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NOVEL SYNTHETIC ROUTE FOR QUATERNARY $MoBiGaSe_5$ MIXED METAL CHALCOGENIDE (MMC) THIN FILMS

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Quaternary $MoBiGaSe_5$ mixed metal chalcogenide thin films have been deposited onto a conducting and non conducting glass substrates using simple and low cost arrested precipitation technique (APT). Ammonium molybdate, bismuth nitrate, gallium nitrate-triethanolamine (TEA) complex agent and sodium selenosulphite are used as precursors for Mo^{+4}, Bi^{+3}, Ga^{+3} and Se^{-2} ions respectively. Thin uniform and tightly adhesive thin films were obtained by controlling various preparative parameters such as concentration of precursors, complexing agent, surfactant, pH of bath solution, temperature, deposition time, rate of substrate rotation in reaction bath etc. As deposited films were characterized by physical and chemical techniques. The optical absorption spectra reveal that optical transition is direct and allowed and the band gap of as deposited film is 1.30 eV. The structural property was investigated by XRD analysis and it shows nanocrystalline nature with hexagonal structure. SEM micrograph clearly reveals well defined, nanocrystalline grains. The compositional analysis was carried out by using EDAX and it shows films are chemically stoichiometric. One of the important property observed during DC conductivity measurement study that ternary $MoBi_2Se_5$ is n-type while on addition of Ga, $MoBi_2Se_5$ exhibits p-type conductivity.

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1. Introduction

Novel energy systems based on renewable and clean energy sources have brought more attention due to the rise in energy consumption and environment concern. In this regard, photovoltaic and photoelectric based on thin film absorber have a potential to reach stable and electrical conversion efficiencies on a commercial level. The semiconducting ternary (I^B-III^A-VI^A), (VI^B-V^A -VI^A) and quaternary (I^B-III^A-III^A-VI^A),(VI^B-V^A-III^A-VI^A) group metal chalcogenide thin films deposited on conducting and non-conducting substrates have considerable attention due to their use in photoelectrochemical cells [1-5]. As p- type semiconducting materials acquire stronger anti-corrosive property since they are cathodically protected under light illumination as compared to that of n-type semiconductors [6]. We are interested in the development of p-type quaternary $MoBiGaSe_5$ mixed metal chalcogenide thin films, which would be used to construct photoelectrochemical cell as working electrode because of its well matched band gap energy to cover maximum visible radiation of solar spectrum.

Semiconductor thin films can be prepared by a variety of deposition methods, such as chemical bath deposition (CBD), chemical vapor deposition (CVD), metal organic chemical vapor deposition (MOCVD), spray pyrolysis, sputtering, molecular beam epitaxy (MBE), etc. [7-12]. Each method has some merits and demerits; therefore it is necessary to develop a hybrid

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deposition technique. Arrested precipitation technique (APT), used for the deposition of quaternary thin films which is a combination of chemical bath deposition and controlled precipitation method. The arrested precipitation technique (APT) largely depends on complexing agent which should be stable at low temperature and avoid bulk precipitation of metal selenide. The ion-by-ion condensation took place which results in the formation of thin quaternary films of $MoBiGaSe_5$. The growth of quaternary $MoBiGaSe_5$ thin films observed due to uniform condensation of metal ions and chalcogen ions on the active surface of substrate [13-15]. The precursors used have important role in developing performance of quaternary thin films [16-18].

In the present investigation, we have deposited device quality quaternary $MoBiGaSe_5$ thin films by simple and low cost arrested precipitation technique (APT). In APT, deposition of thin films takes place from aqueous solution at just above the room temperature (30^oC) by chemical reaction between complexed precursors in TEA complexing agent. We have used several complexing agents to arrest the Mo^{+4}, Bi^{+3} and Ga^{+3}, however TEA forms stable complex in aqueous medium at about 7.5 pH, however metal complex should get dissociated at particular pH value. A better quality film of mixed metal chalcogenide thin films (MMCTF) are obtained on plane substrates as well as FTO and ITO coated conducting glass substrates. As deposited films were characterized for its optostructural, morphological and compositional studies.

