Optimization of rotation speed for CuSCN hole transport layer in perovskite solar cell using spin coating

J Sulistianto, R W Purnamaningsih, and N R Poespawati*

Department of Electrical Engineering, Universitas Indonesia, Depok 16424, Indonesia

Email: pupu@eng.ui.ac.id

Abstract. Organometal lead halide has gained immense popularity as solar cell active layer due to their unique optical characteristic, low cost, and simple fabrication technique. Transport layer is important component to maximize overall performance of perovskite solar cell. Inorganic CuSCN have good transparency and high hole mobility as p-type transport layer for perovskite solar cell. In this work, we investigated the effect of rotational speed on spin coating to grow CuSCN thin film. Rotational speed is ranging from 1000 rpm to 4000 rpm. The best performing devices is when CuSCN layer deposited at 2000 rpm with V_{OC} 0.96 V, I_{SC} 5.29 mA, and FF 0.48.

1. Introduction
The escalation of world population growth is becoming an attraction for development of new energy sources to meet global energy demand. Photovoltaic based on crystalline silicon is one of the promising devices and has been investigated in past 40 years [1]. Over the last few years, the emerging solar cell such as dye sensitized solar cell (DSSC) and other organic solar cell are also continuously investigated to comply high efficiency and low cost solar energy sources [2]. Perovskite is organic-inorganic material that has crystal structure of ABX_3 and has similar structure with CaTiO_3. First organometal halide perovskite as solar cell active layer was performed by Kojima et al at 2009 [3]. They used organic-inorganic lead halide perovskite compounds CH_3NH_3PbX_3 (X = I, Br) as active layer in similar fabrication method to DSSC. The result was a cell with efficiency 3.81% by using CH_3NH_3PbI_3 and TiO_2 as photoanode. These research gained immense popularity and extensively investigated by researcher until 2018, the power conversion efficiency (PCE) of perovskite solar cell can exceed 20% [4]. Such rapid improvement is also caused by low-cost, simple fabrication technique (solution processed or doctor blade), long diffusion length and high absorption coefficient of lead-based perovskite which meet the requirements for mass production and industrial applications [5–7].

From their first appearance, significant progress has been made with various device configurations, including the improvement of transport layer. PEDOT:PSS, spiro-OMETAD, P3HT, and PTAA is organic transport layer and widely used as hole transport layer (HTL). Advantage of using organic material is high performance solar cell can be achieved. However, organic transport layer easily degrades under open environment and accelerates the degradation of perovskite film [8]. In addition to high efficiency, stability of perovskite solar cell must be considered for long term use in applications. Several studies has been conducted and the result mentioned that inorganic material can be used as transport layer. CuSCN [9] and NiO_x [10] were utilized as p-type transport layer, and TiO_2 [11] and
were used as electron transport layer (ETL). These metal oxides are known in its stability at moisture and possesses higher mobility carrier compared to other types.

CuSCN is inorganic $p$-type which has higher hole mobility ($0.01 - 0.1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) and better transparency compared to organic transport layer spiro-OMETAD ($4\times10^{-5} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) [13]. Solution processed in low temperature and simple fabrication method becomes an advantage to apply it in flexible surfaces. There have been several reports about CuSCN as hole transport with different method of fabrication and device configuration. Ye et al reported an inverse architecture with PCE 15.6% using electrodeposited method for forming CuSCN thin film [14]. The effect of thickness and annealing temperature of CuSCN has also been studied [15]. Fan et al improved the CuSCN surface by modified annealing technique to obtain high quality film [16] and then Xiong et al improved CuSCN surface by using PEDOT:PSS to form bilayer HTM [17]. However, it has been observed that reported studies focused on the investigation in inverted configuration and novel technique to improve efficiency instead of $n$-$i$-$p$ architecture with simple fabrication method that has been investigated in this paper. Thickness of CuSCN thin film was already studied but not exclusively for optimization of spin coat rotation speed in CuSCN layer. Therefore, in this research we present optimized rotation speed of CuSCN as HTL in perovskite solar cell using spin coating method.

2. Experimental method

2.1. Device structure

In this research, perovskite solar cell was fabricated based on figure 1. FTO coated glass slide was used as front contact and back contact. The device was made on top of fluorine doped tin oxide (FTO) coated glass slide. As an $n$-type transport layer, mesoporous TiO$_2$ was used which also works as scaffold for perovskite layer. For the optimization, the rotation speed of spin coat has been varied when deposited CuSCN thin film. Different rotation speed will change the thickness of thin film and control the thickness of CuSCN layer. Furthermore, spin coating is one of an important process to obtain a good thin film.

![Figure 1](image.png)

Figure 1. Fabricated perovskite solar cell structure.

TiO$_2$ was used as electron transport layer because of their ability to collects electron from perovskite into the FTO glass front contact. Due to its wide bandgap ($E_g = 3.2 \text{ eV}$), TiO$_2$ provides great transparency as a thin film, thus it permits more light to perovskite as an active layer. Furthermore, TiO$_2$ has excellent photocurrent response for visible light when it used together with perovskite [11]. As a hole transport layer in this device, CuSCN was used to collect holes from active layer. It has wide band gap ($E_g = 3.6 \text{ eV}$) which has excellent transparency and suitable energy level ($E_{VB} = -5.4 \text{ eV}$ and $E_{CB} = -1.8 \text{ eV}$) for collecting hole [15].

