

The preparation of CuInSe₂ films by direct selenization of the CuIn oxides precursors

PAIFENG LUO*, YUANKUI DING, ZHAOFAN LIU, LI ZHOU, YUEQIANG DIAO

Department of Materials Science and Engineering, Hefei University of Technology, Hefei, Anhui, 230009, P.R. China

A low-cost non-vacuum process for the deposition of CuInSe₂ (CIS) films is reported in this work. First, Cu-In oxides precursors are prepared by the traditional grinding method. Second, the precursor layers are deposited via spin-coating from oxides slurry. Finally, CIS films are achieved after direct selenization reaction without the complicated hydrogen reduction process. The desired near stoichiometric CIS films with up to micron-scaled grain size show the dominant chalcopyrite structure with preferred (112) orientation by XRD, Raman spectra, SEM and XRF. A band gap about 1.0 eV and an absorption coefficient exceeding 10⁵ cm⁻¹ are also obtained by absorption spectroscopy measurement in our study.

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1. Introduction

CIS and its chalcopyrite compounds are considered the best optical absorber layer materials used in thin film photovoltaic devices due to their favorable electrical and optical properties, and long term stability [1,2,3]. So many techniques including co-evaporation [4], sputtering [5,6], and pulsed laser deposition (PLD) [7,8,9] have been employed for fabrication of the CIS films. However, the general vacuum routes are not readily adaptable to the low cost production of large area thin films, mainly because uniform deposition on large-scale substrates is not so easy, the composition control of the film is difficult, the vacuum equipments are also very expensive and the utilization of the raw materials is limited. On the other hand, low-cost non-vacuum techniques for CIS thin films deposition are inherently suitable for large-scale applications, which benefit from mature commercial industries of coating, paints, inks and electronic ceramics. Therefore, more research and development on simple non-vacuum deposition techniques are necessary for breakthrough in the industrial manufacture of CIS solar cells.

The non-vacuum recipe has been pioneered by Kapur [10] and Eberspacher [11] respectively, and high efficiency of up to 13% has been demonstrated. But there are several drawbacks to these methods, such as the high-temperature hydrogen reduction steps are potentially explosive, the mechanical milling may result in the non-uniform distribution of the particle size and incorporating undesired impurities. In this work, a non-vacuum approach of fabrication CIS films includes preparation of Cu-In oxides precursors, synthesis the slurry, thin film spin-coating, post-heat treatment, and selenization process. The key advantages of our recipe are (1) Employing the most convenient grinding process to obtain precursor powder and also the first applied in the CIS solar cells, (2)

Direct selenizing the Cu-In oxides precursors and avoiding the terrible hydrogen reduction process, (3) Low cost of processing equipment and high materials utilization. The structure and the optical properties of the Cu-In oxides precursors and the CIS films are also investigated.

2. Experimental

Fig. 1 shows the schematic diagram of CIS films fabrication with non-vacuum process. First, the Cu-In oxides precursors are prepared by simple solid-state reaction. CuCl₂·2H₂O and NaOH are mixed and milled at ambient temperature in an agate mortar until the color of the powder changes from blue to black. Then the mixed precursors need to be washed three times in DI water to remove the soluble impurities. All vacuum-dried CuO powder shows deep black color. Using the same route, In(NO₃)₃·4H₂O and NaOH are mixed and milled to at ambient temperature in an agate mortar. The fine powder of In₂O₃ can also be obtained after washed and dried the mixed precursors. Then CuO and In₂O₃ are weighed in exact amount to obtain the desired Cu/In ratio and grinded for 2 hours at room temperature. Second, a suitable dispersant is selected to formulate the slurry containing Cu-In oxides components with suitable viscosity to fabricate CIS precursor layer through spin-coating. Finally, the precursor films are heated to remove solvent and burnt organic additive, and then placed in a tubular furnace for selenization reaction at 500°C for 1 hour in a quasi-closed quartz tube and using Se powder as the Se-source. The schematic diagram of the selenization furnace is shown in Fig. 2.

