A simple synthesis of transparent and highly conducting p-type Cu_{x}Al_{1-x}S_{y} nanocomposite thin films as the hole transporting layer for organic solar cells

Xin Dai, Hongwei Lei, Cong Chen, Yaxiong Guo and Guojia Fang

Inorganic p-type films with high mobility are very important for opto-electronic applications. It is very difficult to synthesize p-type films with a wider, tunable band gap energy and suitable band energy levels. In this research, p-type copper aluminum sulfide (Cu_{x}Al_{1-x}S_{y}) films with tunable optical band gap, carrier density, hole mobility and conductivity were first synthesized using a simple, low cost and low temperature chemical bath deposition method. These in situ fabricated Cu_{x}Al_{1-x}S_{y} films were deposited at 60 °C using an aqueous solution of copper(ii) chloride dihydrate (CuCl₂·2H₂O), aluminium nitrate nonohydrate [Al(NO₃)₃·9H₂O], thiourea [(NH₂)₂CS], and ammonium hydroxide, with citric acid as the complexing agent. Upon varying the ratio of the precursor, the band gap of the Cu_{x}Al_{1-x}S_{y} films can be tuned from 2.63 eV to 4.01 eV. The highest hole mobility obtained was 1.52 cm² V⁻¹ s⁻¹ and the best conductivity obtained was 546 S cm⁻¹. The Cu_{x}Al_{1-x}S_{y} films were used as a hole transporting layer (HTL) in organic solar cells (OSCs), and a good performance of the OSCs was demonstrated using the Cu_{x}Al_{1-x}S_{y} films as the HTL. These results demonstrate the remarkable potential of Cu_{x}Al_{1-x}S_{y} as a hole transport material for opto-electronic devices.

1. Introduction

Industrialization in the past years has yielded an increasing energy demand, which was resolved using non-renewable resources. However, utilization of these resources results in serious environmental pollution and depletion of the fossil fuel energy. To avoid this green renewable energy must be developed and solar cells are a promising material because of its high band gap energy (E_g) and hole conductivity. There are various methods used to prepare CuAlS₂, such as chemical vapor transport deposition, solid phase reaction, solvothermal deposition, chemical spray pyrolysis, hydrothermal methods and chemical bath deposition (CBD). However, these methods involve either high temperature or high pressure and the prepared CuAlS₂ always has a low conductivity, whereas the film prepared using CBD is not very uniform and lacks measureable electrical properties.

In this research, a CBD technique was used to grow Cu_{x}Al_{1-x}S_{y} thin film with a tunable band gap in situ. Compared with other deposition methods, this method has several advantages such as: (1) the precursors are dissolved in distilled water, which is non-toxic, low cost and environmentally friendly, (2) the chemicals are commercially available and inexpensive, the deposition temperature is 60 °C which is really low and very

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safe, and (3) the process is simple. With this method Cu\textsubscript{x}Al\textsubscript{1-x}S\textsubscript{y} films with a large area can easily be grown without using sophisticated instruments. In addition, citric acid and ammonium hydroxide are used to adjust the speed of the reaction to obtain the required film.

In comparison with copper(II) sulfide (CuS)\textsuperscript{29–31} film, the Cu\textsubscript{x}Al\textsubscript{1-x}S\textsubscript{y} film is easy to grow without needing any sophisticated instruments. Most importantly, the variable energy levels of Cu\textsubscript{x}Al\textsubscript{1-x}S\textsubscript{y} films with a tunable band gap are very attractive.

In this research, non-toxic and earth-abundant Cu\textsubscript{x}Al\textsubscript{1-x}S\textsubscript{y} thin film was used as HTL for OSCs with a blend of poly(3-hexylthiophene) (P3HT) and 6,6-phenyl C\textsubscript{61} butyric acid methyl ester (PCBM) was used as the active layer. Photovoltaic devices were made with the structure of fluorine doped tin oxide (FTO)/Cu\textsubscript{x}Al\textsubscript{1-x}S\textsubscript{y}/P3HT:PCBM/Al. The optimized OSCs illuminated under simulated AM1.5G, 100 mW cm\textsuperscript{-2} white light.