Figure 2 shows energy band diagram of fabricated devices. FTO glass has an energy level -4.4 eV [18]. Energy level for TiO$_2$, perovskite, and carbon are known from research by Wang et al [19]. TiO$_2$ energy level is -7.3 eV and -4.1 eV for valence and conduction band respectively. Energy level of perovskite is -5.43 eV and -3.93 eV for valence band and conduction band respectively. Carbon has an energy level -5 eV. Perovskite will generate charge when exposes to light and creates electron-hole
pairs. Electron from perovskite conduction band will be transferred to TiO$_2$ conduction band because of lower energy level in TiO$_2$ conduction band.

![Energy level of perovskite solar cell](image)

**Figure 2.** Energy level of perovskite solar cell.

These mechanisms work similarly for hole from perovskite. Hole will move from perovskite valence band to CuSCN valence band due to higher energy level in CuSCN valence band. Carbon was being used to improve performance of hole transfer from HTL to FTO glass.

2.2. Device fabrication

In this research, perovskite solar cell was fabricated on a 2 x 1.5 cm$^2$ FTO glass. Before fabrication process were conducted, all FTO glass was cleaned using deionized water, acetone, and ethanol, respectively in ultrasonic cleaner bath for 5 minutes each. TiO$_2$ solution was prepared using 0.2 M titanium (IV) isopropoxide (TTIP) and 0.1 M HCl in anhydrous ethanol. The resultant solutions then stirred for 20 minutes in room temperature. Perovskite solution was prepared from precursor made of methylammonium iodide (MAI) 1.5 M diluted in N,N-dimethylformamide (DMF) and 0.5 M lead(II) chloride. Perovskite precursor then stirred at temperature 80$^\circ$C for 1 hour before deposited and the solution would become yellow. CuSCN solution was made using 6 mg copper (I) thiocyanate dissolved in 1 ml dipropyl sulphide (DPS) followed by stirring the solution for 8 hours at room temperature.

Fabrication procedure is shown in figure 3. TiO$_2$ was deposited to FTO glass through spin coating at 2000 rpm for 30 s followed by annealing at 425$^\circ$C for 30 minutes. Afterward, the sample was being waited until it was cooled down to room temperature. Perovskite solution then deposited above FTO/TiO$_2$ by spin coating with rotation speed 1000 rpm for 30 s. Sample then being dried at 120$^\circ$C for 15 minutes and yellow solution of perovskite precursor would turn into grey.

![Step by step fabrication of perovskite solar cell](image)

**Figure 3.** Step by step fabrication of perovskite solar cell.
All samples were fabricated with same configuration except for CuSCN layer which has different rotation speed for each sample. CuSCN was made above perovskite layer by spin coat CuSCN solution at 1000 – 4000 rpm for 30 s followed by annealing at temperature 80°C for 15 minutes. After CuSCN layer was made, carbon powder sprinkled on top of it. Finally, clean FTO glass placed above carbon layer as electrode contact.

3. Result and discussion

Dark I-V curve has been obtained from semiconductor parameter analysis (SPA) HP4145B. Solar cell performance under illumination was performed directly under sun with average irradiance of 800 W/m² and measured using multimeter. Photovoltaic parameters of varied CuSCN rotation speed are shown in table 1. Typical I-V curve also is shown in figure 4. All devices perform same fabrication method except in rotational speed for CuSCN layer.

Devices with 1000 rpm and 2000 rpm exhibited better performance in every parameter compared to high speed rotation at 3000 rpm and 4000 rpm. Best result from all devices was obtained by using rotational speed 2000 rpm for CuSCN layer with fill factor (FF) 0.48, short circuit current (Isc) 5.29 mA, and open circuit voltage (Voc) 0.96 V. This result is in line with research that has been conducted by Ye et al [14]. It was reported that thin CuSCN film would generate low performance on photovoltaic parameter compared to thicker one. It is important to noting that rotational speed on spin coating has direct consequences to film thickness. Generally, the thickness of spin coated film is proportional to the inverse of the spin speed [20]. This means that low rotation speed will produce thicker film than high rotation speed.

Table 1. Photovoltaic parameters of varied CuSCN rotation speed of perovskite solar cells.

| Variation | Voc (V) | Isc (mA) | FF  |
|-----------|---------|----------|-----|
| 1000 rpm  | 0.96    | 3.82     | 0.43|
| 2000 rpm  | 0.96    | 5.29     | 0.48|
| 3000 rpm  | 0.54    | 1.88     | 0.37|
| 4000 rpm  | 0.62    | 2.99     | 0.36|

Low photovoltaic performance for 3000 rpm and 4000 rpm can be attributed to thickness of CuSCN layer was too thin. CuSCN with thickness lower than 40 nm will produce inhomogeneous and rough surface that lead to inefficient charge transport as mentioned by Jung et al [15]. Therefore, smooth CuSCN layer need to be achieved in order to get high performance of perovskite solar cell.
The fabricated cell has relatively low performance compared to similar structure demonstrated by Qin et al [13]. This might be caused by fabrication process were perform outside clean room or glove box. Moisture and high humidity in not controlled environment can caused perovskite layer degrade. Moisture will decompose MAPbI\textsubscript{3} into PbI\textsubscript{2} and make perovskite layer turn back into yellow. Nevertheless, it can take into account that perovskite solar cell is possible to fabricate in such environment.

