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Investigation of Copper(I)Thiocyanate (CuSCN) as a Hole Transporting Layer for Perovskite Solar Cells Application

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ABSTRACT

Copper(I) Thiocyanate (CuSCN) is an inorganic hole transporting layer (HTL) used in perovskite solar cells (PSC). This material offers higher stability and reliability compared to conventional HTL. In this work, for depositing CuSCN (inorganic compound) we were using spin coating technique. The annealing temperature of CuSCN is varied in order to analyze the structural and electrical characteristics. The structural characteristics are determined by scanning electron microscopy (SEM), Raman spectroscopy and X-ray diffraction (XRD). Meanwhile, the electrical characteristic is measured by the I-V characteristics measurement. SEM images show the material surface features such as crystallinity morphology and density. XRD and Raman spectroscopy are used to confirm the coated surface on the ITO substrate is CuSCN. Besides, the I-V characteristic reveals that the conductivity with respect to annealing temperature. As a result, the optimized annealing temperature of CuSCN is 80 °C and showing conductivity of 62.96 S/m. In conclusion, CuSCN has a significant conductivity, hence suitable for the application as the HTL for perovskite solar cells.

Keywords:
CuSCN; Hole transporting layer; Perovskite solar cells

1. Introduction

In 2009, the first Perovskite Solar cell (PSC) was developed [1]. The fabricated PSC produced merely 3.8% of power conversion efficiency (PCE) and also exhibited low stability. The PSC consists of 6 layers which are substrate glass, transparent electrode, electron transporting layer (ETL), perovskite, hole transporting layer (HTL) and metallic electrode. 2,2′,7,7′-Tetrakis[N,N-di(4-methoxyphenyl) amino]-9,9′-spirobifluorene (Spiro-OMeTAD) is the most commonly used as HTL because it has low charge conductivity which can be increased by doping. However, spiro-OMeTAD has few drawbacks such as performance degradation in chemical reaction and reliability issues. On

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the other hand, the spiro-OMeTAD can be replaced by other HTL material such as CuSCN and CuI. These materials are solid state based that offers better stability and reliability. Therefore, short circuit current density (Jsc) will be increased as the HTL has better conductivity. HTL will also prevent charges recombination because it has low resistance [2].

To date, the highest PCE of CuSCN-based PSC is 20.4% which is fabricated by Arora *et al.,* [3]. This research group demonstrated that the CuSCN-based PSC remains stable as over 95% of its initial efficiency and remained after aging for 1000 hours. It proved the stability of CuSCN is higher than the conventional HTL which is spiro-OMeTAD. Lv *et al.,* [4] confirmed that the stability and electron lifetime is improved by using CuSCN as HTL for PSC. This research team also proved that CuSCN can be effectively reduced the charges recombination. Jung *et al.,* [5] used also the spin-coating method to deposit CuSCN on ITO glass and 16% of PCE is achieved. Besides, Yaacobi-Gross *et al.,* [6] state that CuSCN is high hole mobility and ultra-high transparency. Therefore, CuSCN has the potential to be applied to optoelectronic devices. CuSCN is deposited by spin-coater had achieved 6.49% of PCE.

A study on comparing the CuSCN and conventional HTL, spiro-OMeTAD had been conducted [7]. This researcher team used a spray deposition technique to deposit CuSCN with different thicknesses. Hence, the optimized thickness computes PCE as high as 17.1%. Others had demonstrated the different types of solvents are used to identify the most suitable solvent for CuSCN [8]. The highest PCE is 10% with the use of propylsulfide + isopropanol (1:2) + MAI (10 mg/ml) as the solvent for CuSCN. Moreover, a study had been done to compare among a few common HTLs which are CuSCN, CuI, and spiro-OMeTAD in order to find out the most stable HTL for PSC [9]. Therefore, the maximum PCE of 9.6% can be achieved by using a doctor blading deposition method of CuSCN layer on ITO. Hence, CuSCN has higher J-V hysteresis compare to CuI. In addition, doctor blading deposition method also used by Qin *et al.,* [10] and Ito *et al.,* [11] with the PCE above 10% which are 12.4% and 11.96% respectively. Furthermore, a potentiostatically electrodeposited method for depositing CuSCN layer had also been used [12,13].