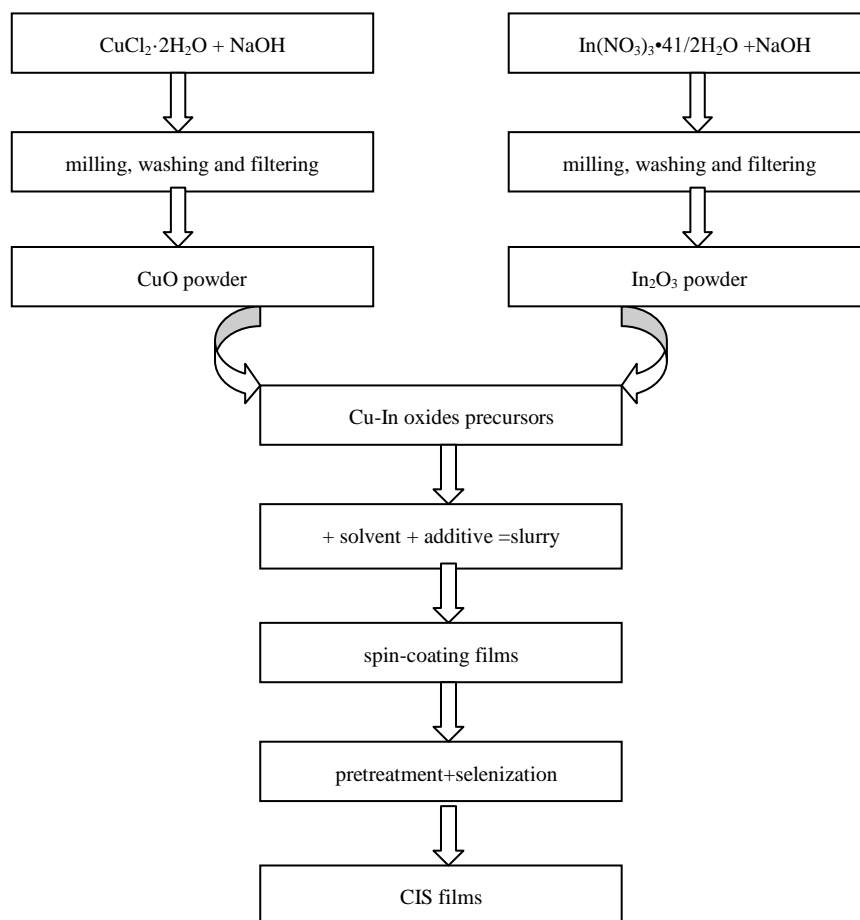


Fig. 1. The schematic diagram of CIS films fabrication with non-vacuum process.

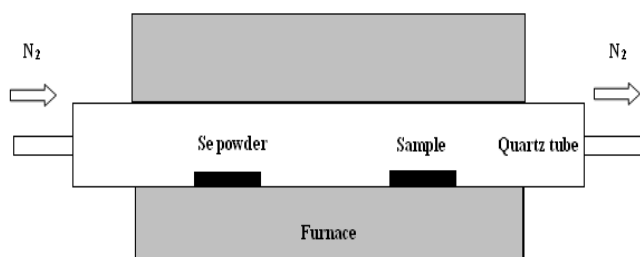


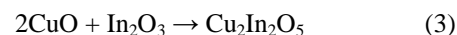
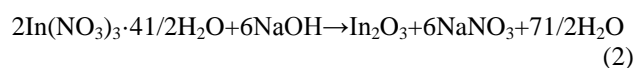
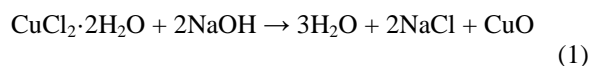
Fig. 2. The schematic diagram of the selenization furnace.

