Control of III/VI ratios in the preparation of In_2Se_3 thin films

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$CuInSe_2$ (CIS) thin films on glass substrates were successfully grown by the metal organic chemical vapour deposition method by using three precursors [Cu-precursor, trimethyl-indium (TMI) and hydrogen selenide (H_2Se)]. The flow rates of TMI and H_2Se can be adjusted independently to gain different III/VI ratios, which is different from the single-precursor technique. Good chalcopyrite phase from CIS films was demonstrated by X-ray diffraction. The optical band gap of CIS thin films can be adjusted by controlling the growth conditions.

Keywords: metal organic chemical vapour deposition, $CuInSe_2$ thin films, photoluminescence

$CuInSe_2$ (CIS) thin films have attracted extensive attention due to their potential applications in solar cells. For photovoltaic applications, CIS thin films have the advantages of a strong absorption coefficient as well as good thermal stability.[1] A high conversion efficiency of 19.5% has been achieved for the CIS solar cells.[2] Therefore, CIS thin films are promising materials for thin-film solar cells. Methods reported for growing CIS thin films include: molecular beam epitaxy (MBE),[3] electrochemical synthesis,[4] evaporation,[5] selenisation[6] and metal organic chemical vapour deposition (MOCVD).[7,8] MOCVD is a well-known technique, that can control the structure of deposited films and grow high-quality thin films by using proper precursors. Single-source precursors have been used for deposition of CIS thin films by MOCVD.[7,8] Lee *et al.*[7] used the single-source precursor, bis(ethylbutyrylacetato)copper(II), on glass substrates, and treated it with tris(N,N-ethylbutyldithiocarbamato)indium (III) to produce CIS films by MOCVD. This technique can successfully grow CIS thin films on various substrates such as glass and ITO glass. Yoon *et al.*[8] fabricated CIS thin films on molybdenum substrates by using bis(ethylisobutyrylacetato) copper(II) with a single-source precursor (dimethylindium). In recent years, CIS-based solar cells have been proposed to be fabricated from In_2Se_3 thin films. We have studied CIS thin films grown by MOCVD whilst controlling the III/VI ratio. The growth method used the three-precursor technique, which is easy for mass production and the developments of CIS-based solar cells. This technique is different from single-source precursor MOCVD, which has a fixed III/VI ratio. The structural and optical properties of the grown CIS films were analysed by X-ray diffraction and photoluminescence (PL).

Experimental

CIS thin films were grown on glass substrates through MOCVD using three precursors: *i.e.*, Cu-precursor, trimethylindium (TMI) and hydrogen selenide (H_2Se). The flow rate of Cu precursor is fixed, however, the flow rate of TMI and H_2Se can be adjusted independently to gain different III/VI ratios. The III/VI ratio is defined by the rate of the indium atoms and selenium atoms. Before growth, the glass substrate was coated with a copper thin film by electron beam deposition. The precursors of indium and selenium were TMI and H_2Se, respectively. The flow rate of TMI was kept at 3 μmol min^{-1} and that of H_2Se varied from 3 to 40 μmol min^{-1}. We utilised N_2 as a carrier gas and the flow rate was kept at 5 L min^{-1}. The InSe thin films were deposited at 480 °C for 40 minutes and subjected to *in situ* annealing at 550 °C for 100 minutes. The growth conditions for the investigated CIS thin films are shown in Table 1.

Optical properties of the grown CIS thin films have been investigated by PL. The PL measurements were performed by using a pulsed laser operating at a wavelength of 635 nm as the excitation source. The light pulse was produced with 50 ps duration and a repetition rate of 5 MHz. The luminescence was detected with an extended InGaAs detector and a high-speed photomultiplier tube. PL decay signals were measured by using the technique of time-correlated single-photon counting. The overall temporal response function of the system was 250 ps.

Results and discussion

Figure 1 shows a representative scanning electron micrograph (SEM) of the surface morphologies of CIS thin films (sample CIS-55) annealed at 550 °C for 100 minutes on glass (100) substrates. The SEM pictures show that the films are polycrystalline with large grains. The average grain size in the top view is about 1μm. Figure 2 is a representative electron microscope image of the cross section of CIS thin films (sample CIS-55) grown on glass (100) substrates. The estimated thickness of the films is about 1.06 μm. Compared with the CIS thin films grown by other methods,[1,6,8] our thin films reveal better polycrystalline morphology.

