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ELECTRICAL PROPERTIES OF $MoBiGaSe_5$ THIN FILMS DEPOSITED BY HEATING RESISTIVE VACUUM DEPOSITION TECHNIQUE

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ABSTRACT

In the present study, nanocrystalline $MoBiGaSe_5$ thin films with primary semispherical balls and secondary diffused nanograins have been prepared onto glass substrates by vacuum deposition technique. Ammonium molybdate $(NH_4)_6Mo_7O_{24}\cdot4H_2O$, Bismuth nitrate $Bi(NO_3)_3\cdot5H_2O$, Gallium nitrate $Ga(NO_3)_3\cdot xH_2O$, and Selenium Se metal powder were used as a precursors of Mo^{+4}, Bi^{+3}, Ga^{+3} and Se^{-2} ions respectively. The as deposited and vacuum annealed thin films were characterized for their optostructural, morphological and electrical properties using different characterization techniques. Optical absorption studies reveal that as deposited and annealed $MoBiGaSe_5$ films show absorption in the wavelength range of 400 to 800 nm. Scanning electron microscopic (SEM) images of as deposited films showed uniform, well defined granular morphology, besides annealed samples have diffused granular growth of uniform spheres. X-Ray diffraction (XRD) analysis of annealed thin film shows, the phase transition from orthorhombic Bi_2Se_3 to stoichiometric hexagonal Bi_2Se_3 phase. Phase transition confirms the formation of hexagonal nanocrystalline $MoBiGaSe_5$ pure phase. Electrical conductivity (EC) of as deposited and vacuum annealed sample was measured by two probe method. An EC increase with temperature indicates semiconductor nature with p-type conductivity.

KEYWORDS : *characterization techniques, hexagonal nanocrystalline.*

1. INTRODUCTION

Recently nanocrystalline Mixed Metal Chalcogenide (MMC) thin films have great potential in solar cell application. MMC and chalcopyrite semiconductors have been widely used as the most promising candidates for low cost solar absorbers and significant efficient thin film photovoltaic devices [1-3]. The ternary and quaternary thin films of VIB-VA-VIA, VIB-VA-IIIB-VIA and IB-IIIA-VIA groups have high conversion efficiency due to its tunable band gap in the range of 1.1 to 1.6 eV which absorbs maximum solar spectrum. Recently quaternary MMC materials are at front because of similar band gap energy as that of $Cu(In,Ga)Se_2$ (CIGS) and Cu_2ZnSnS_4 (CZTS) [4,5]. Quaternary materials are synthesized by various methods such as electrodeposition [6], spray pyrolysis [7], hydrothermal [8], chemical vapor deposition [9], hot injection method [10], sputtering [2] and arrested precipitation technique [11]. In those studies researchers paid more attention on absorption coefficient, band gap and photo response of the material. Recently S. S. Mohite et. al. [12] showed the vacuum evaporation method is more promising for the synthesis of quaternary MMC thin film materials. The preparative parameters like evaporation rate, deposition time and easy of precursor selection are the key factors for achieving good quality MMC thin films. In this investigation, we report deposition of quaternary $MoBiGaSe_5$ thin films by heating resistive vacuum evaporation technique and their electrical properties.

2. EXPERIMENTAL DETAILS

All the reagents are of analytical grade (AR) and were used without further purification. Ammonium molybdate $(NH_4)_6Mo_7O_{24}\cdot4H_2O$, Bismuth nitrate $Bi(NO_3)_3\cdot5H_2O$, Gallium nitrate $Ga(NO_3)_3\cdot x\cdot H_2O$ and Selenium metal powder were used as a precursors for Mo^{+4}, Bi^{+3}, Ga^{+3} and Se^{-2} ions respectively. The

$MoBiGaSe_5$ thin films were deposited on to cleaned glass substrates by sequential evaporating Mo^{+4}, Bi^{+3}, Ga^{+3} and Se^{-2} precursors using vacuum deposition technique (HIND-HIVAC model: 15 F6-India) by resistive heating. Molybdenum boat was used as resistive heating source. Pressure was maintained at 10^{-6} mbar and time 7 minutes during deposition for all materials. The distance between the source and substrate was kept 25 cm. The thickness of the film measured using surface profilometer and was found to ~750 nm, which was in agreement with the value obtained through quartz crystal monitor mounted in the evaporation unit. Deposited $MoBiGaSe_5$ thin films were blackish in colour with reflecting surface. Optimized deposition parameters for $MoBiGaSe_5$ samples by vacuum evaporation technique are summarized in Table 1. As deposited samples were annealed at 80 ^{0}C in vacuum furnace and used for further characterizations.

