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# Characterizations of ZnS/$CuInS_2$ Film Fabricated by Electrochemical Deposition Process for Solar Cell Devices

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***Abstract:*** *In this study, $CuInS_2$ (CIS) films were fabricated by a two-step, non-vacuum process. Electrochemical deposition (ECD) was first used to prepare Cu-In precursors on Mo substrate under constant current. Then, $CuInS_2$ films were prepared by sulfurization of the Cu-In precursors in sulfur atmosphere. The surface morphologies, compositions, and transmittance of the $CuInS_2$ and ZnS films were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), energy dispersive spectroscopy (EDS), and UV-VIS, respectively. The results show that a high-quality CIS thin film solar cells by low-cost, non-vacuum process could be obtained.*

*Keywords: ZnS/$CuInS_2$ layer, electrochemical deposition, chemical bath deposition, CIS thin film solar cells*

## 1. INTRODUCTION

$CuInS_2$ (CIS) is a kind of direct-band-gap semiconductor material. Because of its low cost, long life, and high absorption rate of light can reach up to $10^5 cm^{-1}$, it can function as the absorption layer of solar cells [1]. After 1970s, researchers started to incorporate the $CuInS_2$ film as the solar cells, its electro-optical efficiency can reach to 13% in the laboratory [2-3]. Nowadays, preparation of $CuInS_2$ film has been conducted in various methods such as sputtering [4], evaporation[5-9], spray pyrolysis [10-13], sulfurization after Cu-In deposition[14], chemical bath deposition [15]. Among these fabrication techniques, the electro-depostion with sulfurization has advantages of fast, low cost, and large area production [16]. In addition, the technique can effectively manipulates the thickness, the amount of apertures, and optmize the performance by adjusting the fabrication condition [17].

In this research, we fabricated the $CuInS_2$ film with electrodeposited sulfurization. The Cu-In precusor film was grown on the Mo glass, followed by sulfurization to form $CuInS_2$ thin film. During sulfurization, ambient temperature was an important factor related to crystallization and the change of phase. Therefore, a suitable sulfurization temperature could improve the crystallization and enhance the uniformity of the film. The transformation of phases from Cu-In binary compounds to ternary compounds of Cu-In-S was storngly dependent on a proper sulfurization temperature. Furthermore, a ZnS buffer layer was grown on top of the $CuInS_2$ film. To explore the fabrication condition, the surface morphologies, compositions, and transmittance of the $CuInS_2$ and ZnS films were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), energy dispersive spectroscopy (EDS), and UV-VIS, respectively. The results show that a high-quality CIS thin film solar cells by low-cost, non-vacuum process could be fabricated.

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## 2. EXPERIMENTAL

The electrodeposition system consisted of Pt as the counter electrode and the conductive Mo glass as the working electrode. The composition of electrolyte in the plating solution and electrodeposition conditions are shown in table 1. After the Cu-In alloy film was deposited on the Mo glass, the Cu-In alloy was sulfurized with sulfur powder in a vacuum tube to form a high-quality $CuInS_2$ film. Then, a 70 nm ZnS layer was grown on top of the $CuInS_2$ film by chemical bath deposition (CBD). The solution of the CBD process was $ZnSO_4$ (0.15M), $SC(NH_2)_2$ (0.15M), $NH_4OH$ (25%), and $(NH_4)_2SO_4$ (0.25M), and $(NH_4)_2SO_4$ (0.25M). The ZnS/ $CuInS_2$/Mo film was analyzed by various material and optical measurements. The flowchart of our experiment is shown in Fig. 1.