2. Experimental

2.1 Synthesis of $MoBiGaSe_5$ mixed metal chalcogenide thin films

Quaternary $MoBiGaSe_5$ mixed metal chalcogenide thin films were prepared by APT on glass substrates. Analytical reagent grade ammonium molybdate [$(NH_4)_6\ Mo_7O_{27}.4H_2O$], bismuth nitrate [$Bi(NO_3)_3.5H_2O$] and gallium nitrate [$Ga(NO_3)_3.xH_2O$] were triturated separately in triethanolamine, an organic chelating agent, which helps to arrest metal ion below 8.5 pH precipitation. Elemental selenium metal (99.95%) was refluxed in aqueous solution of sodium sulphite 6 hours at 90^oC to form a partial unstable sodium selenosulphite, which is good source of selenium ions [19-20]. The deposition bath was prepared in 100 ml beaker containing aqueous solution of Mo-TEA, Bi-TEA, Ga-TEA complex and 0.25 M sodium selenosulphite solution slowly added to form $MoBiGaSe_5$ thin films on substrate support by ion by ion condensation. The preparative parameters such as concentration of solutions, pH of bath, temperature, rotations of substrate were optimized for better growth of films on the substrate support. In alkaline medium at pH 9.80 there is slow release of metal ions in aqueous solution at 30^oC temperature. The growth of film involves slow release of precursor ions when ionic ratio is high enough then ion by ion condensation on substrate takes place, ions of Mo, Bi, Ga and Se so formed hits on substrate support which are mounted perpendicular to each other and rotated at constant speed in aqueous reaction bath. The thickness of the film is monitored by simple eye observations and it is found that after deposition time one and half hour, there is no further increase in terminal thickness of the film indicates completion of reaction. Then substrates were removed from bath and washed with deionised water and kept in desiccator. Both the sides of the glass substrate were coated with $MoBiGaSe_5$ films are dried in constant temperature oven for one hour.

2.2 Characterization of as deposited $MoBiGaSe_5$

Various characterization techniques such as UV-Vis spectroscopy, scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDAX), X-ray diffraction (XRD) etc were employed to study optostructural, morphological and electrical characterization of films. The structure of the film was determined by X-ray diffraction (XRD) analysis [Bruker Axs Model D8 Advance X-ray diffractometer] with Cukα target having wavelength 1.542 A^o. The surface morphology of the film was studied using scanning electron microscopy [SEM: JEOL-6360 A Analytical scanning electron microscope]. The compositional analysis was carried out using energy dispersive X-ray analysis [EDAX: JEOL-6360A Analytical scanning electron microscope]. The thickness of $MoBiGaSe_5$ thin film was measured by surface profiler [AMBIOS XP-1]. The

optical study was done by using a UV-Vis spectrophotometer [UV-1800 Shimadzu, Japan] in wavelength of range 300-1100 nm. All characteristics were measured at room temperature.

3. Results and discussion

3.1 Growth kinetics and reaction mechanism of thin film formation

The quaternary $MoBiGaSe_5$ mixed metal chalcogenide thin films were deposited by using self organized growth process arrested precipitation. Arrested precipitation from inorganic aqueous ions, which form stable complexes at lower pH value < 8 are selected for preparing quaternary semiconducting mixed metal chalcogenide thin films. In the present investigation it was observed that Mo^{+4}, Bi^{+3}, Ga^{+3} forms stable complex with triethanolamine complexing agent. Experimental results showed that Mo^{+4}, Bi^{+3}, Ga^{+3} in aqueous medium forms Mo-TEA, Bi-TEA and Ga-TEA stable complex than EDTA, Ethylene diammine, Dimethyl glyoxime and pyridine. Further it was observed that while increasing pH above 8 these complexes slowly releases metal ions which readily reacts with Se^{-2} ions added drop wise with constant stirring resulting in to ion by ion condensation to form mixed metal chalcogenide thin films on substrate support [21,22] as per following reaction,

$$\underset{\text{Mo-TEA Complex}}{(NH_4)_2[Mo\ 2N(CH_2\text{-}CH_2\text{-}O)_3]} + \underset{\text{Bi-TEA Complex}}{(NH_4)_3[Bi\ 2N(CH_2\text{-}CH_2\text{-}O)_3]} + \underset{\text{Ga-TEA Complex}}{(NH_4)_3[Ga\ 2N(CH_2\text{-}CH_2\text{-}O)_3]}$$

$$5\ Na_2SeSO_3 + 13H_2O \xrightarrow{p^H\ 9.80} MoBiGaSe_5 + 6(N(CH_2\text{-}CH_2\text{-}OH)_3) + 5Na_2SO_4 + 8\ NH_4OH \quad (1)$$

i.e.

$$Mo^{+4} + Bi^{+3} + Ga^{+3} + Se^{-5} \xrightarrow{p^H\ 9.80} MoBiGaSe_5 \quad (2)$$

