Journal of Alloys and Compounds 502 (2010) 220–224

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Preparation and characterization of vacuum thermal evaporated trilayer Cu/Se/Al thin films

S.P. Nehra [a,*], Deepshikha Sharma [b], M. Singh [a], Y.K. Vijay [a]

[a] Thin Films and Membrane Science Laboratory, Department of Physics, University of Rajasthan, Jaipur 302004, India
[b] Department of Physics, Banasthali Vidya Pith, Tonk 304022, India

ARTICLE INFO

Article history:
Received 5 January 2010
Received in revised form 8 April 2010
Accepted 22 April 2010
Available online 5 May 2010

PACS:
73.21.Ac
67.80.dm
61.72.Cc

Keywords:
Trilayer thin films
Annealing
XRD
I–V characteristics
Optical band gap
Surface topography

ABSTRACT

Trilayer thin films of Cu/Se/Al have physically deposited using vacuum thermal evaporation technique at pressure of 10^{-5} Torr onto a glass substrate. Before and after annealing at different temperatures, various properties of these trilayer thin films, including the structure, optical absorption, optical band gap, current–voltage measurements and morphology have been studied and discussed. These properties have been characterized by X-ray diffraction (XRD), UV–vis spectrophotometer, 2 point probe and optical microscope at room temperature. Crystalline nature, resistance and band gap of annealed Cu/Se/Al trilayer thin films have been found to be increased comparative to the as deposited samples. Surface topography of as deposited and annealed trilayer thin films has been confirmed by 2D and 3D images of optical micrographs.

1. Introduction

The $A^{I}B^{III}C^{IV}$ chalcopyrite semiconductor compounds have recently received increased attention because of their wide range of physical properties, compared with those of elemental semiconductors [1]. Ternary and multinary compounds have been attracting attention mainly from the view point of semiconductor researches for the next generation. However, it should be noted that multinary compounds are commonly seen material in the field other than semiconductors [2]. The $CuAlSe_2$(1 1 2)/GaAs (1 0 0) heteroepitaxial layers were grown by the hot wall epitaxy (HWE) method. From the measurements of the Laue patterns and the double crystal X-ray diffraction, the $CuAlSe_2$ epilayer was confirmed to be the epitaxially grown layer along the ⟨1 1 2⟩ direction onto a GaAs (1 0 0) substrate [3]. Investigations on the $CuIn_{1-x}Al_xSe_2$ (CIAS) system as a potential alternate to CIGS are quite important due to replacement of Ga by inexpensive and abundant Al. In addition to single junction solar cells, CIAS thin films can also find application in tandem solar cells [4]. $CuAlSe_2$ is a ternary chalcopyrite semiconductor with a wide gap of 2.67 eV [5]. Thin layer of copper, aluminum and chalogen sequentially deposited by evaporation and annealed to synthesize $CuAlX_2$ (X = Se, Te) films. These films crystallized in the chalcopyrite structure. For $CuAlSe_2$, three characteristic energy gap of 2.66, 2.78, 2.91 eV were obtained for an analysis of the optical transmission spectra [6]. Initially the researchers faced some problems in preparing good quality single crystal of $CuAlSe_2$ because of high reactivity of aluminum.

$CuIn_{1-x}Al_xSe_2$ is an alternative material for the fabrication of low cost heterojunction solar cells and tandem cells. By gradually substituting indium by aluminum, band gap can be varied from 1.04 eV to 2.67 eV. $CuIn_{1-x}Al_xSe_2$ system can also be used for other optoelectronic devices because of its wide coverage of the electromagnetic spectrum [7]. The ternary compound $CuInSe_2$ (CIS) is one of the most widely used material in the production of high efficiency solar cells [8]. The optical constant of vacuum deposited $CuInSe_2$ films was determined from the measured transmission and reflection at normal incidence of light in the wavelength range 500–2000 nm [9].