Herein, the annealing temperature of CuSCN is varied in order to analyze the structural and electrical characteristics. Scanning electron microscopy (SEM), Raman spectroscopy and X-ray diffraction (XRD) are used to determine the structural characteristics. Meanwhile, the electrical characteristic is measured by the I-V characteristics measurement. Then, the deposition method for CuSCN is spin-coating which can provide the uniform coating surface and thin surface.

2. Methodology

2.1 Deposition of CuSCN Layer

ITO substrate glass of size is 50 mm by 50 mm. Then, it was cut into four pieces by a diamond glass cutter and the size of each small piece was 25 mm by 25 mm. After that, ITO was socked in a beaker fill with ethanol and placed the beaker in the ultrasonic cleaner for 10 min. After 10 min, the substrates were dried on a hot plate at 70 °C for 20 min.

The CuSCN solution was prepared by diluting the CuSCN powder (precursor) with ethylene glycol as a solvent. Then his solution was preheated in the ultrasonic bath for 2 hours at 70 °C.

CuSCN was deposited on the ITO glass substrate by spin-coater. CuSCN solution was dropped ten times for each sample. Then, it was spin-coated for two times at 500 rpm for 5 s and at 2500 rpm for 30 s. First, spin-coating was used to produce a uniform coating surface, while the second spin-coating was used to produce a thin layer on the ITO glass substrate. CuSCN coated glass was annealed at different temperature for each sample. The CuSCN coated glass was annealed at 60 °C, 70 °C, 80 °C, 90 °C and 100 °C for 10 min on the hot plate.

2.2 Characterization

In this work, both structural and electrical characterizations were investigated. Scanning electron microscopy (SEM, Zeiss EVO 18) was used to characterize the surface morphology of CuSCN layer. The crystal structure of CuSCN layer was investigated by X-ray diffraction (XRD, PANalytical X'pert Pro). Raman spectroscopy was used to examine the crystalline structure of CuSCN (UniRAM-3500). Meanwhile, the electrical characteristic is measured the measurement of the I-V characteristic.

3. Results, Analysis and Discussion

3.1 Structural Performance of CuSCN

Based on Figure 1, the SEM images of CuSCN annealed at different temperatures are recorded. The images are magnified to 3000 or 5000 times in order to identify the crystal structure of CuSCN annealed on ITO glass. For the annealing temperature at 60 °C, the structure of CuSCN is not fully crystallized and less dense as shown in Figure 1(a). The image of annealing temperature at 70 °C also came out the result as 60 °C which is not fully crystallized and less dense.

Then, CuSCN showed crystalline and dense when the annealing temperature is 80 °C based on Figure 1(c). According to Figure 1(d) and Figure 1(e) which annealing temperature at 90 °C and 100 °C, the structure of both images is dense but starts to dissolve from the crystalline structure. However, the worst structure of CuSCN is shown in Figure 1(e) which annealed at 100 °C. In conclusion, the annealing temperature at 80 °C is most suitable for CuSCN according to SEM images and this conclusion is confirmed by electrical measurement which is I-V characteristics.

