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Characterization of chalcopyrite Cu(In,Al)Se_2 thin films grown by selenization of evaporated precursors.

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Abstract

Chalcopyrite Cu(In,Al)Se_2 (CIAS) thin films were prepared by a two-stage process onto soda-lime glass substrates. Different Cu/(Al+In) atomic ratios have been evaporated in a vacuum chamber to be subsequently heated with elemental selenium in a quasi closed graphite box at 530ºC. The results on the dependence of the crystallite size, preferential orientation, roughness, optical transmittance and aluminium incorporation as a function of the stoichiometry have been studied, concluding that a Cu/(Al+In) atomic proportion near the 1.07 value seems to be the best choice to favour crystalline CIAS formation without substantial CuSe secondary phases segregation.

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Keywords: Cu(In,Al)Se_2; CIAS; Chalcopyrite; Evaporation; Selenization; Roughness; Stoichiometry; CuSe.

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1. Introduction

It has been demonstrated that $CuInSe_2$ (CIS) compound is a good option to be used as absorber in high-efficiency thin-film solar cells [1, 2]. With the aim of enhance the performance of the chalcopyrite systems, Cu(In,Ga)Se_2 based solar cells have shown to be higher efficiencies, reaching up values of 19.9% in laboratory scale [3]. To obtain the best efficiencies in terrestrial applications the band gap is adjusted by the Ga/(Ga+In) atomic ratio. Al appears as a good alternative being more abundant than Ga. Varying the Al ratio in the absorber the band gap can range from 1.0 eV (CIS) to 2.67 eV (CAS) [4],

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which makes this compound very attractive to be used in new concepts of solar devices, such tandem cells.

In order to increase the cells performance it is known that, due to the recombination produced in the lattice defects of the absorber in the conduction mechanisms, the density of grain boundaries should be low. The crystallites should have large size with the aim of reduce this recombination. The formation of copper selenide (CuSe) phases during the growth of the chalcopyrites enhances the crystallite size [5, 6]. Nevertheless the presence of these secondary phases in the absorber layers makes the performance of these films worse. The usual segregation of the CuSe towards the surface makes rougher the films, implying the increase of the light trapping at the surface and of the number of interface states between the absorber layer and the window layer in the solar cells. Additionally, the coexistence of the CuSe phases with the chalcopyrite structure introduces undesirable sub-band gap absorptions.

In this project CIAS thin films were prepared onto soda lime glass (SLG) by a two stage process. Different ratio of Cu/(Al+In) were deposited on the substrate by evaporation, to be subsequently annealing to 530ºC during the selenization. The results on the dependence of the chalcopyrite size, preferential orientation, roughness, optical transmittance and aluminium incorporation as a function of the stoichiometry are studied.

2. Experimental details

Various $Cu(In,Al)Se_2$ absorber layers were deposited by a selenization process onto glass substrates. First, metallic precursor layers were evaporated following the SLG/In/Cu/In/Al sequence in a vacuum chamber with a base pressure below 10^{-4} Pa, where the substrates were rotated during evaporation. The individual layers thicknesses were controlled by quartz crystal microbalance monitoring to obtain different metallic proportions, being m=Cu/(Al+In) and x=Al/(Al+In) the atomic ratios. These precursor samples and elemental selenium were put together within a partially closed graphite container that was loaded into a quartz tube furnace in Ar atmosphere for heating up to 530ºC, achieved in successive annealing steps based on that reported for CIS format [7]. After selenization absorber thin films of about 0.8 ± 0.1 μm of thickness were obtained, as was determined by profilometry.

The optical transmittance (T) and reflectance (R) of the samples were measured with a Perkin-Elmer LAMBDA 9 double beam spectrophotometer in the 300-2000 nm wavelength range at room temperature, taking the air as reference. The thickness and roughness of the CIAS films were obtained by means of a DEKTAK 3030 profilometer. The structural characterization was carried out by means of X-ray Diffraction (XRD) using a PHILIPS X'PERT diffractometer with CuKα (λ=1.54056 Å) radiation. Peak diffraction angles in the XRD patterns were converted to interplanar d-spacing and thus, phase identification has been carried out by comparison of the observed d-spacing with those reported by the Joint Committee on Powder Diffraction Standards.

