

Effect of thermal annealing on the structural, optical and microstructural properties of AgInSe₂ thin films

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Abstract

In the present work, Ag/In/Ag/In multilayers were deposited on glass substrates by DC magnetron sputtering and the films were selenized at 350°C. The selenized films were annealed at 450°C and 500°C. The selenized and annealed films were characterized by X-ray diffraction (XRD), UV-Visible-NIR spectroscopy and Field Emission Scanning Electron Microscopy (FESEM). XRD revealed formation of the desired AgInSe₂ phase along with Ag₂Se as impurity phase. Unlike in previous studies, where conventional approach of optimizing the volume fraction of initial precursor material is adopted to control the phase purity of AgInSe₂, we show that annealing highly impure films at 500°C can suppress the impurity phase and lead to pure AgInSe₂ phase. The suppression of the low band gap Ag₂Se impurity phase on annealing the films at 500°C led to increase in the optical band gap. Copyright © 2016 VBRI Press

Keywords: Chalcopyrite, thin film synthesis, annealing, impurity phase suppression, band gap.

Introduction

AgInSe₂ is a member of I-III-VI₂ chalcopyrite family. It has a tetragonal structure with space group I42d. It is potentially one of the most useful materials for NIR application as well as for the preparation of Schottky diodes and solar cells. AgInSe₂ is a very important material for solar cell due to its high absorption coefficient and its band gap lies in between 0.8-2.0 eV. AgInSe₂ is one of the least exploited compounds and is of special interest since it is the ternary analogue of CdSe, which is reported to have been used for a number of electronic devices [1]. It is direct band gap semiconductor and can be grown either as n or p-type [2].

Various techniques have been used to prepare AgInSe₂ thin films. These include flash evaporation [3–5], RF magnetron sputtering [6], thermal evaporation [7, 8] and electro-deposition [9, 10]. However, the common problem encountered during synthesis is to preserve stoichiometric amount of Se due to high volatility in Se-containing compounds. In the present work we report the synthesis of AgInSe₂ thin films by DC magnetron in which Se volatility can be minimized. We have studied the structural, optical and microstructural properties of these films with different annealing temperature.

Experimental

Materials details

The material used in the present study is 300 nm thick AgInSe₂ thin films. The films were prepared by selenization of Ag/In/Ag/In multilayer deposited on glass substrate using dc magnetron sputtering. Silver target of 2-inch diameter and indium target of 3-inch diameter, both of 99.9% purity were used for the growth of multilayers. Selenization was done at 350°C in selenium vapor.

Material synthesis

The glass substrates of 10 mm × 10 mm surface area and 1 mm thickness were used for deposition of the films. The substrates were cleaned with warm water and soap solution, and then ultrasonically rinsed with de-ionized water. Distance between substrate and targets during sputtering was 15 cm. Multilayer of silver (Ag) and indium (In) were deposited sequentially from Ag and In targets with 50 watt and 20 watt DC power respectively. The deposition rates were 10.2 nm/min and 2.7 nm/min for duration of 5.7 mins and 33.9 mins per layer for Ag and In targets respectively. Ag and In were deposited at a pressure of 10⁻² millibar and 8-9×10⁻³ millibar of argon atmosphere. Substrate temperature was kept at

300 K. Thickness of each Ag layer and In layer was found to be 58.14 nm and 91.53 nm respectively from the deposition rates. Selenization and annealing of the multilayer metallic films were done using a RTP (Rapid Thermal processing) furnace having capacity to reach maximum temperature of 700°C in 5 minutes. The multilayer metal precursor was selenized at 350°C in presence of selenium pellets for 30 minutes at a pressure of 1.8×10^{-2} millibar. After selenization, each of the selenized samples was annealed at temperatures of 450°C and 500°C for one hour at a pressure of 1.8×10^{-2} millibar. The selected temperatures of RTP furnace were reached within a time period of 1-3 mins.

Characterizations

Structural study of the AgInSe_2 films deposited on glass substrates was done using an X-ray diffractometer (Bruker D8 Advance) with CuK_α ($\lambda = 1.5405 \text{ \AA}$) radiation. The X-ray diffraction (XRD) patterns were recorded in 2θ range of 23° - 55° with glancing angle of 2° and scan speed 1min/sec. The optical absorbance spectra of the as-deposited and the annealed AgInSe_2 thin films were recorded at room temperature within a spectral range from 400 to 1200 nm by using UV-Visible NIR spectrometer (Bruker IFS 66v/s). Microstructural study of the films was done by Field Emission Scanning Electron Microscopy (FESEM) (ZEISS SIGMA-40).

