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Archives of Applied Science Research, 2010, 2 (2):275-283
(http://scholarsresearchlibrary.com/archive.html)

ISSN 0975-508X
CODEN (USA) AASRC9

Optical and electrical studies on $MoBi_2Se_5$ thin films prepared by Arrested Precipitation Technique (APT)

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Abstract

The layered molybdenum chalcogenides and lattice structured bismuth chalcogenides are semiconductors which can be efficient electrodes in the realization of photo electrochemical solar cells. The bismuth chacogenides are thermoelectrically important materials which are used as thermoelectric coolers and sensors. The main advantage of molybdenum chalcogenide semiconductor is the prevention of electrolyte corrosion because of the photo transition involving non bonding d-d orbital of the Mo atoms. $MoBi_2Se_5$ thin films are prepared by simple and low cost arrested precipitation technique (APT). The growth kinetics of the films was studied and the deposition parameters such as bath concentration, bath temperature, time of deposition, P^H of bath etc., are optimized. X-ray diffraction analysis of the films showed the highly textured $MoBi_2Se_5$ films with orthorhombic structure. Surface morphology studies by scanning electron microscopy (SEM) shows that the films are pinhole free and of device quality nature. EDAX spectrum of the surface composition confirms the nearly stoichiometric $MoBi_2Se_5$ thin films. Optical absorption spectra show band gap value 1.78eV. Conductivity measurements carried out at different temperatures and activation energy was calculated. The thermoelectric power measurements showed material to be n-type.

Keywords: X-ray diffraction, Growth from Solution, Thin film, Semiconducting ternary compounds.

INTRODUCTION

Interest in the use of photo electrochemical (PEC) solar cells for low cost energy conversion has lead to an extensive research in the search for novel and suitable thin film semiconductor materials [1]. Materials belonging to V group of periodic table like bismuth and antimony are thermoelectrically important materials which are used as thermoelectric coolers and sensors.

Recent investigation have shown that the layered type semiconducting group VI transition metal dichalcogenides ($MoSe_2$, MoS_2) which absorb visible and near IR light are particularly interesting materials for photo electrochemical solar energy conversion. The most efficient system till date turned out to be $MoSe_2$ [2].

The best materials for thermoelectric application at room temperature were $V^A{}_2$, $VI^A{}_3$ compounds and VI^B, $VI^A{}_2$ compounds and their alloys because of high thermoelectric figure of merit. Various researchers are investigating new materials for use in the solar energy conversion [3-6]. Our research in new PEC materials has identified several ternary bismuth chalcogenide thin films to have promising properties for PEC applications. Bi_2Se_3 materials have possible application as thermoelectric generator or photoconductors [7, 8] and $MoSe_2$ have special application in interaction superconductors or photo electrochemical cells [9, 10]. The techniques presently used for synthesis of molybdenum chalcogenide and bismuth chalcogenide semiconductors thin films are CBD, MOCBD, spin coating , electro deposition, spray pyrolysis, sputtering, crystal growth, APT and chemical bath deposition [11-16]. All these deposition techniques required specific sophisticated instrumentation. In this regard APT is more attractive and relatively inexpensive presently used by us for deposition of binary V^A-VI^A, II^B-VI^A, VI^B-VI^A and ternary III^B-V^A-VI^A group chalcogenide thin films.

In present investigation we attempt to prepare ternary $MoBi_2Se_5$ thin films by arrested precipitation technique (APT). The purpose of work is to establish and optimize the growth condition to produce $MoBi_2Se_5$ thin films. The as grown films are then used for characterization studies like structural, surface composition, surface morphology, optical and electrical.

MATERIALS AND METHODS

Experimental Details:

