*Materials Science-Poland*, *Vol. 28*, *No. 1*, *2010*

# Characterization of laser ablated $AgInSe_2$ films

D. PATHAK[1*], R.K. BEDI[1], D. KAUR[2]

[1]Department of Physics, Guru Nanak Dev University, Amritsar, India

[2]Department of Physics and Center of Nanotechnology,
Indian Institute of Technology Roorkee, India

$AgInSe_2$ (AIS) thin films have been grown directly on silicon by means of a pulsed laser deposition technique. The X-ray diffraction studies show that the films are textured in the (112) direction. Increase of the substrate temperature results in a more ordered structure. Composition of the samples has been analysed by EDAX. It was found that the stoichiometry is better maintained with the PLD technique than with other traditional methods like thermal evaporation. The optical studies of the films show that the optical band gap is about 1.20 eV. The results of investigations may be of interest for a better understanding of the growth processes of chalcopyrite thin films on silicon materials.

Keywords: *pulse laser ablation; silicon wafers; heterojunction; FESEM; direct band gap materials*

## 1. Introduction

The I–III–$VI_2$ compounds are ternary analogues of II–VI compounds having high absorption coefficient and good thermal stability [1]. The chalcopyrite semiconductor $AgInSe_2$ (AIS) is one of the most attractive materials in thin film solar cell applications because of its high optical absorption coefficient. These compounds crystallize in chalcopyrite structure which is closely related to a zinc blend structure. Ternary chalcopyrite compounds have photovoltaic properties that have potential use in solar cells since their optical band gap lies between 0.8 eV and 2.0 eV and can be grown either as n or p type [2]. The efficiency of 19.5% has been reported by Contreras et al. in $CuInGaSe_2$ [3]. $AgInSe_2$ having a band gap of 1.20 eV and the melting point of 780 °C has applications in photovoltaic and optoelectronic devices. Matsuo et al. studied $AgInSe_2$ films grown by the thermal evaporation technique, taking $Ag_2Se$ and $In_2Se_3$ as starting materials [4]. Ramesh et al. obtained the efficiency of 7.5% in p-$AgInSe_2$/n-CdS solar cells in which $AgInSe_2$ is used as the absorber material [5].

*Corresponding author, e-mail: dineshpathak80@gmail.com

A number of physical and chemical deposition techniques such as flash evaporation [6], radio frequency sputtering [7], thermal evaporation [8–10], solution growth [11, 12] and hot pressing [13] have been used for the preparation of $AgInSe_2$ under various experimental conditions. All these techniques have advantages and disadvantages, depending on the type of application intended for the films. It is important to obtain high quality AIS films for improving solar cell performance. However, the common problem encountered during synthesis is to preserve the stoichiometric amount of selenium due to high volatility in Se containing compounds. The pulsed laser deposition (PLD) technique has been shown to be an excellent way to fabricate high temperature superconductors [14] and multicomponent oxide films [15, 16], especially with respect to compositional reproduction and high deposition rate. PLD has many advantages and technological possibilities. These advantages are the effectiveness and simplicity of the deposition equipment, high deposition rates and low temperature deposition, a wide spectrum of deposition parameters for the control and optimization of film properties. In addition, PLD enables accurate control both the stoichiometry and the film thickness. The growth of AIS on Si substrates is of interest, since it is regarded to be a prerequisite for the direct integration of this material with the more dominant Si-based technologies. In this paper, an attempt has been made to grow $AgInSe_2$ films on Si substrates with (100) orientation by laser ablation. We report on the synthesis of AIS thin films using the (PLD) technique in which Se volatility can be minimized. Structural and optical properties depending on substrate temperature of films fabricated by pulse laser deposition have also been studied.

## 2. Experimental

Ablation of a polycrystalline target 25 mm in diameter was achieved using a multitarget, ultra high vacuum (UVH) pulse laser deposition (PLD), KrF excimer laser system ($\lambda$ = 248 nm, the laser rate of 3 Hz and the pulse energy density of 1–2 J/cm$^2$). The complete set up of the system is shown in Fig. 1. The synthesis of the target was performed using a stoichiometric mixture of Ag, In and Se, followed by sealing in a quartz tube ampoule. The sealed quartz tube was heated at 900 °C for 48 h and cooled slowly. A polycrystalline chalcopyrite structure was obtained as the resulting compound. The details of the synthesis of the AIS target have been described elsewhere [10]. The target substrate distance was kept at 40 mm. The chamber was evacuated to the pressure lower than $2.7\times10^{-6}$ Pa before ablation. The (100) oriented Si substrates were chemically cleaned and etched in a dilute HF solution prior to introduction into the chamber. All substrates were also cleaned in an ultrasonic bath before deposition. The ablated AIS was collected on a Si(100) wafer. The silicon substrates were then mounted on a direct heating sample holder made of a stainless steel sheet. AIS/Si films were grown with the deposition temperatures 300 K and 473 K. Laser pulses were incident at the angle of 45° on the target, over the surface scanned

by the focused laser beam. The deposited films were finally cooled to room temperature in vacuum.