![Fig. 1 SEM images of Cu\textsubscript{x}Al\textsubscript{1-x}S\textsubscript{y} films fabricated on FTO substrates. (a) x = 0.2, Cu:Al = 2 : 8. (b) x = 0.3, Cu:Al = 3 : 7. (c) x = 0.5, Cu:Al = 5 : 5. (d) x = 0.7, Cu:Al = 7 : 3. (e) x = 0.8, Cu:Al = 8 : 2. (f) x = 0.9, Cu:Al = 9 : 1. (g) x = 1, Cu:Al = 10 : 0.](image-url)
yielded a power conversion efficiency (PCE) of 2.67% with an open-circuit voltage ($V_{oc}$) of 0.596 V, a short-circuit current density ($J_{sc}$) of 9.21 mA cm$^{-2}$, and a fill factor (FF) of 48.7%, which was comparable to that obtained with reference organic photovoltaics with PEDOT:PSS as HTL.

2. Experimental details

2.1 Material

The polymer donor (P3HT) and acceptor PC$_{61}$BM was obtained from Nano-C. Copper(II) chloride dihydrate (CuCl$_2$·2H$_2$O), aluminium nitrate non-oxydrate [Al(NO$_3$)$_3$·9H$_2$O], thiourea [(NH$_2$)$_2$CS], citric acid (all analytically pure reagents) and ammonium hydroxide were purchased from traditional Chinese chemical companies. All the materials were used without further purification. The solvent used was deionized water.

2.2 Preparation of Cu$_{x}$Al$_{1-x}$S$_y$ films on FTO glass

The FTO substrate was cleaned using ultrasonic cleaning in deionized water, followed by acetone and alcohol for 10 min each. Finally, the substrates were dried in a temperature controlled drying oven.

Aqueous solutions of 0.01 M CuCl$_2$·2H$_2$O, 0.01 M Al(NO$_3$)$_3$·9H$_2$O, 0.04 M (NH$_2$)$_2$CS, 0.02 M citric acid and pH adjuster (ammonium hydroxide) was used to prepare a CuAlS$_2$ thin film. Firstly, CuCl$_2$·2H$_2$O, Al(NO$_3$)$_3$·9H$_2$O and citric acid were placed into a beaker using deionized water as the solvent and then stirred continuously for a few minutes until the solution became homogenous. Then, ammonium hydroxide was added dropwise into the solution until it became a bluish violet colour, and solution was denoted as solution A. The (NH$_2$)$_2$CS was placed into another beaker and dissolved in deionized water, which was denoted as solution B. Solution A and solution B were mixed together to obtain the final solution, and ammonium hydroxide was added dropwise to adjust the pH to 8.8. Subsequently, the FTO substrates were placed into the final solution at 60 °C to obtain the required CuAlS$_2$ film. To prepare the Cu$_x$Al$_{1-x}$S$_y$ film ($x = 0.2, 0.3, 0.5, 0.7, 0.8, 0.9, 1$), the molar ratio of CuCl$_2$·H$_2$O and Al(NO$_3$)$_3$·9H$_2$O was varied, while maintaining the total concentration at 0.02 M, as the remaining steps were processed as described previously. Then the Cu$_x$Al$_{1-x}$S$_y$ films were annealed at 150 °C for 10 min and cooled down to room temperature (RT) prior to use.

2.3 Fabrication of solar cells

The organic solution was prepared by dissolving 10 mg of P3HT and 10 mg of PCBM in 0.5 ml of chlorobenzene with vigorous magnetic stirring for 24 h before use. The organic solution was used for the active layer deposition. It was spin-coated onto Cu$_x$Al$_{1-x}$S$_y$ films at 500 rpm for 6 s and then at 1000 rpm for 20 s, to give a thickness of about 200 nm. The 100 nm thick Al top electrodes were thermally evaporated through a shadow mask under a pressure of about 10$^{-4}$ Pa. Finally, the fabricated devices were thermally annealed on a hot plate at 150 °C for 10 min in an argon filled glovebox. The active area of the device was 0.04 cm$^2$ as defined by the shadow mask.

