performance analysis results are presented.

Keywords: Solar Cell, Perovskite, Photovoltaic Device, Renewable Energy

1. Introduction

By the year 2030, the US Department of Energy (USDOE), the International Energy Agency (IEA) and the European Photovoltaic Industry Association (EPIA) project the global power demand to be around 18 terawatts¹. As an estimation, less than 500,000 square kilometers would need to be covered with only 8% efficient solar cells in order to completely satisfy the global demand with clean renewable solar energy. That is less than 0.2% of the earth's surface area, or the approximate sum of all the deserts on the earth. Fossil fuels are depleting quickly and the greenhouse and toxic gases being released into the atmosphere are polluting the environment and contributing to the global warming. Solar energy has the ability to exploit a virtually unlimited reservoir of energy available to the Earth from the Sun. Solar energy possesses a huge potential to reduce the amount of hazardous and greenhouse gases being released in our environment and become the largest source of clean, cost-effective energy for the future, thus substantially reducing the fossil fuel dependency. Therefore, research and development of affordable photovoltaic technology is crucial to realize mass-scale solar power production in the near future.

Currently, 1st generation solar cells are the most dominant in the market while second generation solar cells have just recently been commercialized. 1st generation solar cells use Silicon (poly-crystalline or mono-crystalline) as the light-absorbing material. Silicon (Si)-based solar cells are highly expensive due to highly sophisticated fabrication

technique and the high cost of electronic grade silicon wafers (200 – 300 μm thick at 99.9999999% purity)². Also, Si-based solar modules are rigid and heavy leading to strenuous and costly mechanical support installations. 2nd generation solar cells, also known as thin film solar cells (TFSC) use amorphous Si or other direct bandgap semiconductors (such as Cadmium Telluride or Copper-Indium-Gallium-Selenide) as the light absorbing material. These cells use only a few microns thin film deposited onto a plastic, glass or metal surface. 2nd generation solar cells allow flexible lightweight solar cells and offer high throughput commercial production. However, these cells also use rare and expensive elements^{3,4}. Thus, research on various 3rd generation photovoltaic technologies is currently in progress to develop low-cost solar cells using earth-abundant materials offering scalable manufacturing process for mass-production.

The 3rd generation perovskite-based solar cells use a hybrid organic-inorganic lead or tin halide-based light absorbing material (halogen could be: Iodine, Chlorine, or Bromine)^{5,6}. In this work, we have used a perovskite material – methylammonium lead iodide (MAPbI₃) as the light absorber. Crystal structure of the perovskite (MAPbI₃) is shown in Fig. 1. Compared to Si, MAPbI₃ is a direct bandgap light absorber and has a much higher light absorption coefficient⁵. Hence, light is absorbed within the perovskite more efficiently requiring a much thinner layer. Also, the fabrication of perovskite-based solar cell is much easier and cheaper compared to Si solar cells. Perovskite solar cells can be fabricated with inexpensive equipment making them commercially competitive in today's market. Unlike Si solar cells, perovskite solar cells require less than a micrometer thick (~200 times less than Si) coating thereby greatly reducing the material consumption and raw material cost. Also, it can be fabricated on top of a flexible plastic substrate which will allow roll-to-roll production at increased throughput. Using perovskite materials, it is also possible to fabricate semi-transparent solar cells that can be mounted onto windows, especially for sky scrapers⁷. These lightweight cells can also be integrated into everyday electronic accessories such as smart watches, backpacks, self-charging cellphones etc. For large panels, the installation would be easier without requiring bulky and expensive mechanical structures. In this work, we report on the fabrication, characterization, and resulting photovoltaic performance of the fabricated perovskite solar cells.

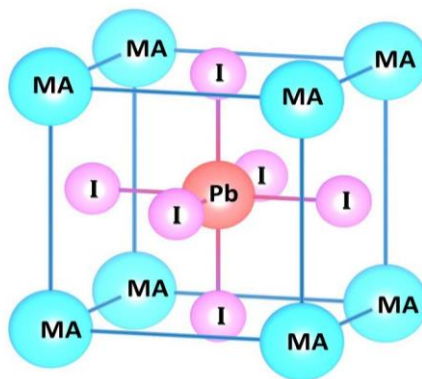


Figure 1. Methylammonium lead iodide (perovskite) crystal structure

2. Solar Cell Structure and Operating Principle

We have fabricated perovskite solar cells with a planar device structure using five layers. The complete device structure is shown in Fig. 2. The first layer is a 2 mm thick transparent soda-lime glass (SLG) substrate that is commonly used in regular windows or glass bottles upon which the cell is fabricated. On top of the glass substrate, there is an electrically conductive fluorine-doped tin oxide (FTO) coating which is the cathode for the device since it will receive and transport the electrons out of the cell.