High–coercivity Au/FePt/Au trilayer samples were prepared by sputtering at room temperature, followed by post annealing at different temperatures by Chen et al. [10]. Crystalline structure and magnetic and magneto-optical properties of MnSbBi thin films

* Corresponding author. Tel.: +91 141 2702457; fax: +91 141 2711049.
E-mail address: nehrasp@gmail.com (S.P. Nehra).

0925-8388/$ – see front matter
doi:10.1016/j.jallcom.2010.04.150

studied by Kang et al. [11]. High conducting trilayer films consisting of a Cu layer sandwiched between Al-doped ZnO (AZO) layers (AZO/Cu/AZO) were prepared on glass substrates at room temperature by radio frequency (RF) magnetron sputtering of AZO and ion-beam sputtering of Cu. These trilayer films have been found with superior photoelectric properties compared the bilayer films by Yang et al. [12]. Shen et al. have done research work on growth and magnetism of metallic thin films and multilayer by pulsed-laser deposition and observed that the improved growth, in particular for the first several monolayer, provides great opportunities to design artificial thin film structures that have promising physical properties [13]. Zn/Se bilayer thin films were prepared and characterized by Singh and Vijay [14]. They prepared ZnSe films by a stacked elemental layer deposition method on glass substrates at pressure 10^{-5} Torr. They found that the band gap and grain size of films increase with annealing time.

In the present work, we are reporting the preparation of Cu/Se/Al trilayer thin films onto glass substrate by thermal evaporation technique and its characterization through X-ray diffraction, UV–vis spectrophotometer, current–voltage measurements and the optical microscopy. An attempt is made to correlate the annealing temperature of the film and observed results. The purpose of this work is to evaluate the role of annealing temperature and mixing of layers leading to the formation of $CuAlSe_2$ and AlCu etc. compounds which are necessary to maximize the sensitivity, fabrication and reproducible condition in the solar energy conversion and energy efficiency studies. The information obtained from these fundamental studies will establish a foundation for high quality trilayer thin films production.

2. Experimental details

2.1. Sample preparation

Trilayer thin films of Cu/Se/Al have been deposited layer-by-layer onto a glass substrate by thermal evaporation technique (Hind High Vacuum) under vacuum of 10^{-5} Torr. Copper wire (98.99% pure), selenium (99.99% pure, pellets < 4 mm) and aluminum foils (99.999% pure) were used for the present study. Copper wire and selenium were kept in tantalum boats separately and aluminum foil was wrapped over tungsten filament. The source to substrate distance was kept 15 cm in each case. To get good adhesion we have used substrate heater having constant temperature of 80–90 °C. The melting point of used materials Cu, Se and Al are 1080, 221 and 660 °C respectively which is not so high to prevent good adhesion. Deposition of trilayer Cu/Se/Al thin films has been performed by stacked layer method. First we have deposited Cu layer and later Se and Al layers respectively to obtain Cu/Se/Al trilayer thin film structures. The thickness of Cu/Se/Al trilayer thin films was 500 nm (150 nm Cu, 200 nm Se and 150 nm Al) measured by quartz crystal thickness monitor (HINDHIVAC THICKNESS MONITOR MODEL DTM-101).

2.2. Annealing

Annealing of trilayer thin films have been performed at constant temperatures of 50–200 °C for half an hour in atmospheric conditions for mixing to get homogeneous structure and interdiffusion of trilayer thin films of Cu/Se/Al. For annealing constant temperatures have been obtained and maintained with the help of Metrex Muffle furnace automatic controlled by digital microprocessor having temperature precision of ±1 K.

2.3. X-ray diffraction

X-ray diffraction measurements have been taken by using an X-ray diffractometer (PANalytical X'pert PRO PW3040/60) having Cu Kα, as a radiation source of wavelength $\lambda = 1.540598$ Å with $2\theta = 10–70°$ at the scan speed 0.09°/min. for determination of structure. The analysis has been performed by using Powder X Software.

