



Preparation and characterization of MnSe thin films

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ABSTRACT

Thin films of manganese selenide (MnSe) were deposited on indium doped tin oxide coated conducting glass (ITO) substrates using potentiostatic electrodeposition technique. The mechanism of formation of MnSe was analyzed in the potential range between -1500 and $+1500$ mV versus SCE. Structural studies reveal that the deposited films exhibit cubic structure with preferential orientation along (200) plane. Structural parameters such as crystallite size, strain and dislocation density are calculated and their dependency with bath temperature is studied. Surface morphology and film composition show that films with smooth surface and well-defined stoichiometry were obtained at bath temperature 70°C . The band gap value of the deposited films was evaluated using optical absorption measurements.

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1. Introduction

Thin films of transition metal chalcogenides are considered important technological materials because of their electrical, optical, magnetic and transport properties which have found applications in spintronics devices [1–3]. Among them, alloys of manganese attract many researchers due to their excellent combination of semiconductivity and magnetism [4,5], impurity-like localized phenomenon [1,6,7] and spin glass behaviour [4]. Manganese selenide (MnSe) is a direct band gap semiconductor with a band gap value ranging from 1.13 to 1.25 eV used for fabricating diluted magnetic semiconductors [8–10]. Thin films of MnSe are usually crystallized in cubic structure (JCPDS 11-0683) with lattice constant ($a = 5.462 \text{ \AA}$) and in hexagonal structure (JCPDS 89-4966) with lattice constants ($a = 3.63 \text{ \AA}$; $c = 5.91 \text{ \AA}$). Various methods such as molecular beam epitaxy (MBE) [11], organometallic vapour phase epitaxy [12], brush plating [13] and thermal evaporation [14] are used for the preparation of MnSe thin films. Heimbrodt et al. [11] have prepared MnSe thin films using molecular beam epitaxy and studied their optical properties. The preparation of MnSe thin films by organometallic vapour phase epitaxy technique and their structural and thermal properties were investigated by Tomashini et al. [12]. Thanigaimani and Angadi [8] have prepared MnSe thin films and studied their properties using X-ray diffraction and optical absorption measurements, respectively. Murali

and Trivedi [13] have obtained MnSe thin films by brush plating method and studied their properties using X-ray diffraction, scanning electron microscopy, energy dispersive analysis by X-rays, optical absorption and Raman spectroscopic measurements, respectively. Among the various deposition techniques mentioned above, electrodeposition is considered to be attractive due to its low cost, low temperature growth and the possibility to control film thickness and morphology by readily adjusting the electrical parameters as well as the composition of the electrolytic solution [15,19]. To the best of our knowledge based on the literature survey, this paper is the first one related to the electrodeposition of MnSe thin films.

In the present investigation, we report our work on the preparation and characterization of MnSe thin films from an aqueous solution mixture containing MnSO_4 and SeO_2 . Structural properties such as crystallite size, strain and dislocation density are calculated from X-ray diffraction analysis and their dependency with bath temperature is studied. Also the morphological, compositional and optical properties of the deposited films are studied and the results are discussed.

2. Experimental details

MnSe thin films were deposited on indium doped tin oxide coated conducting glass substrates using potentiostatic cathodic electrodeposition technique from an aqueous acidic bath containing 0.01 M MnSO_4 and 0.002 M SeO_2 . The chemicals used in the present work were of AnalaR Grade reagents (99.5% purity, SD Fine, Mumbai, India). All the depositions were carried out using

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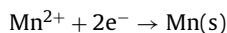
a PAR scanning potentiostat/galvanostat unit (EG&G, Model 362, Princeton Applied Research, USA) employing three electrode configurations with indium doped tin oxide coated glass substrate as cathode, platinum electrode as anode and saturated calomel electrode as reference electrode, respectively. The electrolytic processes were monitored by cyclic voltammetry and governed potentiostatically. In cyclic voltammetric studies, indium doped tin oxide coated glass substrate was used as working electrode with constant potential plating. The voltammetric curves were scanned in the potential range from -1500 to 1500 mV. The deposition potential was fixed as -700 mV versus SCE using cyclic voltammetry. The solution pH and deposition time were fixed as 2.5 ± 0.1 , 40 min, respectively after undertaking several depositions. The preparation of MnSe thin films is carried out at various bath temperatures ranging from 30 to 90°C .