Table 1. Various optimized parameters during vacuum deposition of the $MoBiGaSe_5$ films having substrates at Room temperature.

Element	Precursor	Deposition rate (Å/sec)	Pressure (mbar)	Current (Amp)
Mo	$(NH_4)_6Mo_7O_{24}.4H_2O$	20	10^{-5}	105
Bi	$Bi(NO_3)_3{\cdot}5H_2O$	20	10^{-5}	110
Ga	$Ga(NO_3)_3{\cdot}xH_2O$	20	10^{-5}	118
Se	Se metal powder	20	10^{-5}	68

3. CHARACTERIZATIONS

The optical absorption study was done by using a UV-Vis spectrophotometer (UV-1800 Shimadzu, Japan). The surface morphology of $MoBiGaSe_5$ thin films were studied using Scanning Electron Microscopy (SEM: JEOL-6360). The thickness of films was measured by surface profiler (AMBIOS XP-1, USA). The structural properties of as deposited and annealed thin films are analyzed by X-ray Diffraction (XRD) analysis (Bruker AXS Model D8 Advanced X-ray Diffractometer) with Cukα target having wavelength 1.542 Å, radiation (I) the 2θ ranges from 20 to 60^0. Electrical conductivity was measured by two probe method.

4. RESULTS AND DISCUSSION

4.1 Optical Absorption Studies

The optical absorption of as deposited and vacuum annealed nanocrystalline $MoBiGaSe_5$ thin films was carried out in the wavelength range 300-1100 nm. The thickness of as deposited film is near about 750 nm while on annealing thickness of the film slightly decreases due to diffusion of the smaller grains to larger grains. The variation of optical coefficient with wavelength was further analyzed to find out the nature of electronic transition across the optical band gap. The nature of transition was determined by using the relation,

$$\alpha h\nu = A(h\nu - Eg)^{n/2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

Where, A is a constant, hν is a photon energy, n = 1 for a direct gap material and n = 2 for an indirect gap material. The plot of $(\alpha h\nu)^2$ versus hν for the $MoBiGaSe_5$ thin films for as deposited and annealed samples are shown in fig. 1.

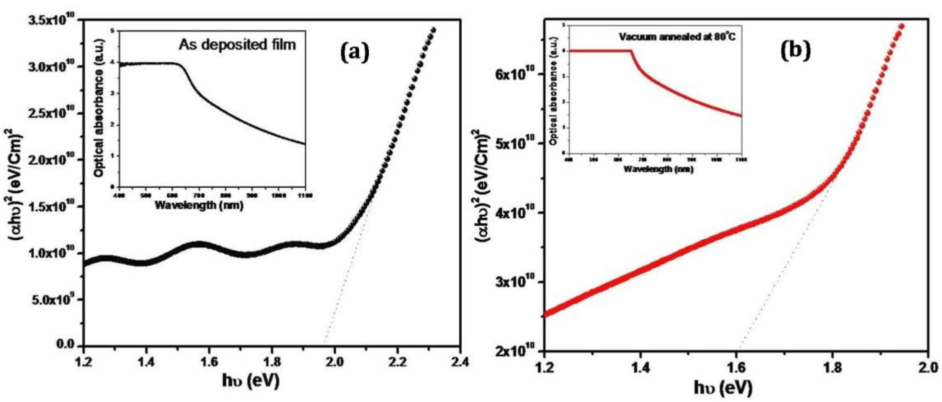

Fig.1. Optical absorption of the $MoBiGaSe_5$ thin films a) as deposited and b) vacuum annealed at 80^0C.

The nature of plot suggests direct allowed transition. The extrapolating of straight line portion to the X-axis leads to the determination of band gap energy of the material. Fig. 1 clearly reveals that the band gap energy decreases for annealed sample from 1.96 to 1.60 eV. The band gap energy decreases due to compact grain growth after annealing grain size of the film.