2.4 Films and device characterization

The transmittance of the films was measured with an ultraviolet-visible -near infrared (UV-Vis-NIR) spectrophotometer (Cary 5000, Varian) in the 300–800 nm wavelength range at RT. The film thickness was measured using ellipsometry. Field-

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Summary of optical and electrical properties of the Cu$<em>x$Al$</em>{1-x}$S$_y$ film annealed at 150 °C for 10 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x$</td>
<td>$E_g$ (eV)</td>
</tr>
<tr>
<td>---------</td>
<td>------------</td>
</tr>
<tr>
<td>0.2</td>
<td>4.01</td>
</tr>
<tr>
<td>0.3</td>
<td>3.76</td>
</tr>
<tr>
<td>0.5</td>
<td>3.60</td>
</tr>
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<td>0.9</td>
<td>2.91</td>
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<td>2.63</td>
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</table>
emission scanning electron microscopy (SEM; FEI XL-30) was used to observe the morphology of the samples. Transmission electron microscopy (TEM; Jeol JEM-2010) was used for the observation of the ultrastructure. Energy dispersive spectrometry (EDS; FEI XL-30) was used to determine the components of the samples. X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) were performed using a XPS/UPS system (ThermoScientific, ESCLAB 250Xi, USA). The compositions and chemical states of the CuAlS₂ films were examined using XPS. Before being tested, the samples were sputter cleaned, to remove atmospheric contamination in the XPS chamber for approximately 30 s, using the lower energy of Ar⁺, and the Ar⁺ gun was operated at 0.5 kV under a pressure of \(1 \times 10^{-7}\) Pa. The vacuum pressure of the analysis chamber was greater than \(1 \times 10^{-8}\) Pa. A whole survey scan to identify the overall surface composition and chemical states was performed, using a monochrome Al Kα X-ray source (1486.68 eV), with detection of photoelectrons at a 150 eV energy pass and a channel width of 500 meV. The surface carbon signal at 284.6 eV was used as an internal standard. The work function and band energy levels were measured using UPS. UPS was carried out using helium \(I_\alpha\) radiation from a discharge lamp operated at 90 W, a pass energy of 10 eV, and a channel width of 25 meV. A \(-9\) V bias was applied to the samples, in order to separate the sample and determine the low kinetic energy cutoffs. The conductivity, carrier concentration and mobility were measured using a Hall effect measurement system (Lake Shore Cryotronics, 7704A). The current–voltage (\(I–V\)) curves of the devices were obtained using a computer controlled Source Measure Unit (Keithley 2400) and the device test was carried out in a glove box under illumination of AM1.5G, 100 mW cm\(^{-2}\) (the light intensity was calibrated using a silicon photodiode) at RT using a solar simulator.

3. Results and discussion

The SEM images of Cu\(_x\)Al\(_{1-x}\)S\(_y\) thin films annealed at 150 °C for 10 min with various composition are shown in Fig. 1. The ratio shown in each SEM image is the ratio of Cu:Al which refers to \(x\)

<table>
<thead>
<tr>
<th>(x) in precursor</th>
<th>Cu (atom%)</th>
<th>Al (atom%)</th>
<th>S (atom%)</th>
</tr>
</thead>
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<tr>
<td>0.2</td>
<td>23.50</td>
<td>76.02</td>
<td>0.48</td>
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<td>23.8</td>
<td>52.9</td>
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<td>0.5</td>
<td>47.17</td>
<td>22.04</td>
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<td>0.7</td>
<td>54.46</td>
<td>14.32</td>
<td>33.22</td>
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<td>0.8</td>
<td>53.62</td>
<td>11.34</td>
<td>35.04</td>
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<tr>
<td>0.9</td>
<td>58.78</td>
<td>6.9</td>
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<tr>
<td>1</td>
<td>61.12</td>
<td>0</td>
<td>38.88</td>
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</table>
0.2, 0.3, 0.5, 0.7, 0.8, 0.9, or 1. The films deposited at 60 °C for 10 min were very uniform. The particle size was defined by testing several small particles using a scaleplate when magnifying the picture. The average size of the particles was about 50–100 nm. As observed, both a cluster-by-cluster process and an ion-by-ion process occurred in the reaction, and the ion-by-ion process was dominant in the formation which could be seen from the small crystal domains in the films. The CuAlS2 (5 : 5) and CuS (10 : 0) films show a similar, smoother film because of their structure, whereas the Cu$_x$Al$_{1-x}$S$_y$ (8 : 2) film has similar round domains.