After one and half hour almost all arrested metal ions have been released from complex and this shows terminal growth of the of the metal chalcogenide thin films. Effect of bath temperature and pH plays important role in the ion by ion condensation results in layer deposition of $MoBiGaSe_5$ on substrate support. The bath temperature was maintained at 45^{o}C while, pH 9.80. The quaternary thin film obtained after terminal growth was taken out from bath and rinsed with double distilled water and dried in constant temperature oven in absence of air at 110^{o}C for one hour. Finally thin films of $MoBiGaSe_5$ are characterized for its compositional, structural, optical and surface morphology and electrical properties.

3.2 Characterization of $MoBiGaSe_5$ thin films

The films composition and morphology were studied using energy dispersive spectroscopy (EDS) and scanning electron microscopy (SEM) respectively. The EDS pattern for $MoBiGaSe_5$film is shown in Fig. 1.

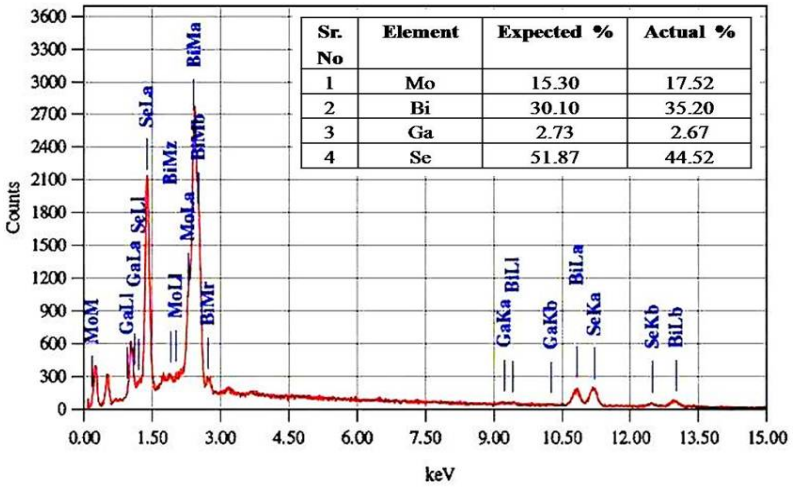


Fig 1. EDAX spectrum of $MoBiGaSe_5$ thin film

The Spectrum reveals the presence of Mo, Bi, Ga and Se at 2.293, KeV 2.419, KeV 9.241 KeV and 1.379 KeV respectively, which confirms the presence of Mo, Bi, Ga and Se in the film. It is observed from composition analysis results there is little deviation from ideal stoichiometry. It can be noted that the composition of as deposited $MoBiGaSe_5$ thin films is closer to stoichiometric ratio. It is evident that the intensity of Se is weaker hence its atomic percentage is low, the atomic percentage of Mo and Ga well matched with theoretical values actually taken for thin film growth. However atomic percentage of Bi is found to be more than theoretically expected percentage, this may due to formation of antisite defects [23] as well as among the elements of the thin films composition, bismuth is more metallic [5].

3.3 X-ray diffraction analysis

The XRD pattern for as deposited $MoBiGaSe_5$ thin films is displayed in figure 2; it is shown that the thin film material have hexagonal structure (JCPDS No. 02-1223, 80-1179, 80-2271, 82-2442, 29-0246). The typical feature of XRD pattern is that, the sample exhibit most intense peak at about 30^o i.e. (200) plane and five different diffraction peaks at (103), (217), (117), (109), (213) corresponding to $MoBiGaSe_5$

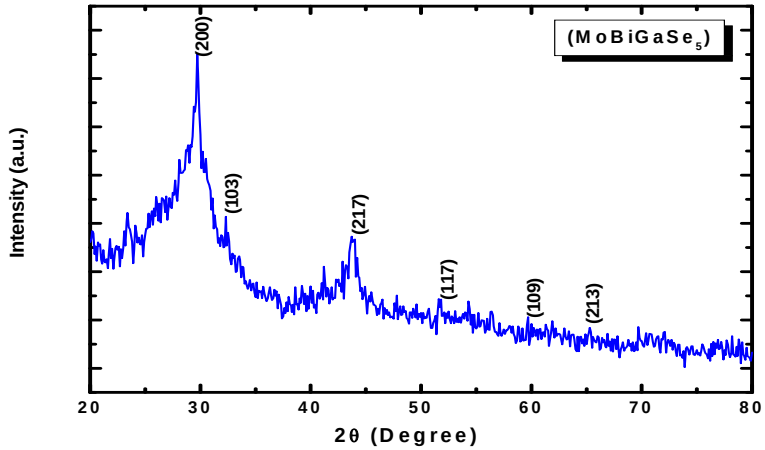


Fig. 2. X-ray diffraction pattern of $MoBiGaSe_5$ thin film.

