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$AgInSe_2$ thin films prepared by electrodeposition process

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Abstract: In this work, the one step electrodeposition process was used to prepare Ag-In-Se thin films. The films were deposited at room temperature from a bath containing 1-3x10^{-3} M $AgNO_3$, 6x10^{-2} M $InCl_3$ and 3x10^{-2} M of H_2SeO_3. The KSCN at a concentration of 0.681 M was used as complexing agent. The pH value of the solution was 1.4. Applied potentials to SCE were chosen between -0.3 V and -1.1 V. Films were deposited onto molybdenum/glass and ITO/glass substrates. We showed that the films' compositions are strongly function of the growth conditions. Heat treatment at 320 °C during 30 minutes under nitrogen led to $AgInSe_2$ chalcopyrite p-type semiconductor. Also, the morphology and crystallinity of the films is improved by annealing. $AgInSe_2$ films deposited on indium tin oxide showed a band gap value of about 1.24 eV.

Keywords: Thin Films, Electrodeposition, $AgInSe_2$, Physical Properties

1. Introduction

Ternary chalcopyrite compounds offer numerous possibilities of applications such as absorber materials in solar cells and optoelectronic devices. The optical band gap E_g can be varied from 1.2 eV ($AgInSe_2$) to 3.1 eV ($AgAlS_2$) for the Ag-based Chalcopyrite materials and they can be grown either as *n* or *p* type.

$CuInSe_2$ (CIS) and CIGS based-materials such as $Cu(In,Ga)Se_2$ solar cells have achieved a single junction efficiency of 19.5 % [1] comparable to that of the best multicrystalline silicon devices. Thus, they are real alternative to crystalline-silicon technologies.

Silver indium diselenide $AgInSe_2$ (AIS) ternary I-III-VI$_2$ compound is a direct gap and a promising absorber semiconductor since its gap value is about 1.2 eV [2,3]. It has been used in various heterojunction solar cells like (*p*)AIS-(*n*)CdS [4,5] and glass/SnO_2:Sb/1.5at.%In-doped*n*-$Zn_{0.35}Cd_{0.65}S$/*p*-$AgInSe_2$/Au polycrystalline thin film heterojunctions where the efficiency conversion was around 7.5 % [6]. Schottky barrier diodes with aluminum and nickel [7,8] and AIS nanorods have also been elaborated [9].

AIS semiconductors have been produced by several techniques such as: co-evaporation [3,10-12], ultra-high vacuum pulsed laser deposition [13], horizontal Bridgman method [14], molecular beam epitaxy [5], vertical gradient temperature freezing method [15] and solid state microwave irradiation [16].

In this work, we have prepared Ag-In-Se thin films by simultaneous electrodeposition process, followed by an adequate annealing treatment. This technique is a low-cost, high deposition speed, possibility of large-area films and does not require the use of vacuum. However, the preparation of ternary compounds is rather difficult due to the different values of equilibrium potentials for each constituent. We have carried out the effect of conditions growth on composition of the films. Morphology, structural, electrical and optical measurements are presented.

2. Experimental

$Ag_xIn_ySe_z$ (AIS) films were deposited by the potentiostatic electrochemical method by using EG&G Princeton Applied research Potentiostat Model 6310. The electrodeposition solution is composed of 1-3x10^{-3} M $AgNO_3$, 6x10^{-2} M $InCl_3$ and 3x10^{-2} M of H_2SeO_3. The KSCN of concentration 0.681 M was used as complexing agent as it has been reported by Tzvertkova et al. [17] for $CuInSe_2$ prepared by one-step electrodeposition process and Cesiulis et al. [18] for electrodeposited Ag. The pH value of the solution was 1.4. Saturated calomel electrode and Pt gauze were used as reference electrode and counter electrode, respectively. Mo/glass substrates were chosen to be the working electrodes. They were degreased with acetone and methanol and dried in air before electrodeposition. AIS films were electrodeposited at room temperature for 5 to 60 min. The potentials used to deposit the films were based upon the results of cyclic voltammetry. Applied potentials to SCE were chosen between -0.3 V and -1.1 V. Annealing treatment of AIS films was achieved in a quartz tube at 230-400 °C temperature range under N_2 atmosphere for 30 min.

