The Influence of CH$_3$NH$_3$I/ PbI$_2$ Ratio on The Absorption and Electrical Characteristics of Perovskite/Polymer Solar Cell

Shobih$^{1,*}$, Erlyta Septa Rosa$^1$, and Endang Lestari$^2$

$^1$Research center for Electronics and Telecommunication Indonesian Institute of Sciences
Kampus LIPI Gd. 20 Jalan Sangkuriang Bandung 40135 West Java Indonesia
$^2$Faculty of Mathematics and Natural Sciences Sebelas Maret University
Jl. Ir. Sutami No. 36A, Solo 57126 Jawa Tengah Indonesia

* Corresponding author, tel/fax: 022-2504661/2504659, email: sho99bih@gmail.com
Co-author 1, email: erlytasr@gmail.com
Co-author 2, email: endanglestari46@gmail.com

ABSTRACT

In this paper, we report a simple solution processed perovskite/polymer solar cell using CH$_3$NH$_3$PbI$_3$ as an absorber, PCBM (6,6 phenyl C61-butyric acid methyl ester) as an electron transport layer, and PEDOT:PSS (poly (3,4-ethylene dioxy thiophene):poly(styrene sulfonate)) as a hole transport layer. The absorber solution was prepared by mixing of CH$_3$NH$_3$I (methyl ammonium iodide) with PbI$_2$ (lead iodide) in DMF (dimethyl formamide) solvent. The absorber, electron transport, and hole transport layers are deposited by spin coating of the solutions. In order to obtain the optimum optical and electrical characteristics, the mixture of CH$_3$NH$_3$I and PbI$_2$ are varied by the molar ratio of 1:1, 1:3, and 3:1, respectively. Because of CH$_3$NH$_3$PbI$_3$ layer degrades, the fabricated cells have low performance. However, the cell using a molar ratio of 1:1 CH$_3$NH$_3$I and PbI$_2$ gives the best electrical characteristics, results in an open circuit voltage of 0.04 V, a short circuit current density of 0.08 mA/cm$^2$, and a power conversion efficiency of 0.002 %.

Keywords: perovskite solar cell, CH$_3$NH$_3$PbI$_3$, CH$_3$NH$_3$I, PbI$_2$, PCBM, PEDOT/PSS

ABSTRAK

Di dalam tulisan ini kami melaporkan proses pembuatan sel surya berbasis perovskite/polimer yang diproses dalam bentuk larutan. Sel surya perovskite/polimer menggunakan CH$_3$NH$_3$PbI$_3$ sebagai lapisan penyerap cahaya, PCBM (6,6 phenyl C61-butyric acid methyl ester) sebagai lapisan transport elektron, dan PEDOT:PSS (poly (3,4-ethylene dioxy thiophene):poly(styrene sulfonate)) sebagai lapisan transport hole. Larutan penyerap cahaya dibuat dengan mencampurkan CH$_3$NH$_3$I (metil ammonium iodida) dengan PbI$_2$ (timbal iodida) berupa larutan DMF (dimetyl formamida). Lapisan-lapisan penyerap cahaya, transport elektron, dan transport hole dibuat dengan cara mendeposikan larutan-larutan tersebut menggunakan metoda spin coating. Untuk mendapatkan karakteristik listrik dan optik yang optimum campuran CH$_3$NH$_3$I dan PbI$_2$ divariasikan dengan perbandingan molar masing-masing 1:1, 1:3, dan 3:1. Karena lapisan lapisan perovskite CH$_3$NH$_3$PbI$_3$ mengalami degradasi, sel yang dibuat mempunyai perfomansi rendah. Namun demikian, sel yang menggunakan perbandingan molar CH$_3$NH$_3$I dan PbI$_2$ 1:1 memberikan karakteristik listrik yang paling baik, dengan tegangan sirkit terbuka sebesar 0,04 V, densitas arus sirkit pendek sebesar 0,08 mA/cm$^2$, dan efisiensi konversi energi sebesar 0,002 %.

Kata Kunci: sel surya perovskite, CH$_3$NH$_3$PbI$_3$, CH$_3$NH$_3$I, PbI$_2$, PCBM, PEDOT:PSS
I. INTRODUCTION

Nowadays hybrid halide perovskites enable outstanding photovoltaic performance due to their good electrical and optical properties. Hybrid perovskites are solids formed by an inorganic framework, usually a metal halide, intercalated by organic cations filling its voids, resulting in a polycrystalline material with octahedral arrangement. The formation of the crystals occurs spontaneously, driven by the self-assembly of the two precursors upon deposition [1]. One of the known perovskite material that is often used for the solar cells preparation is methyl ammonium lead iodide (CH₃NH₃PbI₃).