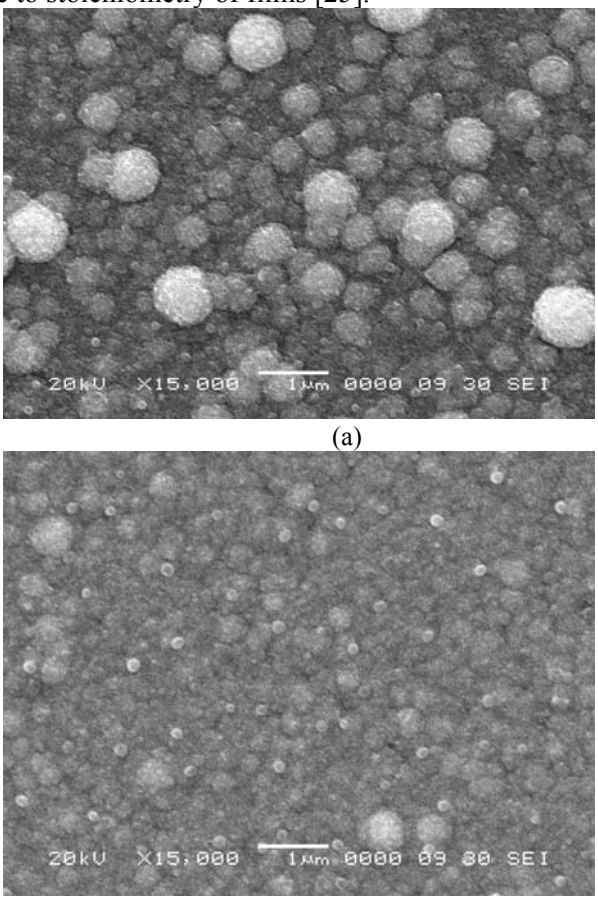
The structural analysis of the thin film indicates that the material crystallizes in hexagonal structure. The crystallite size of the material was calculated from XRD using Scherer's relation [24].

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (3)$$

Where K is 0.94 is a constant λ is wavelength of radiation β is full width at half maximum
θ is Bragg's angle of diffraction
The crystallite size calculated for (200) reflection is 10.73 nm.

3.4 Scanning electron microscopy analysis

The SEM micrographs (magnification of 15,000X) of the as deposited and without pretreatment are shown in figure 3 (a, b) respectively. The SEM micrograph of $MoBiGaSe_5$ shows fibrous nanosphere close to stoichiometry of films [25].



(a)

(b)

Fig. 3. (a)SEM micrographs of $MoBi_2Se_5$ thin film, (b) SEM micrographs of $MoBiGaSe_5$ thin film.

Grain is small with visible boundary and voids. The largest grain about 400 nm can be seen in the film. The surface morphology shows that the Ga rich composition has small grain size and smooth, uniform, fine grained dense surface. The ternary $MoBi_2Se_5$ film composition shows much larger grain size 800 nm

3.5 Optical absorption spectroscopy analysis

An optical absorbance study of $MoBiGaSe_5$ films was carried out in the wavelength range 300 – 1100 nm at room temperature. The films show good absorbance in the visible region. The optical band gap was determined by analyzing the optical data with optical absorption coefficient (α) and the photon energy (hν) using equation [26].

$$\alpha = \frac{A\,(h\nu - E_g)^{n/2}}{h\nu} \quad (4)$$

Where, A is a constant hν is a photon energy n = 1 for a direct gap material n = 2 for an indirect gap material
The optical absorption coefficient α was calculated for the thin film using the equation,

$$\alpha = \frac{1}{t}\log\left(\frac{Io}{It}\right) \quad (5)$$

t is the film thickness.
I_t and I_0 are the intensity of transmitted and initial light respectively.

The thickness (t) of the film is measured by surface profiler and average thickness of films under investigation was 633 nm. Log (Io/It) is the optical density. The optical absorption coefficient is of order 10^5 cm^{-1} supporting the allowed and direct band to band transition of material.