3. Results and discussion

The structural properties of the thin films were analyzed by XRD technique. Fig. 1 shows the spectra of the selenized films for the m=Cu/(Al+In) atomic ratios of 0.85 and 1.25, the extreme values in study. These X-ray diffraction patterns indicate that both films have chalcopyrite structure and preferential orientation along the (1 1 2) direction. The displacement of the main peak toward higher angles is principally observed in the m=1.25 sample. Since no standard files are available for CIAS, $CuInSe_2$ [8] and $CuAlSe_2$ [9] standards were used to identify the $Cu(InAl)Se_2$ formation, for which diffraction peaks are located between both. As it is observed, the increment of the m ratio makes to appear the CuSe diffraction signal, indicating that the film has been transformed from copper-poor to copper-rich sample. It is known that copper selenide phases formed during copper-rich growth are an excellent medium for

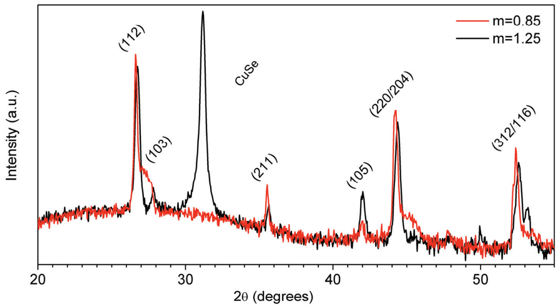

Fig. 1 XRD patterns of the selenized CIAS samples with different Cu proportion

enhancing the crystallization of chalcopyrite absorbers. According to this fact in Fig. 2 are depicted the crystallite sizes of the thin film samples. The average crystallite size in the (1 1 2) plane direction was estimated according to the Scherrer's formula:

$$S = \frac{0.9\lambda}{B\cos\theta}$$

where S is the crystallite mean size in nm, λ the X-ray wavelength in nm, θ the diffraction angle and B is the value of the full width at half maximum (FWHM). Although for the lowest m proportion it has been obtained the highest size, since m=0.9 it is observed the tendency to improve the crystallinity with increasing copper content in the film, according with previous results [10].

The preferential orientation of the crystallites along the (1 1 2) plane, F (1 1 2), was estimated from the XRD patterns as the ratio between the peak intensity of the most intensive (1 1 2) reflection and the sum of the intensity of the secondary peaks (2 2 0/2 0 4) and (3 1 2/1 1 6) as follows:

$$F(112) = \frac{I(112)}{I_0(112)} \Big/ \sum_{hkl} \frac{I(112)}{I_0(112)}$$

where I(hkl) is the measured intensity of the peak (hkl) for the film and I_0(hkl) the relative powder intensity. The obtained data (Fig. 2), ranging from 0.38 to 0.66, increase with the Cu proportion.

It has been found in addition that the Cu/(Al+In) proportion influences the aluminium incorporation to the CIS matrix. Fig. 3 shows the main peak of three samples with m=0.85, m=1.07 and m=1.25 corresponding with x=Al/(Al+In) atomic proportions of x= 0.29, x=0.20 and x=0.19 respectively. It is noticeable that the shift toward higher angles occurs when the samples are stoichiometric or Cu-rich. However, the sample with higher aluminium content has not undergone the incorporation of this element to form CIAS compound, remaining as CIS crystalline structure. It should be noted that this sample has the lowest Cu proportion and the highest grain size achieved should be related with CIS compound instead of CIAS.

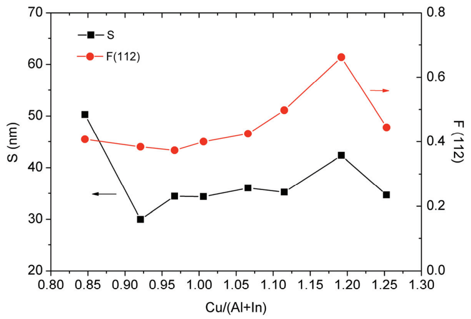

Fig. 2 Variation in the grain size and preferential orientation as a function of Cu/(Al+In) proportion..