4.2 Scanning Electron Microscopy (SEM) Analysis

Fig. 2 show SEM images of as deposited $MoBiGaSe_5$ thin film sample exhibits a uniform deposition with granular morphology. When $MoBiGaSe_5$ thin film annealed at 80^0C in a vacuum, the granular morphology converted into diffused grains. The grain size of as deposited and vacuum annealed samples is about 600 nm and 900 nm respectively.

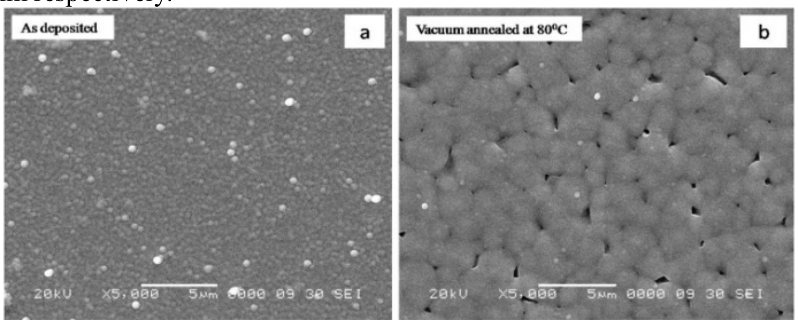

Fig. 2. SEM micrographs of $MoBiGaSe_5$ thin films deposited by vacuum evaporation; a) as deposited and b) vacuum annealed at 80^0C.

4.4 X-ray Diffraction (XRD) Analysis

For the structural analysis of as deposited and annealed $MoBiGaSe_5$ thin films, the diffraction angle 2θ is varied in the range of 20 to 60^0. Fig. 4 show the XRD patterns for as deposited and vacuum annealed samples.

Different intensity peaks in X-Ray spectra are indexed and the corresponding values of interplaner spacing 'd' are calculated and compared with standard values of JCPDS data and). The X-ray diffraction pattern for as deposited thin film displayed diffraction peaks at 2θ values of approximately at 27.165^0 corresponds to (230) plane of orthorhombic structure of Bi_2Se_3 (Card No. 77-2182 and hexagonal Bi_2Se_2 (card No. 72-2182) phase, 37.863^0 corresponds to (103) plane of hexagonal structure of $MoSe_2$ (Card no. 17-0887), 22.359^0 and 32.365^0 corresponds to (004) and (103) planes of hexagonal structure of GaSe (Card No. 37-0931) phase. XRD analysis of vacuum annealed thin film shows peak at 2θ value approximately at 29.74, 43.67^0 corresponds to (104), (109) planes of hexagonal Bi_2Se_2 phase. The XRD analysis reveals that the transition from Orthorhombic Bi_2Se_3 to stoichiometric Hexagonal Bi_2Se_2 phase. Phase transition confirms the formation of Hexagonal nanocrystalline $MoBiGaSe_5$ pure phase.

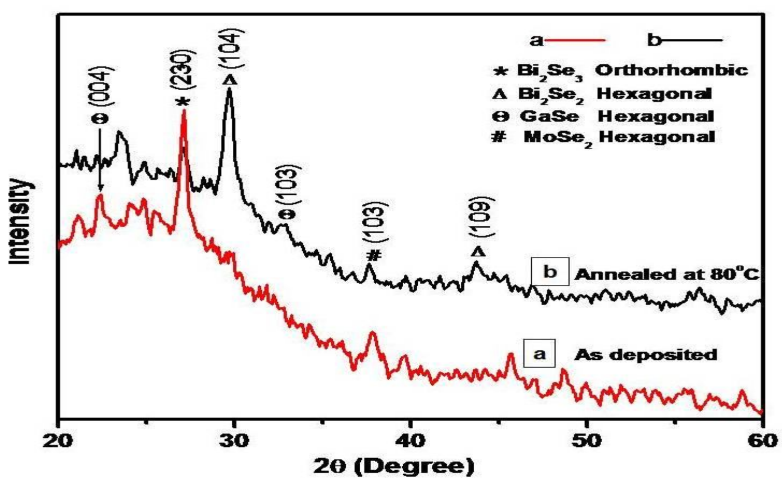

Fig.3. XRD patterns of the $MoBiGaSe_5$ thin films a) as deposited and b) annealed at 80^0C.