X'Pert Pro diffractometer was used to determine the X-Ray Diffraction (XRD) patterns with Cu K radiation. The surface morphology and Energy Dispersive X-ray Analysis (EDX) of the films was investigated using Scanning Electron Microscopy (SEM) SEI Quanta 200. The type of conductivity of the films was determined by the hot-probe method and the electrical resistivity at room temperature was measured by Van der Pauw method. Transmittance measurements were performed using a Perkin-Elmer spectrophotometer 900 λ.

3. Results and Discussion

Figure 1 shows the cyclic voltammograms of Ag-In-Se on Mo coated glass substrates in the plating solution of pH 1.4 at room temperature.

Three potential regions are observed:

- Zone I: from 0 V (vs.SCE) to -0.55 V (vs.SCE)
- Zone II: from -0.55 V (vs.SCE) to -0.95 V (vs.SCE
- Zone III: from -0.95 V (vs.SCE) to -1.2 V (vs.SCE)

In order to vary the composition of the films, two parameters were used: the deposition potentials and the protocol of heat treatment. According to the voltammograms results, the applied potentials were -0.3V, -0.7V, -0.8V, -0.9V, -1.1 V and -1.2 V /ECS.

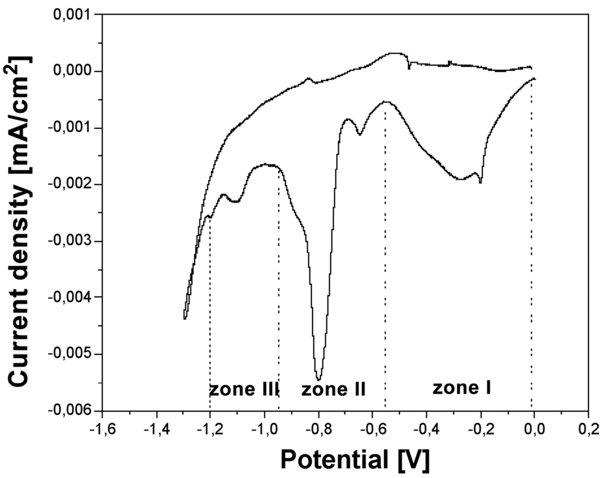

Figure 1. *Cyclic voltammogram recorded at a sweep rate of 50 mV/s for Ag-In-Se thin films on Mo coated substrates.*

All films were prepared without stirring because we noted that the indium concentration decreased in the films for stirred solution but not for the other elements, as it has been observed by Diaz et al. [19] for Cu-In-Se electrodeposited films.

Table 1 presents the typical composition of some Ag-In-Se thin films electrodeposited under different applied potential on molybdenum-coated glass during 30 min and annealed at 320 °C for 30 min. For synthesis at –0.3 V vs SCE, indium is weakly deposited while Se and Ag are deposited with concentration ratio Ag/Se of about 2, which corresponds to deposits of Ag_2Se. When the potential becomes very negative (-1.1 V and -1.2 V vs SCE), we observe a very high concentration of indium (more than 80 %). These observations are in agreement with Ueno et al. results [20] obtained on Ag-In-Se films simultaneously electrodeposited on titanium substrates from sulphate bath. The best stoichiometry was obtained for -0.8 V vs SCE applied voltage. For Ag content, one can note that it decreases with increasing negatively applied potential. More important is the fact that repeatability of results for stoichiometric samples is remarkable.