Fig. 1. Complete PLD set up

The structure of the as prepared powder and pulse laser ablated films on Si(100) wafers was observed with a $\theta$–$2\theta$ X-ray diffractrometer using $CuK_\alpha$ radiation to study the orientation and crystallinity of the films. The analysis of the composition of the product has been carried out by the energy dispersive analysis through X-rays (EDAX), together with field emission scanning electron microscopy (FESEM). The optical studies were performed on films grown on glass substrates, using the same conditions as used for the deposition on Si substrates [9, 17]. Glass was chosen only for the optical measurements. It is noted that AIS/glass exhibits a similar composition to that found in AIS/Si films. The absorption spectra of $AgInSe_2$ films were recorded in the wavelength range 200–1100 nm, using a UV-VIS Perkin-Elmer spectrophotometer.The microstructure was studied using field emission scanning electron microscopy (FESEM-FEI Quanta 200 F). To prevent the charge build up during FESEM observation, samples were coated with gold using a sputtering system.

## 3. Results and discussion

The XRD profile of the as-prepared powder is shown in Fig. 2a. The pattern indicates that AIS is polycrystalline in nature and exhibits a prominent (112) peak of chalcopyrite phase, in addition to other (220), (204), (312) and (116) peaks of very small intensity. The films prepared on the Si(100) wafers at room temperature are characterized by the absence of diffraction peaks, indicating their amorphous nature. However the AIS films obtained at 473 K indicate high orientation in the (112) plane, parallel to the silicon substrate along with a reflection from the (204) plane of comparatively small intensity (Fig. 2b).

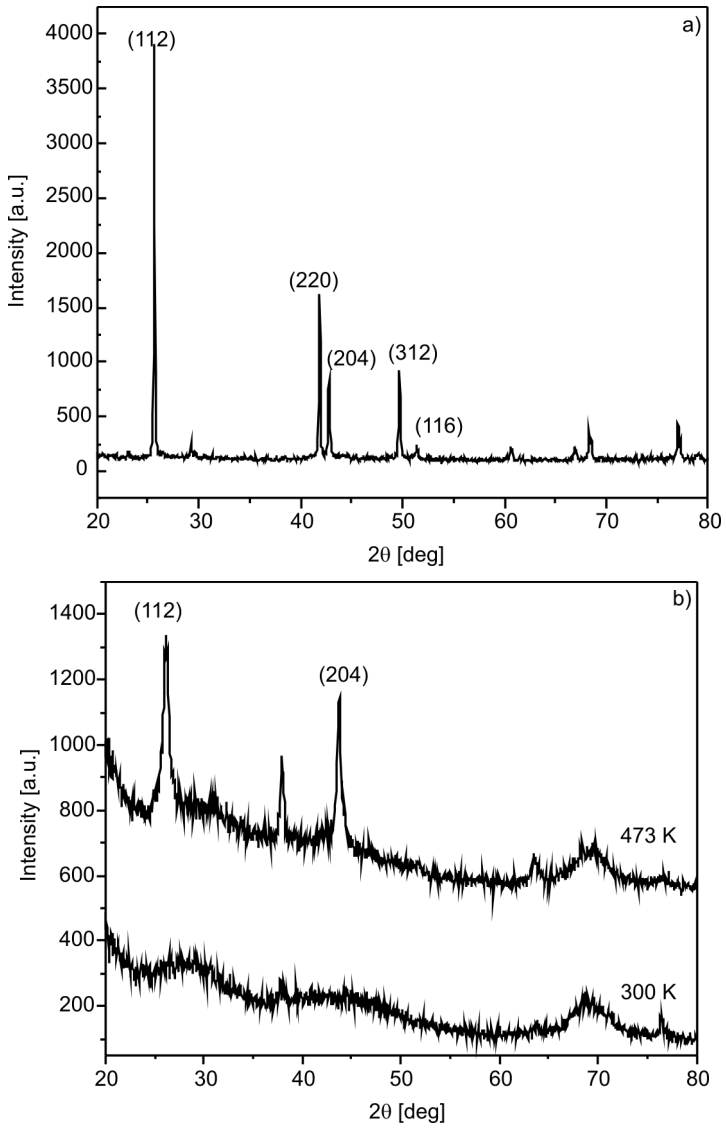


Fig. 2. XRD pattern of as synthesized powder (a) and films (b) fabricated by PLD on Si(100) wafers at 300 K and 473 K