2.4. Optical characteristics

The optical absorption spectra of as deposited and annealed Cu/Se/Al trilayer thin films were recorded in the range 200–1100 nm with the help of Hitachi spectrophotometer model-U3300.

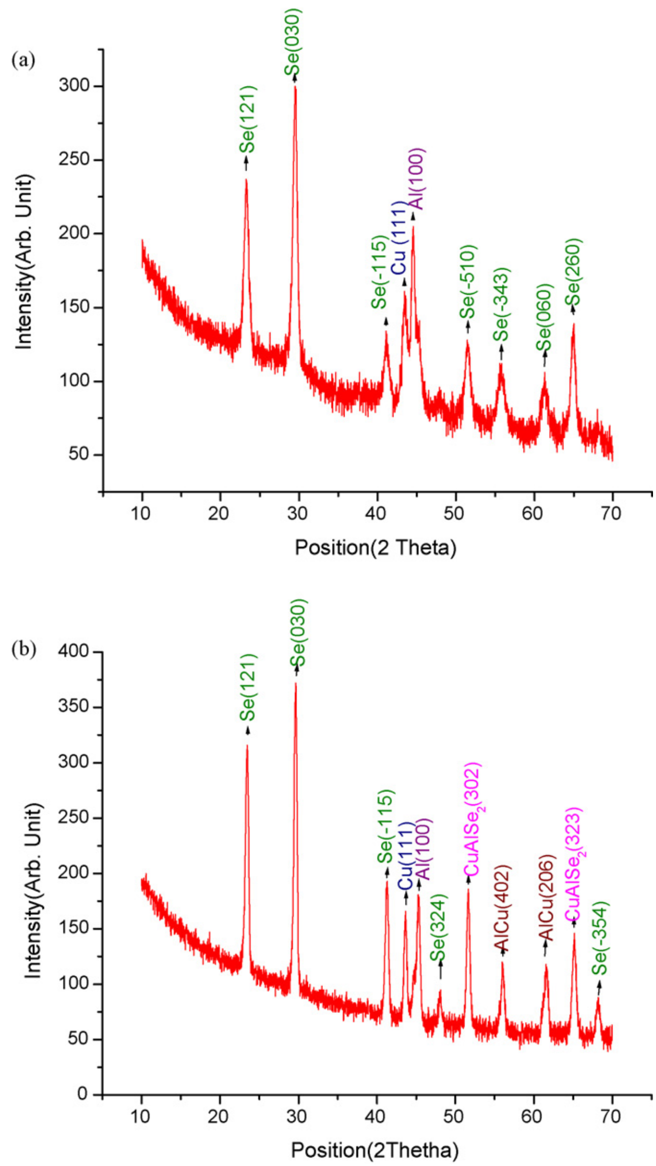

Fig. 1. (a) X-ray diffraction pattern of as deposited Cu/Se/Al trilayer thin film. (b) X-ray diffraction pattern of annealed at 200 °C Cu/Se/Al trilayer thin film.

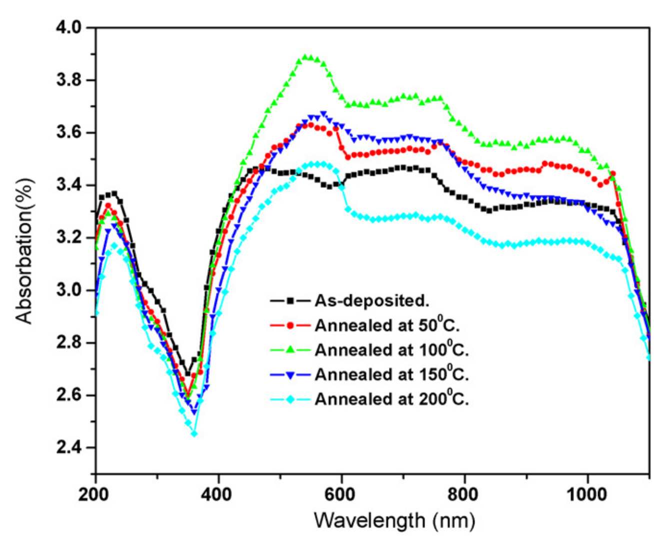

Fig. 2. Optical absorption spectra of as deposited and annealed Cu/Se/Al trilayer thin films.