The next layer is the Electron Collection Layer (ECL) for which we have used zinc oxide (ZnO). The ECL is responsible for extracting the excited electrons out of the perovskite material and transporting them to the electrically conductive FTO layer. Next is the light absorbing perovskite layer where electrons and holes are generated. After the perovskite, we deposited a hole transport layer (HTL), and for this layer, we have used Spiro-OMETAD (2,2',7,7'-Tetrakis-(N,N-di-4-methoxyphenylamino)-9,9'-spirobifluorene), which collects and transports the holes to the anode. Finally, silver back contact is used as the anode for the device. Sunlight ($h\nu$) enters through the SLG substrate and most of the incoming light is transmitted to the perovskite layer.

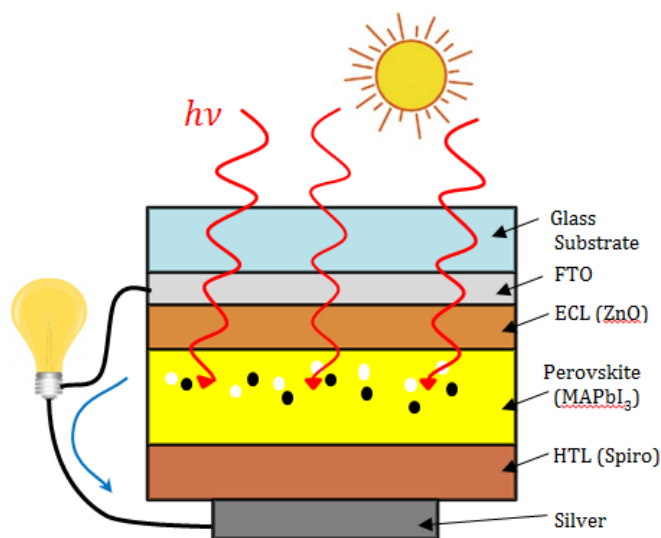


Figure 2. Planar perovskite solar cell structure

ZnO has a much higher bandgap ($E_g = 3.4 \text{ eV}$), hence light easily passes through it. As the light is absorbed by the perovskite layer, charge carriers (electrons and holes) are generated and are selectively diffused onto opposite directions due to the specific bandgap alignment of the ZnO ECL and Spiro HTL.