The phase composition and the crystal structure of the films are identified by XRD method (D/Max-rA). The morphology of the films is observed on a field emission scanning electron microscope (FESEM, JEOL-JSM-6700F). The composition of CIS films is measured by X-ray fluorescence (XRF) (SHIMADZU, VF-320) method. The optical absorption spectrum is recorded on a UV-vis-365-type spectrophotometer in a range 800-1500 nm.

3. Results and discussions

3.1 Preparation of Cu/In oxides precursors

Fig. 3 shows the X-ray diffraction patterns of the Cu-In oxides precursor. After milling the Cu-In oxides precursors at room temperature, it shows the dominant CuO, In_2O_3 and $\text{Cu}_2\text{In}_2\text{O}_5$ phases. CuO phase shows the preferred (111) orientation and the In_2O_3 film has the preferred (400) orientation. It also can be proved that the Cu-In oxides precursors react with each other from the XRD result. The possible reactions as follows:



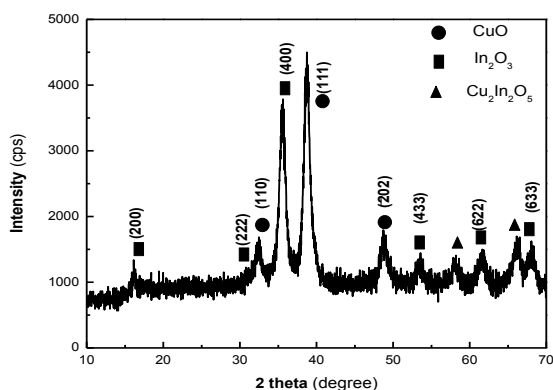


Fig. 3. The XRD pattern of the Cu-In oxides precursors.

The planar SEM micrograph of pretreatment oxides precursors after spin-coating on glass substrate are shown in Fig. 4. A large number of spherical particles with approximately 100 nm in diameter are observed in the organic package and it has the uniform distribution of the particle size which can be easily controlled by milling time. The organisms also can volatilize from the precursors during the pretreatment process.

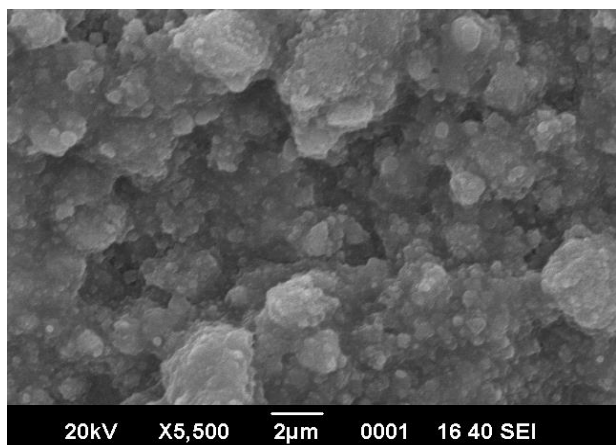


Fig. 4. The SEM micrograph of the Cu-In oxides precursors after spin-coating.

The composition of the Cu-In oxides precursors is accurately determined by XRF method. In considering the volatilization of In element during the high temperature selenization process, the ratio of Cu/In in the raw materials is 0.9. As shown in Table 1, the ratio of Cu/In is not changed after the pretreatment process, which is well corresponding to the composition of the raw ingredients.

Table 1. The composition of the Cu-In oxides precursor by XRF method.

Name	Cu%	In%
Ar.%	47.37	52.63

From the XRD, SEM and XRF results, it can be concluded that the uniform oxides precursors are obtained through the solid-state reaction at room temperature, which should be the simplest technology for preparing the Cu-In oxides precursors. Other methods, such as the mechanical milling and high temperature oxidation, may cause the non-uniform distribution of the particle size, incorporate impurities and also increase the cost.