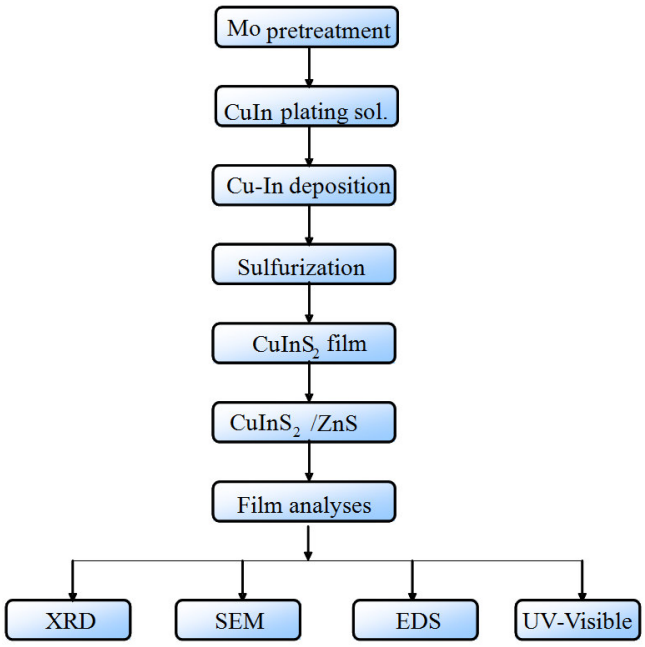



Figure 1. The flow chart of our experiment

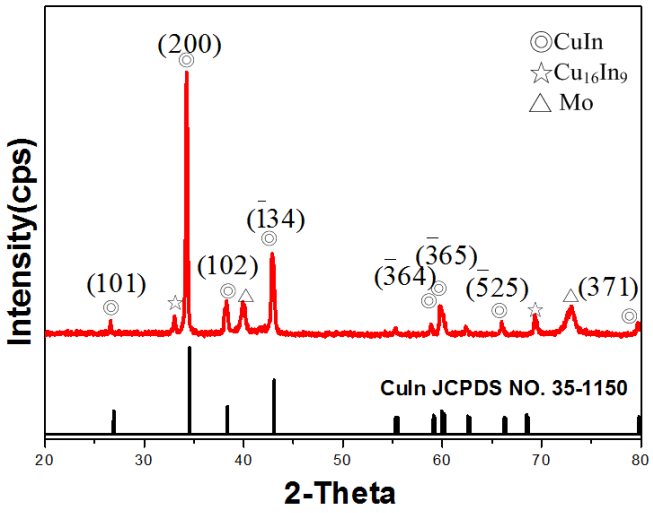



Figure 2. The XRD of the Cu-In film on top of Mo glass

## 3. RESULT AND DISCUSSION

To investigate the Cu-In precusor film, the XRD analysis of the film is shown in Fig. 2. In the XRD spectrum, the highest Cu-In phase (200) peak with a diffraction peak at 34.5˚ can be clearly observed, indicative of formation of a good crystalline phase. The $Cu_{16}In_9$ of intermetallic phase was relatively small compared to the preferable binary compound of the Cu-In film on the Mo glass owing to the proper deposition condition [18]. The surface morphology of the precusor film is shown in Fig. 3. Consistent with the XRD analysis, well-crystallized Cu-In grains can be seen in the SEM image. Sulfurizing the Cu-In film with heating was used with two-step “low temperature - high temperature” heat treatment after electrodeposition [19]. At the beginning, we kept the sulfurization temperature at 150°C for 10 mins. Then, we raised the temperature a final temperautres of 450, 500, and 550°C in a short time. Keep the sample sulfurized in different final temperatures for 120 mins. Figure 4 shows the XRD analysis of $CuInS_2$ film that after sulfurization. According to JCPDS for

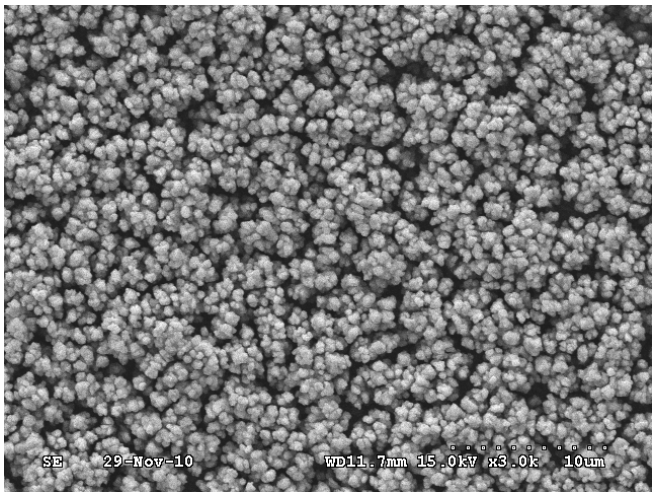



Figure 3. The SEM image of the Cu-In film on top of Mo glass

Table 1. Compositions of the plating solution and the deposition conditions

| Cu-In plating solutions | |
|---|---|
| $CuCl_2$ | 0.008M |
| $InCl_3$ | 0.02M |
| $H_3Cit$ | 1.142M |
| TEA | 0.4M |
| pH | 2.0 |
| Current densities | 1.0～2.0 mA·cm$^{-2}$ |

