Study on the application of cuprous thiocyanate in lead perovskite solar cells as a hole transport layer

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Abstract

In recent years, in order to solve the increasingly serious energy and environmental problems, people have turned their attention to the development and utilization of new energy. Among various new energy technologies, photovoltaic solar cells are undoubtedly one of the most promising directions. Among many new types of solar cells, perovskite thin-film solar cells have attracted a lot of attention from many solar energy researchers because of their high photoelectric conversion efficiency.

In perovskite solar cells, in addition to the active layer material affecting the photoelectric conversion efficiency of the device, the interface layers(hole transport layer and electron transport layer) between the active layer and the electrode are also key factors. Therefore, in the current material structure of perovskite cells, the interface layer material has become an important research field.

In this study, the inorganic copper thiocyanate (CuSCN) film was prepared by gas-assisted spin coating method, which was used as the hole transport layer(HTL) of perovskite solar cell to replace the traditional polymer material PEDOT:PSS.

The thickness, crystallization characteristics, interface structure, annealing temperature and photoelectric conversion efficiency of the perovskite solar cell will be carefully investigated in this study. The experimental results show that cuprous thiocyanate can effectively replace PEDOT:PSS as a hole transport layer in perovskite solar cells. The cell with the best photoelectric conversion efficiency has a J_{sc} of 21.4 mA/cm^2, a V_{oc} of 1.0 mV, and a photoelectric conversion efficiency of 15.1%.

Key words: cuprous thiocyanate, perovskite solar cells, hole transport layer, spin coating

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I. INTRODUCTION

Traditionally, the most commonly used hole transport layer for perovskite solar cells is poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) polymer material[1-2]. However, the PEDOT:PSS corrodes the indium tin oxide film which is a conductive and transparent electrode material used in perovskite solar cells. Besides it is also easy to absorb water vapor and is expensive. Therefore, it is imperative to find more stable and cheap alternative hole transport layer materials. In this study, the cuprous thiocyanate inorganic material was used to replace the PEDOT:PSS hole transport layer to avoid corrosion and moisture absorption and improve the conversion efficiency of the perovskite solar cell. Many researches have studied the cuprous thiocyanate film as a hole transport layer in perovskite solar cells[3-4]. Since the process conditions are quite sensitive to the properties of the material, various experimental results are obtained. In 2014, the Seigo Ito [5] team used cuprous thiocyanate as a hole transport layer to prepare a cuprous thiocyanate film by doctor-blade method. They found that the cell conversion efficiency reached 4.85%, and the short-circuit current would increase substantially. In 2014, Peng Qin used CuSCN as an alternative to the hole transport layer. Through the combination of CuSCN and TiO_2, the perovskite cell structure completely uses the inorganic hole transport layer and the electron transport layer, and the conversion efficiency is up to 12.4% [3]. Neha Arora et al. replaced organic hole transport layers with CuSCN to improve thermal stability [6]. Their research proves that CuSCN can effectively replace the expensive organic material hole transport layer and the conversion efficiency can still reach 20%. In Seok Yang et a.l enhances the open circuit voltage of CuSCN-based perovskite solar cells by controlling the perovskite/CuSCN interface of functional molecules [7]. Inorganic P-type semiconductors are an ideal choice compared to organic hole transport materials because of their high mobility, stability, ease of synthesis, and low cost. From the literatures show that the P-type semiconductor CuSCN also has good hole mobility (0.01–0.1 cm^2 /V● S) and high transparency in the visible and near-infrared spectra [8-9], also has better chemical stability than the commonly used small molecule Spiro-OMeTAD [10]. In this study, we chose the copper thiocyanate P-type semiconductor material as the hole transport layer material. The CuSCN solution was deposited at room temperature by a gas-assisted spin coating method to form a hole transport layer.

II. MATERIALS AND METHODS

The cuprous thiocyanate powder was dissolved in a dipropyl sulfide (98%, Alfa) liquid and stirred at 60 ° C overnight. The solution was filtered through a filter head of

polyfluoroethylene (PVDF) having a pore size of 0.45 um to remove undissolved solid particles. Then the solution was spin-coated on the ITO substrate at 3000 rpm to form a CuSCN layer. After the layer was dried, it was transferred to a baking plate and heated at 100 ° C for 15 minutes to remove excess solvent.