3.2 Selenization of Cu/In oxides precursors

Fig. 5 shows the X-ray diffraction patterns of CIS films on glass substrate. The CIS film exhibits preferential orientation along the chalcopyrite phase α -CIS (112) direction at 26.74°. The other prominent peaks correspond to the (204)/(220) and (116)/(312) phase. In addition to these commonly observed orientations, the weak orientations such as (101), (211) and (008) are also observed in the XRD pattern, distinguishing the chalcopyrite phase from the sphalerite phase. After selenization of the Cu-In oxides precursors, almost all peaks observed on the patterns are well accord with the diffraction lines in the chalcopyrite structure of CIS, and no peaks excepting Cu_{2-x}Se, which is usually observed in the CIS films and can be removed by KCN, are found from any other phases. Kaelin [12,13] has revealed difficulties in converting the stable compound In₂O₃ into their selenide phase using selenium vapor. But the In₂O₃ phase is not found in our study which would result in poor quality of CIS films and detrimental the efficiency of the solar cells. It may be caused by a quasi-closed quartz crucible used in our experiment and thus produces a higher vapor pressure of selenium.

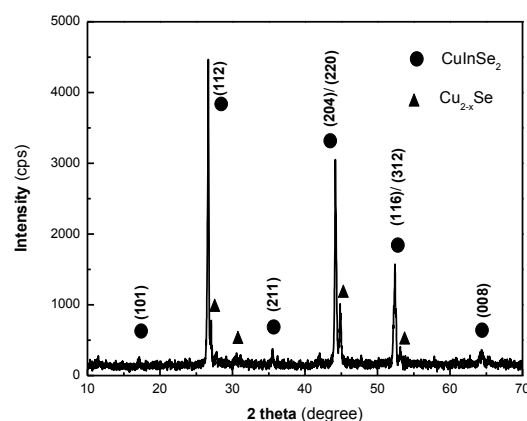


Fig. 5. The XRD pattern of the CIS films.

The planar SEM micrograph of CIS films is shown in Fig. 6. The dense and well-defined uniform grains with larger sizes which attain micron levels are formed on the glass substrate. The photovoltaic devices are typically fabricated using a uniform absorber layer applied in solar cells in order to avoid the formation of undesirable shunt paths, so the distribution of the particles and the roughness must be the key issues. According to the experiment result, high quality CIS films with large grain size were achieved in this study.

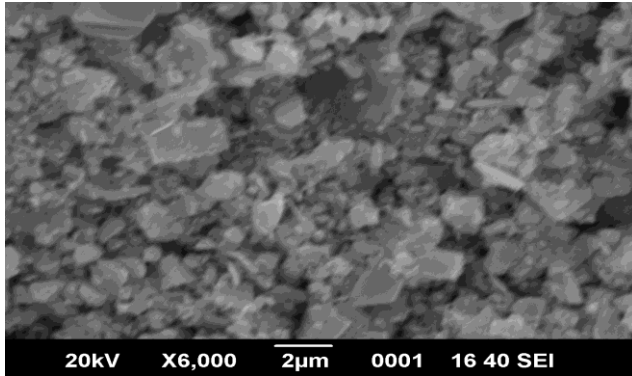


Fig. 6. The planar SEM micrograph of CIS films.

As shown in Table 2, the composition of the CIS films is also accurately determined by XRF. The ratio of Cu/In/Se is very close in composition to 1/1/2. Contrasting with the ratio of Cu/In in the raw materials, it can be observed that a little amount of In is lost during the course of selenization, which seems probably due to the slow rate of heating temperature. Finally, the high quality and the typical near stoichiometric little Cu-rich CIS films are obtained in our work.

Table 2. The composition of the CIS films determined by XRF method.