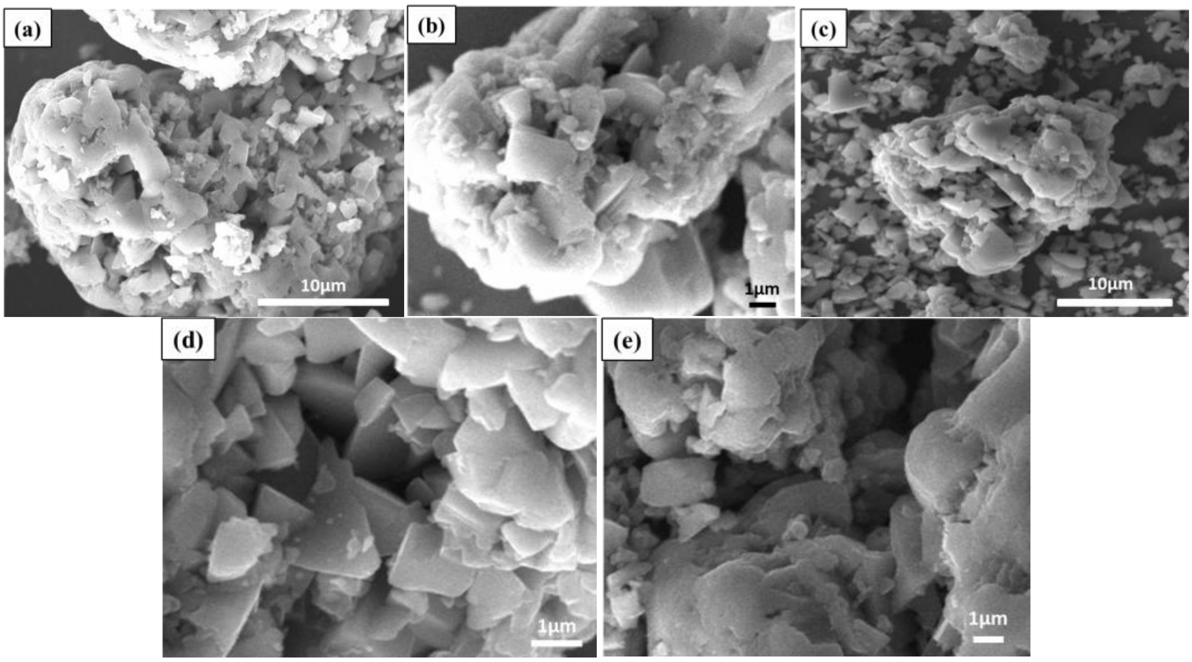

Fig. 1. Top view of SEM images of CuSCN annealed at different temperature. (a) 60 °C, (b) 70 °C, (c) 80 °C, (d) 90 °C and (e) 100 °C

XRD pattern is used to identify the crystal structure of the CuSCN film. From Figure 2, CuSCN and ITO are showed the respective peaks on the graph of intensity versus 2θ. The diffraction peaks of CuSCN can be categorized into two different formations of phase which are rhombohedral and orthorhombic phase or call it as β-CuSCN and α-CuSCN. The XRD distinct peaks at 16.1°, 27.2°, 32.6° and 47.1° are corresponding to the (003), (101), (006) and (110) planes of rhombohedral (β-CuSCN)

CuSCN phase. Besides, the intense diffraction peaks at 21.3°, 30.3°, 37.4° and 55.5° are corresponding to the (120), (131), (141) and (014) planes of orthorhombic (α-CuSCN) CuSCN phase.