The crystallite size is calculated from the FWHM value of the (112) peak by using Scherrer's formula

$$D = \frac{0.9\lambda}{\beta \cos\theta} \tag{1}$$

and is found to be 6 nm, where $\lambda$ is the wavelength of X-rays, $\beta$ is the FWHM in radians, $\theta$ is the Bragg angle. XRD studies confirm that by performing laser ablation,

$AgInSe_2$ can be grown on silicon wafers. These preliminary results indicate the possibility of producing device quality chalcopyrite–$AgInSe_2$/Si heterojunctions by pulse laser ablation for photovoltaic applications.

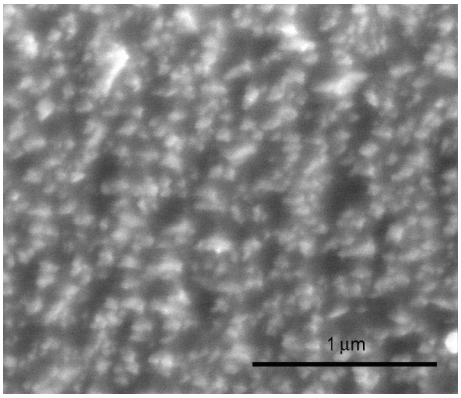


Fig. 3. FESEM of laser ablated AIS films on Si(100) wafer at 473 K

Field emission scanning electron micrograph of an AIS nanostructured film deposited by pulse laser deposition at 473 K on Si(100) substrate is shown in Fig 3. It delineates the shape and distribution of crystallites. Densely packed grains elongated in one direction are exhibited by AIS film grown at 473 K. It is also observed that grains are more homogeneous, uniformly distributed and densely packed as compared with the films deposited by thermal evaporation on the same substrate, Si(100), and at the same deposition temperature [9]: these are the major advantages of PLD, along with pore free growth.

Analysis of the composition of AIS films grown on 100 oriented silicon wafers was carried out by the energy dispersive analysis through X-rays. This elemental analysis showed that films obtained at 473K are almost as stoichiometric those prepared by thermal evaporation with Ag 28.96%, In 27.41% and Se 43.63%. The selenium percentage deviates to some extent due highly volatile nature of the element.

The optical studies were carried out on AIS films grown on glass substrates under the same conditions as those used for deposition on Si substrates [9, 17]. It is noted that AIS/glass has a similar composition to that found in AIS/Si films. The linear nature of the plot near the absorption edge confirms that ablated $AgInSe_2$ films show semi-conducting behaviour with direct band gap [18]. The band gap energy ($E_g$) was estimated based on the recorded optical spectra from the equation of Bardeen [19].

$$\alpha h\nu = A\left(h\nu - E_g\right)^n \tag{2}$$

where $A$ is a constant, $\alpha$ is the absorption coefficient, $h\nu$ is the photon energy, and $n$ depends on the nature of the transition. For direct transition, $n$ =1/2 or 3/2, while for the indirect one $n$ = 2 or 3, depending on whether they are allowed or forbidden, respectively. Here the best fit to the experimental data was obtained for $n$ = 1/2. The

dependence of $(\alpha h\nu)^2$ on $h\nu$ yields a straight line, indicating that the fundamental absorption edge could be due to direct allowed transition.