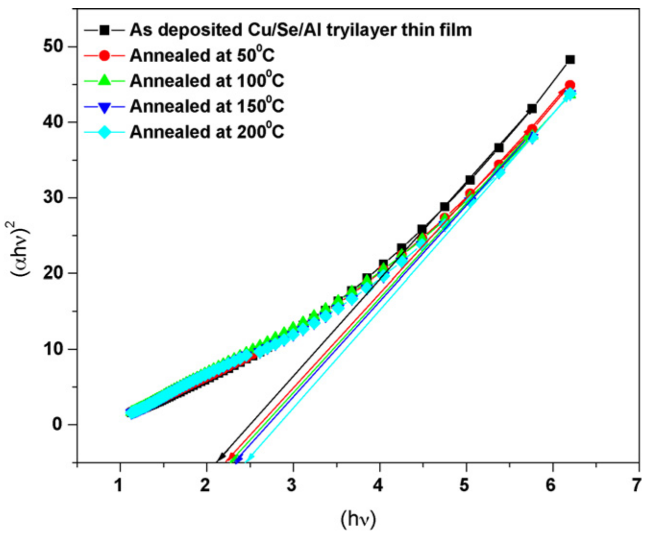

Fig. 3. Optical band gap spectra of as deposited and annealed Cu/Se/Al trilayer thin films.

2.5. I–V characteristics

Transverse *I–V* characteristics of as deposited and annealed samples have been recorded using Keithley-238 high current source measuring unit. The applied voltage was kept within the range of −2.0 to +2.0 V with increasing step of 0.1 V. For *I–V* characteristics, electrode contacts of copper wire have been made using silver (Ag) paste on Cu and Al layer across the Se layer. *I–V* characteristics of bilayer thin films have been monitored with the help of SMUSweep computer software. All the measurements have been performed at room temperature.

2.6. Optical microscopy

The optical micrographs have been observed with the help of Labomed optical microscope at 10× magnification having resolution of the order of 1 μm and the microscope was kept in reflection mode. The micrographs were stored in computer through standard software (PixelView). Two dimensional images captured from optical microscope have been converted into three dimensional images with the help of Scanning Probe Image program.

3. Results and discussion

3.1. Structural characteristics

Fig. 1 shows the X-ray diffraction trace for as deposited Cu/Se/Al trilayer thin film. It is found that the diffraction peaks at 2θ angles

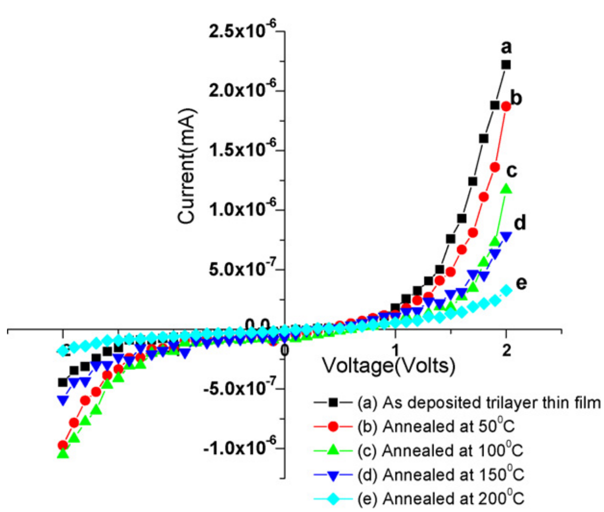

Fig. 4. *I–V* characteristics of as deposited and annealed Cu/Se/Al trilayer thin films.