The perovskite film was prepared by gas-assisted spin coating method. The perovskite solution is prepared by dissolving methyl iodide amine (0.159 g, MAI, CH_3NH_3I, 99.995%, Ruilong Technology) and lead diiodide (0.461 g 0.461 g PbI_2, 99.999%, Aldrich) in 1 mL of mixing solvent of γ-butyrolactone and Dimethyl sulfoxide (γ-butyrolactone: dimethyl hydrazine = 7:3, volume ratio) to form 1 molar concentration solution. The prepared solution deposits a perovskite layer on top of CuSCN layer. Then, the layers of fullerene(C_{60}), hole barrier layer (BCP) and Al electrode are sequentially deposited to form a solar cell. The electron transport layer(fullerene,C_{60}) and the hole barrier layer are prepared by a thermal evaporation process. First of all, the chamber pressure is pumped to below $6x10^{-6}$ torrs for deposition these films. The electron transport layer and the hole barrier layer are sequentially deposited to a thickness of 20 nm and 10 nm, respectively. Finally, an aluminum electrode having a thickness of 100 nm was also deposited in a thermal evaporator.

Compared with the vacuum thermal evaporation process, the solution method has the advantages of time and cost saving. This is also the mainstream method for producing perovskite film in the world. Since the perovskite film was highly susceptible to moisture, the process of making the perovskite film was carried out in a glove box. Blowing nitrogen(N_2) on the surface of the perovskite film during spin coating enables the solute in the film to accelerate to a supersaturated state, rapidly inducing a large number of nuclei and resulting in forming a dense crystalline perovskite film [11]. The advantage of this method is that it can be uniformly deposited over a large area at room temperature and can quickly obtain a smooth and high crystalline perovskite film.

The crystallographic properties of the perovskite $CH_3NH_3PbI_3$ absorption layer and CuSCN hole transport layer were characterized using X-ray diffraction (XRD) measurements using a Cu Kα (λ = 0.15418 nm) radiation source operated at 40 kV. The morphologies of the $CH_3NH_3PbI_3$ films and CuSCN layer were investigated with a scanning electron microscope (SEM, HITACHI SU8000, Japan) operated at 10 kV.
The current density-voltage (J-V) curves were measured using a Keithley 2400 Source Meter under the standard 1 sun AM 1.5G simulated irradiation (100 mW cm^{-2}) from a Newport-Oriel Instruments Model 69911 300 W Solar Simulator (Class A) in a nitrogen-filled glove box.

III. RESULTS AND DISCUSSION

The structural layer of the perovskite solar cell in this study is sequentially from bottom to top by anode(ITO) / hole transport layer(CuSCN) / active layer(perovskite) / electron transport layer(fullence) / hole blocking layer(BCP) / cathode(Al). A schematic diagram of the overall component structure is shown in Figure 1(a). Figure1(b) is a schematic diagram of the energy levels of the components in this study. It can be seen from the energy level diagram in figure1(b) that the CuSCN layer uses as a hole transport layer theoretically facilitates to transfer holes to the anode in the built-in electric field of the cell.

Figure 2 shows the XRD patterns of perovskite films deposited on unannealed and annealed CuSCN layers at different temperatures. All perovskite films were found to have distinct diffraction peaks at 14.08°, 28.40°, and 31.86°, each corresponding to (110), (220), and (310) crystal planes. Therefore, it was confirmed that the prepared perovskite films belong to typical tetragonal crystal system structures. In addition, we can clearly see that the perovskite film prepared by the gas-assisted solution method has strong and obvious diffraction peaks in the three crystal planes, which means that the perovskite films prepared by this process has good crystallization. A film with a high degree of crystallinity will have a better transport ability of carriers in the film, so this also explains why the solar cell element prepared by the gas assisted solution method has higher efficiency.

Figure 3 is surface topographies of CuSCN layers before and after annealing at different temperatures. The CuSCN grain sizes are less uniform before annealing and become more uniform after annealing. However, whether it is annealed or not, the crystals of CuSCN are clearly visible. This means that CuSCN is easily prepared by wet aqueous chemical method to obtain a deposit with good crystallinity.

Figure 4 show surface topography of perovskite layers deposited on top of CuSCN layers. Whether or not the CuSCN was annealed, the perovskite layers exhibit flat and dense grain structures. These results confirm that the gas-assisted chemical wet method contributes to the nucleation and growth of the material. The crystallinity of the underlying CuSCN layer seems to have little effect on the crystallization characteristics of the perovskite layer.

