Nano-structured CuO-Cu$_2$O Complex Thin Film for Application in CH$_3$NH$_3$PbI$_3$ Perovskite Solar Cells

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Abstract

Nano-structured CuO-Cu$_2$O complex thin film-based perovskite solar cells were fabricated on an indium tin oxide (ITO)-coated glass and studied. Copper (Cu) thin films with a purity of 99.995 % were deposited on an ITO-coated glass by magnetron reactive sputtering. To optimize the properties of the nano-structured CuO-Cu$_2$O complex thin films, the deposited Cu thin films were thermally oxidized at various temperatures from 300 to 400 °C. A CH$_3$NH$_3$PbI$_3$ perovskite absorber was fabricated on top of CuO-Cu$_2$O complex thin film by a one-step spin-coating process with a toluene washing treatment. Following optimization, the maximum power conversion efficiency (PCE) exceeded 8.1 %. Therefore, the low-cost, solution-processed, stable nano-structured CuO-Cu$_2$O complex thin film can be used as an alternative hole transport layer (HTL) in industrially produced perovskite solar cells.

Keywords: Nano-structured, CuO-Cu$_2$O complex-based, CH$_3$NH$_3$PbI$_3$ perovskite

Background

Organic–inorganic hybrid perovskite (such as CH$_3$NH$_3$PbX$_3$, X = I, Cl, Br) solar cells has attracted much attention because of its superior photovoltaic performance, including excellent light-harvesting ability and potential applications [1–6]. In previous reports, the high power conversion efficiency (PCE) of perovskite solar cells was achieved when a conducting polymer PEDOT:PSS thin film that was formed using TiO$_2$ nano-particles that had been sintered at high temperature was used as the electron transport layer (ETL) (hole transport layer (HTL)) [7–9]. However, a trade-off must be between fabrication cost and device stability, impeding the development of commercialized solar cells. Inorganic p-type materials as hole transport media have the double advantage of excellent chemical stability and simplicity of preparation [10–12]. Along with some inorganic HTLs (copper iodide (CuI) [13], copper thiocyanate (CuSCN) [14–16], graphene oxide (GO) [17], nickel oxide (NiO) [18], cuprous oxide (Cu$_2$O), and copper oxide (CuO) [19] have attracted substantial interest owing to their direct gaps of 1.9–2.2 eV [20–22], and these have been widely used as HTLs in solar cells. Cu$_2$O and CuO thin films can be prepared by various methods, including reactive sputtering [23], electrochemical deposition [24–27], chemical dissolution [28–30], thermal oxidation [31], and successive ionic layer adsorption and reaction (SILAR) method [12, 32].

In this work, CuO-Cu$_2$O complex thin films were prepared from thermally oxidized Cu thin films to form HTLs for use in perovskite solar cells. The structural, optical, and surface properties of CuO-Cu$_2$O complex thin films were investigated to elucidate the performance of CuO-Cu$_2$O complex thin film-based photovoltaics. The device with an optimized CuO-Cu$_2$O complex thin film as the HTL exhibited superior photovoltaic performance, revealing that the CuO-Cu$_2$O complex thin film is a potential inorganic HTL for use in perovskite solar cells.

Methods

Firstly, Cu layers were deposited on an indium tin oxide (ITO) glass substrate by RF magnetron reactive sputtering from Cu targets in gaseous argon (Ar) at a flow rate...
Fig. 1  a Preparation of nano-structured CuO-Cu$_2$O complex films, b photograph image of shadow mask, and c structure of device.
of 15 sccm and a stable working pressure of 3 × 10⁻³ Torr. The nano-structured CuO-Cu₂O complex thin films were formed by thermally oxidizing Cu on ITO substrate at various annealing temperatures from 300 to 400 °C for 1 h in air, and these acted as HTLs. 1.25 M PbI₂ and 1.25 M methylammonium iodide (MAI) were dissolved in a cosolvent mixture of dimethyl sulfoxide (DMSO) and γ-butyrolactone (GBL) (vol. ratio = 1:1), and the resulting solution was used as the perovskite precursor solution. The CH₃NH₃PbI₃ perovskite precursor was spin-coated on top of the nano-structured CuO-Cu₂O complex/ITO/glass and underwent in situ non-polar solvent washing treatment [1–3] in a glove box that was filled with highly pure nitrogen. The CH₃NH₃PbI₃ perovskite precursors were then coated onto the CuO-Cu₂O complex/ITO/glass samples in two consecutive spin-coating steps at 1000 and 5000 rpm for 10 and 20 s, respectively. At 5000 rpm for 20 s, the wet spinning film was quenched by dropping 100 μl of anhydrous toluene onto it. After spin coating, the film was annealed at 100 °C for 5 min. Finally, C₆₀, BCP, and the Ag electrode were sequentially deposited by thermal evaporation at a base pressure of 5 × 10⁻⁶ Pa. The thicknesses of C₆₀, BCP, and Ag were 50, 5, and 100 nm, respectively. Figure 1a presents the steps in the preparation of CuO-Cu₂O complex thin film-based perovskite solar cells. The C₆₀ thin film, CH₃NH₃PbI₃ perovskite thin film, and CuO-Cu₂O complex thin film in the cell structure acted as the ETL, the active layer, and the HTL, respectively. A shadow mask firmly covered the sample to define an active area of 0.5 cm × 0.2 cm during C₆₀/BCP/Ag deposition. Figure 1b shows the photo image of the shadow mask. Figure 1c schematically depicts the complete structure.