The transmission spectra of CuAlS2 films on FTO glass (a), (b), (c), (d), (e) and (f). The energy gap $E_g$ was calculated from the equation:

$$a h v = B (h v - E_g)^2$$
where $\alpha$ is the absorption coefficient, which can be calculated from the equation:

$$\alpha = \frac{1}{d} \ln \left( \frac{1}{T} \right)$$

$B$ is a constant and $r$ is an index, which could have values of 1/2, 3/2, 2, and 3, depending on the nature of the electronic transition. The exponent $r = 1/2$ is for allowed direct transition, $r = 3/2$ is for forbidden direct transition, $r = 2$ is for forbidden indirect transition, and $r = 3$ is for allowed indirect transition.

The CuAlS$_2$ film exhibited allowed direct transition. The optical band gap of Cu$_{x}$Al$_{1-x}$S$_y$ film according to the dependence of $(ahv)^2$ on $hv$ was confirmed. The estimated band gaps of the Cu$_{x}$Al$_{1-x}$S$_y$ films at different Cu concentrations are illustrated in Fig. 2(b). Using Fig. 2(b), the CuAlS$_2$ film ($x = 0.5$) was calculated to have a band gap of 3.60 eV which matched well with those figures reported in the literature. Also, as expected, CuS film ($x = 1$) had an optical gap of 2.63 eV, which was very close to the reported values (2.4 eV). As can be seen in Fig. 2(b), starting from CuS, the band gap of the films increased from 2.63 eV to 4.01 eV with the decrease of $x$ (which means that the ratios of Cu to Al became smaller) and the transmittance increased with the decreasing Cu content. Thus, metal chalcogenides with a tunable optical band gap could be obtained by varying the precursor ratio of Cu and Al, and this is promising for applications in optoelectronic devices.

The electrical properties were characterized using Hall effect measurements. As seen in Table 1, there was a variation of optical and electrical parameters of the Cu$_{x}$Al$_{1-x}$S$_y$ thin films which were annealed at 150 °C for 10 min. For each composition with a particular molar ratio, more than three samples were made and tested to ensure the reproducibility, and all the films displayed p-type conductivity. The data listed in Table 1 for the reference was the one which was closer to the average result. Overall, the resistivity shows a tendency to decrease with increasing Cu concentration, as shown in Fig. 3(b). A maximum conductivity of 546 S cm$^{-1}$ in films with $x = 0.7$ was achieved, which was much higher than the values reported for the p-type HTLS.$^{32,33}$ It is interesting that the resistivity of the films between $x = 0.7$ and $x = 0.8$ has a sudden rise, the reason for this is not known at the moment. Hole concentration and mobility were measured using a 7704A Hall system (Lake Shore Cryotronics). As shown in Fig. 3(c), hole mobility appears to increase gradually as the Cu concentration increased, within the range of 0.2 < $x$ < 0.5, and then gently decreased and this takes no account of the CuS film. Compared with other samples, the high conductivity of the film with $x = 0.7$ originates from the relatively higher carrier concentration and mobility. In Fig. 3(d), hole concentration varies from (1–4) × 10$^{21}$ cm$^{-3}$, which is in the range of a highly doped degenerate semiconductor.