Results and discussion

Fig.1 shows the XRD pattern of selenized and annealed AgInSe_2 (AIS) films. Comparison of these XRD patterns with that of different phases that can form out of Ag, In and Se, as reported JCPDS files, indicated the formation of AgInSe_2 and Ag_2Se (AS) phases. The JCPDS data of these two phases presented as vertical lines along with our observed XRD pattern in **Fig. 1** clearly supports this conclusion.

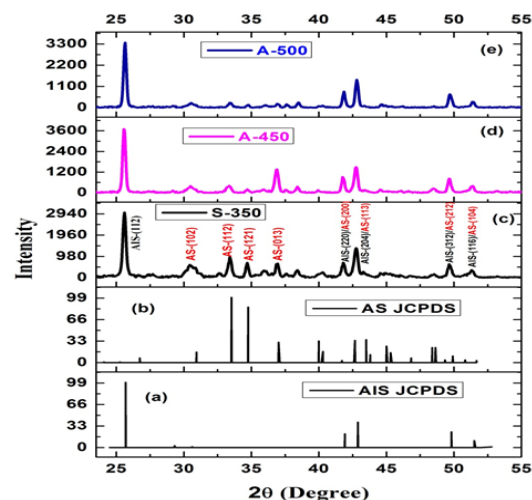


Fig. 1. XRD pattern of (a) JCPDS of AIS (b) JCPDS of AS (c) 350°C selenized film (d) 450°C annealed film (e) 500°C annealed film

Though our starting material was multilayer of Ag and In, which was selenized at 350°C and annealed at 450°C and 500°C, XRD of any of these films does not show peaks due to Ag and/or In. It also did not show peaks due to In_2Se_3 phase. Absence of these phases clearly indicates that all the silver and indium have been consumed for the formation of AgInSe_2 and Ag_2Se phases. Absence of In_2Se_3 phase and appearance of Ag_2Se phase indicate that our precursor multilayers were indium deficient. The excess Ag after the formation of AgInSe_2 phase, reacted with selenium vapour and led to the formation of Ag_2Se phase.

To examine the evolution of AgInSe_2 and Ag_2Se phases with annealing temperature, the most commonly followed approach is to extract the volume fraction of the two phases from the area under their XRD peaks [11]. This however could not be done in the present study since most of the peaks of AgInSe_2 overlapped with those of Ag_2Se . We therefore considered the area under the highest peak only of each phase to ascertain the content of that phase. These are (112) peak of AgInSe_2 and (112) peak of Ag_2Se occurring at 2θ values of 25.6° and 33.4° respectively. Fortunately, these peaks do not overlap with any other peak of the same or of the other phase.

Fig. 2 shows the variation of the area under these peaks with annealing temperature. The area of the peak for each phase is normalized with respect to its area in the selenized film. The area under the (112) peak of AgInSe_2 shows only a small variation with annealing temperature.

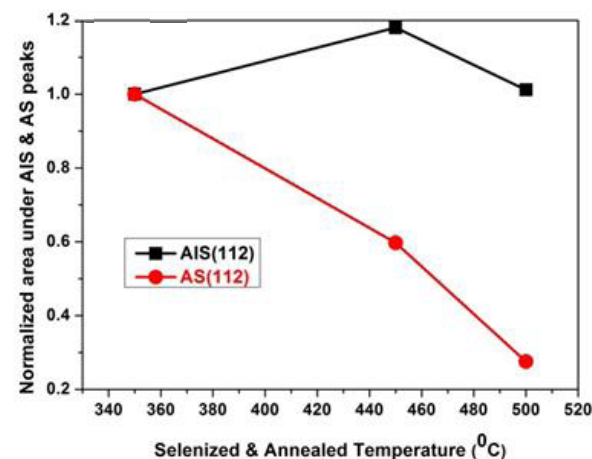


Fig.2. Selenized and annealing temperature vs normalized area of AIS and AS phase

