**Preparation of CuInS₂ Thin Film Using Sulfides Nanoparticle Precursor Ink**

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A low cost spin coating route of fabricating CuInS₂ polycrystalline thin films by reactive sintering method was put forward. The ink for spin coating was optimized by pre-reducing the precursor powders in hydrogen, which turned the nanoparticle precursor powders from mixed sulfides into a mixture of CuInS₂ and Cu-In metal alloys. The results of scanning electron microscopy, energy dispersive spectroscopy, X-ray diffraction, and Raman spectra showed that this optimization could highly improve the performance of CuInS₂ polycrystalline thin films, including higher packing density, less impurity phases, and better quality. The energy gap of optimized CuInS₂ thin film was determined to be about 1.45 eV by absorption spectroscopy measurement.

**Key words:** CuInS₂ thin film, Nanoparticle, Ink, Spin coating

I. INTRODUCTION

As a member of the chalcopyrite family, CuInS₂ is a very promising material for thin film photovoltaics due to its direct band gap (1.50 eV) and high absorption coefficient (>10⁵ cm⁻¹) and non-degradable properties compared to other solar cell materials [1, 2]. The highest efficiency of CuInS₂-based solar cells reported up to now is 12.5% in laboratory prepared by co-evaporation as well as sequential processes [3]. However, the vacuum evaporation method is hardly applied to an industry relevant area because of the high cost of the vacuum equipment. Therefore, a low-cost method is required for the mass production of CuInS₂-based solar cells.

Slurry or Ink deposition by large-area non-vacuum coating methods are attractive low cost approaches for the growth of thin film solar cell absorbers. Precursor films obtained from precursor ink by wet printing method, such as screen printing, spin coating, roll coating, spraying or doctor blade, can be transformed into CuInSe₂ or CuInS₂ layers after annealing treatment in selenium or sulfur containing ambience. Now there have been attempts of precursor inks containing nanoparticle oxides [4-6] or selenides [7, 8], but no attempts of ink containing sulfides. Due to the difficulty of sintering the film dense and forming the pure phase for sulfides, reactive annealing through chemical reaction has been chosen in this article. Sulfides produced by co-precipitation were reduced in H₂ ambience, so pre-reducing the ink containing sulfides. Reactive sintering annealing process flow by non-vacuum method. Nano-powder mixture of sulfides of copper and indium metals was obtained by the co-precipitation method. Cu(NO₃)₂ (A.R.), In(NO₃)₃ (A.R.) and Na₂S (A.R.) were chosen as the initial reactants. Cu(NO₃)₂ and In(NO₃)₃ mixture solution was dropwise added into Na₂S solution with continuous stirring. Polyethylene glycol 10000 was used as additive to prevent aggregation of the precipitated particles [9]. The pH value was controlled between 1.0 and 3.0 by adding nitric acid, while the precipitation reaction temperature was controlled at 65 ºC throughout the precipitation process. After filtered and washed by deionized water and ethanol in sequence several times, a gelatinous precipitate of mixed sulfides was obtained, followed by drying at 60 ºC to yield sulfides particles with an average size of approximately 10 nm. Afterwards, part of the sulfides powder was reduced in H₂ ambience in an annealing furnace for 1 h.

Inks for spin coating were prepared by mixing and milling the precursor powders with organic dispersing agent consisting of ethyl cellulose and terpineol. Two kinds of inks were prepared in this work: ink 1 was prepared by milling the non-reduced powders and the organic dispersing agent mentioned above, while ink 2 was prepared by milling the partly reduced powders and the organic dispersing agents. After spin coating and annealing, two samples were obtained to make a comparison: sample 1 obtained from ink 1, sample 2 ob-
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FIG. 1 CuInS$_2$ absorber layer preparation process flow chart.

B. Process of spin coating and sulfidation

CuInS$_2$ polycrystalline thin films were obtained by the two-step spin coating method. Precursor inks mentioned above were spin coated on soda lime or Mo-coated soda lime glass substrates. The spinning speed was set at 1000 r/min for 9 s and 3000 r/min for 50 s. Precursor thin films were gained after being dried in a vacuum oven at 100 °C. Then the films were sulfurized in a quasi-closed quartz tube in a vacuum furnace of 1 Pa. The evaporation temperature of sulfur powder was 300 °C, while the substrate was fixed at 550 °C for 30 min to form CuInS$_2$ polycrystalline phase, then the temperature of the furnace decreased from 550 °C to room temperature at a rate of 6 °C/min, which could prevent the CuInS$_2$ films from falling off substrates [10].

C. Characterization

The phase composition and the crystal structure of the films were identified by X-ray diffraction (XRD) method (D/Max-rA). Microstructure of the obtained powders and absorber layers were examined by field emission scanning electron microscope JEOL-JSM-6700F and a JEOL JSM-6390LA scanning electron microscope respectively, while chemical compositions were measured using energy dispersive spectroscopy (EDS) technique. The Raman spectra were obtained in backscattering configuration at room temperature on a LABRAM-HR spectrometer using a 514.5 nm wavelength as a light source. The optical properties of the sample were investigated using an UV-VIS-365-type spectrophotometer in the wavelength range of 400–1200 nm at room temperature.

