

STRUCTURAL AND MORPHOLOGY STUDIES OF Cu-In-Se (CIS) THIN FILMS BY SCREEN-PRINTING AND SINTERING METHOD

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ABSTRACT

CuInSe (CIS) thin films are the best candidate as absorber material for solar cell application and successfully produced by screen-printing and sintering method. Screen printing and sintering of CIS layers is a low cost technique for obtaining homogeneous layers on a large scale. Pure Cu, In and Se powders were mixed and ground with ethyl alcohol to a grain size of 1.5 μm . CuInSe₂ paste was screen-printed on FTO glass substrate and sintered at 350 °C for 60 min. The pastes were tested by X-ray diffractometer (XRD) for crystallinity, Scanning Electron Microscope (SEM) for grain size and thickness, and Energy Dispersive X-ray Spectroscopy (EDX) for CuInSe₂ paste composition. The results indicated that there is non-homogenous agglomeration and random surface texture in SEM images. The grain size of the samples is in average around 10 – 15 μm meanwhile the thickness measured is around 23 – 60 μm . From EDX analysis, there is higher amount of copper indicating the building of a secondary phase at the surface. XRD analysis revealed the high diffraction of CIS peaks are at 2 Theta of 44.3 and 26.6 correspond to the (2 2 0) / (2 2 4) and (1 1 2).

INTRODUCTION

In recent years, there has been a growing interest and considerable attention in CuInSe₂ (CIS), an I-III-VI₂ chalcopyrite, as one of the most promising materials for second-generation solar cell because of its high theoretical efficiency up to 24.8% [1,2]. Various techniques are reported for the preparation of CIS films such as elemental co-evaporation [3], sputtering [4] and electro deposition [5]. However, it becomes necessary to produce device quality CIS films through a low-cost and easily scalable process for PV applications. Screen-printing and sintering is an alternative economical fabrication method for CIS layer. A paste of the material to be screen printed is pressed through the screen by a squeegee. Important screen printing parameters are the viscosity of the paste, the mesh number of the screen, the snap-off distance between the screen and the substrate, the pressure and speed of the squeegee [6]. Sintering is a high temperature step, typically up to 800 °C. The most critical issue when one is to sinter a new semiconductor material is to find a new suitable sinter flux [7]. The aim of this report is to characterize the results of CIS films deposited by screen-printing and

sintering method.

EXPERIMENTAL DETAILS

CIS films were deposited by screen-printing method onto FTO glass substrate at room temperature. Compositions of the films were varied by changing the weight of copper, indium and selenium before the paste was screen-printed. Table 1 show the compositions of copper (Cu), indium (In) and selenium (Se) that have been screen printed on FTO glass substrate. The substrate was cleaned by ethanol – acetone cleaning process. The substrate was sintered at 350°C for 60 min after screen printed process is done. The shape and surface morphology were studied with of high-resolution scanning electron microscopy (SEM) while the crystallinity of the CIS films was determined from X-ray diffraction (XRD).

Table 1: The composition of copper (Cu), indium (In) and selenium (Se) coated onto FTO glass substrate

Parameter	Copper (Cu)	Indium (In)	Selenium (Se)	Cu-In-Se
A	1	1	2	Cu (1) In (1) Se (2)
B	1	2	1	Cu (1) In (2) Se (1)
C	2	1	1	Cu (2) In (1) Se (1)
D	1	2	2	Cu (1) In (2) Se (2)
E	2	1	2	Cu (2) In (1) Se (2)
F	2	2	1	Cu (2) In (2) Se (1)

RESULTS AND DISCUSSION

SEM images have provided the microscopic information of the surface structure and roughness in order to determine the effect of the different copper, indium and selenium composition on the film morphology. Figure 2 shows the microstructure of CIS films where non-homogenous agglomeration and random surface texture were observed. This indicates that the Cu-In-Se powders is not adhered together very well due to the grinding process. The average grain size is up to 10 – 15 μm which is normally measured for films produced in the same way while the thickness is around 23 – 60 μm .

Energy dispersive X-ray analysis (EDX) indicated the presence of copper (Cu), indium (In) and selenium (Se) for CIS films. Deviation from the atomic percentages of Cu/In/Se ratios could be attributed to the presence of atomic percentage of oxygen. Oxygen may be incorporated into the film either from the atmosphere or from the aqueous medium of the paste. EDX analysis revealed a distinctly higher amount of copper in the island areas, indicating the building of a secondary phase at the surface. This phase is segregated by the layer as a reaction to the lack of Se in composition [8]. EDX analysis of CIS thin films with different deposition times are listed in Table 2.

