Investigation of AgInS$_2$ thin films grown by co-evaporation

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Abstract. AgInS$_2$ thin films were grown on soda-lime glass substrates by co-evaporation of the precursors in a two-step process. X-ray diffraction (XRD) measurements indicated that these compounds grow in different phases and with different crystalline structure depending upon the deposition conditions. However, through a parameter study, conditions were found to grow thin films containing only the AgInS$_2$ phase with chalcopyrite type structure. In samples containing a mixture of several phases, the contribution in percentage terms of each phase to the whole compound was estimated with the help of the PowderCell simulation package. It was also found that the AgInS$_2$ films present p-type conductivity, a high absorption coefficient (greater than $10^4$ cm$^{-1}$) and an energy band gap $E_g$ of about 1.95 eV, indicating that this compound has good properties to perform as absorbent layer in thin film tandem solar cells. The effect of the deposition conditions on the optical and morphological properties was also investigated through spectral transmittance and atomic force microscopy (AFM) measurements.

1. Introduction

Chalcopyrite type compounds of the groups I – III – VI$_2$ are direct gap semiconductors, with suitable properties for solar cells manufacturing. The highest conversion efficiency reported until now for simple junction thin film solar cells was obtained with a device fabricated using a layer based on compounds of the Cu-III-VI$_2$ group as absorber [1]; solar modules based on Cu(InGa)Se$_2$ (CIGS) thin films offer additionally good stability and competitive projected production cost. On the other hand, Ag-III-VI$_2$ based compounds are characterized by having energy band gap values ranging from 1.87 to 2.03 eV which makes these compounds suitable as absorber layers in two junction tandem solar cells [2].

Different methods have been used for preparing thin films based on Ag-III-VI$_2$ compounds; thermal evaporation [3], electrodeposition [4] and solution growing [5] are some of them. In this work, thin films of AgInS$_2$ have been grown by co-evaporation of the precursors in a two steps process; for that, the metallic precursors were evaporated from a tungsten boat in presence of elemental sulfur, evaporated from a tantalum effusion cell. The influence of the deposition conditions on the optical, structural and morphological properties were investigated by spectral transmittance, XRD (x-ray diffraction) and AFM (atomic force microscopy) measurements.
2. Experimental

The AgInS$_2$ thin films were prepared by co-evaporation of the precursor species on a glass substrate, using a system constituted by an evaporation chamber connected to a vacuum system which allows working at pressures of about 2x10^{-5} Torr, two tungsten boats (used to evaporate Ag and In respectively), a tantalum effusion cell to evaporate sulfur and a thickness monitor (Maxtec TM-400) with a quartz crystal as sensor, used to measure the evaporated elements flux. The substrate temperature was controlled with a programmable PID controller (Eurotherm 900C). The chemical composition of the AgInS$_2$ films is controlled by controlling the substrate temperature and the evaporated mass of the precursor species.

The deposition of the AgInS$_2$ films was accomplished in two stages. In the first stage an In$_x$S$_y$ layer is grown by simultaneous evaporation of In and S, keeping the substrate temperature at 300º C. During this stage the flux of In is kept around 2.5 Å/s and the evaporation temperature of S is kept around 135ºC. In the second stage the AgInS$_2$ compound is formed by evaporating Ag in a sulfur environment, on the In$_x$S$_y$ layer, keeping the substrate temperature between 400 and 600ºC. During this stage the flux of Ag was kept at about 3 Å/s. The AgInS$_2$ films were submitted to a post-deposition thermal annealing in S ambient during about 1 hour, in order to improve the stability of the chemical composition.

The transmittance measurements were carried out with a VIS – IR Oriel spectrophotometer and the conductivity type was determined through thermoelectric power measurements. The XRD measurements were performed using the Cu Kα radiation of a Shimadzu-6000 diffractometer and the AFM images were obtained with a PSI AP-0100 Scanning Probe Microscope. The film thickness was measured with a Veeco Dektak 150 surface profiler. Thermoelectric power measurements revealed that all the studied AgInS$_2$ films presented p type conductivity.

3. Results and discussion

3.1 Optical characterization

The AgInS$_2$ thin films were characterized through spectral transmittance measurements, in order to study the effect of the synthesis parameters on the optical constants (refractive index n, absorption coefficient $\alpha$ and optical gap $E_g$). In figure 1 are depicted typical transmission spectra of AgInS$_2$ films, deposited varying the mass of Ag to mass of In ratio as well as the substrate temperature. The studied AgInS$_2$ films were grown varying the deposition parameters as follows:

i) The mass of Ag to mass of In ratio was varied between 0.7 and 1.13, keeping constant the substrate temperature at 300ºC and 500ºC during the 1st and 2nd stages, respectively, and the masses of In and S at 0.15 and 3 grams, respectively.

ii) The substrate temperature (2nd stage) was varied between 400 and 600ºC, keeping constant the amounts of Ag, In and S at 0.15, 0.17 and 3 grams, respectively.

It is observed in figure 1 that the Ag or In rich AgInS$_2$ films, present low transmittance values. This behaviour is seemingly caused by absorption of photons through states within the energy band gap associated to donor states generated by S-vacancies and by anti-site defects. Transmittances around 70% were obtained with AgInS$_2$ films deposited under the following parameter set: $M_{Ag}/M_{In}=0.9$, substrate temperature of 300ºC and 500ºC during the 1st and 2nd stages respectively, $M_S=3$ gr. and evaporation rate of In and Ag of about 2.5 and 3.0 Å/s, respectively.
Figure 1: Spectral transmittance measurements of AgInS\textsubscript{2} thin films showing the effect of a) substrate temperature and b) mass of Ag to mass of In ratio.