Initially CH₃NH₃PbI₃ is utilized as sensitizers for liquid-state dye-sensitized solar cells in the form of nanoparticles which self-organized on the surface of a mesoporous TiO₂ films, replacing the dye in a liquid electrolyte-based device [2]. CH₃NH₃PbI₃ has a band gap of 1.55 eV, close to the optimum band gap for single junction which gives maximum efficiency (1.4 eV). This coupled with the good extinction coefficient (one order of magnitude higher than standard dyes, allows excellent external quantum efficiency spectra (EQE) until 800 nm, harvesting the photons in the visible range and part of the near-infrared of the solar spectra [3]. However, by this device structure the performance of these electrolyte-based perovskite solar cells degraded within only a few minutes due to the rapid decomposition of the hybrid halide perovskite in the redox electrolyte [4]. To solve this problem, Kim et al. developed solid-state perovskite-sensitized solar cells employing spiro-MeOTAD as the hole transport material (HTM), mesoscopic TiO₂ film as the electron transport material (ETM) and CH₃NH₃PbI₃ as a sensitizer forming perovskite solar cells with a planar structure. By using this structure, it was obtained more stable cell with higher efficiency[5].

The use of mesoscopic TiO₂ as ETM requires high temperature processing, and as it has been known that the concentration and chemical composition of precursor solution strongly influence the thickness and microstructure of lead halide thin film and further more to the photovoltaic performance of the cells [6]. In order to be processed at low temperatures, here we report the fabrication of perovskite/polymer solar cells using CH₃NH₃PbI₃ as an absorber, PCBM (6,6 phenyl C₆₁-butyric acid methyl ester) as an electron transport layer, and PEDOT/PSS as a hole transport layer. The device comprises a glass/ITO/PEDOT:PSS/CH₃NH₃PbI₃/PCBM/Ag structure, where perovskite and polymers are deposited by spin coating. Spin-coating is a well-known, rapid technique used for producing uniform, quality thin films on a variety of substrates. This coating method is widely used in fabrication of organic electronics and optical device coatings, among many others [3]. In this research, we prepared a thin film of the low temperature solution-processed organometallic trihalide perovskite (CH₃NH₃PbI₃) absorber by mixing CH₃NH₃I (methyl ammonium iodide) with PbI₂ (lead iodide) in DMF (dimethyl formamide) solvent. The absorber, electron transport, and hole transport layers are deposited by spin coating of the solution. In order to obtain the optimum electrical characteristics, the mixture of CH₃NH₃I and PbI₂ are varied by the molar ratio of 1:1, 1:3, and 3:1, respectively.

II. EXPERIMENTAL SECTION

2.1 Materials

In this experiment we use materials as follow, indium tin oxide (ITO) coated glass substrates (Sigma Aldrich, 12 Ω/sq), HCl (Merck, 37%), CH₃NH₃I (Sigma Aldrich), PbI₂ (Sigma Aldrich), DMF (Sigma Aldrich), PCBM (Sigma Aldrich), PEDOT:PSS (Sigma Aldrich), aerosol spray paint (PT Difan Prima Paint), paint thinner solution, acetone (Sigma Aldrich), isopropyl alcohol, and silver wire (Sigma Aldrich).

2.2 Instrumentation

All solution deposition processes are carried out on spinner coating equipment (Integrated Tecnologies, Inc.). Dryings of deposited layers are carried out in vacuum oven (The Grieve Corporation). Digital hotplate/stirrer (Cimarec) is used to mix perovskite solution. Deposition silver metal is carried out in Auto 306 Vacuum Coater (Edwards). Ultraviolet spectrophotometer (Hewlett Packard 8453 Agilent Technologies) is used to measure the absorbance of perovskite layer. Solar simulator (Oriel Newport) is used as light source, and National Instrument source meter for measuring I-V characteristics.
2.3 Procedure

Fabrication of perovskite/polymer solar cells

In this work all chemicals are commercially available and used without further purification. The substrates used are indium tin oxide (ITO) coated glass in 12.5×12.5 mm dimensions with a sheet resistance of 12 Ω/sq. ITO is a transparent conductive oxide which serves to drain the generated hole. To avoid short circuit of the cell, it is necessary to form an ITO pattern by etching ITO partially. A black aerosol spray paint is sprayed on the ITO surface which has been patterned by adhesive tape mask previously. The substrates are then dried in room temperature overnight, and when they have dried, the masks are removed. The next step is etching process which aims to eliminate undesired ITO layer. Etching process is performed by dipping the substrates into 50% HCl solution for 5 minutes, followed by washing in DI water and dried. The remaining paint then removed by immersing the substrates into paint thinner solution, acetone, isopropyl alcohol, and DI water, respectively, for 10 minutes in ultrasonic bath.

