

Structural and Optical Studies of Stepwise Flash Evaporated AgIn_3Te_5 Thin Films†

C. RANGASAMI^{1,*} and S. KASIVISWANATHAN²

¹Department of Physics, Erode Sengunthar Engineering College, Erode-638 057, India

²Department of Physics, Indian Institute of Technology Madras, Chennai-600 036, India

*Corresponding author: E-mail: kkaumaran@gmail.com

AJC-12851

AgIn_3Te_5 thin films have been grown on glass substrates by stepwise flash evaporation. Powder sample of bulk AgIn_3Te_5 has been used as source material. Bulk AgIn_3Te_5 has been synthesized by melt-quench technique, starting from the stoichiometric mixture of constituent elements. Phase homogeneity and crystal structure of thin films have been investigated by X-ray diffraction. The film grown at room temperature has showed amorphous nature while the film deposited at 673 K has exhibited crystalline nature. Analysis of X-ray powder diffraction data of thin films has revealed that the films have crystallized in P-chalcopyrite structure with space group $P\bar{4}2c$. The lattice parameters are calculated to be $a = 6.243 \text{ \AA}$ and $c = 12.504 \text{ \AA}$, close to that found in bulk AgIn_3Te_5 . Analysis of optical transmittance data of thin film grown at 673 K has yielded band gap value around 1.06 eV.

Key Words: AgIn_3Te_5 , Thin film, X-ray diffraction, P-type tetragonal, Optical band gap.

INTRODUCTION

Ag-III-VI₂ based ternary and quaternary chalcopyrite semiconductors have been investigated widely for applications in the field of photovoltaics and non-linear optics. For example, AgGaTe_2 (band gap 1.16 eV) thin film based solar cells exhibit efficiency of 4.8 % at laboratory scale¹. Efficiency of 7.3 % has been reported² for a tandem solar cell with AgInGaSe_2 absorber layer. AgGaSe_2 , another compound of this family, exhibits large non-linear optical coefficient and high transmission in the IR region³. In fact, AgGaSe_2 crystals for second harmonic generation in the IR region are commercially available (<http://www.ekspla.com>). When the occupancy of cations in the ideal chalcopyrite lattice is disturbed, a series of compounds with general formula $A^I B_{2n+1}^{III} C_{3n+2}^{VI}$, where $n = 0, 1, 2$, have been reported to stabilize⁴. These compounds have been studied with equal interest, ever since the experimental observation of CuIn_3Se_5 as a segregated phase over CuInSe_2 film surface⁵. While a number of Cu based compounds have been investigated, Ag based systems have attracted much less attention. Reported works on Ag-based vacancy compounds mainly concern with Ag-III₅-VI₈ and only two reports^{6,7} on AgIn_3Te_5 are available in the literature. AgIn_3Te_5 is located in between the compounds AgInTe_2 ($I\bar{4}2d$) and AgIn_5Te_8 ($P\bar{4}2m$) on the $\text{Ag}_2\text{Te-In}_2\text{Te}_3$ tie line in the Ag-In-Te ternary

phase diagram⁸. The structure of AgIn_3Te_5 has been resolved by Rangasami *et al.*⁷. It also inferred from the literature that there are no elaborate reports available on the growth and characterization of AgIn_3Te_5 thin film.

The aim of the present study is to grow AgIn_3Te_5 thin films by stepwise flash evaporation and to characterize the grown films using X-ray diffraction (XRD) and optical transmittance measurements. Since the source material to be evaporated is fed in small steps, spluttering and the consequent wastage of material are greatly reduced in stepwise flash evaporation method^{9,10}. This method has been successfully used to grow thin films of CuInSe_2 and CuIn_3Se_5 in our laboratory. The details of the melt-quench technique⁷ and the stepwise flash evaporation can be found elsewhere^{9,10}.