$MoBi_2Se_5$ thin films were deposited on micro glass slide substrates using hybrid arrested precipitation technique (APT). The ammonium molybdate and bismuth nitrate were crushed with complexing agent tri-ethanol ammine (TEA) to get Mo-TEA and Bi-TEA complexes respectively. The precursor for Se^{2-} ions was aqueous solution of Na_2SeSO_3 obtained by refluxing sodium sulphite with selenium metal powder for 8 hours [17, 18]. The film growth involves the reaction of Mo^{4+}, Bi^{3+}, and Se^{2-} ions in aqueous medium. The concentration of procures, P^H of the bath solution, temperature, rate of substrate rotation were finalized at initial stages to get good quality uniform and adherent thin films on substrate support. At alkaline P^H (9.5) Mo-TEA and Bi-TEA arrested metal ions slowly dissociates form complex and reacts with chalcogen ion Se^{2-}. At this stage ion by ion condensation took place which results in thin films formation on substrate surface. Na_2SeSO_3 in aqueous alkaline solution ionizes to yield Se^{2-} and SO^{3-} ions, reducing species $SO_3{}^{2-}$ ions at P^H 9.5 ionic product k exceeds solubility product K_{sp} which result in condensation of metal ions and chalcogen ions into quasi binary thin film formation $MoSe_2$ and Bi_2Se_3 to $MoBi_2Se_5$. The complete characterization of $MoBi_2Se_5$ thin films was done for opto-structural and morphological characteristic such as a phase analysis, compositional analysis, structural elucidation, micro-structural analysis and surface morphology which have strong bearing on the properties of materials.

The structure of thin films was determined by X- ray diffraction (XRD) analysis [Philips PW-1710 X-ray diffractometer] with Cr Kα target having wavelength 2.289Å for the 2θ ranging from 20° to 100°. The thickness of film was determined by surface profiler (AMBIOS XP-1). The elemental composition of the as deposited thin was determined by energy dispersive X-ray analysis (EDAX) attached to scanning electron microscope (SEM) model JEOL-JSM- 6360A scanning electron microscope. The optical transmittance was measured using UV-Visible NIR-spectrophotometer Hitachi model 330, Japan in the wavelength range 350 to 850 nm. DC electrical conductivity was measured by two probe method in the temperature range 300K to 500K. Thermoelectric power measurement was carried out under the condition of maximum temperature difference and minimum contact resistance.

RESULTS AND DISCUSSION

3.1.Growth kinetics and reaction mechanism for thin film formation:

The novel structural behavior and properties of thin films can largely be described to their growth process which is therefore basic importance to the science and technology thin films. During synthesis parameters such as temperature, reaction time, P^H, complexing agent and respective precursor product system can be tuned to maintain a high simultaneous nucleation rate and good size distribution.

In present investigation we have successfully deposited $MoBi_2Se_5$ thin films by arrested precipitation technique. In this method metal ions of the precursors are arrested using stable complexing agent in slightly alkaline medium. The metal complex is P^H sensitive and at P^H value 9.5 arrested metal ions slowly released in aqueous alkaline solution where it reacts with Se^{2-} results in ion by ion condensation to uniform thin film formation on substrate surface [19, 20].

In alkaline medium Mo-TEA complex slowly releases Mo^{4+} ions at 9.5 P^H

$$(NH_4)_2[Mo_2N\ (CH_2\text{-}CH_2\text{-}O)_3] + 6H_2O \xrightarrow{P^H\ 9.5} Mo^{4+} + NH_4OH + 4OH^- + 2[N(CH_2\text{-}CH_2\text{-}OH)_3] \quad \ldots. (1)$$

In alkaline medium Bi-TEA complex slowly releases Bi^{3+} ions at 9.5 P^H

$$(NH_4)_3[Bi\ 2N\ (CH_2\text{-}CH_2\text{-}O)_3] + 6H_2O \xrightarrow{P^H\ 9.5} Bi^{3+} + 3NH_4OH + 3OH^- + 2\ [N(CH_2\text{-}CH_2\text{-}OH)_3] \ldots. (2)$$

Na_2SeSO_3 dissociates in alkaline medium to produce Se^{2-} ions

$$Na_2SeSO_3 + OH^- \rightarrow Na_2SO_4 + HSe^-$$
$$HSe^- + OH^- \rightarrow H_2O + Se^{2-} \quad \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

When the reaction (1), (2) and (3) is slow enough, the heterogeneous nucleation of $MoBi_2Se_5$ would occur slowly on the immersed substrate and on the inner wall of the beakers, and deposition of material can be expected as per reaction

$$Mo^{4+} + 2Bi^{3+} + 5\ Se^{2-} \rightarrow MoBi_2Se_5 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