Table 1. *Composition of Ag-In-Se films deposited on Mo for different applied voltages, during 30 min and annealed at 320°C for 30 min*

Sample/potential V/SCE	Ag (%at)	In (%at)	Se (%at)
-0.30	58.94	3.66	37.40
S1/-0.80	25.34	26.05	48.61
S2/-0.80	24.91	22.26	52.83
S3/-0.80	24.14	23.97	51.89
S4/-0.80	23.15	22.49	54.36
-0.90	19.84	16.74	63.42
-1.10	4.86	83.60	11.53
-1.20	4.79	87.85	7.36

The effect of annealing on morphology of Ag-In-Se surface is shown in figure 2 for films deposited on Mo and ITO during 30 min under -0.8 V applied potential. Before annealing (figure 2a), one can note the high density of clusters with average size of about 240-400 nm. After annealing under nitrogen atmosphere at 320 °C during 30 min, we observe an increase of the cluster sizes (figure 2b). Figure 2c presents a cross section of AIS films annealed at 320 °C for 30 min under nitrogen atmosphere where the thickness is around 1.5 µm. A micrograph of AIS film deposited on ITO is presented in figure 2d.

Figure 3 depicts the XRD diffractograms of as grown and annealed samples. As grown, the films always show the characteristic profile of an amorphous material. Only a pronounced peak at 2θ =40.95° due to the Mo substrate is present. A heat treatment at 250°C under nitrogen atmosphere during 30 min leads to large increase in the intensity and number of diffraction peaks, indicating crystallization. We note the presence of <112> characteristic peak of $AgInSe_2$ tetragonal chalcopyrite structure (JCPDS file n° 38-0952). We also note peaks attributed to the Mo substrate and to In_2Se_3

secondary phase. When the annealing

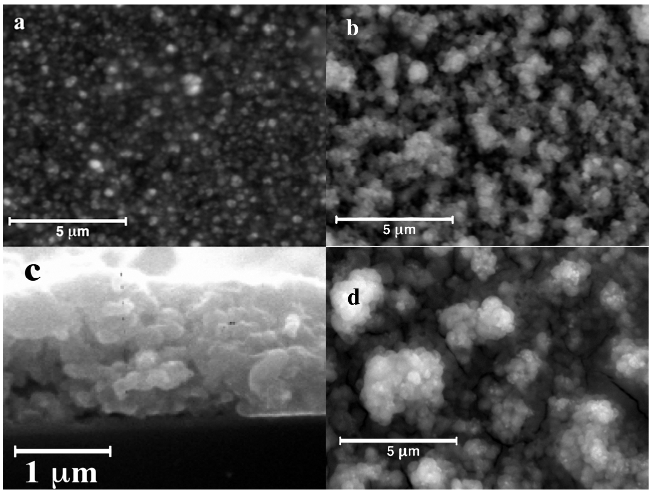

Figure 2. *SEM photomicrographs of electrodeposited AIS films. (a) As deposited on Mo; (b) deposited on Mo and annealed at 320 °C for 30 min in N_2 atmosphere; (c) cross section of AIS deposited on Mo and annealed at 320 °C for 30 min in N_2 atmosphere; (d) deposited on ITO and annealed at 320 °C for 30 min in N_2 atmosphere.*

temperature treatment is increased to 320°C, the spectrum shows a prominent peak at 2θ =26.08°, and a smaller ones at 2θ =50.19° and 2θ =59.08°, corresponding to <112>, <312> and <323> directions, respectively, characteristic peaks of $AgInSe_2$ tetragonal chalcopyrite structure, without any secondary phase in the limit of XRD detection. This is in agreement with results on co-evaporated AIS [3] and AIS prepared by vertical gradient temperature freezing method [15] and sealed quartz ampoule [21]. This improvement of XRD spectra by a heat treatment has been also observed on evaporated AIS [22]. The lattice parameters a and c computed from XRD data were a=5.92 Å and c= 11.82 Å, respectively. Average AIS crystallite's size of about 50 nm was obtained for the <112> direction as calculated using the well known Scherrer's formula [23]. For higher temperatures, we observe an evaporation of the film.