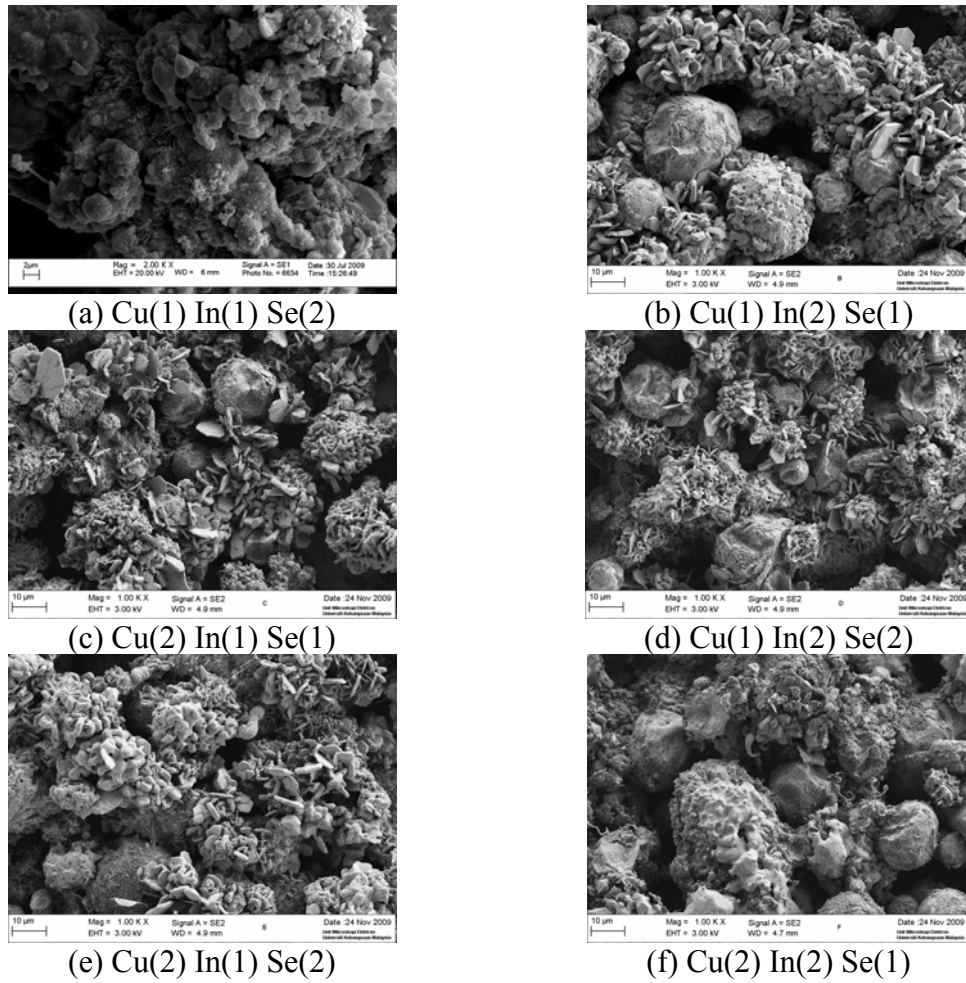


Figure 1: SEM images of nanoparticle CuInSe thin film.

Table 2: Atomic ratios (%) of Cu-In-Se obtained by EDX

Sample	Cu (%)	In (%)	Se (%)
A	45.53	13.94	34.64
B	58.04	31.54	10.42
C	50.63	23.53	25.84
D	55.78	42.09	22.58
E	47.32	27.82	30.10
F	65.36	31.01	16.83