The variation is within 20% and that also is not monotonic. The volume fraction of the AgInSe_2 phase thus seems not to be affected by annealing. On the contrary, area under the XRD peak of the impurity Ag_2Se phase showed a dramatic decrease with increasing annealing temperature to 500°C. The impurity phase decreased to about one fourth of its initial value in the selenized sample. Cheng et al. [12]

also showed appearance of Ag_2Se as the impurity phase along with the desired AgInSe_2 phase, but in a set of Ag/In bilayers deposited by RF magnetron sputtering and selenized at 250°C . These authors could reduce the Ag_2Se phase content by increasing In concentration. On the contrary, our study shows that Ag_2Se phase content can be reduced simply by heating the sample at 500°C without being constrained by the chemical composition to arrive at the pure AgInSe_2 phase. Our study has thus established the importance of a physical route like thermal annealing in controlling the chemical composition of a material.

To probe into the possible mechanism of such a novel phenomenon as discussed above, we note that the suppression of the Ag_2Se phase on annealing at high temperature can have a bearing on the structural evolution of this phase with temperature. Extensive studies undertaken since 1935 [13] have established a first-order reversible phase transition around 139°C from a semiconducting orthorhombic (β phase) to a metallic, cubic structure (α phase) of this compound [14-18]. The high temperature cubic phase is a super-ionic conductor in the bulk state [19-21]. The high ionic conductivity in the high temperature α phase of Ag_2Se is due to a statistical distribution of the silver atoms in an ordered chalcogen sub-lattice (body centered cubic) together with low activation energy for diffusion of the silver ions [22]. Annealing the $\text{AgInSe}_2/\text{Ag}_2\text{Se}$ composite films at 450°C and 500°C , which are far above the onset temperature for superionicity in Ag_2Se , is expected to accelerate diffusion of silver ions in this phase and collapse of its structure as is seen in the present study.

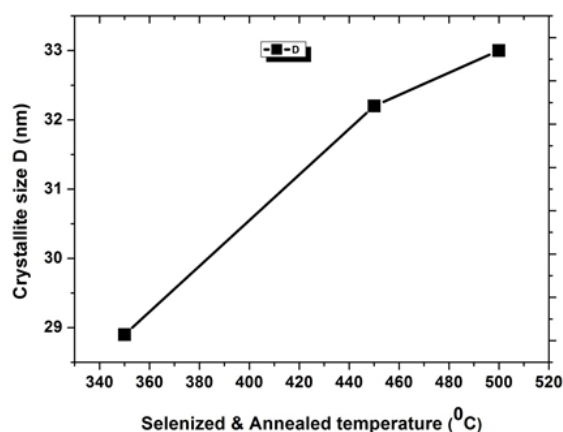


Fig. 3. Plot of annealing temperature vs crystallite size of AIS phase.

Overlap of most of the XRD peaks corresponding to the AgInSe_2 and Ag_2Se phases as discussed above was also a constraint for us to extract crystallite size and strain using Williamson-Hall equation. We therefore calculated only the crystallite size using Debye-Scherrer formula [23] by taking only the most intense peak (112) of AgInSe_2 phase.

$$D = \frac{0.9\lambda}{\beta_{2\theta} \cos \theta}$$

where, D is the crystallite size, $\beta_{2\theta}$ is full width at half maximum (FWHM) and λ is wavelength of X-rays (1.54\AA). The crystallite size showed a very small increase with increasing annealing temperature (Fig. 3). The increase however being monotonic, clearly indicates improvement of crystal quality of AgInSe_2 with increasing annealing temperature. We studied the electronic band structure of AgInSe_2 thin films by using the UV-Visible NIR spectrometer. From the absorbance data we calculated the absorption coefficient (α) by using the equation [24]

$$\alpha = \frac{2.303 \times A}{t}$$

where, A is absorbance and t is thickness of the film. The optical band gap energies were calculated using the equation [24]

$$\alpha h\nu = B E_g - h\nu^n$$

where, E_g is the band gap, α is the absorption coefficient, ν is the frequency, B is a constant and n can have values $1/2$, $3/2$, 2 and 3 depending upon the mode of inter band transition i.e. direct allowed, direct forbidden, indirect allowed and indirect forbidden transition respectively. We find best fit for the optical absorption data of AgInSe_2 thin films with $n = 1/2$, indicating direct allowed transition for the absorption in the as-prepared and annealed thin films of AgInSe_2 . Extrapolating the linear portion of the $h\nu$ versus $(\alpha h\nu)^2$ curve (Fig. 4) to $\alpha h\nu = 0$, we got the band gap (E_g).