3.2. X-ray diffraction studies

The diffraction pattern of ternary thin film is illustrated in figure 1 the diffraction angle was varied between 20° to 100°. Three peaks observed at diffraction angle of 37.77°, 65.59° and 84.76 °corresponding to 3.537, 2.114 and 1.698 'd' values. These values are matched with standard JCPD data (Card No.40-0908 and 81-0834) showing (311), (025) and (2012) orthorhombic peaks. The XRD data shows $MoBi_2Se_5$ thin films are composed of quasi binary $MoSe_2$ and Bi_2Se_3 phases. The strongest peak for all films occurred at $2\theta = 37.77^o$. It indicates that the preferred orientation lies along (311) direction for $MoBi_2Se_5$ thin films deposited by arrested precipitation technique. The crystallite size D of the deposits was calculated by using Debye Scherer formula [21] for (311) peak assuming that micro strain can be neglected

$$D = \frac{k\lambda}{\beta \cos\theta} \qquad \text{..... (5)}$$

Where, k constant varies with hkl and crystallite shape but usually nearly equal to 0.94, λ is wavelength of source radiation, β full width half maximum of the peak in radian, θ is Braggs angle. The calculated crystallite size is 20.8nm**.**

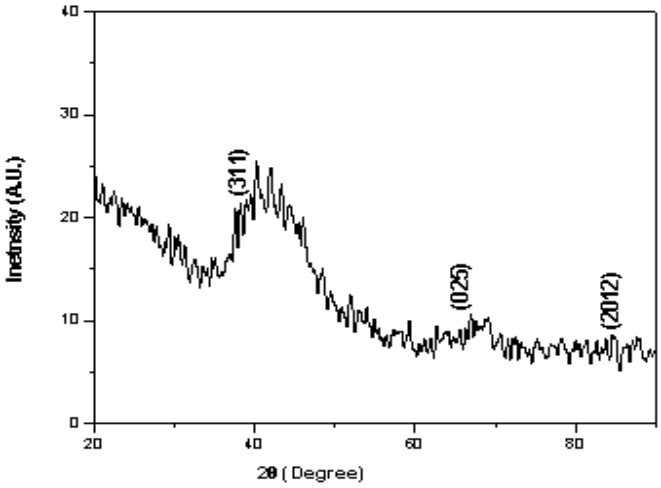


Figure 1. X-ray diffraction pattern of $MoBi_2Se_5$ thin film

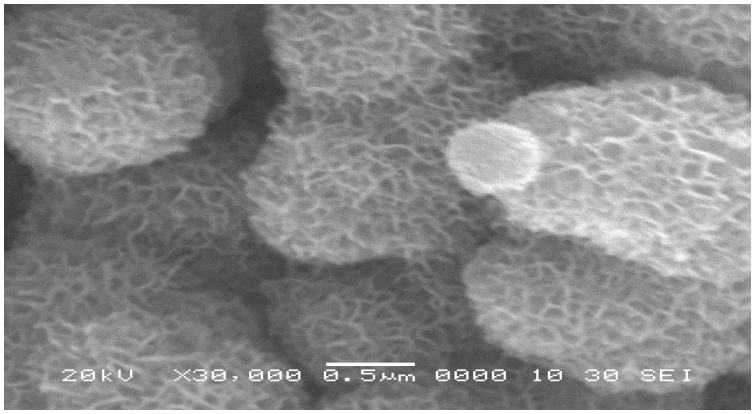


Figure 2. SEM micrograph of $MoBi_2Se_5$ thin film

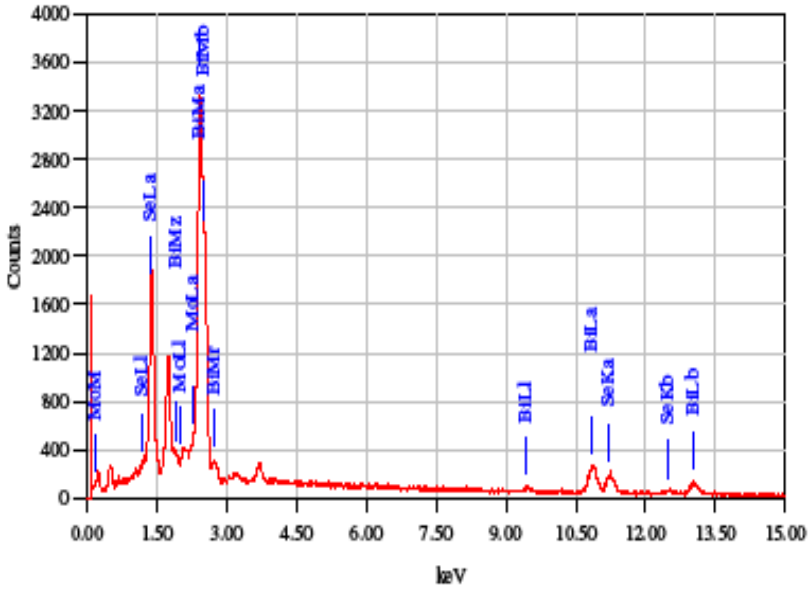


Figure 3. EDS spectrum of $MoBi_2Se_5$ thin film

3.3. SEM / EDAX Studies

The SEM micrograph shows well adherent, smooth and uniform film surface without cracks and pinholes. Figure 2 shows surface morphology of $MoBi_2Se_5$ thin film prepared under optimized condition which exhibits fibrous nature all over the surface.