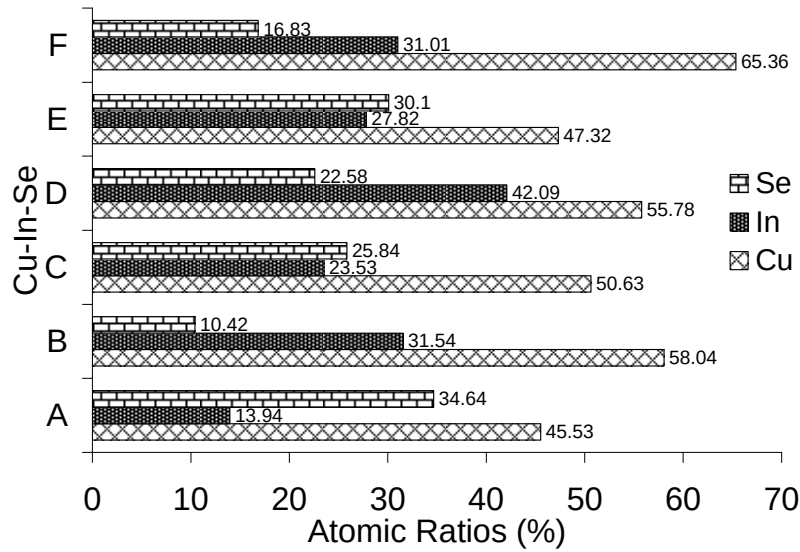


Figure 3: Plot of atomic ratios (%) of Cu-In-Se thin films (a) Cu(1)In(1)Se(2), (b) Cu(1)In(2)Se(1), (c) Cu(2)In(1)Se(1), (d) Cu(1)In(2)Se(2), (e) Cu(2)In(1)Se(2) and (f) Cu(2)In(2)Se(1)

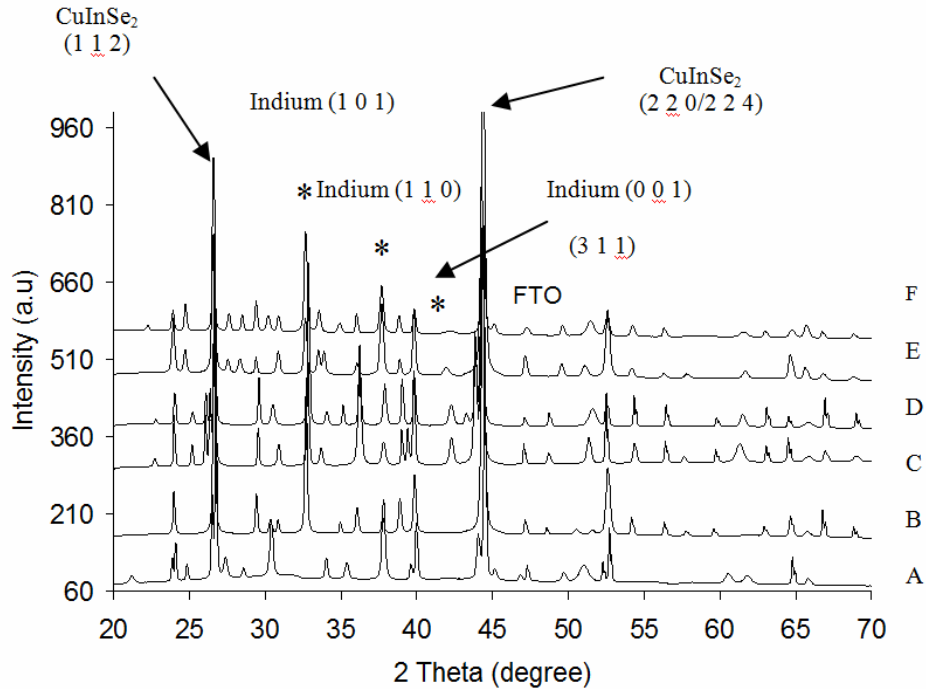


Figure 4: XRD spectra for CIS film with different composition of copper, indium and selenium. (a) Cu(1)In(1)Se(2), (b) Cu(1)In(2)Se(1), (c) Cu(2)In(1)Se(1), (d) Cu(1)In(2)Se(2), (e) Cu(2)In(1)Se(2) and (f) Cu(2)In(2)Se(1)

The structural property of CIS films were characterized by X-Ray Diffraction. Figure 4 shows the XRD spectra for CIS film with different composition of copper, indium and selenium on FTO coated glass. The XRD spectrum for this film shows several CIS peaks, some with slight shifts, indicating crystals with different selenium incorporations. XRD analysis shows the presence of CuInSe in the material. The CuInSe₂ diffraction peaks are observed at 2 Theta of 44.3 and 26.6 and these peaks correspond to the (2 2 0) / (2 2 4) and (1 1 2) respectively. At 32.7, 37.7 and 39.9 of 2 Theta scale is indium correspond to (1 0 1), (1 1 0) and (0 0 1) peaks. There also appears to be a few amounts of FTO presents in the film as well. CuInSe peaks are shifted to higher values due to a decrease in the lattice constant of the material.

CONCLUSION

The CIS films on FTO glass substrate was prepared by using screen-printing and sintering method. From SEM images of CIS films show that there is non-homogenous agglomeration and random surface texture due to the screen-printing method. The grain size of the samples around 10 – 15 µm meanwhile the thickness measured is around 23 – 60 µm. EDX analysis revealed a distinctly higher amount of copper indicating the building of a secondary phase at the surface. XRD analysis revealed the high diffraction of CuInSe₂ peaks are at 2 Theta of 44.3 and 26.6 corresponding to the (2 2 0) / (2 2 4) and (1 1 2), respectively.

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