III. RESULTS AND DISCUSSION

According to Eberspacher et al., the size of mixed nano-particles for preparing ink needed to be sub-micron scale (e.g. size below 100 nm) [11]. The mixed sulfides of copper and indium metals powder prepared by co-precipitation method had the proper size. As can be seen in Fig.2(a), the average size of obtained mixed metal sulfides was only about 10 nm. After reduction by H$_2$, the average size of the particles was around 60–70 nm, still below 100 nm (Fig.2(b)). So both the mixed metal sulfides and the partly reduced powders were suitable to prepare inks.

The surface micrographs of sample 1 and sample 2 were shown in Fig.3. In Fig.3(a), the film was not continuous and lots of large particles which represented an impurity phase could be observed. However, no large particles could be found in the surface of sample 2 in Fig.3(b), which indicated that sample 2 had more uniform and dense surface than sample 1. In order to confirm the composition and phase structure of these large-particles, local EDS was used to analysis their composition and XRD was used to investigate their phase structure.

The results of EDS showed that the large particles in sample 1 contained 48.89% of Cu, 10.62% of In, and 40.49% of S in atom. Since the atom ratio of Cu:In:S reached 4.6:1:3.8 and little In element could be detected, the large particles in sample 1 could be considered as
CuS phase. It could also be seen in Table I that Cu accounted for 23.65%, In 25.53%, and S 50.82% of the composition of sample 2 in atom. The atom ratio of Cu:In:S could be calculated to be very near 1:1:2, where the composition agreed with CuInS$_2$ phase.

Figure 4 showed the XRD patterns of sample 1 and sample 2. In the XRD patterns no peaks of CuS could be observed. From Fig.4(a), three main peaks observed at $2\theta$=27.96°, 46.42°, and 55.14° corresponded to the (112), (204)/(220), and (312) phase of CuInS$_2$ respectively, which indicated a chalcopyrite phase of CuInS$_2$. Besides these three peaks, two other peaks were observed at $2\theta$=32.54° which was attributed to the CuInS$_2$ (200) phase and $2\theta$=40.56° belonging to the Mo in the XRD spectrum for sample 2. This pattern was in agreement with the reported features of the stoichiometric CuInS$_2$ with a tetragonal chalcopyrite phase. The pattern also exhibited that the crystal structure of sample 2 was better than that of sample 1 from the intensities of peaks.

Figure 5 showed Raman spectra of sample 1 and sample 2. In the Raman spectrum of sample 2, there were two peaks observed at 298 and 305 cm$^{-1}$ assigned to CuInS$_2$ phase, another mode at 475 cm$^{-1}$ could be observed obviously, which indicated the presence of CuS and/or Cu$_2$S phase. According to the research of Podder et al., both the CuS and Cu$_2$S have the dominate mode at 475 cm$^{-1}$ [13, 14]. The results of SEM and EDS analysis of sample 1 were furthermore confirmed by the Raman spectra. The reason of secondary phase existing in sample 1 was that the melting point of sulfides was so high that it was difficult to sinter at sulfidation. The metal alloy existed in sulfides not only improved the quantity of thin films, but also provided a reactive annealing at the process of fabricated CuInS$_2$ films. This could be explained that the metal alloy in sulfides would react with sulfur in sulfur atmosphere and improved sintering character of sulfides.

The photon energy dependence of the absorption coefficient for CuInS$_2$ films was shown in Fig.6. The optical absorbance of CuInS$_2$ thin film prepared from ink 2 was measured on an UV-VIS-365-type spectrophotometer in the wavelength range of 400–1200 nm at room temperature. In order to achieve the exact optical bandgap ($E_g$) of the film, the following equations

\[
\frac{(\alpha h\nu)^2}{h\nu} = \frac{A}{E_g - h\nu}
\]
were calculated (Eq.(1) and Eq.(2)) [15]:

\[ h\nu = \frac{1240}{\lambda} \]  

(1)

\[ \alpha = \frac{A}{h\nu} \sqrt{h\nu - E_g} \]  

(2)

where \( h\nu \) is the radiation energy, \( \lambda \) is the detected wavelength, \( \alpha \) is the absorption coefficient, \( A \) is a constant of 0.4343 here, and \( E_g \) is the transition energy. Eq.(3) was transformed from Eq.(2):

\[ E_g = h\nu - \frac{1}{A^2} (\alpha h\nu)^2 \]  

(3)

Eq.(3) indicates that the optical bandgap can be obtained by plotting the straight line between \((\alpha h\nu)^2\) and \(h\nu\), making use of the extrapolation of the energy axis. By making a proper tangent, the bandgap value was obtained at the intersection point of the tangent and the \( h\nu \) axis. Using these equations, the optical bandgap was determined to be approximately 1.45 eV, as shown in Fig.6. Moreover, the linear nature of the plots through the absorption range indicates that the compound \( \text{CuInS}_2 \) thin film prepared from precursor ink containing partly reduced powders has a direct band gap [16].

IV. CONCLUSION

Nanoparticle sulfides of copper and indium metals were obtained by co-precipitation method. Copper indium disulfide thin films were prepared by spin coating method using sulfide nanoparticle ink. But this method led to the presence of secondary phase, so the necessity of reduction process was confirmed. The XRD, SEM, and EDS results of \( \text{CuInS}_2 \) thin films fabricated by this route showed a good stoichiometric phase and no secondary phase was found. Raman spectra confirmed that no sulfide of copper or indium compounds appeared in the thin films. A band gap of about 1.45 eV of \( \text{CuInS}_2 \) thin film was obtained by absorption spectroscopy measurement.

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