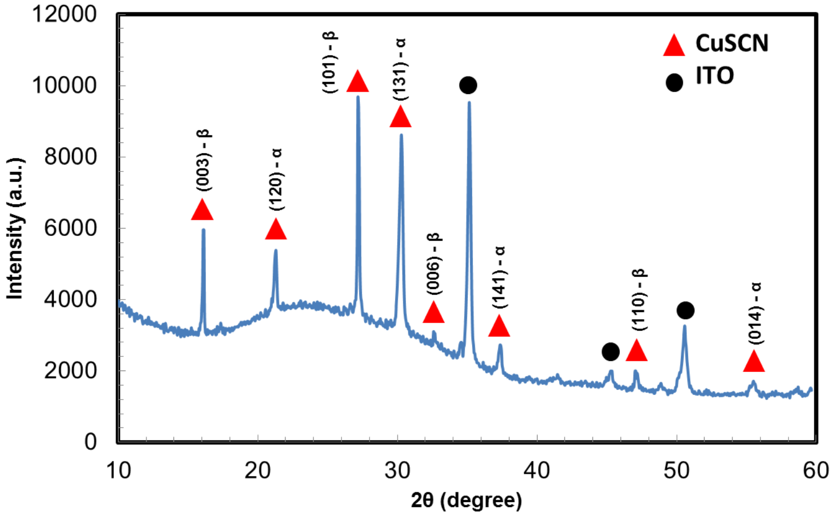

Fig. 2. XRD pattern of CuSCN deposited on ITO glass

Raman spectrum is obtained by Raman spectroscopy. Raman peaks of CuSCN substrate are in the regions of 100 cm-1 to 1000cm-1 and 2100 cm-1 to 2200 cm-1. There are four Raman peaks which at 229 cm-1, 415 cm-1, 728 cm-1 and 2147 cm-1 indicated CuSCN. The highest Raman peak is at 2147 cm-1 which showed the intensity of 509916. For the other peaks, the intensity is 57113, 108406 and 80430 which respect to 229 cm-1, 415 cm-1 and 728 cm-1. Based on the peaks obtained, it proved the presence of CuSCN is deposited on ITO glass (Figure 3).

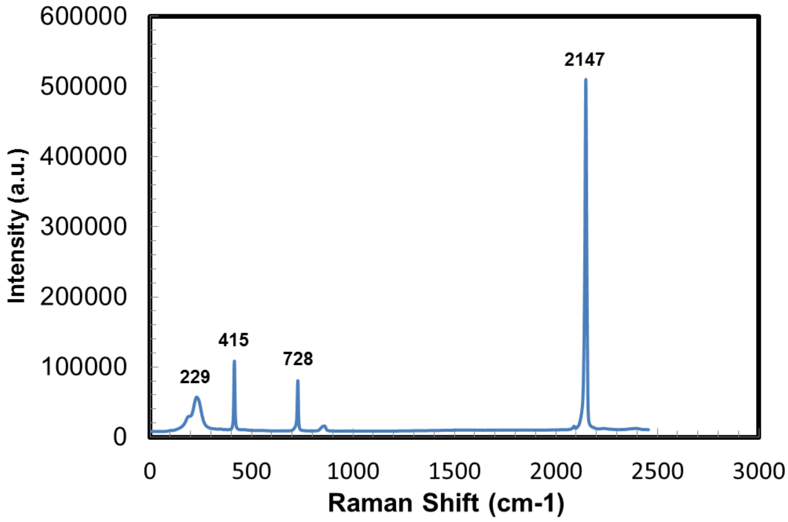

Fig. 3. Raman spectrum of CuSCN deposited on ITO glass

3.2 Electrical Performance of CuSCN

The current of ITO and CuSCN substrates is measured by supplying the voltage between the range of 0.5 V to 4 V and each voltage measure five times. Therefore, the mean, standard deviation and error bar of current is calculated based on five measurements. Then, the mean of current and voltage are used to plot the graph as shown in Figure 4. Error bar is calculated to prove the five measurements of each voltage consists of a bit different during each measurement. Figure 4 showed the current is increased with the increase of voltage supply and each line is directly proportional.