The crystal characteristics of the CuO-Cu₂O complex thin films were determined using an X-ray diffractometer (XRD) (D8, Bruker). Raman scattering spectroscopy was used to analyze the CuO-Cu₂O complex thin films. A field-emission scanning electron microscope (FESEM) (LEO 1530) was used to observe the cross-section and surface morphology of the cells. The current density–voltage (J-V) characteristics were measured using a Keithley 2400 programmable source/meter unit under irradiation by a 1000 W xenon lamp. To evaluate the photovoltaic performance, the irradiation power density on the surface of the sample was calibrated as set to 100 mW/cm² (AM 1.5G). Table 2 and 3 list the characteristic parameters of these devices. The PCE is improved from 3.15 to 7.32 % as the thermal oxidation temperature increases from 300 to 400 °C, mainly owing to the increase in the photo-generated carriers extracted and injected into the electrode caused by the carrier mobility and series resistance in the device, and then to result in the increase in the short-circuit current density (Jsc). The PCE decreases from 7.32 to 6.43 % as the thermal oxidation temperature increased from 350 to 400 °C. As listed in Table 2, for the device annealing at 400 °C, the series resistance (Rs) increases and the shunt resistance (Rsh) decreases. The degradation of the performance may be attributed to the degradation of ITO electrode and leakage between CuO-Cu₂O complex and perovskite layer. The PCE of CuO-Cu₂O complex thin film-based perovskite solar cells is improved from 7.32 to 8.10 % as the thickness of CuO-Cu₂O complex thin film increased from 30 to 60 nm. However, further increasing the thickness of the CuO-Cu₂O complex thin film to 120 nm reduced the PCE from 8.10 to 5.20 % due to the series resistance effect in the cell, as listed in Table 3. According to the J-V curve and PCE value, the optimized thickness of the CuO-Cu₂O complex thin film is 60 nm.

### Results and Discussion

Table 1 presents the Hall measurements of the CuO-Cu₂O thin films. The increase in the carrier mobility at 250–300 °C could be attributed to an improvement in the crystallinity as well as a decrease in the carrier density because carrier mobility is generally affected by grain boundary scattering and by impurity scattering due to the native defects. However, as the annealing temperature increased to 400 °C, the mobility in the sample decreased from 33.5 to 9.7 cm²/V-s for owing to the decrease in the size of the grains caused by the phase transformation from Cu₂O to CuO. As the thermal annealing temperature increased, the reduction of resistivity of the CuO-Cu₂O complex films post-annealing may be attributed to both the carrier concentration and carrier mobility were decreased gradually, resulting in an increase in resistivity. The reduction of mobility is attributable to the transportation of carriers from one grain to another grain.