Thickness of the deposited films was measured using stylus profilometer (Mitutoyo SJ 301). An X-ray diffractometer system with $\text{CuK}\alpha$ radiation ($\lambda = 1.540 \text{ \AA}$) was used to identify the crystalline nature and phases of the deposited films. The structural parameters such as crystallite size, strain and dislocation density are evaluated from X-ray diffraction data. The surface morphology and film composition were analyzed using an energy dispersive X-ray analysis set up attached with scanning electron microscope (JEOL JSM 840). Optical absorption measurements of the deposited films were recorded using an UV–Vis–NIR spectrophotometer (HR-2000, M/S Ocean Optics, USA) in the wavelength range between 350 and 1100 nm.

3. Results and discussion

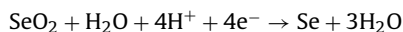
3.1. Electrochemistry of MnSe thin films

The electrochemical deposition of transition metal chalcogenides occurs through three processes such as electrochemical reduction, compound formation and crystallization [19]. In electrodeposition, the formation of alloy is more complex, because they involve thermodynamic problems. The growth mechanism of tellurium-based chalcogenides is well studied by Kröger and his co-workers [16–18]. In electrodeposition of MnSe thin films the less noble constituent of the alloy (here Mn) is deposited at potentials more positive than their standard reduction potential. The energy is brought about by the gain of free energy from compound or alloy formation. This process is also referred as under potential deposition [16,18–20]. Another case is electrocrystallization, here the alloy formation takes place through electrochemical reduction and by direct ionic reactions. The basic electrochemical reactions for the formation of MnSe electrodeposits are described by the following Eqs. (1)–(3):



$$E_{\text{Mn}} = E_{\text{Mn}}^0 + \left[\frac{RT}{2F} \right] \ln \left[\frac{a_{\text{Mn}}^{2+}}{a_{\text{Mn}}} \right] \quad E_{\text{Mn}}^0 = -1.185 \text{ V} \quad (1)$$

$$= -1.185 + \left[\frac{RT}{2F} \right] \ln \left[\frac{a_{\text{Mn}}^{2+}}{a_{\text{Mn}}} \right]$$



$$E_{\text{Se}} = E_{\text{Se}}^0 + \left[\frac{RT}{4F} \right] \ln \left[\frac{a_{\text{SeO}_2}}{a_{\text{Se}}} \right] + \left[\frac{RT}{4F} \right] \ln (a_{\text{H}^+})^4 \quad E_{\text{Se}}^0 = 0.740 \text{ V} \quad (2)$$

$$= 0.740 + \left[\frac{RT}{4F} \right] \ln \left[\frac{a_{\text{SeO}_2}}{a_{\text{Se}}} \right] + \left[\frac{RT}{4F} \right] \ln (a_{\text{H}^+})^4$$

where E_{Mn}^0 and E_{Se}^0 are the standard electrode potentials for Mn and Se respectively, with respect to saturated calomel electrode and a_{Mn}^{2+} , a_{SeO_2} are the activities of respective atoms in the deposited

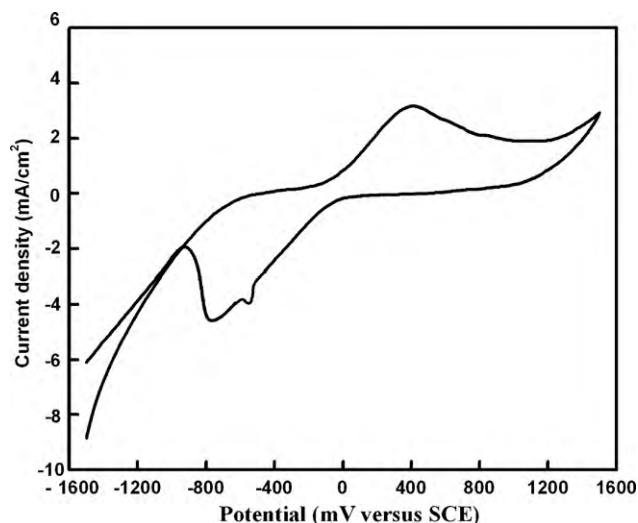


Fig. 1. Cyclic voltammogram of MnSe thin films obtained from an aqueous electrolytic bath consists of 0.01 M MnSO_4 and 0.002 M SeO_2 .