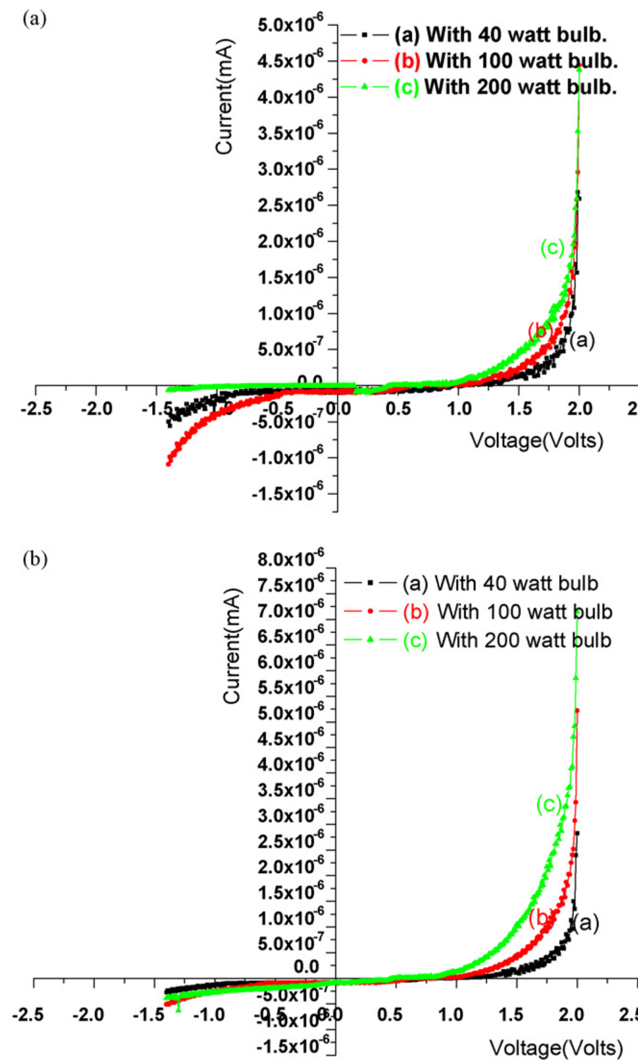

Fig. 5. (a) *I–V* characteristics of as deposited Cu/Se/Al trilayer thin film with different heating power of bulbs. (b) *I–V* characteristics of annealed at 200 °C Cu/Se/Al trilayer thin film with different heating power of bulbs.

of 23.25°, 29.49°, 41.17°, 51.44°, 55.82°, 61.28°, 65.00° corresponds to the (1 2 1), (0 3 0), (−1 1 5), (−5 1 0), (−3 4 3), (0 6 0), (260) planes of the monoclinic structure of Se. The diffraction peaks at 2θ angles of 43.35°, 44.72° corresponds to the (1 1 1) and (2 0 0) planes of the cubic structure of Cu and Al respectively.

Fig. 1b shows dramatic changes in the X-ray diffraction spectra of annealed Cu/Se/Al trilayer thin film at 200 °C for half an hour in air. The sharp diffraction peaks have been observed at 2θ angles of 23.25°, 29.49°, 41.17°, 48.09, 68.22° corresponds to the (1 2 1), (0 3 0), (−1 1 5), (3 2 4), (−3 5 4) planes of the monoclinic structure of Se. Some additional peaks of selenium are observed in the case of annealed Cu/Se/Al trilayer thin film. The diffraction peaks at 2θ angles of 43.35°, 44.72° corresponds to the (1 1 1)

Table 1
Variation in band gap values of Cu/Se/Al trilayer thin films with annealing temperatures.