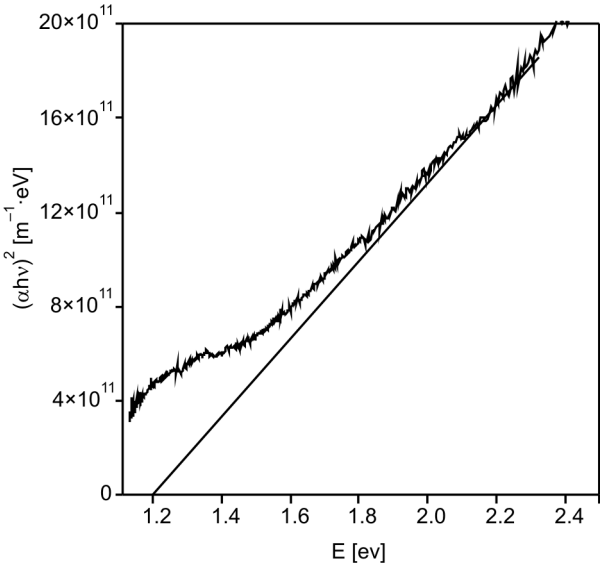


Fig. 4. Dependence of $(\alpha h\nu)^2$ on $E$

These results are in conformity with those reported earlier for thermally evaporated AIS [6, 8–10]. The band gap energy is estimated to be 1.20 ev (Fig. 4). Various authors reported different values for the band gap energy of $AgInSe_2$ films [6,8], which may be attributed to different proportions of Ag/In/Se in the composition.

## 4. Conclusions

We have successfully deposited silver indium selenide films directly on Si (100) substrates by the pulse laser deposition technique. The films show a tetragonally distorted chalcopyrite structure. Room temperature deposited films are amorphous in nature while AIS films deposited at 473 K appear to have preferential texture oriented in the (112) direction. Crystallites of 6 nm size were obtained. On silicon wafers, from optical measurements, the band gap energy is estimated to be 1.20 eV. We believe that these preliminary results may be of interest for a better understanding of the growth of chalcopyrite thin films on silicon materials, since it is regarded to be a prerequisite for the direct integration of these materials with the dominant Si-based technologies.

**Acknowledgements**

One of the authors (D. P.), acknowledges the Council of Scientific and Industrial Research (CSIR), New Delhi, India, for awarding a Senior Research Fellowship (SRF) grant to carry out this project.

## References

[1] TELL B., SHAY J., KASPER H.M., J Appl. Phys., 43 (1972), 2469.
[2] JOSEPH C.M., MENON C.S., Semicond. Sci. Techn., 11 (1996),1668.
[3] CONTRERAS M.A.,RAMANATHAN K., ABUSHAMA J., HASOON F., KEANE J., YOUNG L., EGAAS B., NOUFI R., Prog. Photovolt. Res. Appl.,13 (2005), 209.
[4] MATSUO H., YOSHINO K., AND IKARI T., Phys. Stat. Sol. (c), 3 (2006), 2644.
[5] RAMESH P.P., UTHANA S., SRINIVASALU B.N., JAYARAMA P.R., Vacuum, 47 (1996), 211.
[6] PATEL S.M., PATEL A.D., Thin Solid Films, 111 (1984), 53.
[7] WEIR R.D., JESSOP P.E., GARSIDE B.K., Can. J. Phys., 65 (1987), 1033.
[8] KORASHY A.E., ABDEL-RAHIM M.A., ZAHED H.E., Thin Solid Films, 338 (1999), 207.
[9] PATHAK D., BEDI R.K., KAUR D., Appl. Phys. A, (2009), DOI 10.1007/s00339-009-5083-8.
[10] BEDI R.K., PATHAK D., DEEPAK, KAUR D., Z. Cristallogr. Suppl., 27 (2008), 177.
[11] SHARMA R.P., Indian J. Pure Appl. Phys., 33 (1995), 711.
[12] MENG A., CHRIS B., JAGDESE J.V., J. Am. Chem. Soc.,128 (2006), 7118.
[13] YOSHINO K., KINOSHITA A., SHIRAHTA Y., OSHIMA M., YOSHITAKE T., OZAKI S., IKARI T., J. Phys., Conf. Ser. 100 (2008), 042042.
[14] DIJKKAMP D., VENKATSAN T., WU X.D., Appl. Phys. Lett., 51 (1987), 619.
[15] OTUBO S., MAEDA U., MINAMIKAWA T., YONEZWA Y., MORIMOIO A., SHIMIZU.T., Jpn. J. Appl. Phys,. 29 (1990), 133.
[16] KIDOH H., YASHIMA H., MORIMOTO A., SHIMIZU T., Jpn J. Appl. Phys., 33 (1994), 4094.
[17] BECHIRI L., BENABDSLEM M., BENSLIM N., DIEKOUN A., OTMANI A., MAHADDJOUBI L., MADELON R., RUTERANA P., NOUET G., Catal. Today, 113 (2006), 226.
[18] PANKOVE J.I., *Optical Processes in Semiconductors*, Prentice Hall, New York, 1971.
[19] *Photoconductivity Conference*, J. Bardeen (Ed.), Wiley, New York, 1956.

*Received 5 June 2009*
*Revised 13 October 2009*