Inferior in FF might be associated with lack of proper metal contact. Thin film of Au or Ag is usually used as metal contact and deposited with thermal evaporation method. Moreover, it has small difference in energy level to CuSCN. In this research, FTO glass and carbon powder was being used as a contact, which have lower conductivity from mentioned metal contact. Furthermore, enormous difference in energy level from HTL to carbon and FTO back contact might inhibit charge transport. Energy level tailoring is crucial in perovskite solar cell. It can increase $V_{OC}$ and facilitate charge transfer which increase $I_{SC}$ and FF [21].

4. Conclusion

In summary, optimization of rotational speed for CuSCN thin film in perovskite solar cell using spin coating has already achieved. Rotational speed 1000 – 4000 rpm of spin coating was used to deposit CuSCN layer. It was found that devices with high rotational speed such as 3000 rpm and 4000 rpm exhibited low performance. Best devices with $V_{OC}$ 0.96 V, $I_{SC}$ 5.29 mA, and FF 0.48 can be achieved with spin coat rotational speed 2000 rpm. Relatively low photovoltaic parameters might be due to high humidity condition during fabrication. However, this works implies that spin coating rotation speed can be optimized for further application in other layers of perovskite solar cell.

References

[1] Snaith H J 2013 J. Phys. Chem. Lett. 4 3623–30
[2] Li F and Liu M 2017 J. Mater. Chem. A 5 15447–59
[3] Akihiro Kojima, Teshima K, Shirai Y and Miyasaka T 2009 J Am Chem Soc 131 6050–1
[4] Mesquita I, Andrade L and Mendes A 2018 Renew. Sustain. Energy Rev. 82 2471–89
[5] Burschka J, Pellet N, Moon S J, Humphry-Baker R, Gao P, Nazeeruddin M K and Grätzel M 2013 Nature 499 316–9
[6] Lin Q, Armin A, Nagiri R C R, Burn P L and Meredith P 2015 Nat. Photonics 9 106–12
[7] Wehrenfennig C, Liu M, Snaith H J, Johnston M B and Herz L M 2014 Energy Environ. Sci. 7 2269–75
[8] Habrisreutinger S N, McMeekin D P, Snaith H J and Nicholas R J 2016 APL Mater. 4
[9] Arora N, Dar M I, Hinderhofer A, Pellet N, Schreiber F, Zakeeruddin S M and Grätzel M 2017 Science. 358 768–71
[10] Jiang F, Choy W C H, Li X, Zhang D and Cheng J 2015 Adv. Mater. 27 2930–7
[11] Etgar L, Gao P, Xue Z, Peng Q, Chandiran A K, Liu B, Nazeeruddin M K and Grätzel M 2012 J. Am. Chem. Soc. 134 17396–9
[12] Farrag A A G and Balboul M R 2017 J. Sol-Gel Sci. Technol. 82 269–79
[13] Qin P, Tanaka S, Ito S, Tetreault N, Manabe K, Nishino H, Nazeeruddin M K and Grätzel M 2014 Nat. Commun. 5 1–6
[14] Ye S, Sun W, Li Y, Yan W, Peng H, Bian Z, Liu Z and Huang C 2015 Nano Lett. 15 3723–8
[15] Jung J W, Chueh C C and Jen A K Y 2015 Adv. Energy Mater. 5 1–7
[16] Fan L, Li Y, Yao X, Ding Y, Zhao S, Shi B, Wei C, Zhang D, Li B, Wang G, Zhao Y and Zhang X 2018 ACS Appl. Energy Mater. 1 1575–1584
[17] Xiong Q, Tian H, Zhang J, Han L, Lu C, Shen B, Zhang Y, Zheng Y, Lu C, Zeng Z, Hu Z, Wu L and Zhu Y 2018 Org. Electron. 61 151–6
[18] Akkerman Q A, Gandini M, Di Stasio F, Rastogi P, Palazon F, Bertonì G, Ball J M, Prato M, Petrozza A and Manna L 2017 Nat. Energy 2
[19] Wang H, Hu X and Chen H 2015 RSC Adv. 5 30192–6
Acknowledgments
This work has been supported by International publications indexed for the Final Project of Students (PITTA) Research Grant 2018 from Universitas Indonesia with Nr. 2502/UN2.R3.1/HKP.05.00/2018.

[20] Chaki S H, Joshi H J, Tailor J P and Deshpande M P 2017 Mater. Res. Express 4 076402
[21] Kim H, Lim K-G and Lee T-W 2016 Energy Environ. Sci. 9 12–30