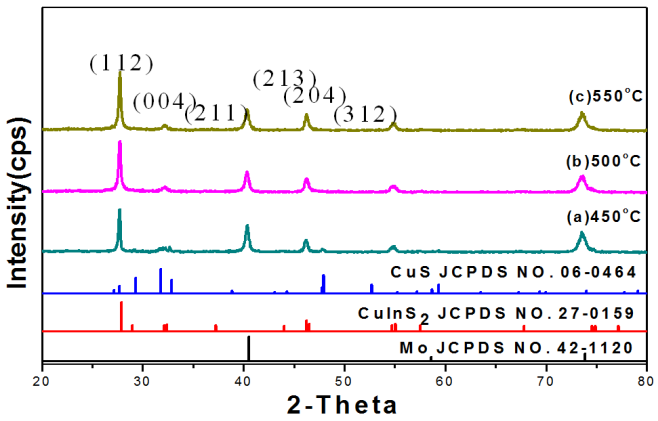
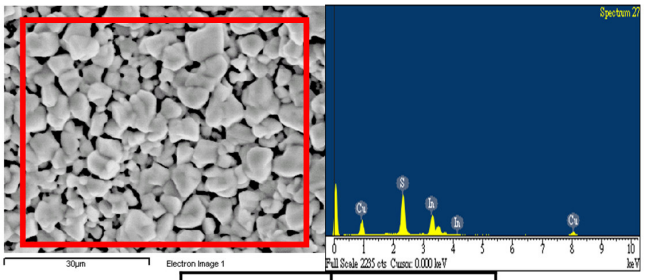



Figure 4. The XRD of the film after sulfurization




| Element | Atomic% |
|---|---|
| S K | 49.77 |
| Cu K | 25.58 |
| In L | 24.66 |