The next step is coating of Poly(3,4-ethylene dioxy thiophene)-poly(styrene sulfonate) (PEDOT:PSS) which serves as a hole transport layer. PEDOT:PSS coating is carried out by spin coating method at a rotation speed of 1000 rpm for 60 seconds. The PEDOT:PSS layer is then dried in a vacuum oven at 120 °C for 60 minutes.

The organometallic halide perovskites are made by mixing CH₃NH₃I with PbI₂ in 1 mL DMF. The mixtures of CH₃NH₃I and PbI₂ are varied by the molar ratio of 1:1, 1:3, and 3:1, and stirred at room temperature for 24 hours. Subsequently, the mixtures are spin coated onto PEDOT:PSS layer at 2000 rpm for 30 seconds and annealed in a vacuum oven at 100 °C for 45 minutes.

The polymer solution is prepared by dissolving of 20 mg PCBM in 1 mL chlorobenzene and stirred for 60 seconds. The polymer layer is deposited onto perovskite layer by spin coating of the PCBM solution at 1000 rpm for 30 seconds, and then annealed in a vacuum oven at 100 °C for 10 minutes. Finally, a 60 nm-thick silver electrode is deposited by thermal evaporation onto the polymer layer at vacuum pressure of 5×10⁻⁵ mBar. The active area obtained of each cell is about 5.5×6 mm. The final structure of perovskite/polymer based solar cells is shown in Figure 1.

![Figure 1. The structure of the fabricated perovskite/polymer solar cells](image)

2.4 Characterization

The ultraviolet-visible absorption spectra of the CH₃NH₃PbI₃ layer are recorded by the ultraviolet spectrophotometer (Hewlett Packard 8453 Agilent Technologies). The photovoltaic performance of solar cells is measured with National Instrument source meter which is controlled by Lab-view software and using solar simulator (Oriel, Newport, USA, AM1.5) as a light source. The irradiation intensity is adjusted to 50 mW/cm² at 25 °C.

III. RESULTS AND DISCUSSION

3.1 Absorption Spectra of CH₃NH₃PbI₃

Figure 2 presents ultraviolet-visible absorption spectra of the CH₃NH₃PbI₃ layers resulted from the precursor solution of the mixed CH₃NH₃I and PbI₂ in the molar ratio of 1:1, 1:3, and 3:1, respectively. It can be seen that all perovskite layers exhibit a broad range of optical absorption with from 280 to 440 nm. According to the previous works [7], [8], the absorbance spectra of CH₃NH₃PbI₃ perovskite layer has a sharp
increase on the right edge of the curve at a wavelength (cut off wavelength) of about 780-800 nm. This wavelength is attributed to the band gap value of CH3NH3PbI3 perovskite of about 1.55 eV. However, in this study the obtained absorbance spectra, has cut off wavelength in the range of about 440-540 nm (average = 480 nm). This wavelength value corresponding to the band gap of about 2.6 eV, which is the band gap of PbI2. Therefore, it can be ascertained that the perovskite layer formed mainly dominated by PbI2, and contains only a little of CH3NH3PbI3. As a note that in this work, the preparation of CH3NH3PbI3 perovskite layer, from mixing CH3NH3I and PbI2 precursors until the deposition using a spin coating technique all performed in atmospheric environment without using a glove box. According to Niu et.al. [8], CH3NH3PbI3 perovskite will be decomposed back into CH3NH3I and PbI2 when exposed to humid air. They stated further that when CH3NH3PbI3 perovskite layer is exposed to humid air under sun light for 18 hours the cut off wavelength of the absorbance spectra will shift sharply from the origin, from the wavelength of 800 nm shifts to a wavelength of 540 nm, due to CH3NH3PbI3 decomposed into CH3NH3I and PbI2. The wavelength less than 520 nm corresponds to the PbI2 band gap of about 2.6 eV [8].

![Figure 2. Ultraviolet-visible absorption spectra of the CH3NH3PbI3 layer resulted from the precursor solution of the mixed CH3NH3I and PbI2 in the molar ratio of 1:1, 1:3, and 3:1](image)

Generally, there are two peaks between the wavelength ranges, first peak at shorter wavelength presumed for CH3NH3I, and second peak at longer wavelength for PbI2. The absorption peaks of each ratio are listed in Table-1. The first peak absorption of the molar ratio of 1:1 is located at 320 nm, and the second peak is located at ~405 nm. When the PbI2 content increased, the first peak does not shift. However, the second peak shifts to blue region ~418 nm. If the PbI2 content decreased, both of absorption peaks do not shift significantly. The highest absorption intensity is obtained by the 1:1 molar ratio. The intensity decreases with the increasing both of the CH3NH3I and PbI2 content. However, the increasing of PbI2 amount significantly influences the absorption intensity of the layer and shifts the cut off wavelength of the absorption spectra to higher wavelength compared to that of CH3NH3I amount. Higher cut off wavelength indicates that the layer contains more CH3NH3PbI3.