Figure 5 is a graph showing the electrical characteristic of the perovskite solar cell using the CuSCN(annaled at 250ºC) as the hole transport layer. Its open circuit voltage and short circuit current density are 1.00V and 21.6mA/cm^2 respectively and the conversion efficiency reaches 15.1% as shown in table1. It can also be seen from the table1 that the FF value reaches 0.7. Since the FF value has a direct correlation with the process, the value of 0.7 represents that the gas phase assisted solution method does

have a positive effect on the preparation of perovskite cell. We also find that the open circuit voltage is as high as 1.00V. Since no buffer layer is added at the interface in this study, the open circuit voltage can still reach 1.00V, indicating that the carriers have a low recombination probability at the interface. Therefore, we preliminarily speculate that the gas-assisted solution method not only makes the perovskite film surface coverage higher, but also has high crystal compactness, which helps to reduce the carrier recombination.

IV. CONCLUSIONS

The CuSCN layer can be prepared by wet aqueous chemical method to obtain a deposit with good crystallinity. It can replace the expensive PEDOT:PSS as the hole transport layer of perovskite solar cells. Good crystallinity can be obtained regardless of the perovskite coating deposited on the annealed or non-annealed CuSCN layer. This contributes to the transport of the carriers and thus improves the conversion efficiency of the solar cell. The gas-assisted solution method not only makes the perovskite film surface coverage higher, but also has high crystal compactness, which helps to reduce the carrier recombination. The cell with the best photoelectric conversion efficiency has a J_{sc} of 21.4 mA/cm^2, a V_{oc} of 1.0 mV, and a photoelectric conversion efficiency of 15.1%.

V. ACKNOWLEDGMENT

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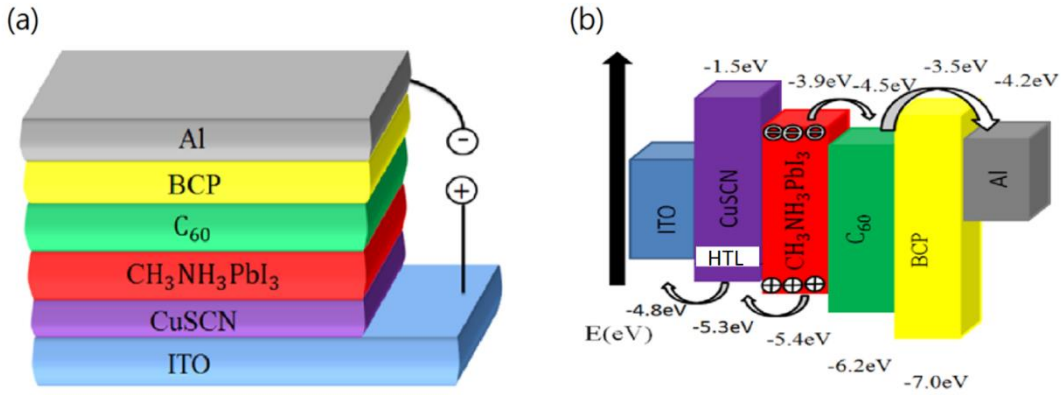

Figure1 (a) Schematic diagram of the cell structure (b) Energy level diagram of components

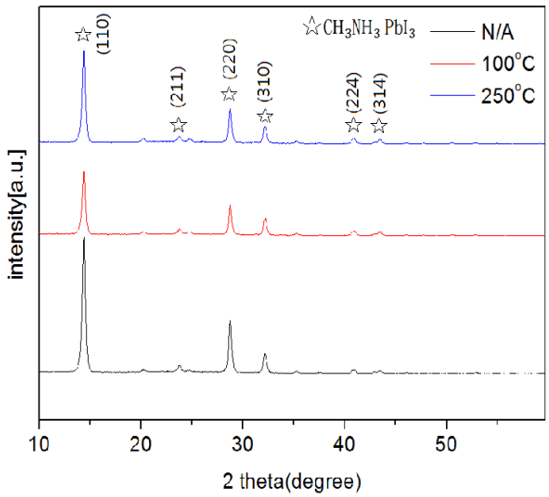

Figure2 X-ray diffraction patterns of perovskite layers on top of CuSCN layers after annealing at different temperatures