Figure 5. The EDS composition of the $CuInS_2$ film

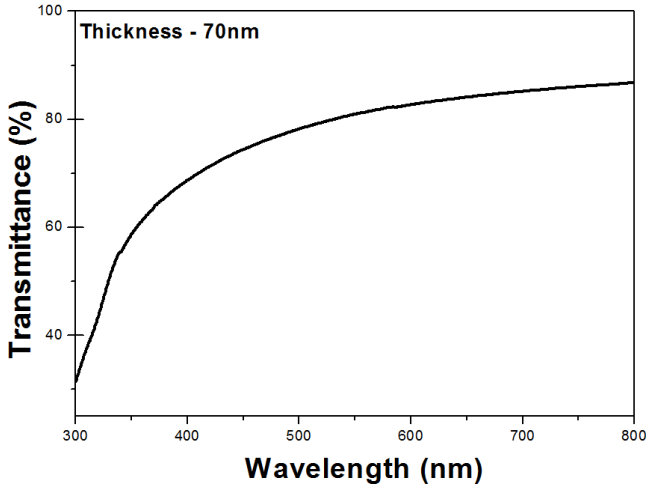



Figure 6. The transmittance of the ZnS film

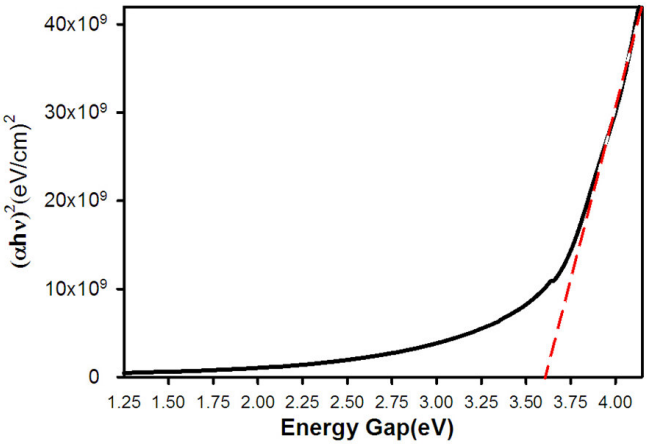



Figure 7. The ZnS energy band gap measurement

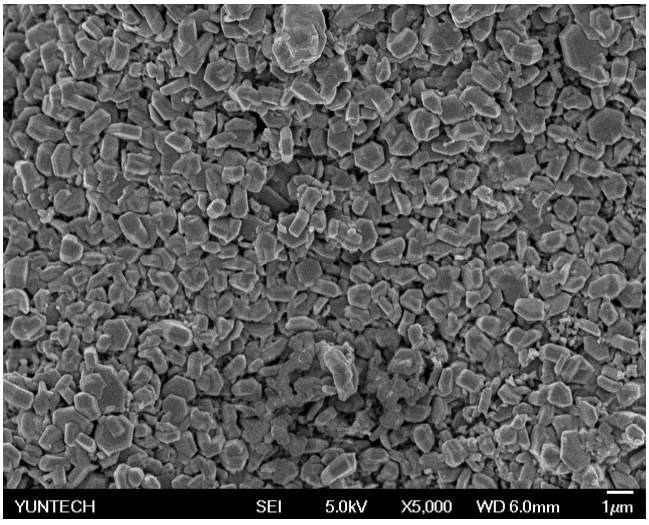



Figure 8. The SEM image of the ZnS film on top of the $CuInS_2$ layer

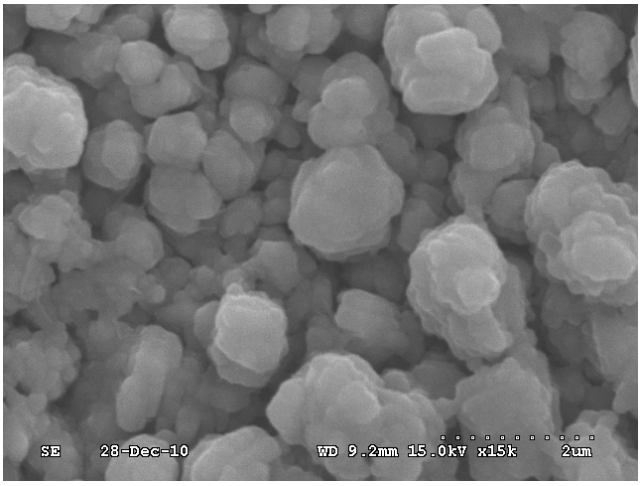



Figure 9. The top-view of the CIS solar cell

diffraction peak (No.27-0159), strong $CuInS_2$ structures can be observed in the XRD spectra. In addition, when the temperature is over 500°C, the diffraction peak of CuS disappeared. According to a previous research [18], an intermediate state of CuS during surfuization might be present near 400°C. A high sulfurzation temperature above 500°C can enhance the formation of Cu-In-$S_2$. In accordance with EDS analysis as shown in Fig. 5, the composition ratio of Cu, In, and S was close to the ideal ratio of $CuInS_2$ (1:1:2). The EDS results further confirm the removal of CuS impurity and the formation of well-crystallized $CuInS_2$. Therefore, the sulfurzation temperature of 550°C could fabricate high-qualtiy $CuInS_2$ film on top of the Mo glass.

Since electron-hole pairs induced by sunlight in the absorption layer would rapidly recombine again, a ZnS layer was required as a buffer layer of the CIS film solar cells to decrease probability of carrier recombination. Based on previous research [20] [21], a ZnS

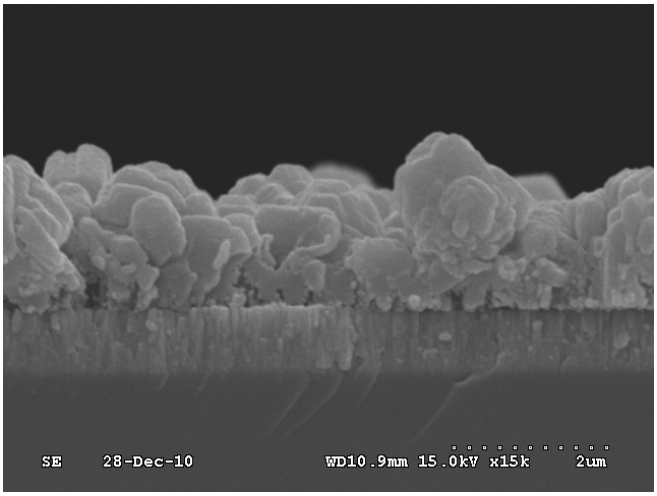



Figure 10. The cross-section of the CIS solar cell.

buffer layer with high performance can be fabricated by CBD. Because the buffer layers must have high light penetration rate lest blocking the the light absorption, we conducted the penetration measurements with UV/VIS spectrophotometer with the wavelength range of scanning from 300nm ~ 800nm. Figure 6 shows that the penetration rate of the ZnS layer fabricated by CBD was about 80% in the visible light range. Also, from the energy bandgap measurements as shown in Fig. 7, we observed that the energy bandgap of ZnS was about 3.6 eV corresponding with wide energy gap requirements of general CIS buffer layers. Therefore, most of light in the solar spectrum could pass the buffer layer. Furthermore, In addtion, a SEM image of the high-quality well-crystallized ZnS film is shown in Fig. 8, which is consistent with the good optical properties of the ZnS film.

Finally, we sputterd a 100nm ZnO (n-type) layer and a 450nm AZO (ZnO: Al) layer on top of the ZnS/ $CuInS_2$/Mo film [22]. Figure 9 shows the top-view SEM image of the solar cell structure, and Fig. 10 shows a SEM image of the cross-section solar cell structure. Well-contacted interfaces and well-grown Cu-$InS_2$/ZnS/ZnO/AZO can be seen in the cross-section [23]. The film structure was composed of Mo/$CuInS_2$/ZnS/ZnO/AZO (from bottom to top) with the thickness of whole components is about 2.5μm.

## 4. CONCLUSION

In this research we fabricated a ZnS/$CuInS_2$/Mo film compatible with the CIS solar cell structure with electro-deposition, sulfurization, and CBD. The composition ratio of three element Cu/In/S close to a standard stoichiometric ratio of 1:1:2 at a temperature of 500°C. Furthermore, a well-crystallized $CuInS_2$ layer and a high penetration ZnS buffer layer have been fabricated and examined by mutiple material and optical analyses. The ZnS/$CuInS_2$/Mo shows great promises for future solar cell applications.

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