films. The electrochemical reactions in Eqs. (1) and (2) which take place at the surface of cathode are at standard equilibrium potentials for Mn and Se. The potential values in Eqs. (1) and (2) depend upon the activity of the respective ions in the solution and the component in the deposited films. In Eq. (2) the value of potential also depends upon the pH of the electrolytic solution for the formation of MnSe. Hence, Eqs. (1) and (2) are important in this case. The cathodic electrodeposition is classified into two categories by Kröger which depend upon whether the difference between the equilibrium potential is larger or smaller than the shift in potential due to variation of component activity in the deposited films resulting from the alloy formation. The activity of MnSe depends on the stoichiometric composition of constituent elements prior to MnSe formation. In order to obtain stoichiometric formation of MnSe thin films, it is necessary to use higher concentration of less noble constituent (here Mn) and lower concentration of more noble constituent (here Se) in the solution. For the deposition of MnSe thin films, deposition potential is fixed in the range between -650 and -750 mV versus SCE using Pourbaix diagram approach. The deposition potential of Mn and Se is different which can be evaluated from Eqs. (1) and (2) and pourbaix diagram approach. In order to obtain co-deposition of Mn and Se, the solution pH and composition of the electrolyte are so varied that the deposition potential of the individual elements comes closer to each other. Hence, in the present work, we have used higher concentration of Mn that shifts the deposition potential of Mn in positive direction closer to Se. The reaction of formation of MnSe is described using the following Eq. (3):



Cyclic voltammetric studies were carried out in a standard three compartment cells comprising of indium doped tin oxide coated conducting glass substrate as cathode, platinum electrode as anode and saturated calomel electrode as reference electrode, respectively. The scan rate employed was 20 mV/s. The voltammetric curves were scanned in the potential range from -1500 to $+1500$ mV versus SCE. A typical cyclic voltammogram recorded for ITO glass electrode in an aqueous solution mixture containing 0.01 M MnSO_4 and 0.002 M SeO_2 is shown in Fig. 1. During cathodic scan, two reduction peaks are observed as shown in Fig. 1. The reduction peak 1 observed at -540 mV versus SCE is due to the reduction of Se according to Eq. (2). Reduction peak 2 observed nearly at -700 mV versus SCE may be due to the reduction of

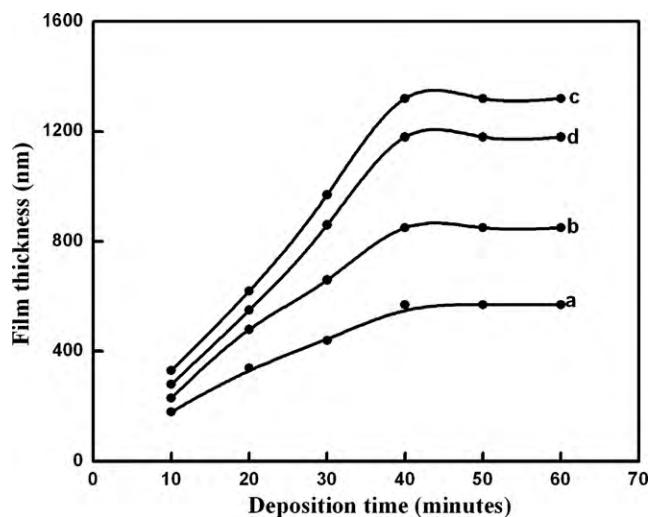


Fig. 2. Variation of film thickness with deposition time for MnSe thin films obtained at various bath temperatures: (a) 30 °C, (b) 50 °C, (c) 70 °C, and (d) 90 °C.

