Vapor deposited perovskites solar cells

Jiayan Huo

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Vapor deposited perovskites solar cells

by

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in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Major: Electrical Engineering

Program of Study Committee
Vikram L. Dalal, Major Professor

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Abstract

Owing to the advantages such as low cost and high efficiency, Perovskites solar cells have attracted widespread attention in the past few years. In this report, thermal co-evaporation method is employed for perovskites solar cell fabrication. We focus on light I-V characterization under different co-evaporation ratios in order to figure out the best conditions based on our experiment setup.
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1. Introduction

Energy plays a key role in human development. Tremendous energy is required in modern society for different purposes, such as heating houses, producing food, transportation and electronic consumption. Considering the fact that energy cannot be produced but always converted from one way to another, challenges arise with greater demand for energy by rapidly increased population. Another challenge that we are facing is relying too much on fossil fuels as shown in Fig. 1.

![Global Primary Energy Consumption 2017](image)

**Fig. 1 The primary energy consumption of the world by source in 2017[1].**

Oil, natural gas and coal are just solar energies that stored on earth for millions of years, which means they cannot be refilled in a short time. Thus, the desire for renewable energy, for example, solar energy, is universal. Photovoltaic effect refers to the solar energy converting into electricity directly based on semiconductor materials[2], which is the main working principle of solar cells.

1.1 Solar cells

Fig. 2 shows the cross-sectional view of a solar cell. Light shining on the solar cell and photons are absorbed by the semiconductor materials by which exciting electron from the valence band to the conduction band, generating the electron-hole pairs(EHPs). Usually, electron-hole pair trends to recombine and photon absorption energy will then be released as the thermal or radiative energy and no current or power can be utilized. However, the built-in electric field between a p-n junction makes the separation of EHPs happen and prevents this recombination.
By sandwiching p-n junction between metallic electrodes, generated carriers can be collected, producing current in the external load by movement and finally recombine with the counterpart on the other contact. Though silicon is the most popular material for photovoltaics, people never stop seeking new materials with even lower cost and higher efficiency.

### 1.2 Perovskites

High efficiency is one of the most exciting parts of perovskites, the power conversion efficiencies (PCE) can be more than 20% based on the lab calculations[4]. Advantages such as high absorption coefficient, high dielectric constant make perovskites a material for high efficiency solar cell with a great potential. Fig. 3 is the power conversion efficiency table for thin-film solar cells. In only a span of 6 years, the PCE of perovskites has improved from only 4% to nearly 20%, indicating the promising potential of perovskites solar cells.
A general perovskite crystal structure is in the form of $\text{ABX}_3$, where A and B are cation with +1 and +2 vacancies of the electron, respectively, and X is an anion which can be halogen. In our study, the perovskite structure is a combination of Cesium(A), Lead(B), Iodine and Bromine(X).

Multiple compositions can be served as solar cell absorption layer, such as $\text{CsPbI}_3$, $\text{CsPbI}_2\text{Br}$, $\text{CsPbBr}_2$ and $\text{CsPbBr}_3$. The bandgap of $\text{CsPbBr}_3$ is too large, leading to a low efficiency as the solar cell. $\text{CsPbI}_3$ with small bandgap can absorb more photons but it is very unstable to moisture and oxygen. Thus $\text{CsPbI}_2\text{Br}$ is chosen for our study since it is stable under the higher temperature for annealing.
2. Fabrication

In this section, the fabrication process of perovskites solar cell will be introduced, starting with cleaning steps for preparation. Focus is given on co-evaporation deposition and then followed by the fabrication process flow including electron, hole transportation layers, and aluminum contacts deposition.

2.1 Cleaning Steps

We use the standard cleaning process to prepare the substrate (Indium Tin Oxide (ITO) coated glass). First, sonicate the ITO in 5% wt surfactant bath at 60 °C for 60 minutes, followed by 20 minutes DI water hot bath for 3 times. Then sonicate in methanol, acetone and finally in isopropanol for 15 minutes each process. The cleaned ITO substrates will then be stored in the fresh methanol and cleaned by plasma to remove organic materials before further deposition.

2.2 Co-evaporation

Thanks to the co-evaporation method, perovskites manufacturing is highly scalable, controllable with a lower cost. Co-evaporation thermal evaporator is shown in Fig. 5. Like any other thin film deposition system, high vacuum environment is required for good quality which can be achieved with the help of roughing and turbopumps. At the same time, ion gauges are used for measuring the chamber pressure. Deposition rate, monitored by a crystal thickness sensor, is related to source temperatures which are precisely controlled by the current of two power supplies. Each source is equipped with a shutter to prevent evaporation when it is unnecessary.
The main idea of co-evaporation is that deposit CsBr and PbI₂ thin films with exact thickness alternatively by turn on/off the shutter for the specific source as shown in Fig. 6. The thickness ratio is 20:30 (CsBr: PbI₂) to form a Perovskites structure. Annealing the sample after the deposition will cause a reaction between thin layers, leading to Perovskites film.