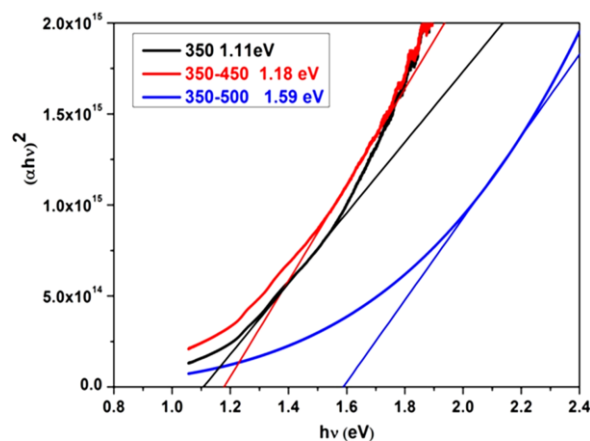


Fig. 4 Plot of $h\nu$ vs $(\alpha h\nu)^2$

The band gap was found to be 1.11 eV for selenized AgInSe_2 thin films. The selenized films annealed at 450°C causes a small increase in the band gap to

1.18 eV. Further annealing at 500°C makes a large increase of the band gap to 1.59 eV (**Fig. 5**). The increase in band gap with increasing annealing temperature is in accordance with the decrease in impurity phase as revealed from XRD study (Fig. 2). In the as-prepared AgInSe_2 thin film, the concentration of Ag_2Se impurity phase with low band gap (0.15 eV) is more which leads to the lowest value of the optical band gap.

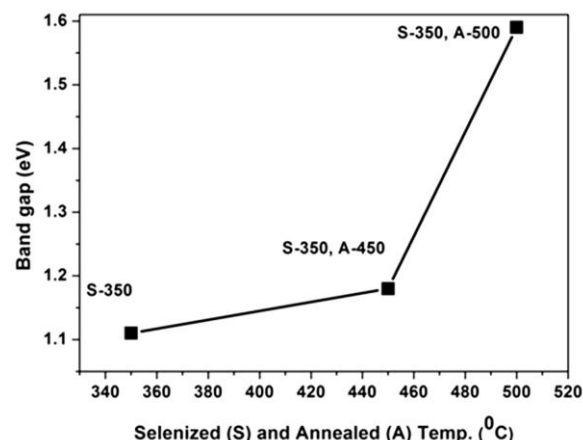


Fig.5 Plot of the variation of band gap with Selenized and Annealed temperature

Field emission scanning electron micrograph of the selenized and the annealed $\text{AgInSe}_2/\text{Ag}_2\text{Se}$ composite thin films is shown in **Fig. 6**. The size of the grains shows a wide distribution from very small size of ~ 60 nm to very large size of more than a micron. The large size grains did not show any regular shape, but had facets with agglomeration of small crystallites. In case of 500°C annealed samples, large size grains seem to agglomerate and form rod shaped structure oriented in arbitrary direction. Their number is very small. On the contrary, a large number of small size grains show up.

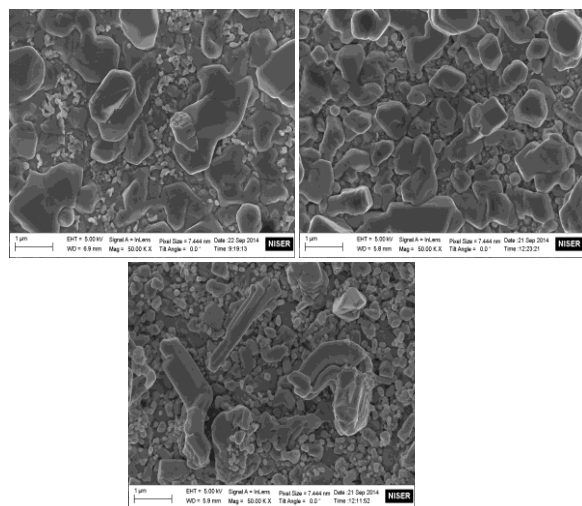


Fig. 6 FESEM images of the 350°C selenized film and 450°C and 500°C annealed films respectively.