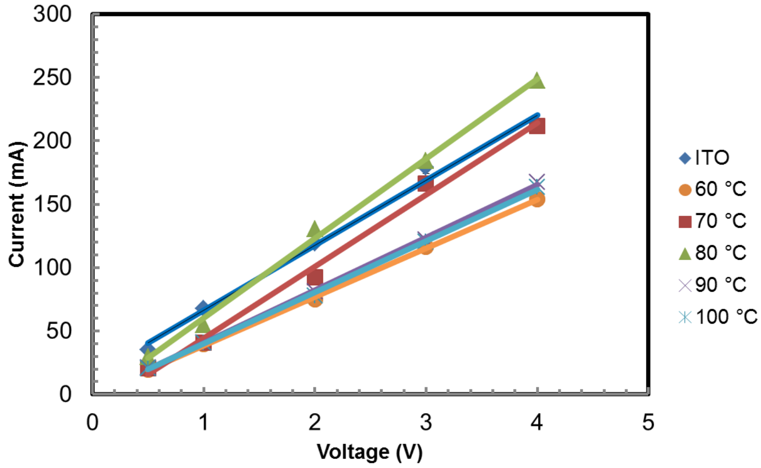

Fig. 4. I-V characteristics of CuSCN at different temperature

Based on Figure 4, the gradient of ITO is 51.311 which as the guidelines for CuSCN. The gradient obtained from the graph indicated the conductivity as it is equal to 1/R. The high performance due to high conductivity, so the highest performance is the most suitable to be applied on the CuSCN substrate. Therefore, the CuSCN substrates annealed at 70 °C and 80 °C showed the gradient higher than ITO which is 56.717 and 62.961. Thus, this indicated CuSCN annealed at 70 °C and 80 °C has better electrical performance than ITO. At 60 °C, 90 °C and 100 °C, annealed CuSCN substrates displayed its gradient lower than ITO which are 38.422, 41.671 and 40.61 respectively. Hence, the CuSCN substrate annealed at 60 °C, 90 °C, and 100 °C has low electrical performance than ITO. The highest conductivity obtained from Figure 5 is the CuSCN substrate annealed at 80 °C which is the best electrical performance for CuSCN.

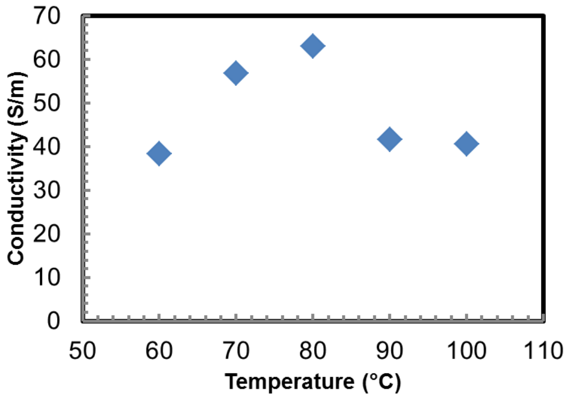

Fig. 5. Graph of conductivity versus temperature for CuSCN

4. Conclusion

HTL of PSC can affect the performance of PCE in terms of stability and reliability. Therefore, CuSCN as unconventional HTLs are introduced to replace the conventional HTL which is spiro-OMeTAD. CuSCN is deposited on the top of ITO glass by using a spin-coater. The speed and duration of spinning are fixed for both HTL which performed two times of spinning. The first spin-coating is used to produce a uniform coating surface, while second spin-coating is used to produce a thin layer of HTL on ITO glass.

Then, the annealing temperature of CuSCN is optimized based on the analysis of structural and electrical characteristics. The structural characteristics are determined by scanning electron microscopy (SEM), X-ray diffraction (XRD) and Raman spectroscopy. Meanwhile, the electrical characteristic is measured by I-V characteristics. SEM images show the material surface characteristics such as crystallinity and density. XRD and Raman spectroscopy are used to prove the coated surface on ITO is CuSCN. Besides, the I-V characteristic reveals that the conductivity with respect to annealing temperature. In summary, the SEM images of CuSCN at 80 °C showed the result of highly dense and crystalline compared with other annealing temperature. From the I-V characteristics, the optimized annealing temperature of CuSCN is 80 °C resulting in conductivity of 62.96 S/m. As a result, CuSCN has a significant conductivity, hence suitable for HTL application. This is suggested that the CuSCN offers high stability, longer electron lifetime and effectively reduces charges recombination.

The annealing temperature of CuSCN is optimized which is 80 °C. Therefore, the development of a full PSC by using CuSCN as inorganic HTL is needed in order to obtain the PCE. Full PSC can accurately determine the effect of CuSCN on the perovskite layer. HTL is the layer that transporting holes from the perovskite layer, so it can directly affect the PCE performance of PSC. By developing full PSC, PCE can be calculated in order to determine the performance. Besides, the annealing duration of CuSCN can also be optimized according to its optimized annealing temperature. By varying this parameter, the SEM image will show the different crystallinity and density of a material, while the electrical performance will change according to the annealing duration. Moreover, the thickness of CuSCN can also become a research parameter as it will affect the performance of transporting holes.

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