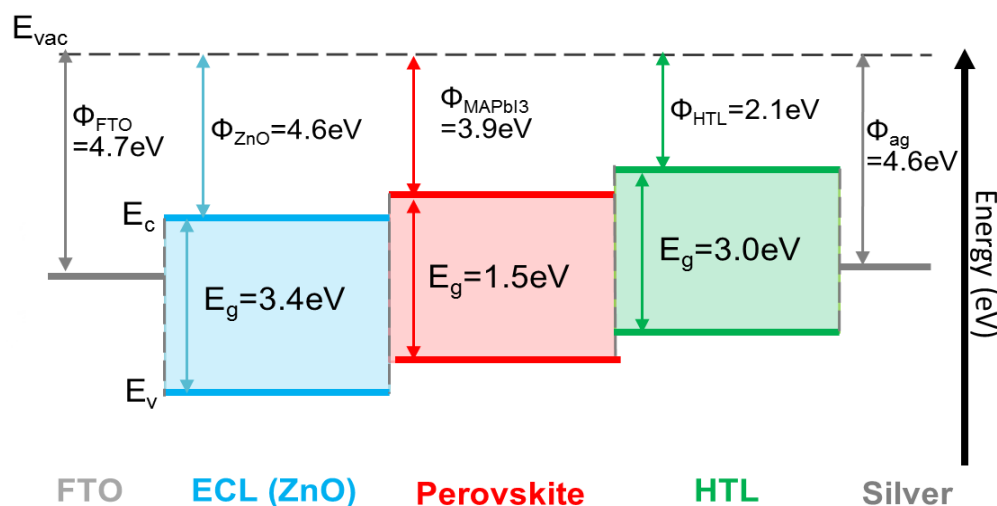


Figure 3. Energy band diagram of the fabricated perovskite solar cell

Operating principle of the perovskite solar cell is explained with the help of the energy band diagram as shown in Fig. 3. As the light is absorbed by the perovskite layer, it creates free electrons and holes. Electrons accumulate in the perovskite layer and because electrons always want to occupy the lowest possible energy level, they naturally begin to diffuse toward the conduction band of the ECL (ZnO). Electrons will be blocked from diffusing into the HTL (Spiro-MeOTAD) since its conduction band is at a higher energy state than the conduction band of the perovskite. Similarly, the holes in the valence band of the perovskite naturally begin to diffuse into the HTL (Spiro), because hole energy reduces upward. Hole diffusion toward the cathode (ZnO) is blocked due to the lower position of the ZnO valence band. Finally, electrons are transported to the FTO cathode and holes are transported to the Silver anode which can power an electrical load connected externally.

3. Solar Cell Fabrication

Fabrication of the perovskite solar cell is done on a fluorine-doped tin oxide (FTO) coated soda-lime glass (SLG). The major fabrication steps are schematically represented in Fig. 4. The FTO is a conductive layer on which the subsequent layers are fabricated. In the first step (step 1 in Fig. 4) of the fabrication process, a portion of FTO is etched off from the substrate to make room for anode contacts. The etched glass substrate is then cleaned thoroughly under sonication with soap water, organic solvents, and de-ionized (DI) water. The substrate is then dried in air. On this partially etched substrate, ZnO (the electron collection layer) is deposited using radio frequency (RF) sputtering (step 2 in Fig. 4). The etched FTO coated substrate is mounted on the rotating stage inside the sputtering chamber. Pressure inside the chamber was kept at 10 millitorr during the sputtering process. High-energy Ar ions are bombarded on the ZnO target; thereby lifting the target molecules that are deposited onto the FTO-coated glass substrate creating the ZnO film. Thickness of the ZnO layer depends on the amount of time the sputtering is done.

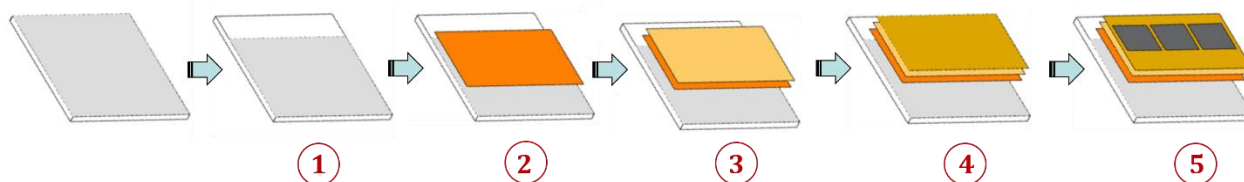


Figure 4. Major steps for the planar perovskite solar cell fabrication: (1) FTO etching, (2) ZnO deposition, (3) Perovskite deposition, (4) Hole transport layer deposition, and (5) Silver back contact deposition

After the deposition of ZnO layer, the deposition of light absorbing Perovskite layer is carried out (step 3 in Fig. 4). Deposition of perovskite layer is done by a low-cost, single-step spin-coating method followed by multistep annealing⁸. This technique is industrially scalable and would allow high-throughput mass production. In this method, the ZnO-coated substrate is mounted onto the spin-coater. The substrate is then rotated at a very high speed (between 2000-4000 rpm), while the precursor solution is dropped onto the rotating substrate. This results in the deposition of ~300 nm thick light absorbing perovskite layer. The substrate is then annealed at 110°C for 30 minutes. Annealing is carried out in a glovebox in multi steps with gradual increase in temperature until the perovskite layer crystallizes. The quality and surface morphology of the perovskite layer depends on the concentration of the precursor solution, the speed at which the substrate is rotated and the annealing process parameters.

Next step is the deposition of the hole transport layer (HTL) which also acts as the electron blocking layer. Spiro-OMETAD hole transport layer is also deposited by spin coating (step 4 in Fig. 4). The HTM is layer is deposited onto the perovskite layer at 2000 rpm. Finally, silver back contacts are deposited using thermal evaporation of silver (step 5 in Fig. 4). Silver pellets placed on a tungsten boat is heated inside the vacuum chamber for evaporation and subsequent deposition.