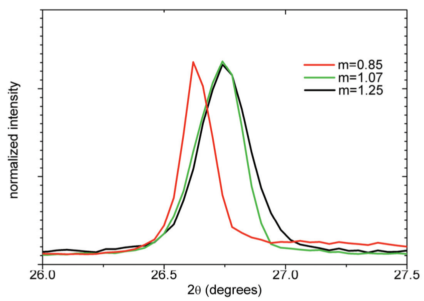

Fig. 3 Variation in the main peak obtained by XRD for three samples with different Cu proportion

Transmission spectra of the Cu-poor, stoichiometric and Cu-rich samples are depicted in Fig. 4. It is observed clearly that the films with higher Cu content show a decrease of their transmission in the high wavelengths region. The transmission average in the 1400-2000 nm range (Fig. 5) shows that there is significant sub-band gap absorption for near stoichiometric and Cu-rich films, indicating the presence of many impurity states in the gap which are related to the CuSe secondary phases found with XRD.

The roughness of the absorber samples has been measured by profilometry. The roughness average of absolute values in an interval of 200 μm has been calculated by means of:

$$r_a = \frac{1}{n}\sum_{i=1}^{n}|y_i|$$

The results are represented in Fig. 5 as a function of the Cu/(Al+In) ratio. It can be seen that in the change from Cu-poor to Cu-rich samples, the surface is modified as the segregation of the CuSe phases to the surface began to appear. As can be observed in Fig. 6, the surface of the film with m=1.25 is rough, while the stoichiometric and Cu-poor samples show a smoother surface. This behaviour also has been observed in previous works [5, 11].

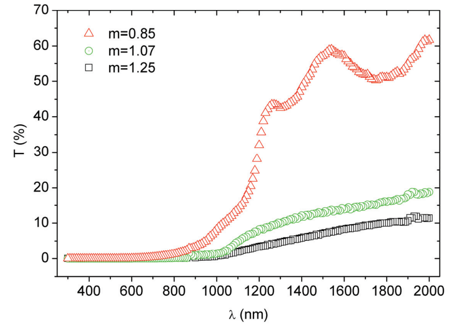

Fig. 4 Optical transmission curves T(%) of CIAS samples with different Cu proportion

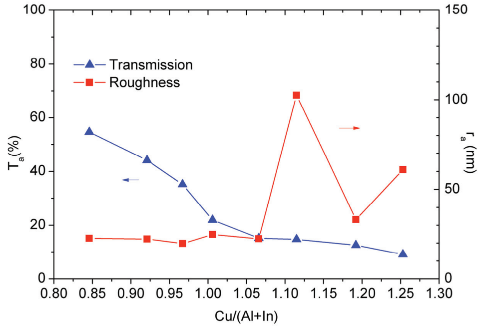

Fig. 5 Variation in the transmission average in high wavelengths region and roughness average as a function of Cu/(Al+In) proportion.

4. Conclusions

The Cu/(Al+In) ratio has a great influence on the structural, optical and morphological properties of the CIAS compound. The increment of Cu proportion improves the Al incorporation, the grain size and the preferential orientation. However, with a Cu/(Al+In) proportion > 1.11 the segregation towards the surface of CuSe secondary phases increases, increasing the roughness average and decreasing the transmission associated with the sub-band gap transitions.

A Cu/(Al+In) proportion near the m=1.07 value seems to be the best choice to favour crystalline CIAS formation without substantial CuSe secondary phases segregation.

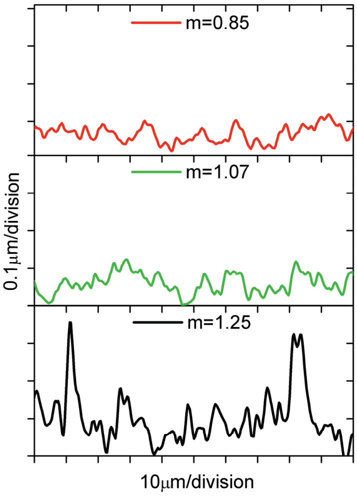

Fig. 6 Roughness measured for three samples with different Cu/(Al+In) proportions

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