Mn^{2+} to elemental Mn according to Eq. (1). In between -550 and -700 mV versus SCE, current plateau is observed. In this region, Mn is in adsorbed state and the Se is reduced to Se^{2-} state because at the potential more negative than Se reduction to Se^0 (i.e. -540 mV versus SCE), Se forms H_2Se , which is highly reactive, this immediately reacts with adsorbed Mn^{2+} and forms MnSe. This plateau region gives the co-deposition range for MnSe with in -550 and -700 mV versus SCE. Hence, the deposition potential is fixed as -700 mV versus SCE, in order to obtain MnSe thin films.

3.2. Film thickness

The electrochemical growth of MnSe thin films was controlled by two separate variables such as (i) film thickness and its uniformity and (ii) surface morphology [19]. The stylus profilometer was used to measure the thickness of the deposited films. By controlling the plating current and plating time thickness of the deposited films could be controlled. An irregular growth with rough surface was obtained for films prepared at lower bath temperature such as 30 °C. At higher bath temperature such as 90 °C the formation of films may be hindered due to hydrogen evolution. The temperature of the bath is maintained at 90 °C the hydrogen gas is evolved from the electrolytic bath leads to bubble formation which is termed as hydrogen evolution. The variation of film thickness with deposition time for MnSe thin films prepared at various bath temperatures ranging from 30 to 90 °C is shown in Fig. 2 a–d. Fig. 2 represents that the film thickness increases linearly with deposition time and tends to attain saturation after 40 min of deposition. The temperature of the electrolytic bath plays an important key role to control the rate of deposition and film thickness by: (i) increase of precursor solubility and (ii) increasing the diffusion coefficient of the species and decrease of viscosity [19]. Increase in bath temperature results in increase of film thickness for films prepared at bath temperature 70 °C. It is observed from Fig. 2 that the maximum value of film thickness was obtained from a single deposition within 40 min for bath temperature varying from 30 to 90 °C. The increase in value of film thickness is described by the following two mechanisms: first one is the deposition of MnSe which leads to the film growth, and the second one is the reaction of formation of MnSe with acid in the solution which results in decrease of film thickness after certain intervals of time. In the initial stage, the source materials are sufficient and the solution has high conductivity. The process of deposition plays a more important role than the dissolution process which leads to increase in film thickness. With the deposition

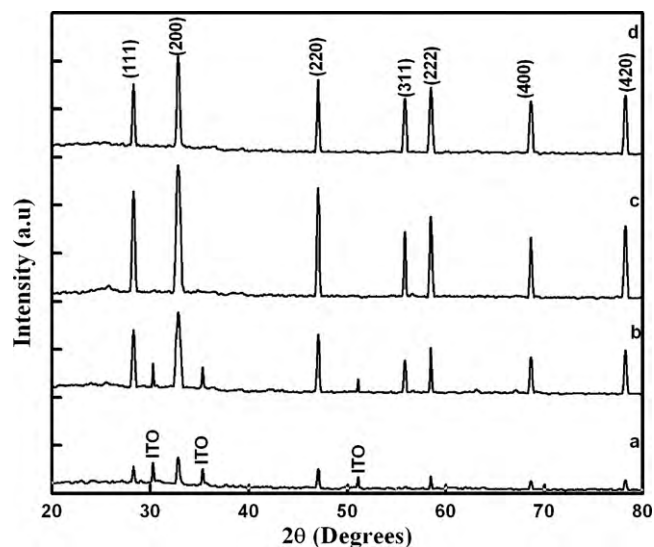


Fig. 3. X-ray diffraction pattern of MnSe thin films electrodeposited at various bath temperatures: (a) 30 °C, (b) 50 °C, (c) 70 °C, and (d) 90 °C.

time being prolonged, the thickness of the film increases, at the same time the resistance of the film increases. So, the density of electrons decreases relatively and the MnSe films were eroded by acid in the solution. Therefore, after a particular time of deposition, the dissolution process predominates over the deposition thereby resulting a decrease in film thickness. The films obtained a maximum thickness at deposition durations ranging from 30 to 60 min synthesized at all bath temperatures. But the rate of deposition and thickness of the deposited films are different [19].