After loading the sample into the chamber, purge the chamber for 10 times to remove the water and oxygen. Then turn on the power supplies and set to 6.5A and 5.5A for CsBr and PbI₂, respectively for first step preheating.
Wait for 20 minutes and raise the currents to 9.3A and 6.4A for second preheating, at the same time turn off the shutter of two sources. As temperature increases, current adjustments are required to match the temperature at which the deposition rates are desired based on previous data on the logbook. After another 20 minutes, turn on the substrate and CsBr shutter for first layer deposition. Then turn off the CsBr shutter when thickness reaches 20 nm, followed by turning on the PbI₂ shutter for the second layer for 30 nm. Repeat the previous steps until the total number of layer is 16, then the co-evaporation process is completed.

### 2.3 Solar cell fabrication process

Fig. 7 shows the fabrication process flow for Perovskite solar cells in this study. After cleaning ITO substrate described in section 2.1, 1.1 mg/mL PTAA(poly-triaryl amine) solution in toluene is spin coated on the ITO as the hole transportation layer(HTL) at 6000 rpm for 40 seconds followed by 10 minutes annealing at 150 °C. Perovskites is then deposited on PTAA based on co-evaporation method introduced in detail in section 2.2. Next 30 mg/mL PCBM(Phenyl-C61-butyric acid methyl ester) solution in chlorobenzene is spin coated on the Perovskites as the electron transportation layer(ETL) at 2000 rpm for 60 seconds, followed by 100 nm Aluminum deposition via the thermal evaporator.

![Fig. 7 Perovskite solar cell fabrication process flow](image-url)
In order to have a better understanding of perovskite solar cell after fabrication, it is necessary to look into the energy band diagram. Since PTAA is a p-type material and on the other hand, PCBM is an n-type material, a p-i-n structure, as well as an electric field throughout intrinsic layer, is formed. EHPs generated by photon absorption in Perovskites layer will be separated with the help of this electric field.

![Fig. 8 Structure and energy band diagram of Perovskites solar cell.](image)
3. **Light IV characterization**

To analyze the quality as well as to have a better understanding of principle operated by device, optical and electrical characterizations are required. In this chapter, only light IV characterization will be focused on.

### 3.1 Light generated current

The solar cell can be considered as a p-n junction, which means IV characteristic of the solar cell should be the same as a single p-n junction. The IV curve for p-n junction is well known as

\[
I = I_o [\exp\left(\frac{qV}{nkT}\right) - 1]
\]

Eq. 1

Where \( I_o \) is the saturation current density of the p-n junction, \( q \) is the elementary charge \( q = 1.6 \times 10^{-19} C \), \( k \) is the Boltzmann’s constant which is equal to \( 1.38 \times 10^{-23} J / K \), \( T \) is temperature in Kelvin, \( V \) is applied voltage across p-n junction, \( n \) is the ideal factor of p-n junction which is between 1 to 2.

However, light shining on the solar cell has the effect of shifting the IV curve down where power can be extracted from the diode as shown in Fig. 9.

Fig. 9 Light effects on solar cell IV curves[6].

Fig. 9(a) shows the IV curve under no light condition which is exactly same as that of a single diode. When the light is shining, the solar cell generates current due to absorption of the photons, adding a current source in
parallel with the diode which moves the IV curve into the fourth quadrant as shown in Fig. 9(b). The convention is to invert the current axis because the solar cell is generating the power and Eq. (1) becomes:

\[ I = I_L - I_0 \left[ \exp \left( \frac{qV}{nkT} \right) - 1 \right] \]  

Eq. 2

Where \( I_L \) is light generated current.

### 3.2 Important parameters in IV measurement

IV curve gives out important parameters for solar cell such as short circuit current \( I_{sc} \), open circuit voltage \( V_{oc} \), fill factor \( FF \), and PEC. Fig. 10 illustrates the relations between the IV curve and these parameters. As we can see in the figure, the short circuit current is the maximum current from a solar cell and occurs when the voltages across the device is zero, i.e., the interception of the current axis. The generation and collection of EHPs cause the short-circuit current. Likewise, the open circuit voltage is the maximum voltage when the net current is zero, i.e., the interception of the voltage axis. In Fig. 10, the blue curve shows the product of current and voltage, that is the output power, of the solar cell. Though \( I_{sc} \) and \( V_{oc} \) are the maximum value for current and voltage, the output power is zero at these two working points. And fill factor, \( FF \), is a parameter which determines the maximum power. \( FF \) can also be calculated graphically, that is the ratio of the largest rectangle that can fit in IV curve to the product of \( I_{sc} \) and \( V_{oc} \), which is given by:

\[ FF = \frac{V_{mp} \times I_{mp}}{V_{oc} \times I_{sc}} = \frac{areaA}{areaB} \]  

Eq. 3

![Fig. 10 Graph of solar cell output power and current](image)
The most common parameter to appraise the performance of a solar cell is the power conversion efficiency which is defined as the ratio of energy output to the input energy from the sunlight, given by

\[ \eta = \frac{V_{oc} \times I_{sc} \times FF}{P_{in}} \quad \text{Eq. 4} \]

Where \( P_{in} \) is the power input from the sun which is equal to 100 mW/cm\(^2\). PCE must be measured carefully since a lot of factors, for e.g. light spectrum, intensity or temperature, can have a great influence on PCE.