4. Results and Discussion

Fig. 5 (a) shows the optical image of the perovskite solar cell array fabricated on 1 sq. inch glass substrate. There are six isolated solar cells in the array as indicated in Fig. 5 (a). The shiny center regions are the photoactive regions of the solar cells, and the top and bottom regions are the contact areas (anode and cathode) of the cells. It is worth to mention that these are the first set of solar cells fabricated at the Kennesaw State University. Morphology of the light-absorbing perovskite layer of the cells was investigated under a scanning electron microscope (SEM) as shown in Fig. 5 (b). The SEM image (100 $\mu\text{m} \times 100 \mu\text{m}$ scan area) was taken at an acceleration voltage of 10 KV using a JEOL scanning electron microscope. The SEM image clearly shows formation of flake-like perovskite crystals. However, the formation of the perovskite layer was not very uniform and did not cover the entire surface. This is a major reason for the limited efficiency of the cells. Morphology plays a critical role in the resulting performance of thin film solar cells⁹. The morphology and quality of the perovskite crystals are highly dependent on the precursor solution concentration, rotation speed during the deposition, and annealing temperature for crystallization. Hence, optimization of each step is required to obtain a high quality film to further improve the cell efficiency. Also, we fabricated these cells under the ambient conditions in the laboratory. Moisture from the ambient is expected to have detrimental effects on the cell performance. We are currently building a set up to fabricate perovskite cells inside an inert glovebox to avoid the effects of humidity and achieve solar cells with higher power conversion efficiency.

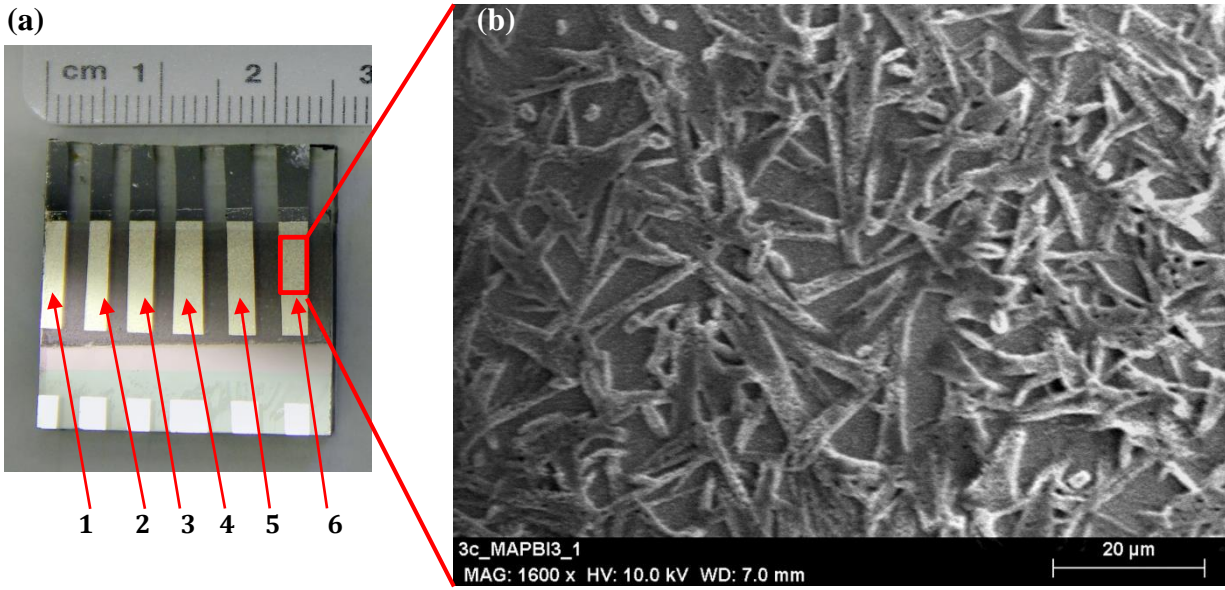


Figure 5. (a) Optical photograph of the fabricated solar cells and (b) SEM Image of the perovskite layer.

Electrical measurements of the fabricated PV devices were performed under the standard laboratory testing procedures for solar cells. Cell # 3 showed the best photovoltaic performance in this array and here we report the electrical parameters for this cell. The J-V (current density vs voltage) curve of the cell taken under AM 1.5 illumination and under dark conditions are shown in Fig. 6 (top).