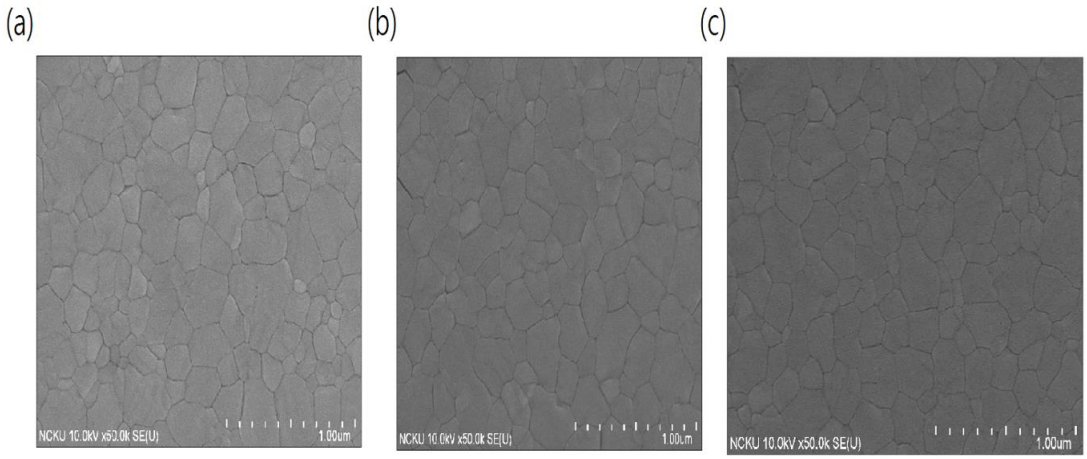

Figure3 The surface topographies of CuSCN layers before and after annealing at different temperatures(a)as deposited(b)100°C(c)250°C

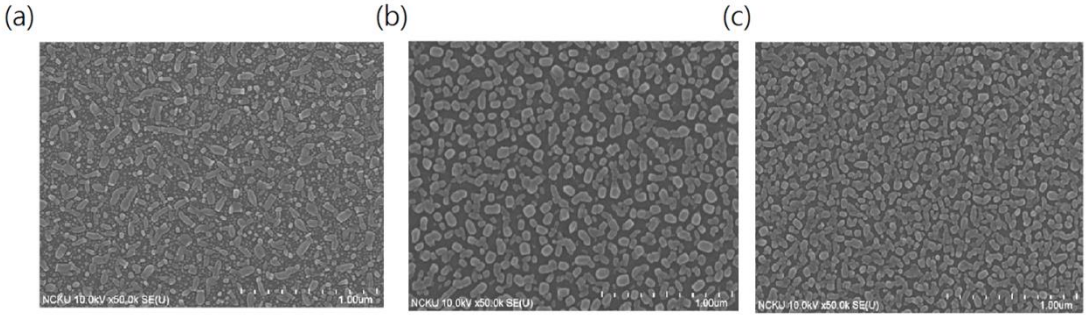

Figure4 The surface topographies of perovskite layers deposited on top of CuSCN annealed at different temperatures(a)as deposited(b)100°C(c)250°C

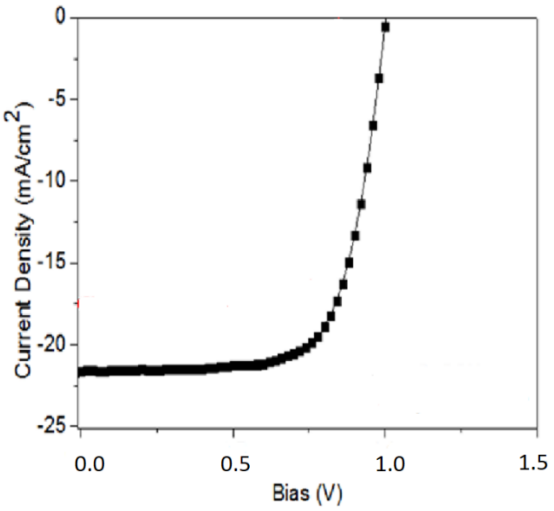

Figure5 a graph showing the electrical characteristic of the perovskite solar cell using the CuSCN(annaled at 250°C) as the hole transport layer.

Table1 Photovoltaic characteristic parameters of perovskite solar cells using CuSCN as the hole transport layer

	V_{oc}(V)	J_{sc}(mA/cm^2)	FF	PCE(%)
CuSCN	1.00	21.6	0.70	15.1