Figure 2 plots the J-V curves for the CuO-Cu₂O complex thin film-based perovskite solar cells under 100 mW/cm² illumination (AM 1.5G). Tables 2 and 3 list the characteristic parameters of these devices. The PCE is improved from 3.15 to 7.32 % as the thermal oxidation temperature increases from 300 to 400 °C, mainly owing to the increase in the photo-generated carriers extracted and injected into the electrode caused by the carrier mobility and series resistance in the device, and then to result in the increase in the short-circuit current density (Jsc). The PCE decreases from 7.32 to 6.43 % as the thermal oxidation temperature increased from 350 to 400 °C. As listed in Table 2, for the device annealing at 400 °C, the series resistance (Rs) increases and the shunt resistance (Rsh) decreases. The degradation of the performance may be attributed to the degradation of ITO electrode and leakage between CuO-Cu₂O complex and perovskite layer. The PCE of CuO-Cu₂O complex thin film-based perovskite solar cells is improved from 7.32 to 8.10 % as the thickness of CuO-Cu₂O complex thin film increased from 30 to 60 nm. However, further increasing the thickness of the CuO-Cu₂O complex thin film to 120 nm reduced the PCE from 8.10 to 5.20 % due to the series resistance effect in the cell, as listed in Table 3. According to the J-V curve and PCE value, the optimized thickness of the CuO-Cu₂O complex thin film is 60 nm.

### Table 1

| Annealing temp. (°C) | Resistivity (Ω-cm) | Carrier concentration (×10¹⁷ cm⁻³) | Mobility (cm²/V-s) |
|---------------------|--------------------|-----------------------------------|-------------------|
| As-deposited         | 2.1                | 2.9                               | 10.3              |
| 300                 | 1.5                | 2.1                               | 19.3              |
| 350                 | 2.0                | 9.2                               | 33.5              |
| 400                 | 9.7                | 36                                | 179               |
Fig. 2 Current–voltage (J–V) characteristics of perovskite solar cell that was constructed using CuO-Cu$_2$O complex thin film under simulated illumination with a light intensity of 100 mW/cm$^2$ (AM 1.5). a Thermal oxidation temperatures. b The thicknesses of CuO-Cu$_2$O complex thin film.

Table 2 Parameters of CuO-Cu$_2$O complex thin film-based perovskite solar cells following thermal oxidation of the film at various temperatures

| Annealing temp. (°C) | $V_{OC}$ (V) | $J_{SC}$ (mA/cm$^2$) | FF(%) | Eff(%) | Rs(Ω) | $R_{sh}$ (Ω) |
|----------------------|--------------|----------------------|-------|--------|-------|-------------|
| 300                  | 0.88         | 8.56                 | 41.42 | 3.15   | 25.8  | 234         |
| 350                  | 0.95         | 13.88                | 55.54 | 7.32   | 7.9   | 738         |
| 400                  | 0.89         | 12.71                | 56.89 | 6.43   | 12.5  | 698         |

Table 3 Parameters of CuO-Cu$_2$O complex thin film-based perovskite solar cells with films of different thicknesses

| CuO-Cu$_2$O complex thickness (nm) | $V_{OC}$ (V) | $J_{SC}$ (mA/cm$^2$) | FF(%) | Eff(%) | Rs(Ω) | $R_{sh}$ (Ω) |
|-----------------------------------|--------------|----------------------|-------|--------|-------|-------------|
| 30                                | 0.95         | 13.88                | 55.54 | 7.32   | 12.9  | 410         |
| 60                                | 0.96         | 14.40                | 58.61 | 8.10   | 10.3  | 789         |
| 120                               | 0.93         | 10.28                | 54.45 | 5.20   | 21.9  | 338         |
In this study, the X-ray diffraction technique was used to elucidate the crystal characteristics of CuO-Cu$_2$O complex thin films. To determine the relationship between thermal oxidation temperature and mechanism, the phase of the CuO-Cu$_2$O complex thin films was identified. Figure 3 shows the XRD patterns of CuO-Cu$_2$O complex thin films that were deposited on a glass substrate. XRD experimental results demonstrate that the crystalline phases of CuO and Cu$_2$O were formed at different thermal oxidation temperatures. Diffraction peaks at 35.84° and 38.85° corresponded to the (−111) and (100) planes of the cubic-structured CuO, and diffraction peaks at 36.8° and 38.63° corresponded to the (111) and (200) planes of the cubic-structured Cu$_2$O. A broad diffraction peak at 35.84° was obtained from the Cu/ITO/glass sample following thermal annealing at 350 °C. This peak may be attributed to a complex layer that comprised the (−111) plane of CuO and the (111) plane of Cu$_2$O. The XRD patterns of Cu$_2$O (CuO) gradually decrease (increase) as the thermal annealing temperature increased from 300 to 400 °C, indicating that the crystalline Cu$_2$O is completely converted to crystalline CuO. The crystal domain size $G$ was calculated according to the Scherrer’s equation: [33]