A careful inspection of the literature on structure refinement of vacancy compounds in general and $\text{CuIn}_3\text{Se}_5/\text{CuIn}_3\text{Te}_5$ in particular suggest that the structure of these compounds depends on composition as well as on thermal cycle followed for sample synthesis. Report⁷ on structural investigation has shown that the defect chalcopyrite phase AgIn_3Te_5 synthesized by melt-quench method has crystallized in P-type tetragonal structure with space group $P\bar{4}2c$. Formation of the defect chalcopyrite phase with compositional ratio 1:3:5 is marked by the existence of characteristic reflections such as 110, 114 and 212 in the diffraction pattern. These reflections are not

†International Conference on Nanoscience & Nanotechnology, (ICONN 2013), 18-20 March 2013, SRM University, Kattankulathur, Chennai, India

present in the XRD pattern of its chalcopyrite counter part, AgInTe_2 . Another important factor that differentiates the defect phases from the corresponding chalcopyrite members is fundamental optical band gaps. The band gaps are always direct in nature for both the compounds, but it is larger for defect phases. The slight increase in band gap values has been attributed to the presence of defect pairs¹¹, which results in a shift in valence band maximum (VBM) and conduction band minimum (CBM). For instance, the reported fundamental gap of CuIn_3Se_5 is ~ 1.12 eV, which is much larger than that of CuInSe_2 (~ 1.04 eV). However, in tellurides, the change in band gap values is comparatively less because the lowering of valence band maximum and conduction band minimum are nearly of same magnitude. The reported values for the band gaps of both AgInTe_2 and bulk AgIn_3Te_5 are around 1 eV.

EXPERIMENTAL

Preparation of bulk and thin films of AgIn_3Te_5 : Bulk AgIn_3Te_5 was synthesized by melt-quench method. Phase homogeneity and crystal structure of the bulk sample were investigated using XRD. Thin films of AgIn_3Te_5 were grown by stepwise flash evaporation using fine powder of bulk sample as source material. The AgIn_3Te_5 films were deposited at a pressure of $\sim 2 \times 10^{-6}$ Torr onto well cleaned glass substrates held at room temperature and 673 K. The substrate temperature of 673 K was chosen based as our earlier studies on CuInSe_2 and CuIn_3Se_5 films, which have exhibited polycrystalline films having well-defined crystallites at 520 K^{9,10}. By optimizing the growth rate, thickness of the films was adjusted to ~ 500 nm, in order to satisfy the requirements of different measurements such as XRD and optical transmittance.

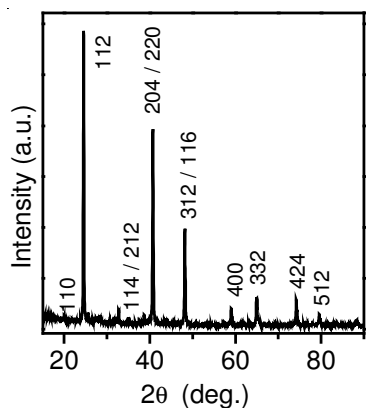
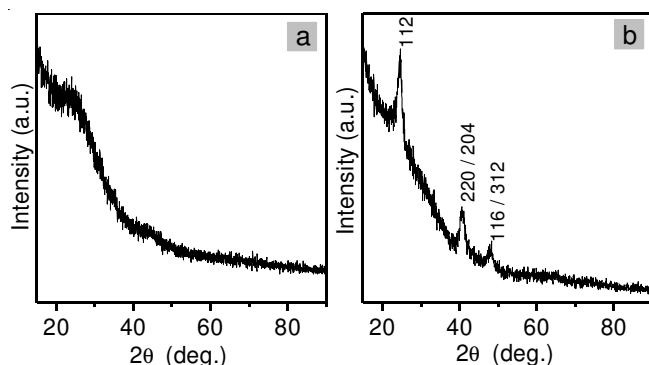
Structural analysis of bulk and thin films of AgIn_3Te_5 : Powder X-ray diffraction measurements were made at 298 K using PANalytical (model-X'Pert PRO, equipped with X'Celerator detector) XRD unit with $\text{Cu-K}\alpha$ radiation source in the 2θ range 10 to 130° with step size of 0.0170° and integration time of *ca.* 40 s. The X-ray generator was operated at 40 kV and 30 mA and the wavelengths of $\text{K}\alpha$ lines were 1.54060 and 1.54443 Å corresponding to $\text{K}\alpha_1$ and $\text{K}\alpha_2$ respectively. Theta compensating slit was fixed at 1° and $\text{K}\beta$ lines present in the diffracted beam were filtered using nickel filter. Prior to the measurements, the unit was calibrated with silicon (external) standard. Specimen (mortar and pestle ground powder) for XRD measurements was taken in an aluminum well and was gently pressed (without affecting its random orientation) to present a smooth flat surface. XRD patterns were also obtained for thin films deposited at room temperature and 673 K. The patterns were recorded in glancing angle XRD (GXRD) mode. In GXRD measurements, the incident X-ray beam was kept stationary at a small angle of incident ($\sim 1^\circ$) with respect to the sample surface while the detector was rotated to receive the diffracted beam. This small angle of incidence increases the path length of X-rays in the film and hence the diffracting volume.