S. No.	Cu/Se/Al trilayer thin films	Value of band gap (eV)
1.	As deposited	2.14
2.	Annealed at 50 °C	2.25
3.	Annealed at 100 °C	2.32
4.	Annealed at 150 °C	2.36
5.	Annealed at 200 °C	2.48

and (2 0 0) planes of the cubic structure of Cu and Al respectively same as observed in case of as deposited trilayer thin film The diffraction peaks at 2θ angles of 51.65°, 65.17° and 55.98°, 61.45° corresponding to the (3 0 2), (3 2 3) and (4 0 2), (2 0 6) planes of the tetragonal structure of $CuAlSe_2$ and orthorhombic structure of AlCu respectively.

These observed additional peaks of Se and new peaks of $CuAlSe_2$ and AlCu in the case of annealed trilayer thin film of Cu/Al/Se indicates the mixing of trilayers at the interface. The intensity of all the diffraction peaks has been increased due to possibility of grain growth. Grain sizes for as grown trilayer thin films have been found small in comparison of annealed in air at 200 °C for half an hour. It is suggested that some limited grain growth has been occurred during the heat treatment in air, indicating that grain growth may be more accelerated in the presence of oxygen.

3.2. Optical properties

Fig. 2 shows the optical absorption spectra of (a) as deposited and (b–e) annealed at different temperature (50–200 °C) trilayer thin films. It may be concluded that the absorption increases with the annealing temperature of thin films due to the possibility of crystal growth due to annealing.

Fig. 3 shows the optical band gap of (a) as deposited, (b) 50 °C air heated, (c) 100 °C air heated, (d) 150 °C air heated, (e) 200 °C air heated Cu/Se/Al trilayer thin films. The optical band gap of these films was calculated using the famous Tauc relation

$$\alpha h\nu = A(h\nu - E_g)^n$$

where $h\nu$ is the photon energy, α is absorption coefficient, E_g is the band gap, A is a constant, $n = 0.5$ for direct band gap material and