The EDAX for $MoBi_2Se_5$ film is shown in figure 3. The spectrum peak reveals the presence of Mo, Bi and Se at 2.293 KeV, 2.419 KeV and 1.379 KeV respectively, which confirms the presence of Mo, Bi and Se in the film. The expected ratio of atomic percentage of Mo, Bi and Se is 1:2:5, which is the required stoichiometric ratio. At optimized condition the observed atomic percentage is given in table 1.

Table 1 : EDAX analysis of the as deposited $MoBi_2Se_5$ thin films

Element	**Mo**	**Bi**	**Se**
Atomic percentage (Observed)	12.40%	34.45%	52.55%
Atomic Percentage (Expected)	16.67%	33.33%	50.00%

The percentage of Bi in the film is higher than expected this is attributed to the fact that bismuth is more metallic and its reactivity towards Se^{2-} is higher moreover bismuth forms antisite defects [22] which is responsible for slightly non-stoichiometry of ternary $MoBi_2Se_5$ thin films.

3.4. Optical Studies

The room temperature optical absorption was measured for the $MoBi_2Se_5$ thin films in the wavelength region of 350-850nm. The general expression for variation of absorption coefficient (α) with photon energy (hυ) is given as [23]

$$\alpha = A(h\nu - Eg)^n/h\nu \quad \text{.....(6)}$$

Where, α is absorption coefficient (cm^{-1}), A is constant, hν is photon energy (eV), Eg is Band gap energy of semiconductor (eV) and n is index number (1/2, 3/2, 2…..) depending on the mode of transition.

The optical absorption coefficient (α) of $MoBi_2Se_5$ thin films was calculated using the absorbance value measured for a particular wavelength (λ) and film thickness (t) using equation:

$$\alpha = \frac{1}{t}\log\left(\frac{Io}{It}\right) \quad \text{.....(7)}$$

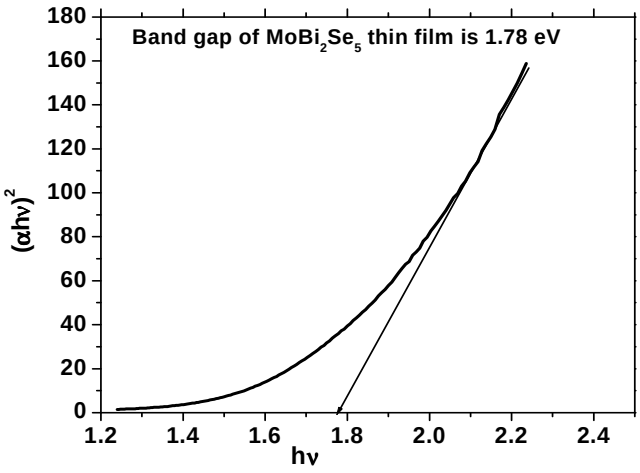
Where, α is optical absorption coefficient, t is thickness of film which is measured by surface profiler and average film thickness for films under investigation was 0.9 μm, log (Io/It) is the absorbance or optical density. The optical absorption coefficient is of the order of $10^4 cm^{-1}$ supporting the allowed and direct band to band transition of material.

The linear portion of graph of $(\alpha h\upsilon)^2$ Vs hυ in eV shown in Figure 4 is extrapolated and it cuts the 'x' axis at 1.78eV, which corresponds to band gap of $MoBi_2Se_5$ films.

3.5. Electrical Properties

Using two point probe technique the electrical resistivity of the film was studied by varying the temperature of the film from 303K to 500K, while doing so the resistivity was found to be decreasing.