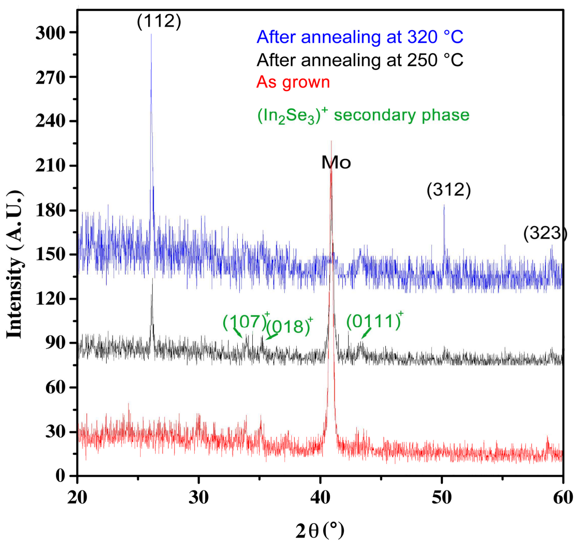

Figure 3. *XRD spectra of Ag-In-Se thin films deposited on Mo.*

For optical measurements, thin films of $AgInSe_2$ were deposited on indium tin oxide (ITO). Figure 4 presents the transmittance spectra of ITO/glass and $AgInSe_2$/ITO/glass substrate thin films. One can note that $AgInSe_2$/ITO/glass films are highly absorbers on the whole visible range, while in the NIR zone they are somewhat transparent, a property that can be very helpful when exposed to sunlight. By a simple and straight calculation, we determine the absorption coefficient, α. The plots of $(\alpha h\nu)^2$ versus $(h\nu)$ and the extrapolation of the linear portion of the plots onto the energy axis gave the band gap value of about 1.24 eV. This value is in good agreement with those reported in the literature for $AgInSe_2$ prepared by other methods [2,4,13,15,24-26].

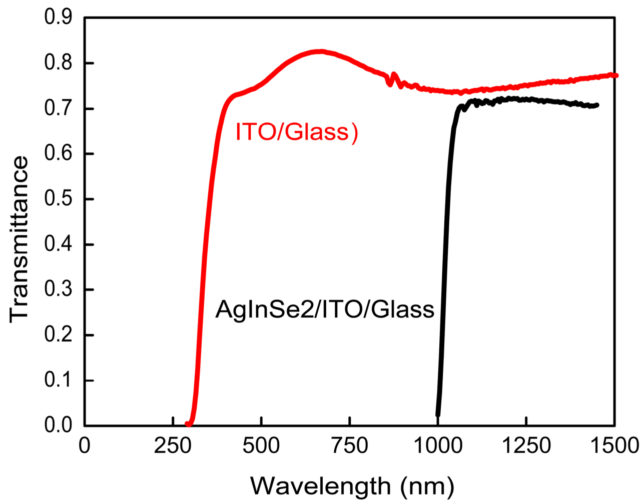

Figure 4. *Transmittance spectra: (a) ITO/glass; (b) $AgInSe_2$ thin films deposited on ITO/glass.*

The electrical resistivity of $AgInSe_2$ thin films, obtained by the Van der Pauw method at room temperature, was around 10^5 Ωcm. By the hot-probe method, we found that our $AgInSe_2$ chalcopyrite films are *p*-type semiconductors, thus making them suitable as absorber material for heterojunction solar cells. Recently, it has been reported for $CuInSe_2$/$AgInSe_2$/CdS double heterojunction Cascade Solar Cells an efficiency of about 10.7 % [27].

4. Conclusions

Ag-In-Se thin films have been grown by one step electrodeposition process, which is a low cost, non vacuum and reproductive technique. The effect of conditions growth on chemical composition of Ag-In-Se films was studied. The best conditions for growing silver indium diselenide $AgInSe_2$ chalcopyrite ternary compound were: – 0.8 V vs SCE applied potential at ambient temperature and without stirring the solution, followed by an annealing treatment under nitrogen atmosphere at 320°C for 30 min. The obtained results on $AgInSe_2$ p-type semiconductor films make them of interest for photovoltaic devices.

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