3.3. X-ray diffraction analysis

X-ray diffraction pattern obtained for MnSe thin films prepared on indium doped tin oxide coated conducting glass substrate with bath composition of 0.01 M MnSO_4 and 0.002 M SeO_2 at various bath temperatures ranging from 30 to 90 °C is shown in Fig. 3. X-ray diffraction patterns revealed that the deposited films possess cubic structure with lattice constant ($a = 5.462 \text{ \AA}$). The diffraction peaks of cubic MnSe are observed at 2θ values of angles 28.27, 32.75, 47.03, 58.49, 68.56 and 78.21 corresponding to the lattice planes (1 1 1), (2 0 0), (2 2 0), (3 1 1), (2 2 2), (4 0 0) and (4 2 0), respectively. The different peaks in the diffractogram were indexed and the corresponding values of interplanar spacing ' d ' were calculated. All the peaks identified are from MnSe and hence no additional lines corresponding to Mn and Se are present. It is also observed that (2 0 0) reflections are of maximum intensity indicating thereby preferential orientation along c -axis. This observation reveals that electrodeposition method is suitable for obtaining single phase MnSe thin films. The ' d ' values observed in the present work are found to be in good agreement with JCPDS values [24]. The effect of orientation of polycrystalline MnSe thin films is determined by evaluating the texture coefficient of the (hkl) plane using the following Eq. (4) [22]:

$$T_c(hkl) = \frac{I(hkl)/I_0(hkl)}{(1/N) [\sum_N I(hkl)/I_0(hkl)]} \quad (4)$$

where $T_c(hkl)$ is the texture coefficient of the (hkl) plane, I is the measured intensity, I_0 is the JCPDS standard intensity and N is the number of diffraction peaks. The variation of texture coefficient with respect to bath temperature for MnSe thin films obtained at different bath temperatures is shown in Fig. 4. The increase in preferential orientation is associated with increased number

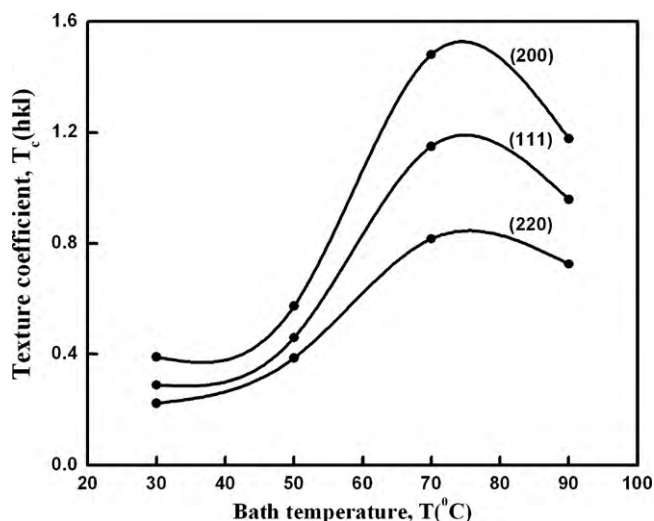


Fig. 4. Variation of texture coefficient along (1 1 1), (2 0 0) and (2 2 0) planes of MnSe thin films deposited at various bath temperatures from 30 to 90°C.

of grains along (200) plane. The diffraction peak corresponding to (200) plane is used for the calculation of crystallite size. It is observed from Fig. 4 that the value of texture coefficient increases while increasing bath temperature from 30 to 70°C, afterwards it decreases slightly. The films prepared at lower bath temperature below 70°C have lower texture coefficient value indicating that the deposited films have poor crystallinity. Also the films prepared at bath temperature 70°C have higher texture coefficient value represents that the films have better crystallinity. It is also evident from Fig. 4 that the value of texture coefficient increases the crystallinity of the film increases. Hence, the films deposited at bath temperature 70°C exhibit better crystallinity and well adherent to the substrates. The crystallite size of the deposited films was calculated using FWHM data and well known Debye–Scherrer formula [19]. The strain ε was calculated using Eq. (5) given below

$$\beta = \left(\frac{\lambda}{D \cos \theta} - \varepsilon \tan \theta \right) \quad (5)$$