3.2. Solar cells performance

The photovoltaic performance parameters of perovskite/polymer solar cells based on CH3NH3PbI3/PCBM are listed in Table 2. From the table, it is clear that the resulted values are very inferior if compared with the results of experiment which was carried out by Jeng et. al. [9]. By using same cell’s configuration, they found greater values for all electrical characteristic parameters, where open-circuit voltage (VOC), short circuit photocurrent (JSC), and power conversion efficiency (PCE) are 0.60 V, 10.32 mA/cm², and 3.9%, respectively. First possibility causing very low performance is the quality of the perovskite layer which is not dominated by CH3NH3PbI3. As discussed before, the cells fabrication was not carried out under controlled
atmospheric conditions but exposed in humid air, so there was degradation of CH$_3$NH$_3$PbI$_3$ layer into CH$_3$NH$_3$I and PbI$_2$. Therefore, with high PbI$_2$ content, only a little portion of semiconductor with narrow band gap which can absorb light to produce significant current. Second possibility is thickness of perovskite layer which is allegedly greater than 100 nm, electron-hole (charge carriers) diffusion length of the CH$_3$NH$_3$PbI$_3$[10]. In the thick perovskite layer, the generated charge carriers can recombine again before the carriers can reach to the respective electrode contact, resulting in the low current. Another possibility is non-uniform and uneven layers in the planar structure cell. This case can result in interpenetrating layers, so energy level of each layer involved in the cell is disturbed, causing the low $V_{OC}$.

Table 1. Absorption peaks and the absorbance of of the CH$_3$NH$_3$PbI$_3$ layer resulted from the precursor solution of the mixed CH$_3$NH$_3$I and PbI$_2$ in molar ratio of 1:1, 1:3, and 3:1.

<table>
<thead>
<tr>
<th>CH$_3$NH$_3$I : PbI$_2$ Molar Ratio</th>
<th>Absorption Peaks (nm)</th>
<th>Absorbance(a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>First</td>
<td>Second</td>
</tr>
<tr>
<td>1:3</td>
<td>317</td>
<td>418</td>
</tr>
<tr>
<td>1:1</td>
<td>320</td>
<td>405</td>
</tr>
<tr>
<td>3:1</td>
<td>318</td>
<td>400</td>
</tr>
</tbody>
</table>

However, in general, Table 2 reveals that molar ratio of 1:1 gave higher performance than the others, with $V_{OC}$, $J_{SC}$, and PCE are 0.04 V, 0.08 mA/cm$^2$, and 0.002%, respectively, due to higher optical absorption and has greater CH$_3$NH$_3$PbI$_3$ content as discussed before. So the perovskite layer with molar ratio of 1:1 has better ability than 1:3 and 3:1 to absorb photons and convert it into current. The high CH$_3$NH$_3$I content significantly contributed on the decrease of the $J_{SC}$ and the $V_{OC}$. While with the higher PbI$_2$ content, the $J_{SC}$ and $V_{OC}$ are not changed.

Table 2. Electrical characteristic of CH$_3$NH$_3$PbI$_3$ solar cells under 50 mW/cm$^2$ irradiation

<table>
<thead>
<tr>
<th>CH$_3$NH$_3$I : PbI$_2$ Molar Ratio</th>
<th>$V_{OC}$ (Volt)</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 : 1</td>
<td>0.039</td>
<td>0.085</td>
<td>0.0020</td>
</tr>
<tr>
<td>1 : 3</td>
<td>0.039</td>
<td>0.083</td>
<td>0.0012</td>
</tr>
<tr>
<td>3 : 1</td>
<td>0.019</td>
<td>0.024</td>
<td>0.0010</td>
</tr>
</tbody>
</table>

IV. CONCLUSION

We prepared a simple solution processed perovskite/polymer solar cell using CH$_3$NH$_3$PbI$_3$, PEDOT:PSS and PCBM as an absorber, an hole transport layer and an electron transport layer, respectively. The absorber solution was prepared by mixing in varied ratio of CH$_3$NH$_3$I with PbI$_2$ in DMF solvent. Because of CH$_3$NH$_3$PbI$_3$ layer degraded into CH$_3$NH$_3$I with PbI$_2$, the fabricated cells have low performance. However, the cell using a ratio of 1:1 CH$_3$NH$_3$I and PbI$_2$ gave the best electrical characteristics, resulted in an open circuit voltage of 0.04 V, a short circuit current density of 0.08 mA/cm$^2$, and a power conversion efficiency of 0.002%.

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