The crystallite size 'D' was calculated using FWHM data and Scherer formula [13],

$$D = K\lambda / \beta \cos\theta \quad \ldots\ldots (2)$$

Where, 'D' is average crystallite dimension, 'K' 0.94 is a constant 'λ' is wavelength of the x-ray used, 'β' is full width at half maximum (FWHM) and 'θ' is Bragg's angle. The crystallite size estimated for as deposited and annealed MoBiGaSe5 films having (230) and (104) planes were 20 and 24 nm respectively. The small crystallite in the range of nanoscale confirms nanocrystalline nature of the films.

4.5 Electrical Properties

Electrical conductivity (σ) measurements of as deposited and vacuum annealed $MoBiGaSe_5$ thin films were carried out in temperature range 300 to 500 K on 1x1 cm^2 area of samples, using standard dc two point probe method. The plot of ln σ versus 1000/T of as deposited and vacuum annealed $MoBiGaSe_5$ thin films are shown in fig. 4.

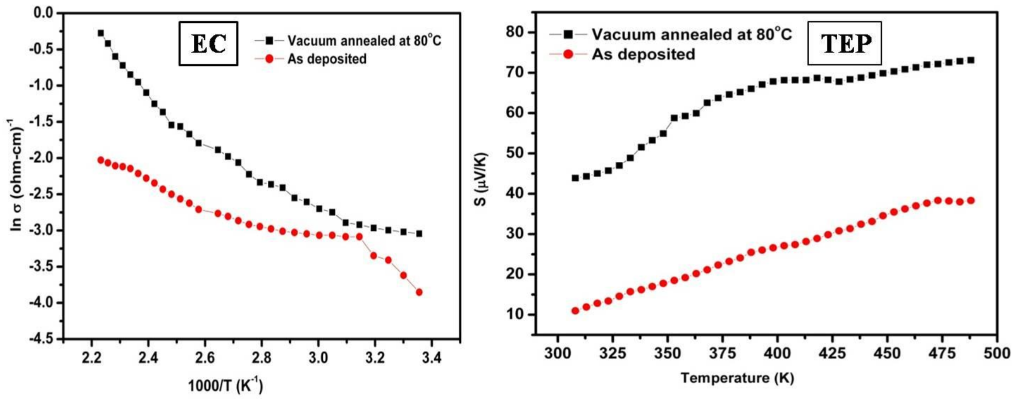

Fig. 4. EC and TEP of as deposited and vacuum annealed $MoBiGaSe_5$ thin films.

An EC of as deposited and vacuum annealed $MoBiGaSe_5$ thin film increases with increasing temperature, exhibiting a characteristic semiconducting nature of the films. When sample is annealed at 80°C in vacuum furnace electrical conductivity of the film increases because of inter mixing of deposited layers shown in fig. 4.

The thermoelectric properties (TEP) of $MoBiGaSe_5$ thin films were measured in the temperature range 300 to 500 K. Fig. 4. shows variation of Seebeck coefficient (S) versus temperature for as deposited and vacuum annealed $MoBiGaSe_5$ thin films. TEP is most sensitive to any change or distortion of the fermi level in the material. The temperature difference between the ends of sample causes transport of carriers from hot to cold end and it creates electrical field which gives rise to thermal voltage. Thermally generated voltage is directly proportional to the temperature difference created across the semiconductor. The plots of Seebeck coefficient versus temperature difference across the sample are shown in fig. 4. TEP measurement gives positive value of Seebeck coefficient throughout the temperature range confirms p-type of conductivity of as deposited and vacuum annealed $MoBiGaSe_5$ thin films.

5. CONCLUSION

Resistive heating vacuum evaporation technique is applied to deposit stoichiometric, adherent and uniform deposition of $MoBiGaSe_5$ thin films. The samples were characterized by using different characterization techniques for optical, structural and compositional studies. As deposited films show granular morphology while on annealing grains get diffused. As deposited and vacuum annealed thin films show good absorption in the visible light. XRD analysis of annealed thin film showed phase transition from Orthorhombic Bi_2Se_3 to stoichiometric Hexagonal Bi_2Se_2 phase. As deposited and vacuum annealed films show semiconducting behavior with p-type conductivity.

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