Optical characterization: Optical transmittance measurement was made on AgIn_3Te_5 thin film deposited at 623 K. By solving the transmittance equations suggested by Neumann *et al.*¹² the absorption coefficient (α) was determined for the

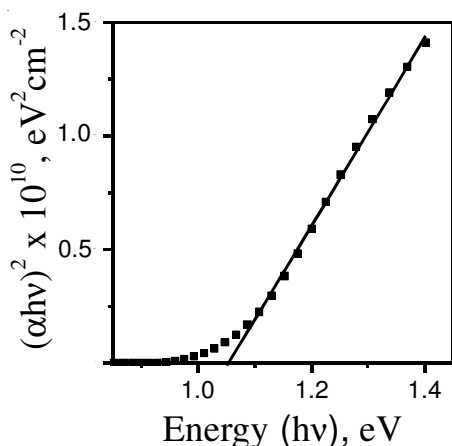
case of a thin absorbing film deposited on a thick non-absorbing substrate. Refractive index (n) and extinction coefficient (k) are the two important parameters which are used to obtain simplified expression for the transmittance. Since AgIn_3Te_5 has not been studied well, parameters n and k are not available in the literature. Therefore, the relevant parameter (n) of its chalcopyrite counterpart, AgInTe_2 , has been used in the present work. The k value is determined by solving the relevant equations¹² using Newton-Raphson method. The value of the band gap was then determined from least squares fit to the plots of $(\alpha hv)^2$ versus (hv) .

RESULTS AND DISCUSSION

XRD analysis of bulk and thin films of AgIn_3Te_5 : Powder XRD pattern of bulk AgIn_3Te_5 synthesized by the melt-quench method is shown in Fig. 1. Quenching in water with cooling rate $\leq 10^3$ K s⁻¹ are widely used for growing polycrystalline ingots of especially covalently bonded systems. This is because, covalent semiconductors such as Si, InSb, when melted turn into a dense 'metallic liquid' rather than a 'semi-conducting liquid' and therefore when quenched they will not become amorphous, but become polycrystalline. Therefore, the nucleation and growth of crystallites cannot be inhibited when the melt is quenched in water¹³. Polycrystalline nature of the sample was confirmed with sharp peaks present in the XRD pattern. Comparison of observed XRD pattern with the reported pattern⁷ revealed that the sample has crystallized in P-type tetragonal chalcopyrite with space group $P42c$. As seen from the XRD pattern, the peak due to (112) plane has the highest intensity. This is expected because the main contribution to this reflection comes from the anion sub-lattice, which remains the same as that of AgInTe_2 . Apart from the reflections which correspond to typical zinc-blende ($h + k + l = 2n$ and even l -indices) and chalcopyrite ($h + k + l = 2n$ and odd l -indices) lattices, the additional reflections specific to defect phase have been attributed to the difference in the atomic arrangement of the cations compared to the chalcopyrite phase. The values of the lattice parameters ' a ' and ' c ' were calculated from the 2θ positions of 112 and 204 reflections using plane-spacing equation and they are $a = 6.243$ Å and $c = 12.504$ Å. These values are having close agreement with the reported values for bulk AgIn_3Te_5 ⁷. Fig. 2a and 2b show a typical XRD patterns obtained for AgIn_3Te_5 films grown at room temperature and 673 K respectively. The broad hump present at the low angle side of the XRD pattern (Fig. 2a) and the absence of diffraction peaks indicate the amorphous nature of the film grown at room temperature. The broad hump is due to glass substrate. The film deposited at 673 K is polycrystalline, as indicated by the presence of well defined peaks. The observed peaks are comparable to the peaks those arising from different planes of bulk AgIn_3Te_5 with space group of $P42c$ ⁷. The dominant peak seen in the pattern is due to the reflection from (112) plane of AgIn_3Te_5 , which is in accordance with the XRD pattern of bulk sample and the reported data⁷. The XRD pattern does not show any peaks which corresponds to secondary or the constituent elements. However, the absence of other allowed reflections as well as the presence of the hump at low angles may be due to the small thickness of the film.