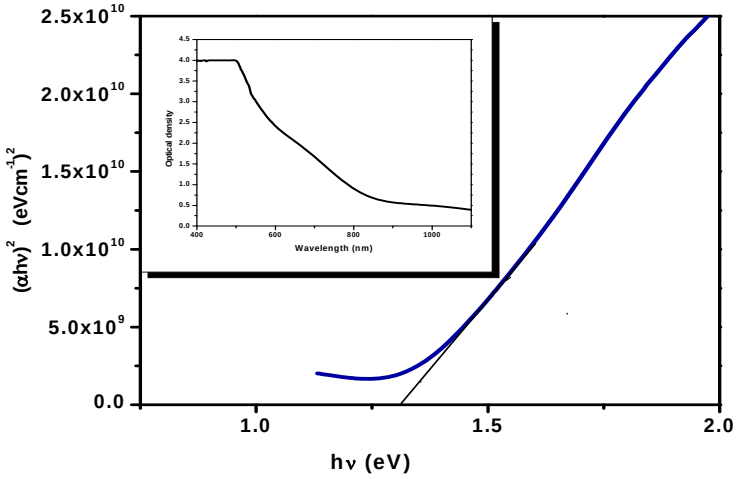


Fig. 4. Band gap of $MoBiGaSe_5$ thin film [Inset- Absorption spectrum]

Plot of $(\alpha h\nu)^2$ Vs hν was drawn using above relation and shown in figure 4. In plot extrapolation of linear portion to the energy axis yielded the direct band gap value of as deposited $MoBiGaSe_5$ film shown in fig. The band gap obtained from $(\alpha h\nu)^2$ Vs hν plot is found to be 1.30 eV

3.6 Electrical analysis

Electrical conductivity (σ) of the $MoBiGaSe_5$ thin film was measured using dc two probe method in the temperature range 300 to 500 K. The variation of electrical conductivity with temperature was studied and is shown in Fig. 5.

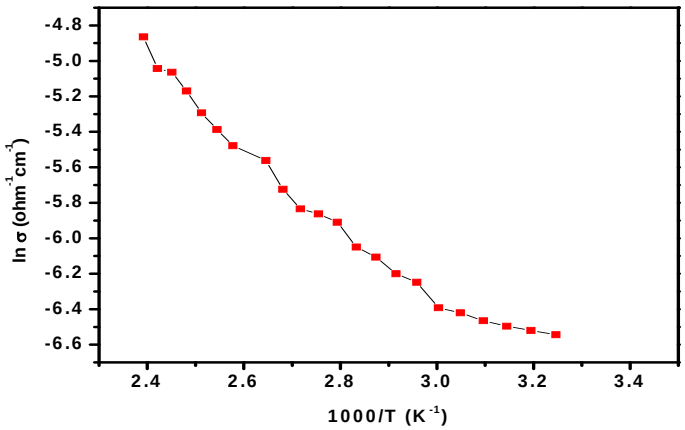


Fig. 5. Temperature dependence of the DC coductivity of $MoBiGaSe_5$ thin film

It is found that the electrical conductivity increases with increasing temperature, exhibiting a semiconducting nature for the $MoBiGaSe_5$ film. The plot shows two regions correspond to high temperature and low temperature. The thermal activation energy was calculated by using following relation.

$$6 = 6_0 \exp^{(-Ea/kT)} \quad (6)$$

Where: σ_o is pre-exponential factor Ea is activation energy for electrical conduction and k is the Boltzmann's constant and T is the absolute temperature.

The values of activation energies are estimated to be 0.2025 eV and 0.05477eV. Activation energy of material at low temperature is low because of impurity scattering and high at high temperature because of phonon scattering.

3.7 Thermoelectric analysis

Thermoelectric power (TEP) means the ratio of thermally generated voltage to temperature difference across the piece of semiconductor. The type of conductivity exhibited by the APT deposited $MoBiGaSe_5$ thin films determined by TEP measurement.