Figure 3 shows the X-ray diffraction chart of a CIS thin film (sample CIS-55) annealed at 400 °C for 55 minutes on a glass

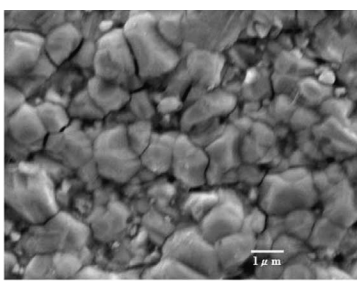

Fig. 1 Surface morphology of typical CIS thin films.

Table 1 Growth conditions of $CuInSe_2$ thin films

	Temperature/°C	H_2Se/μmol/min^{-1}	TMI/μmol/min^{-1}	TMIΔt/min	N_2/sccm
CIS 55	480	40	3	35	5
CIS 56	480	40	3	20	5

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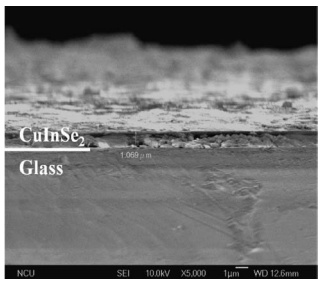

Fig. 2 SEM image of the cross-section of CIS thin films grown on glasses.

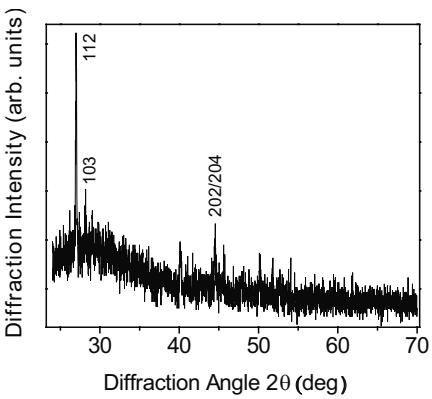

Fig. 3 The XRD charts of the CIS thin films.

substrate. This CIS thin film displays narrow and strong peaks in the XRD chart. The main peak of the (112) reflection and other characteristic peaks, namely (202/204) and (103), show the preferred orientation of crystalline structures. All peaks observed on the charts were in good agreement with the diffraction lines in the chalcopyrite structure of CIS and the previous report from Zaretskaya *et al.*[9] This X-ray diffraction chart demonstrates that good chalcopyrite phases from CIS films can be obtained using the three-precursor method.

Figure 4 shows the PL spectra of CIS thin films for samples CIS-55 and CIS-56 at 15 K. The emission energy of the main peak is 0.89 and 0.87 eV for CIS-55 and CIS-56, respectively. This indicates that the optical band gap of CIS films could be adjusted by changing the TMI deposition time during the growth. Different band-gap energy in CIS thin films has been reported by other groups.[6,8,10,11] Various band gaps of thin films are due to the effects of grain size and thickness of thin films.[11] We demonstrate that an energy band gap of CIS thin films lower than 0.9 eV can be obtained. The optical energy band gap of CIS films could be controlled by adjusting the III/VI ratios through MOCVD using three precursors.

Conclusion

CIS thin films were prepared successfully by MOCVD using three precursors. Based on the X-ray diffraction measurements,

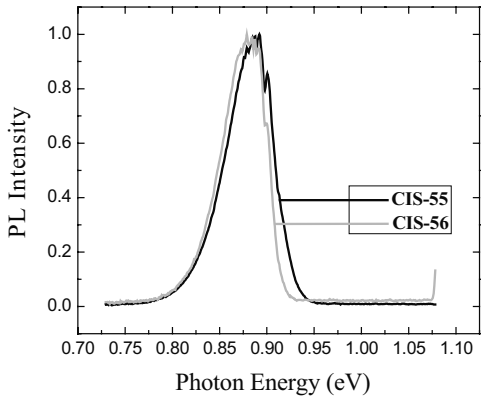

Fig. 4 PL spectra of CIS thin films: CIS-55 and CIS-56.

the chalcopyrite phase of the grown CIS films was found to be good. The optical band gap of CIS thin films can be adjusted by controlling the growth conditions. This technique may be used to develop the CIS-based solar cells and related optical devices.

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