Fig. 3 reveals that the band gaps of 2.63–4.01 eV were comparable to p-type transparent materials such as aluminium copper dioxide (CuAlO$_2$; 3.6 eV), and the hole conductivity was comparable to p-type transparent materials such as aluminium (Al; 3.6 eV), whereas the highest sheet resistance and the highest hole mobility was found at $x = 0.5$. The EDS measurements were used to determine the components of the Cu$_{x}$Al$_{1-x}$S$_y$ films. As shown in Table 2, the atom percentage of Al decreased from 76.02% to 0% when $x$ increased, which may be the main reason for the reduction of the optical band gap. In addition, the
increasing atom percentage of Cu and S when $x$ increases might be responsible for the increasing hole mobility. For the CuS film ($x = 1$), the mole ratio of Cu and S revealed the existence of copper sulfide (Cu$_2$S) and CuS. The possible existence of the O element in the film may result in the higher energy gap (2.63 eV).

The XPS spectra of CuAlS$_2$ films ($x = 0.5$, annealed at 150 °C) deposited on glass are shown in Fig. 4. Fig. 4(a) shows a full scale scan of the results of the XPS which found the peaks of Cu, Al, O, S and C. The magnified peaks of the Al 2p, Cu 2p and S 2p scan are shown in Fig. 4(b), (c) and (d), respectively. Fig. 4(b) shows the peak fitting of the Al 2p spectra. The peak fitting for the Al 2p line was divided into two peaks, the peaks at 77 eV and 74 eV revealed the presence of Cu 3p$_{3/2}$ and Al 2p. The peaks of Cu 2p were at 952.9 eV and 932.9 eV. The core levels of Cu 2p$_{3/2}$ indicated that there was a divalent Cu ion in the product whereas the core level of Cu 2p$_{3/2}$ refers to the Cu$^+$. The peaks at 162.0 eV belonged to S 2p. These results were consistent with...
the results found in the literature and have proved that the atomic ratio of elemental Cu and Al was approximately 2 : 1. For further analysis of the CuAlS$_2$ films, TEM measurements were made to observe the ultrastructure. As seen in Fig. 5(a), the particles seem very large which may be because of the thick film. Fig. 5(b) is a typical high resolution TEM (HRTEM) image of the film of CuAlS$_2$, where 10 crystal planes were tested to get an average interplanar distance for each crystal orientation. It was concluded that there is CuAlS$_2$ (112) in the CuAlS$_2$ film with a corresponding interplanar distance of 3.04 Å. The selected area electron diffraction (SAED) pattern of the CuAlS$_2$ film in Fig. 5(c) shows clearly that the CuAlS$_2$ film is a polycrystalline compound.

The UPS measurement was carried out using helium $I_a$ as the UV source. It can be concluded from Fig. 6 that the binding energies of the Cu$_{x}$Al$_{1-x}$S$_2$ films ($x = 0.2, 0.3, 0.5, 0.7, 1$) were 16.07 eV, 15.89 eV, 16.08 eV, 15.92 eV, 15.89 eV, respectively. Thus, the work function of the Cu$_{x}$Al$_{1-x}$S$_2$ films ($x = 0.2, 0.3, 0.5, 0.7, 1$) annealed at 150 °C for 10 min was 5.15 eV, 5.33 eV, 5.14 eV, 5.30 eV, 5.33 eV, respectively. Fig. 6 also shows the energy difference between the top of valence band ($E_v$) and the Fermi level, and it was concluded that the $E_v$ of the Cu$_{x}$Al$_{1-x}$S$_2$ films ($x = 0.2, 0.3, 0.5, 0.7, 1$) were 0.50 eV, 0.25 eV, 0.21 eV, 0.08 eV, 0.13 eV below the Fermi level, respectively, which were 5.65 eV, 5.58 eV, 5.35 eV, 5.38 eV, 5.46 eV, respectively. Take account of the optical band gap of Cu$_{x}$Al$_{1-x}$S$_2$ films mentioned previously in Table 1, the bottom of the conduction band ($E_A$) is set at 1.64 eV, 1.82 eV, 1.75 eV, 2.13 eV, 2.83 eV for $x = 0.2, 0.3, 0.5, 0.7, 1$, respectively. The device structure and energy level alignment are shown in Fig. 7. From the band alignment, the energy band structure of the Cu$_{x}$Al$_{1-x}$S$_2$ films ($x = 0.2, 0.3, 0.5, 0.7, 1$) was determined, and the energy band levels obtained for the Cu$_{x}$Al$_{1-x}$S$_2$ films with excellent p-type conductivity could be suitable for many opto-electronic devices in the future.