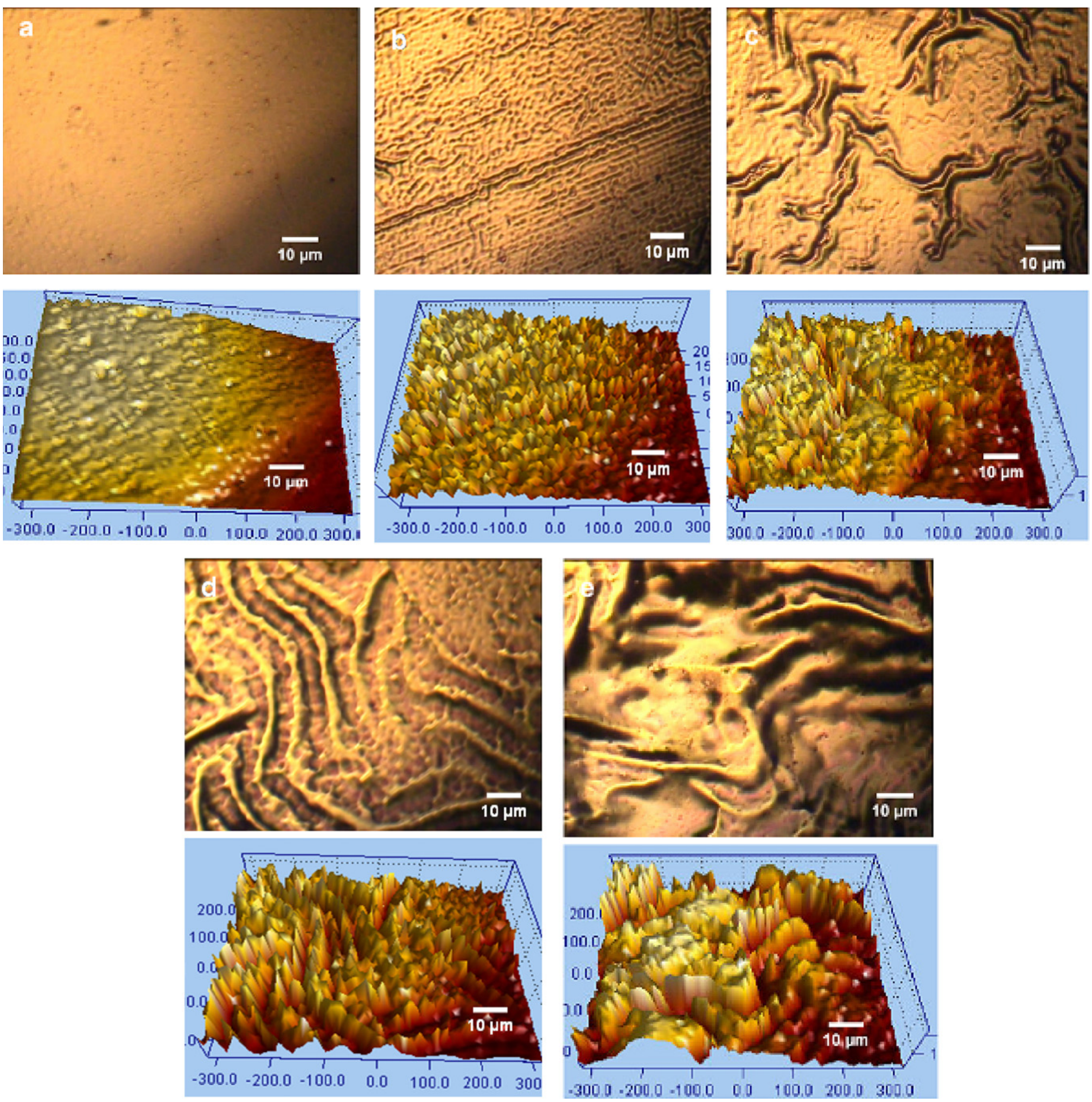

Fig. 6. Surface topography of (a) as deposited, (b) annealed at 50 °C, (c) annealed at 100 °C, (d) annealed at 150 °C and (e) annealed at 200 °C Cu/Se/Al tilayer thin films.

Table 2
Variation in conductivity of Cu/Se/Al trilayer thin films with annealing temperatures.

S. No.	Name of samples	Resistance (MΩ)	Resistivity (Ω m)	Conductivity (Ω^{-1} m^{-1})
1.	As deposited trilayer thin film	0.85	1.0×10^7	9.4×10^{-6}
2.	Annealed at 50 °C	1.3	1.6×10^9	6.1×10^{-8}
3.	Annealed at 100 °C	2.6	3.2×10^9	3×10^{-8}
4.	Annealed at 150 °C	4.5	5.6×10^9	1.7×10^{-8}
5.	Annealed at 200 °C	6.5	8.1×10^9	1.2×10^{-8}

$n = 2$ for indirect band gap material. In the present work, we have used $n = 2$. We have plotted the graph between photon energy ($h\nu$) vs. $(\alpha h\nu)^2$. The intercept of straight line to energy axis is used to find the values of optical band gap of Cu/Se/Al trilayer thin films. The value of band gap is found to vary from 2.14 eV to 2.48 eV with heat treatment as shown in Table 1. The value of band gap was found higher in the case of annealed samples. Due to annealing there is possibility of grain growth and formation of some wide band gap compounds like AlCu, $CuSeAl_2$ etc. which cause increase in band gap.

3.3. Current–voltage characteristics

Fig. 4 shows *I–V* characteristics curves for (a) as deposited and (b–e) annealed at different temperatures Cu/Se/Al trilayer thin films, indicating the partially semiconductor behavior of thin films. It may be attributed that current decreases with increasing temperature of annealing due to the formation of some wide band gap compounds like AlCu, $CuAlSe_2$ etc. by mixing of layers. These compound semiconductors have wide range of physical properties, compared with those of elemental semiconductors. The conductivity has been found to be reduced from 9.4×10^{-6} to $1.2 \times 10^{-8}\,\Omega^{-1}\,m^{-1}$ with increasing temperature of annealing as shown in Table 2.