$$G = \frac{0.9\lambda}{\beta \cos \theta}$$

where $G$, $\lambda$, $\beta$, and $\theta$ denote the grain size, the X-ray wavelength, the full width at half maximum (FWHM) in radians, and the Bragg angle of CuO or Cu$_2$O peak, respectively. The phase transformation from crystalline Cu$_2$O to crystalline CuO reduces the crystal domain size from 31.83 to 29.39 nm, and thereby increases the carrier mobility of the CuO-Cu$_2$O complex thin films, improving the carrier collection at the CH$_3$NH$_3$PbI$_3$/CuO-CuO$_2$ complex interface. However, the phase transformation reduces the grain size and surface roughness of the CuO-Cu$_2$O complex thin films, as presented in Fig. 4, which presents FESEM images of the Cu layers.

![Fig. 3 XRD diffractograms of CuO-Cu$_2$O complex thin film following thermal oxidation at various temperatures](image)

![Fig. 4 FESEM images of CuO-Cu$_2$O complex thin films fabricated using thermal oxidation at various temperatures. a Thermal treatment at 300 °C. b Thermal treatment at 350 °C. c Thermal treatment at 400 °C](image)
that had undergone thermal oxidation at various annealing temperatures. More flat surface favors the coverage of the subsequently coated perovskite layer and C₆₀ layer on the Cu-Cu₂O complex thin films to form the continuous films and so improves the fill factor of the perovskite solar cells (Table 2). The image of the Cu layer that underwent thermal treatment at 350 °C reveals that the surface of the film consisted of small particles. The mean particle size was approximately 20 nm, as displayed in Fig. 4a. When the annealing temperature exceeded 300 °C, thin oxides were formed, particularly in the grain boundary regions, implying that they were formed by fast diffusion processes, as presented in Fig. 4.

To elucidate the relation between the crystal domain size and the grain size in CuO-Cu₂O complex thin films, the Raman scattering spectra of CuO-Cu₂O complex thin films were measured, as shown in Fig. 5. According to two relevant investigations [34, 35], the five peaks at 201, 300, 406, 489, and 638 cm⁻¹ and the three peaks at 274, 328, and 627 cm⁻¹ are the Raman fingerprints of Cu₂O and CuO, respectively. The Cu₂O phase is completely converted to the CuO phase as the annealing temperature increased from 300 to 400 °C, revealing that the Cu₂O is converted to CuO. The results are consistent with the results of XRD patterns in Fig. 3. Therefore, the grain size (Fig. 4) is reduced when the annealing temperature increased from 350 to 400 °C owing to the phase transformation. Figure 6 presents the photoemission spectra of Cu-Cu₂O complex thin films, which were used to determine their work functions. The work function of a CuO-Cu₂O complex thin film is proportional to the Voc of the perovskite solar cell in which it is used.

**Conclusions**

This study examined the characteristics of a nano-structured CuO-Cu₂O complex thin-film for use in perovskite solar cells. A CH₃NH₃PbI₃ perovskite absorber was fabricated on top of a CuO-Cu₂O complex thin film in a one-step spin-coating process, which was followed by toluene washing treatment. The work function of the Cu-Cu₂O complex thin film varied with the annealing temperature. The work function of a CuO-Cu₂O complex thin film is proportional to the Voc of the perovskite solar cell in which it is used. Following optimization, the maximum power conversion efficiency (PCE) exceeded 8.1 %. Therefore, the low-cost, solution-processed, stable nano-
structured CuO-Cu2O complex thin film can be used in alternative hole transport layers (HTLs) in industrially produced perovskite solar cells.

Abbreviations

CuO: cuprous oxide; Cu2O: copper oxide; ETL: electron-transporting layer; FESEM: field-emission scanning electron microscope; HTL: hole transport layer; ITO: indium tin oxide; J-V: current density–voltage; PCE: power conversion efficiency; XRD: X-ray diffractometer

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Authors’ Contributions

LCC wrote the paper, designed the experiments, and analyzed the data. CCC, KCL, SHC, ZLT, and WTW prepared the samples and did all the measurements. SCY, CTC, and CGW made the discussion and suggested the measurements. All authors read and approved the final manuscript.

Competing Interests

The authors declare that they have no competing interests.

Ethics Approval

Not applicable.

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