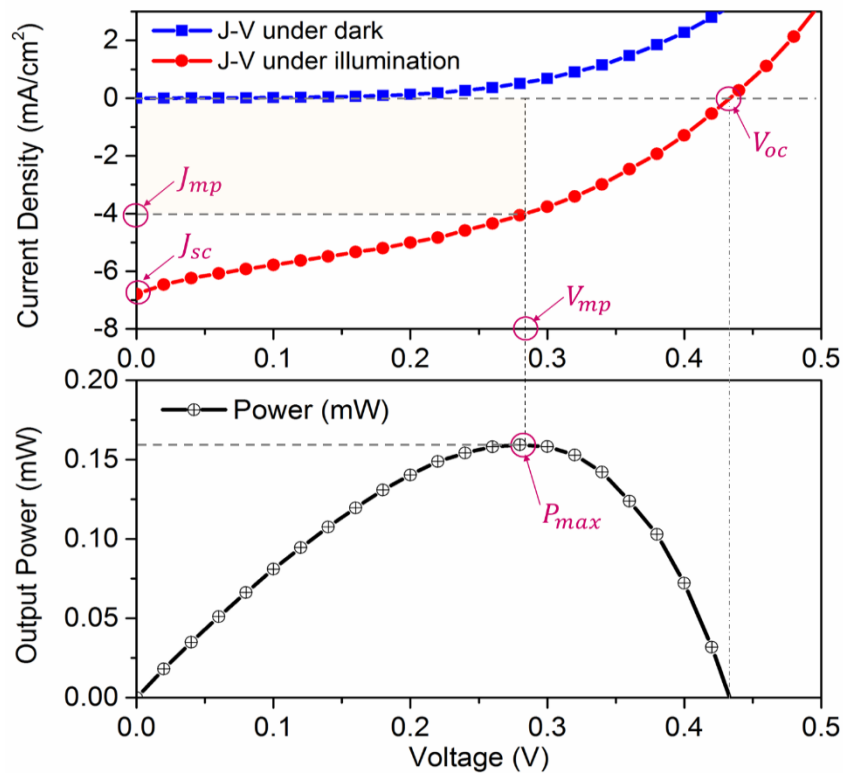


Figure 6. (top) J-V curves under AM1.5 and under dark, and (bottom) power curve of the fabricated cell.

V_{oc} is the highest possible voltage across the cell when no current flows through (open-circuit voltage). J_{sc} corresponds to the maximum current when the voltage across the cell is zero (short-circuit current). Furthermore, J_{mp} and V_{mp} are the respective current density and voltage across the cell at its maximum power point, as shown in the P-V (power vs voltage) graph in Fig. 6 (bottom). Equation 1 is used to find the maximum power output of the solar cell. Cell # 3 showed an open-circuit voltage of 430 mV and a short circuit current density of 6.79 mA/cm². The voltage and current at the maximum power point were found to be 280 mV and 4.07 mA/cm², respectively. Active area of the cell was estimated to be 0.14 cm².

$$P_{max} = V_{mp} \times I_{mp} \quad (1)$$

Fill factor (FF) of the solar cell is the ratio of the actual maximum power output to the theoretical maximum power. This can be expressed by Eq. 2. This ratio is also a measure of the overall quality for the cell. We have calculated a fill factor of 0.39 for the cell # 3. The solar cell efficiency is calculated using Eq. 3.

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

$$\eta = \frac{P_{max}}{P_{in}} \quad (3)$$

Table 1: Measured cell characteristics and electrical parameters

V_{oc}	J_{sc}	FF	V_{mp}	J_{mp}	P_{max}	η
0.43 V	6.79 mA/cm ²	39%	0.28 V	4.07 mA/cm ²	0.159 mW	1.14%

5. Conclusions and Future Work

In conclusion, hybrid perovskite solar cells have the potential to become the future PV technology due to their low production cost, much cheaper raw materials, and ease of fabrication. Compared to silicon solar cells, perovskite cells can be made at low processing temperatures and without the need of expensive equipment. Furthermore, 3rd generation perovskite technology has the opportunity to expand to more novel applications, specifically building-integrated photovoltaics (BIPV). In this research project, we have successfully fabricated thin film perovskite solar cells using low-cost processes and have proven the viability of this technology for easy, inexpensive, fast commercial production for mass-scale solar power generation. The solar cell arrays were fabricated on low-cost glass substrates under ambient laboratory conditions and the photovoltaic performance of the fabricated solar cells were measured under standard test conditions. An open-circuit voltage of 0.43 V, short-circuit current density of 6.79 mA/cm² and a power conversion efficiency of 1.14% is reported in this paper. Our cell efficiency was limited due to non-uniform perovskite film coverage which requires optimization of the film deposition parameters. We are currently in the process of optimizing the fabrication steps to improve the efficiency of these cells. Our future goal is to improve the performance of these solar cells and also fabricate the devices on plastic substrates to realize flexible perovskite solar cells.

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