Fig. 5a and b shows *I–V* characteristics of as deposited and annealed at 200 °C Cu/Se/Al trilayer thin films respectively. These *I–V* measurements have been taken by giving thermal heating with (a) 40 W, (b) 100 W, (c) 200 W bulbs. These measurements indicate the semiconductor nature of trilayer thin films. It may be attributed from these figures that current increases with increasing heating power of bulbs because light of more intensity falls on these films and absorbed. Therefore the number of charges increases across the semiconductor layer which result increase in current. It was found that the current increases linearly within the voltage range of 1–2 V and at the voltage 2 V the current increases drastically in all cases.

3.4. Surface topography

Fig. 6 shows the 2D and 3D images of optical micrographs of (a) as deposited and (b–e) annealed at different temperatures of Cu/Se/Al trilayer thin films, indicating the uniform deposition and mixing of trilayer thin films. From 2D and 3D images it may be attributed that crystal growth has been increased due to the annealing.

4. Conclusion

Trilayer thin films Cu/Se/Al have been prepared by thermal evaporation technique. It is concluded from structural characteristics of trilayer thin films that the intensity of peaks increased and some more peaks are observed in the case of annealed samples. It may be due to the formation of new compounds and growth in grain size because of the mixing of trilayer by annealing.

In the case of annealed Cu/Se/Al trilayer thin films the band gap and current are found to be increased and decreased respectively with increasing annealing temperatures. *I–V* characteristics show the semiconductor nature of Cu/Se/Al trilayer thin films. From *I–V* characteristics of trilayer thin films with bulbs of different heating power it has been observed that the current increases with in the voltage range of 1–2 V. Optical micrographs of as deposited and annealed samples confirm the uniform deposition and mixing of trilayer thin films due to air heating respectively.

Acknowledgements

The authors are highly thankful to University Grant Commission (UGC), Govt. of India for financial assistance. We are also thankful to Department of Physics, University of Rajasthan, Jaipur (India) for providing experimental facilities.

References

[1] A. Rockett, R.W. Birkmire, J. Appl. Phys. 70 (1991) R81–R91.
[2] K. Sato., IPAP Books 1 (2001) 4–5.
[3] S.H. You, K.J. Hong, T.S. Jeong, S.Y. Le, J.J. Bang, J.D. Moon, H.S. Kim, J. Cryst. Growth 290 (2006) 18–23.
[4] Y. Bharath Kumar Reddy, V. Sundara Raja, B. Sreedhar, J. Phys. D: Appl. Phys. 39 (2006) 5124–5132.
[5] Y.B.K. Reddy, V.S. Raja, Semicond. Sci. Technol. 19 (2009) 1015–1019.
[6] C.O. El Moctar, K. Kambas, S. Marsillac, A. Anagnostopoulos, J.C. Bernede, K. Benchouck, Thin Solid Film 371 (2000) 195–200.
[7] K. Srinivas, J.N. Kumar, G.H. Chandra, J. Mater. Sci. 17 (2006) 1035–1039.
[8] K. Ramanathan, G. Teeter, J.C. Keane, R. Noufi, Thin Solid Films 499 (2005) 48–481.
[9] H.S. Soliman, M.M. El Nahas, O. Jamjoum, K.H.A. Mady, J. Mater. Sci. 23 (1995) 4071–4075.
[10] S.K. Chen, F.T. Yuan, W.M. Liao, C.W. Hsu, L. Horng, J. Magn. Magn. Mater. 303 (2006) e251–e254.
[11] K. Kang, V.G. Kravets, A.K. Petford-Long, Thin Solid Film 410 (2002) 28–37.
[12] T. Yang, Z. Zhang, S. Song, Y. Li, M. Lv, Z. Wu, S. Han, Vacuum 83 (2008) 257–260.
[13] J. Shen, Z. Gai, J. Kirschner, Surf. Sci. Rep. 52 (2004) 163–218.
[14] M. Singh, Y.K. Vijay, Appl. Surf. Phys. 239 (2004) 79–86.