Dislocation density is defined as the length of dislocation lines per unit volume of the crystal [23] and can be calculated using the following Eq. (6) [19,23]:

$$\delta = \frac{1}{D^2} \quad (6)$$

Fig. 5a shows the variation of crystallite size and strain with bath temperature for MnSe thin films deposited at various bath temperatures ranging from 30 to 90°C. Also, the variation of dislocation density with bath temperature for MnSe thin films obtained at different temperatures is shown in Fig. 5b. Fig. 5a indicates that the crystallite size increases with bath temperature and the films prepared at bath temperature 70°C are found to have maximum value of crystallite size, thereafter the crystallite size decreases. Due to the release of defects in the lattice, the strain in the films gets released and attained its minimum value for films obtained at bath temperature 70°C. Decrease in strain with respect to bath temperature causes decrease in value of interplanar spacing thus leads to decrease in value of dislocation density in the deposited films (Fig. 5b). Minimum values of strain and dislocation density are obtained for films prepared at bath temperature of 70°C. MnSe thin films with larger crystallite size, lower strain and dislocation density improve the stoichiometry of the films which in turn causes volumetric expansion of MnSe thin films. The type of conductivity of MnSe thin films is due to the presence of Mn ion vacancies within the lattice. Also the increase in crystallinity with

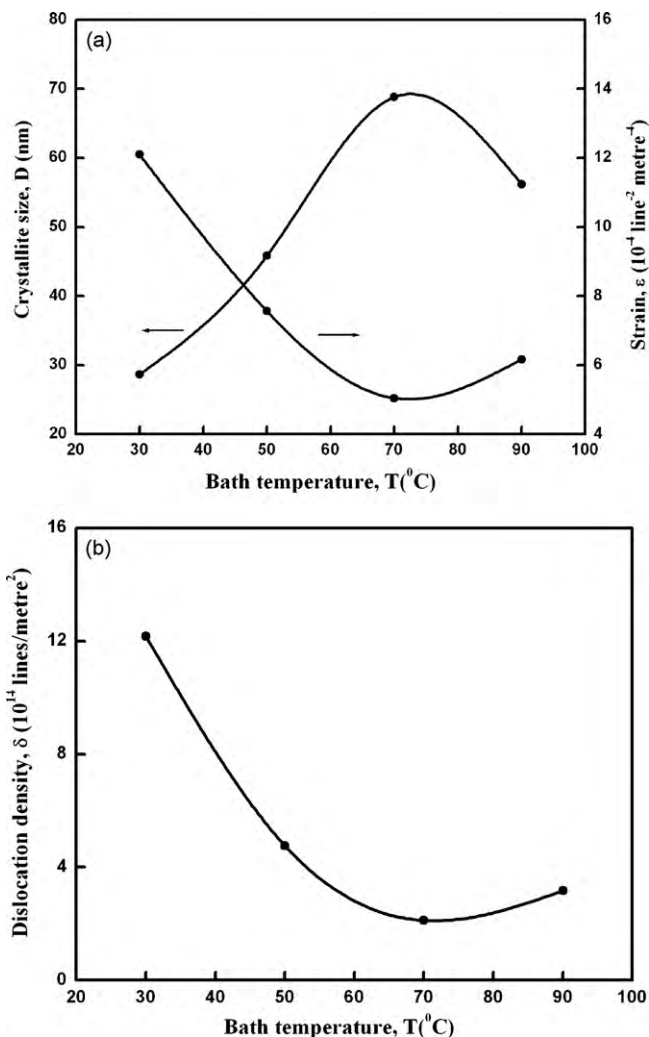


Fig. 5. (a) Variation of crystallite size and strain with bath temperature for MnSe thin films. (b) Variation of dislocation density with bath temperature for MnSe thin films.

bath temperature enhances the crystallinity and mobility of Mn ion vacancies within the lattice and hence reduces the resistivity of the deposited films. The studies on functional dependency of crystallite size, strain and dislocation density with bath temperature indicate that the strain and dislocation density decreases whereas the crystallite size increases. Similar behaviour is exhibited for FeSe thin films as reported earlier [19].