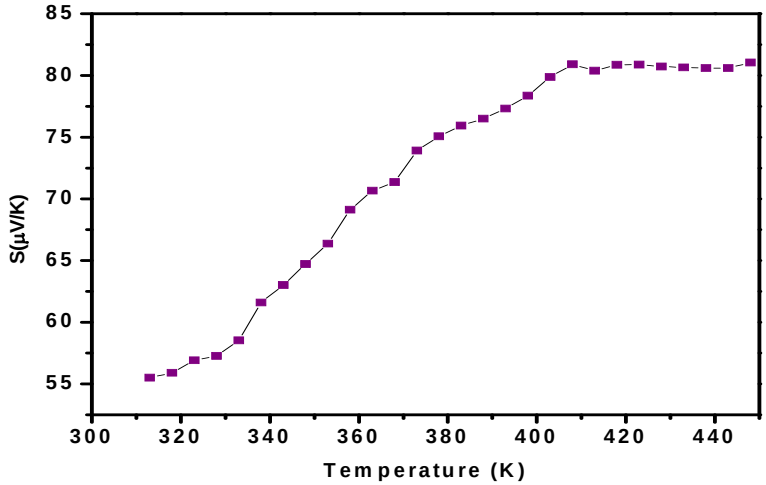


Fig. 6. Temperature dependence of the Seebeck coefficient of $MoBiGaSe_5$ thin film.

Fig. 6 shows the variation of Seebeck coefficient with temperature in the range 300-400 K. The Seebeck coefficient of $MoBiGaSe_5$ thin films has positive sign throughout the temperature

range. The positive sign stems from dominance of p-type charge carriers [27, 28]. The thermoelectric power (TEP) was used to estimate the carrier mobility and carrier concentration using the relation

$$TEP = -\frac{k}{e}\left\{A + \ln[2\,(2\pi m_e^* kT)^{\frac{3}{2}}/nh^3]\right\} \quad (7)$$

Where A is a thermoelectric factor, n is electron density, h is plank's constant, m^*_e is the effective mass of the electron
After substitution of various constants in equation 3 simplifies to [29]

$$\text{Log n} = 3/2\ \text{logT} - 0.005\text{TEP} + 15.719 \quad (8)$$

The electron density was calculated using the above equation and was of the order of 10^{-19} cm^{-3} for the material. The mobility (μ) of the charge carriers is determined from the relation.

$$\mu = \sigma / ne \quad (9)$$

Where n is electron density and σ is conductivity.

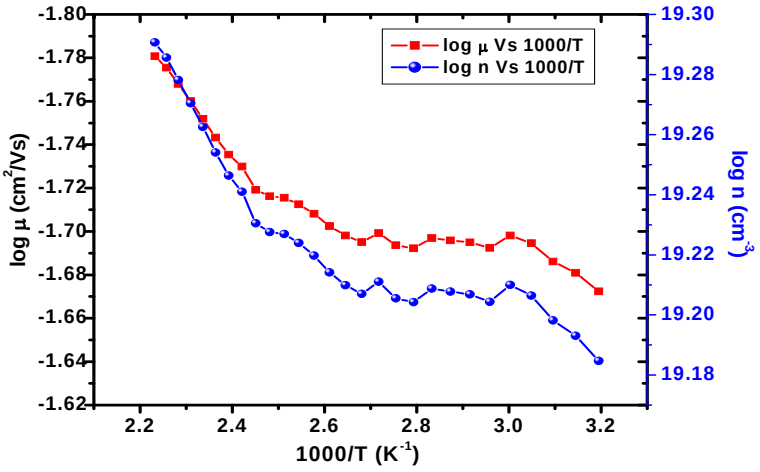


Fig. 7 Variation of log n and log μ as a function of temperature for $MoBiGaSe_5$ thin film

The variation of log n and log μ as a function of temperature is shown in figure 7. It is observed that electron carrier density and mobility increases with temperature. The electron carrier concentration and mobility were estimated to be of order of 2.2×10^{19} cm^{-3} and 1.5×10^{-2} cm^2 V^{-1} s^{-1} respectively.

4. Conclusions

Quaternary $MoBiGaSe_5$ mixed metal chalcogenide thin films were successfully deposited on conducting and non-conducting glass substrate by arrested precipitation technique (APT). Arrested precipitation is simple, low cost and convenient method requires less monitoring. The obtained thin films are mechanically stable and shown uniform growth on the glass substrate. The optostructural and SEM results obtained shows material can be promising candidate for photo convertor and as a photo cathode in solar cells. The good quality thin films have thickness 633 nm containing Mo, Bi, Ga and Se elements. X-ray diffraction study reveals that the formation of nanocrystalline material with hexagonal structure. The activation energy is different for low and high temperature region. $MoBiGaSe_5$ material shown p- type semiconducting behavior. The electron carrier concentration and mobility were estimated to be of order of 2.2×10^{19} cm^{-3} and 1.5×10^{-2} cm^2 V^{-1} s^{-1} respectively.

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