On the other hand, the results of figure 1 show that the substrate temperature (2nd stage) also affects the transmittance of the AgInS\textsubscript{2} films. At temperatures lower than 500\textdegree C, the transmittance decreases significantly, probably because, under this conditions, a high density of native defects are formed in the AgInS\textsubscript{2} films, as a consequence of incomplete chemical reaction of the precursors.

In figure 2 are depicted curves of $\alpha$ vs. $\lambda$ and $(\alpha h\nu)^2$ vs. $h\nu$, which were determined using the transmission spectrum and calculations based on a procedure described in detail in reference [6]. The results of figure 2 show that the AgInS\textsubscript{2} films have an absorption coefficient $\alpha$ greater than $10^4$ cm\textsuperscript{-1} and an optical gap $E_g$ of 1.93 eV, indicating that the AgInS\textsubscript{2} thin films, we have deposited in this work, have suitable properties for using them as absorber layers in two junction tandem solar cells. Theoretical calculations of the conversion efficiency, carried out for two solar cells in tandem operation, revealed that a limit efficiency of 45% can be achieved if the energy gap of the top and bottom cells are 1.75 eV and 1.15 eV respectively [7]. This calculation also predict a limit efficiency of around 40% for a tandem cell fabricated using AgInS\textsubscript{2} ($E_g=1.9$eV) as top cell and AgInSe\textsubscript{2} ($E_g=1.2$eV) as bottom cell.

### 3.2 Structural characterization

The effect of the substrate temperature and of the Ag mass to In mass ratio, on the structural properties of the AgInS\textsubscript{2} films was also studied through XRD measurements. Figure 3 shows typical XRD spectra of AgInS\textsubscript{2} films deposited varying the substrate temperature (2nd stage) between 400 and 600\textdegree C and the Ag mass to In mass ratio between 0.77 and 1.13. The results were analyzed using the data reported in the JCPDS data base for these types of compounds and performing theoretical simulation of the XRD pattern, with the help of the PowderCell package. This procedure allowed us to identify the phases present in the samples with a good degree of confidence. It was found that both, the synthesis temperature and $M_{Ag}/M_{In}$ ratio, affect the phase and structure in which the AgInS\textsubscript{2} films grow. The diffractograms of figure 2 show that only the samples deposited at substrate temperatures around 500\textdegree C, using an Ag mass to In mass ratio of about 0.9, grow in the AgInS\textsubscript{2} phase with tetragonal structure. It was found that, in samples deposited at temperatures greater than 550\textdegree C keeping constant the $M_{Ag}/M_{In}$ ratio at around 0.9, the AgInS\textsubscript{2} compound grows with a mixture of both, orthorhombic and tetragonal structure. The presence of the InS\textsubscript{2} phase was also identified in this type of samples. The AgInS\textsubscript{2} compound grows with both orthorhombic and tetragonal structures when deposited at temperatures below

[Figure 2: Curves of $\alpha$ vs. $\lambda$ and $(\alpha h\nu)^2$ vs. $h\nu$, corresponding to typical AgInS\textsubscript{2} thin films.]
500°C. When deposited around 500°C using a MAg/MIn ratio different from 0.9, a mixture of AgInS$_2$ orthorhombic and tetragonal together with InS$_2$ phases were identified. The lattice parameters determined from the X-ray diffraction spectra, for AgInS$_2$ films grown with chalcopyrite type tetragonal structure, are: $a = 5.8980\text{Å}$ and $b = 11.1935\text{Å}$.

![Figure 3: Typical XRD spectra of AgInS$_2$ films deposited varying: a) the synthesis temperature between 400 and 600°C and b) the mass of Ag to mass of In ratio between 0.77 and 1.13.]

3.3 Morphological characterization

In Figure 4 are shown AFM images taken on typical AgInS$_2$ thin films, deposited varying the M$_{Ag}$/M$_{In}$ ratio (keeping the substrate temperature (2$^{nd}$ phase) in 500°C) and the substrate temperature (keeping the M$_{Ag}$/M$_{In}$ ratio in 0.9). In Figure 4, curves are also depicted showing the effect of the substrate temperature and of the M$_{Ag}$/M$_{In}$ ratio on the grain size of the AgInS$_2$ films.

The results of fig. 4 show that the substrate temperature and the M$_{Ag}$/M$_{In}$ ratio significantly affecting the films morphology. In general, the grain size decreases by increasing both the substrate temperature and the M$_{Ag}$/M$_{In}$ ratio.
Conclusions

P type AgInS\textsubscript{2} thin films with adequate properties to be used as absorber layers in two junction tandem solar cells were grown using a novel procedure based on the co-evaporation of the precursor in a two step process. It was found that the deposition conditions affect the phase and structure in which the AgInS\textsubscript{2} films grow. However, chalcopyrite type AgInS\textsubscript{2} films with tetragonal structure were grown. The results also revealed that the substrate temperature and the MAg/MIn ratio significantly affect the films’ morphology. In general, the grain size decreases by increasing both, the substrate temperature and the MAg/MIn ratio.

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