Figure 4. Plot of $(\alpha h\upsilon)^2$ Vs hυ of $MoBi_2Se_5$ thin films



By plotting *ln* σ (ohm^{-1} cm^{-1}) verses $(1/T)$ as showed in the Figure 5, the activation energy was calculated using the relations:

$\sigma = \sigma_o \exp^{(-Ea/\kappa T)}$

Where, Ea is activation energy. The activation energy was calculated by taking slopes of linear plots in the low and high temperature region. The activation energy for low temperature region is 0.15 eV and in high temperature region is 0.172 eV.

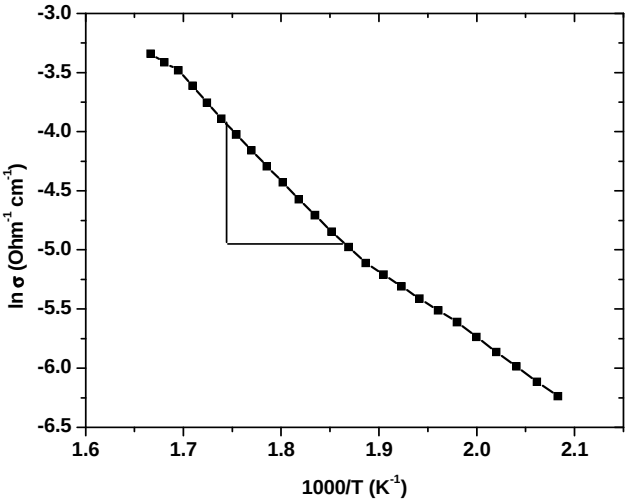


Figure 5. Plot of ln (σ) versus 1000/T for $MoBi_2Se_5$thin film

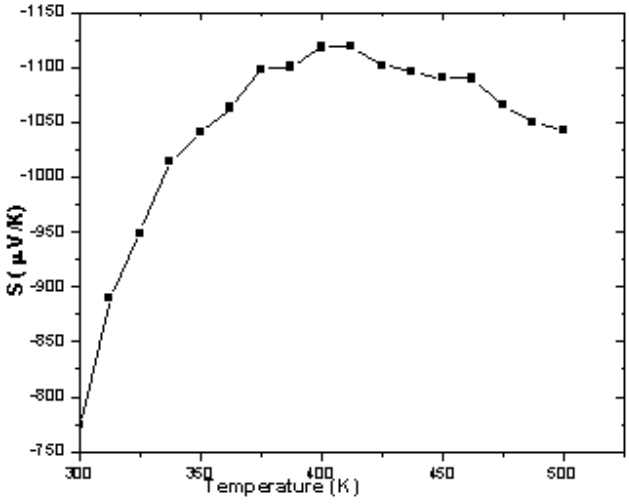


Figure 6. Temperature dependence of the Seebeck coefficient of $MoBi_2Se_5$ thin films

The dark electrical conductivities of the films are studied in the temperature range of 300K to 500K. Figure 6 shows a plot of thermal emf developed across the ends of the film i.e. Seebeck

coefficient as a function of temperature for a film of thickness (0.9µm) during heating and cooling cycles. It is found that thermal emf variation with temperature during heating and cooling cycles is different and this indicates that the as grown films undergo on irreversible transformation due to annealing out of non-equilibrium defects during first heating. The slope of Seebeck coefficient verses temperature plot gives thermoelectric power of the thin film. The increase in thermoelectric power with temperature suggests the degenerate nature of the film. The thermoelectric power is found to be negative indicating that the films are n-type [24-26].

CONCLUSION

The arrested precipitation technique (APT) is found to be most convenient method for deposition of metal chalcogenide thin films. APT is simple, low cost and reliable method. In conclusion, this communication demonstrates that $MoBi_2Se_5$ thin films have been successfully deposited using APT at low temperature. Films prepared using the optimized deposition parameters show preferential orientation along (311) plane. The SEM micrograph shows the device quality nature of the surface without any pinholes. EDAX results confirm the presence of Mo, Bi and Se in 1:2:5 ratios, which shows stoichiometric composition of the films deposited at the optimized condition. From optical studies, the band gap value was found as 1.78eV. From electrical conductivity measurements, the activation energy is calculated for high temperature region and low temperature region as 0.15 eV and 0.172 eV respectively. It reveals that $MoBi_2Se_5$ thin films deposited by APT technique, prepared under the optimized conditions, show semiconductor nature and can be efficiently used for fabrication of efficient PEC solar cells.

Acknowledgement
One of the author (RMM) wish to acknowledge UGC, New Delhi, for the financial support through meritorious Junior Research Fellowship under UGC-SAP-DRS scheme.

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