To demonstrate the application of p-Cu$_{x}$Al$_{1-x}$S$_2$ films in photovoltaic devices, several heterojunction OSCs were fabricated with the Cu$_{x}$Al$_{1-x}$S$_2$ film used as hole transporting layers. The $J$–$V$ characteristics, which were measured under standard test conditions (1000 W m$^{-2}$, air mass 1.5 global (AM1.5G) spectrum and 25 °C) for the 0.04 cm$^2$ device, are presented in Fig. 8(a). Notably, it was found that a 40 nm CuAlS$_2$ film annealed at 150 °C provided superior performance. As summarized in Table 3, for the FTO/Cu$_{x}$Al$_{1-x}$S$_2$/P3HT:PCBM/Al devices, the PCE of the OSCs increased from 1.22% to 2.45% when $x$ increased from 0.2 to 0.5 because of the increasing hole mobility and the better matched band between Cu$_{x}$Al$_{1-x}$S$_2$ and P3HT. However, the PCE decreased while $x$ increased from 0.5
to 1, and the reasons for this phenomenon might be the decreasing band gap and the decline of the valence band edge. Compared with CuS film and other Cu$_{x}$Al$_{1-x}$S$_{y}$ films ($x=0.7$, 0.9) in Fig. 2(a), more light was transmitted by the CuAlS$_{2}$ film with a wider band gap, which allows more use of the incident light under the same conditions. Furthermore, the variation of $E_V$ is in agreement with the changes in PCE, the $E_V$ of CuAlS$_{2}$ film is closer to the highest occupied molecular orbital (HOMO) of P3HT compared with other films as shown in Fig. 7(b). Thus, the solar cells using CuAlS$_{2}$ film as HTL produced the highest PCE. Although the energy levels between Cu$_{x}$Al$_{1-x}$S$_{y}$ and P3HT were not sufficiently matched to achieve good hole collection, the variable energy levels of the Cu$_{x}$Al$_{1-x}$S$_{y}$ films with tunable band gap were still attractive, and there will be more research with better matched bands in future. Finally, the best PCE was achieved using CuAlS$_{2}$ film as HTL, and a $J_{sc}$ of 9.21 mA cm$^{-2}$ and a $V_{oc}$ of 396 mV were observed, delivering a PCE of 2.67%, which is shown in Fig. 8(b). Further comparison with other HTL can be found in Table S1 (ESI†). Therefore, the CuAlS$_{2}$ film is a good material for solar cell applications.

4. Conclusion

In summary, the optical and electrical characteristics of the Cu$_{x}$Al$_{1-x}$S$_{y}$ thin films prepared on glass sheets and FTO glass using CBD were studied. Upon varying the precursor ratio of the CBD solution, p-type Cu$_{x}$Al$_{1-x}$S$_{y}$ films with different optical and electrical properties were obtained. The band gap can be adjusted from 2.63 eV to 4.01 eV. In particular, the CuAlS$_{2}$ film had a band gap of 3.60 eV and a hole mobility of 1.00 cm$^2$ V$^{-1}$ s$^{-1}$.

Consequently, the films could be used as a hole transporting layer for photocells. The addition of a CuAlS$_{2}$ layer between the anode and the active layer in OSCs can significantly improve the device performance, leading to a 2.67% power efficiency with a device structure of FTO/CuAlS$_{2}$/P3HT:PCBM/Al under simulated AM1.5G 100 mW cm$^{-2}$ illumination. This indicates that CuAlS$_{2}$ is a very promising alternative HTL for OSCs and other opto-electronic devices.

Conflicts of interest

There are no conflicts to declare.

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