A visual inspection clearly reveals that based on size, the grains can be clubbed under two categories: small size grains, whose number are quite large and large size grains, which are few in number. The 350°C selenized film in particular shows the widest variation in the size and number of the grains. Annealing the selenized film at 450°C increases the size of small size grains. The size of the large grains, on the contrary decreases on annealing. The latter seems to contradict the Ostwald's principle for grain growth, that large grains absorb the small grains from its neighbors and form a very big grain. In case of 500°C annealed film, grains seem to agglomerate to form rod shaped structure oriented in arbitrary directions. Also very small size grains are present here.

Conclusion

Ternary AgInSe_2 samples were prepared by selenization and annealing of $\text{Ag}/\text{In}/\text{Ag}/\text{In}$ multilayers deposited by DC magnetron sputtering method. XRD study showed improvement of the crystal quality with increasing annealing temperature. More importantly, the Ag_2Se phase which arises at high concentration as impurity in the selenization stage was suppressed to one fourth of its initial value on annealing at 500°C. In contrast to the conventional means of controlling chemical precursors to achieve phase purity, we have showed that phase purity of AgInSe_2 can be achieved just by annealing at high temperatures. The band gap of the films is increased with increasing the annealing temperature due to reduction of impurity phase. FESEM study indicated a wide distribution of grain size ranging from ~ 60 nm to over a micron.

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References

1. Paul, Ramesh P.; Hussain, OM; Uthanna, S.; Naidu, B.S.; Reddy, J.P; *Mater. Lett.*, **1998**, 34, 217.
2. Kumar, M. C. Santosh; Pradeep, B; *J. Mater. Sci. Lett.*, **2003**, 22, 287.
3. Joseph, C.M.; Menon, C.S; *Semicond. Sci. Technol.*, **1996**, 11, 1668.
4. Paul, R.; Uthanna, S.; Naidu, S.B.; Reddy, J.P; *Vacuum*, **1996**, 211, 47.
5. Patel, S.M.; Patel, A.D; *Thin Solid Films*, **1984**, 111, 53.
6. Weir, RD; Jessop, PE; Garside, B.K; *Can. J. Phys.*, **1987**, 65, 1033.
7. El-Korashy, A.; Abdel-Rahim, M.A.; El-Zahed, H; *Thin Solid Films*, **1999**, 207, 338.
8. Abdel-Hady, D.; Salem, A.M; *Physica A*, **1997**, 141, 242.
9. Raviendra, D.; Sharma, J.K; *A Appl. Res.*, **1985**, 365, 88.
10. Ueno, Y.; Kojima, Y.; Sugiura, T.; Minoura, H; *Thin Solid Films*, **1990**, 189, 91.
11. Abbas, M. M.; Oboudi, S.; Raoof, N; *Mater. Sci. Appl.*, **2015**, 6, 310.
12. Cheng, K. W.; Yeh, C. H; *Int. J. Hydrogen Energy*, **2012**, 1.
13. Rahlfs, P; *Z. Phys. Chem. B*, **1935**, 51, 157.
14. Miyatani, S; *J. Phys. Soc. Jpn.*, **1958**, 13, 341.

15. Dalven, R.; Gill, R; *J. Appl. Phys.*, **1967**, *38*, 753.
16. Veale, C. R; *J. Less-Common Met.*, **1966**, *11*, 50.
17. Grønvold, F.; Westrum, E; *J. Chem. Thermodyn.*, **1986**, *18*, 381.
18. Grier, B. H.; Shapiro, S. M.; Cava, R. J; *Phys. Rev. B*, **1984**, *29*, 3810.
19. Schoen, D. T.; Xie, C; Cui, Y; *J. Am. Chem. Soc.*, **2007**, *129*, 4116.
20. Yakshibayev, R. A.; Almukhametov, R. F.; Kh, B.M; *Solid State Ion.*, **1989**, *31*, 247.
21. Junod, P.; Hediger, H.; Kilchor, B.; Wulschleger, J.; *Phil. Mag.*, **1977**, *36*, 941.
22. Fang, C.M.; Groot, R.A. de; Wiegers, G.A.; *J. Phys. Chem. Solids*, **2002**, *63*, 457.
23. Patil, Vikas; Pawar, Shailesh; Chougule, Manik; Godse, Prasad; Sakhare, Ratnakar; Sen, Shashwati; Joshi, Pradeep; *J. Surf. Eng. Mater. Adv. Technol.*, **2011**, *1*, 35.
24. Das, R.; Pandey, S; *IJMS*, **2011**, *1*, 35