Fig. 1. Powder XRD pattern of bulk AgIn_3Te_5 Fig. 2. Typical XRD patterns of AgIn_3Te_5 thin films grown at room temperature and 673 K

Optical transmittance analysis: Fig. 3 shows the plot of $(\alpha h\nu)^2$ versus energy ($h\nu$) for AgIn_3Te_5 film grown at 673 K. The linear variation of $(\alpha h\nu)^2$ in the energy range between 1 and 1.4 eV signifies the direct allowed transition between the band edges. The continuous line is a least square fit to the data in the region where $(\alpha h\nu)^2$ varies linearly with energy. The extrapolated intercept of the line at the x-axis gives 1.06 eV for the optical band gap, which agrees well with the reported value⁶.

Fig. 3. Plot of $(\alpha h\nu)^2$ vs. $h\nu$ of AgIn_3Te_5 film grown at 673 K

Conclusion

AgIn_3Te_5 thin films grown by stepwise flash evaporation at room temperature showed amorphous nature while the film deposited at 673 K exhibited crystalline nature with P-chalcopyrite structure (space group $\text{P}\bar{4}2\text{c}$). The lattice parameters were calculated to be $a = 6.243 \text{ \AA}$ and $c = 12.504 \text{ \AA}$. Optical band gap of the thin film grown at 673 K was determined as $\sim 1.06 \text{ eV}$.

REFERENCES

1. K.C. Mandal, A. Smirnov, U.N. Roy and A. Burger, *Mater. Res. Soc. Symp. Proc.*, **744**, 131 (2003).
2. K. Yamada, N. Hoshino and T. Nakada, *Sci. Technol. Adv. Mater.*, **7**, 42 (2006).
3. D. Xue, K. Betzler and H. Hesse, *Phys. Rev. B*, **62**, 13546 (2000).
4. S.B. Zhang, S.-H. Wei and A. Zunger, *Phys. Rev. Lett.*, **78**, 4059 (1997).
5. D. Schmid, M. Ruckh, F. Granwald and H.W. Schock, *J. Appl. Phys.*, **73**, 2902 (1993).
6. D.F. O'Kane and D.R. Mason, *J. Electrochem. Soc.*, **3**, 546 (1964).
7. C. Rangasami, P. Malar, T. Osipowicz, M.K. Jain and S. Kasiviswanathan, *Powder Diffir.*, **26**, 248 (2011).
8. P.W. Chiang, D.F. O'Kane and D.R. Mason, *J. Electrochem. Soc.*, **114**, 756 (1967).
9. P. Malar and S. Kasiviswanathan, *Sol. Energy Mater. Sol. Cells*, **88**, 281 (2005).
10. P. Malar, V.D. Das and S. Kasiviswanathan, *Vacuum*, **75**, 39 (2004).
11. S.M. Wasim, C. Rincon, G. Marin and J.M. Delgado, *Appl. Phys. Lett.*, **77**, 94 (2000).
12. H. Neumann, W. Horig, E. Reccuis, H. Sobotta, B. Schumann and G. Kuhn, *Thin Solid Films*, **61**, 13 (1979).
13. D.W. He, F.X. Zhang, M. Zhang, R.P. Liu, Y.F. Xu and W.K. Wang, *Cryst. Res. Technol.*, **33**, 43 (1998).