Name	Cu%	In%	Se%
Ar.%	25.13	24.28	50.59

Fig. 7 shows the typical Raman spectra of CIS films. To compare with CIS films, the Raman spectra of Cu_{2-x}Se phase are also shown with dashed line. In general, CIS films show A_1 mode at approximately 175 cm^{-1} , which usually observed in I-II-VI₂ chalcopyrite compounds [14]. Some weak peaks at 217 cm^{-1} and 233 cm^{-1} shown in Fig. 7 are also identical with the predicted modes in CIS [15]. CIS films with poor crystallization property show weak A_1 peak and an additional shoulder peak at 258 cm^{-1} . This peak could be related to the presence of Cu_{2-x}Se secondary phase, as shown by the dashed line in the Fig. 7, with symmetry of lattice vibrations different from

chalcopyrite. The presence of this shoulder peak indicates the formation of a highly distorted structure of the CIS material after the selenization process [9]. In our research, there is a weak peak at 258 cm^{-1} as shown through the solid line which can be explained by the formation of dominant CIS chalcopyrite structure and the additional Cu_{2-x}Se phase.

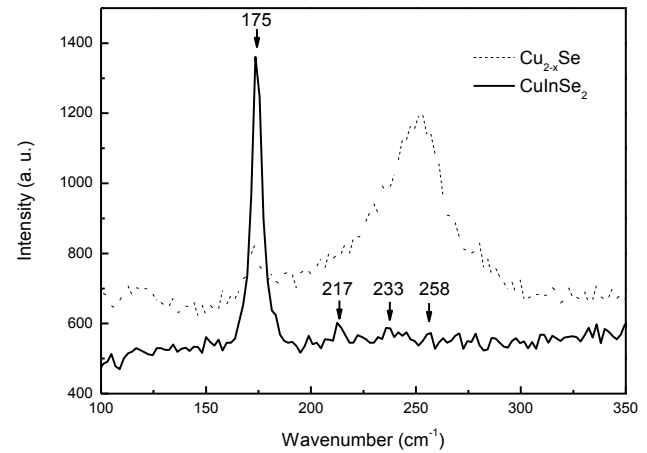


Fig. 7. The raman spectra of CIS thin films.

The optical absorption spectra are detected on a UV-vis-365-type spectrophotometer in a range 800-1500 nm. The photon energy dependence of the absorption coefficient for CIS films is shown in Fig. 8. A high absorption coefficient exceeding 10^5 cm^{-1} is obtained by absorption spectroscopy measurement, which shows a good optical quality of the CIS films. As is well known, CIS is a direct-gap semiconductor with the valence-band maximum and conduction-band minimum at $k = 0$. So an energy band gap about 1.0 eV is obtained by absorption spectroscopy measurement. The energy band gap is very close to the normal value of 1.04 eV at room temperature [16], which can be explained by the little Cu-rich component.

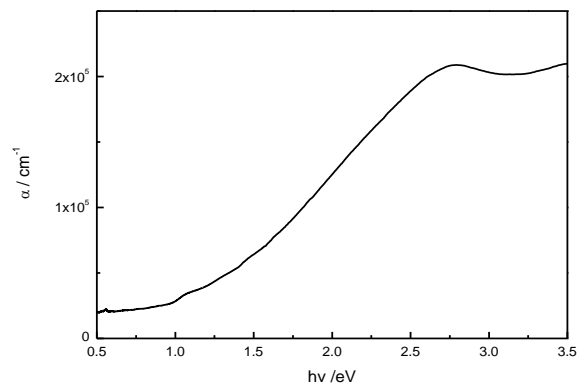


Fig. 8. The photon energy dependence of the absorption coefficient for CIS films.

4. Conclusion

The high-quality CIS films are obtained by a low-cost non-vacuum process. The uniform Cu-In oxides precursors are prepared through solid-state reaction. After spin-coating the slurry and selenization process, the dominant chalcopyrite structure with preferred (112) orientation and the typical near stoichiometric CIS films are achieved in our work. The Raman spectra of grown films show A₁ mode at approximately 175 cm⁻¹, generally observed in I-II-VI₂ chalcopyrite compounds. The energy band gap about 1.0 eV and an absorption coefficient exceeding 10⁵ cm⁻¹ are also determined by absorption spectroscopy measurement. In a word, we develop a simple and low-cost technology for preparing the absorption layer which indicates a promising way for large-scale industrial manufacture of CIS solar cells.

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*Corresponding author: lpfeng@mail.ustc.edu.cn