### 3.3 Experiment setup

As mentioned in the last section, critical requirements need to be met for PCE measurement, moreover, the Perovskites solar cell is also known to degrade in the presence of oxygen and moisture. As shown in Fig. 11, Glove Box providing nitrogen environment is used to get rid of the oxygen and moisture in the air.

![Fig. 11 Glove Box light IV measurement setup](image)

Full solar spectrum of 1.5AM is obtain by using a solar simulator, then light IV characterization can be realized via a probe station. The current flows through two contacts is swept and recorded by LabVIEW software under different voltage controlled by a power supply.
3.4 Data analysis

The purpose is to study the performance of solar cell under different ratios of CsBr to PbI₂. Based on the theoretical calculation, the best ratio to form CsPbI₂Br is around 20:30, we would go further with four different thickness ratios, 16:30, 20:30, 22:30 and 24:30 to see the how this will affect on IV characterization.

The best two contacts for each ratio are selected for comparison. Fig. 12 shows the light IV measurement for 4 different conditions.

**Fig. 12 IV curve for different ratios.**

Fig.12 (a), (b), (c), (d) are for the ratio of 16:30, 20:30, 22:30 and 24:30 respectively. One possible reason for the difference between the two contacts is that the thickness deposited cannot be exactly the same throughout the substrate. As shown in Fig. 6, one side may be CsBr rich and the other side may be PbI₂ rich. Table 1 contains the specific parameters for four situations, with which we can make further comparison. Fig. 13 is the column chart with error bar based on the information given in Table 1.
Combining the Table 1 and Fig. 12, it is obvious that ratio 16:30 is not able to form right Perovskites structure, causing significant decreasing on Voc and Isc which leads to a low PCE.

<table>
<thead>
<tr>
<th>Thickness ratio</th>
<th>Efficiency(%)</th>
<th>Voc(V)</th>
<th>FF</th>
<th>Isc(mA)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>contact1</td>
<td>contact2</td>
<td>average</td>
<td>std</td>
</tr>
<tr>
<td>16:30</td>
<td>1.62862</td>
<td>1.45754</td>
<td>1.54308</td>
<td>0.12097</td>
</tr>
<tr>
<td>20:30</td>
<td>8.08284</td>
<td>8.08119</td>
<td>8.08202</td>
<td>0.00117</td>
</tr>
<tr>
<td>22:30</td>
<td>6.63434</td>
<td>6.63516</td>
<td>6.63475</td>
<td>0.00058</td>
</tr>
<tr>
<td>24:30</td>
<td>6.79437</td>
<td>6.82994</td>
<td>6.81216</td>
<td>0.02515</td>
</tr>
</tbody>
</table>

Fig. 13 Column chart of efficiency, FF, Voc and Isc for four situations.

As ratio increasing to 20:30, the best performance is achieved among 4 situations in this study with 8.04% PCE, 0.98V Voc and 1.34 mA Isc on average. Based on experiment results, 22:30 is way off the best ratio point, decreasing the PEC by 1.27 % and FF by 8 compared with 20:30 situation, though no significant changes in Voc and Isc. It is interesting that when ratio goes further to 24:30, nevertheless Voc and Isc decrease a little, we do have a better FF and PEC compared with 22:30 condition.
4. Conclusions

During this study, we have gone through the working principle and important parameters to evaluate the performance of the solar cell. Then we realized the control of Perovskites layer by using co-evaporation of CsBr and PbI₂, since light IV characterizations show that the performance of the devices is close to each other with the same ratio of two materials.

Then all other variable parameters are controlled such as annealing temperature of PTAA and Perovskites, the devices are fabricated under different ratio ranging from 16:20 to 24:30. As expected, the ratio does have a great effect on Perovskite layer, especially when lacking of CsBr. PCE is significantly decreased under 16:30 condition. Though slightly difference between 22:30 and 24:30, the best ratio in this study for Perovskite solar cell is 20:30 with 8.04% PCE on average for two contacts.

In conclusion, co-evaporated Perovskite solar cell is sensitive to the ratio of two deposited materials. For higher efficiency, precisely control during the co-evaporation needs to be realized. With a smaller step on ratio difference research, it is possible to lead us to an even better ratio other than 20:30 in the future.
Reference