3.4. Morphological and compositional analyses

The surface morphology of MnSe thin films was analyzed using a scanning electron microscope. The scanning electron microscope image of MnSe thin films prepared at different bath temperatures (30 and 70°C) is shown in Fig. 6a and b. It is observed from Fig. 6a that the film surface is observed to be flat and no definite grain structure is observed for films prepared at bath temperature 30°C. It is also observed that some holes are seen at few places in the SEM picture. Fig. 6b represents that the film surface is found to be uniform and covered with small spherically shaped grains. The grains are distributed evenly over the entire surface of the film. The sizes of the grains are found to be in the range between 0.15 and 0.50 μm . The average size of the grains is found to be 0.37 μm .

The film composition was investigated using an EDX microanalytic unit attached with scanning electron microscope. A typical

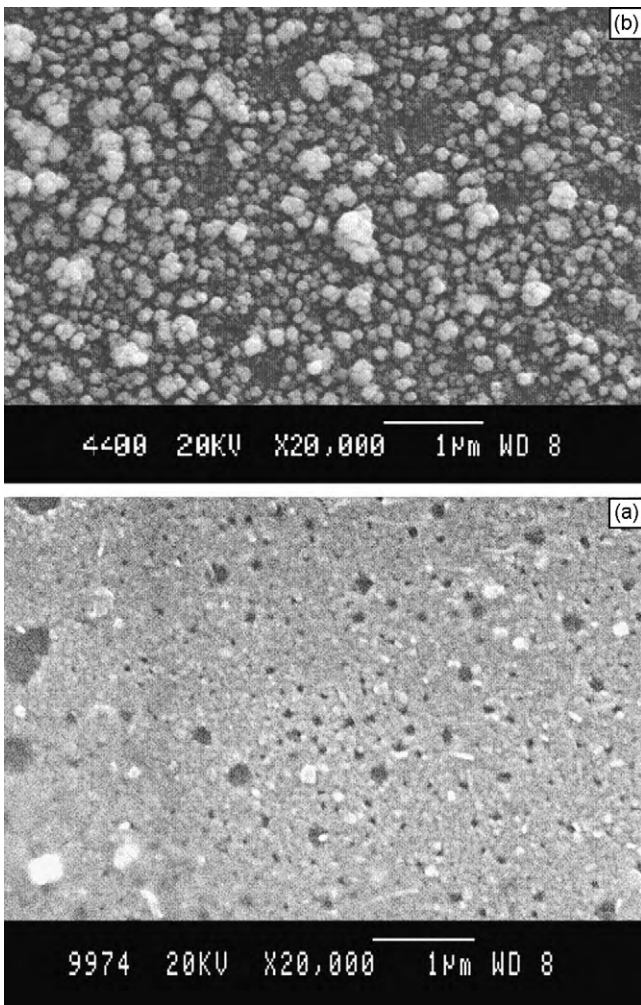


Fig. 6. SEM picture of MnSe thin films obtained at different bath temperatures: (a) 30 °C and (b) 70 °C.

EDX spectrum of MnSe thin films obtained at bath temperature of 70 °C is shown in Fig. 7a. The presence of emission lines in the investigated energy range indicates the formation of MnSe thin films. Fig. 7b shows the variation of Mn and Se content with bath temperature for MnSe thin films obtained at various bath temperatures. It is observed from Fig. 7b that the content Mn increases and the content of Se decreases while increasing bath temperature from 30 to 90 °C. The films prepared at bath temperature below 50 °C have an excess Se content. The presence of excess selenium which causes poor crystallinity of the deposited films. As the bath temperature increases above 30 °C the content of Se decreases (Fig. 7b) which in turn increases the crystallinity of the deposited films. The atomic molar ratio (Mn:Se) of MnSe (52.66:47.34) thin films obtained at bath temperature 70 °C is found to be 1:0.89 indicating stoichiometric formation of good quality MnSe thin films. This result is also consistent with X-ray diffraction analysis of the sample with cubic phase corresponds to MnSe. The atomic percentage of Mn and Se obtained at bath temperature 70 °C is found to be in close agreement with the value reported earlier for brush plated MnSe thin films [13].

3.5. Optical absorption analysis

Optical transmission measurements of electrodeposited MnSe thin films were recorded as a function of wavelength in the range between 350 and 1100 nm. Substrate absorption, if any was cor-

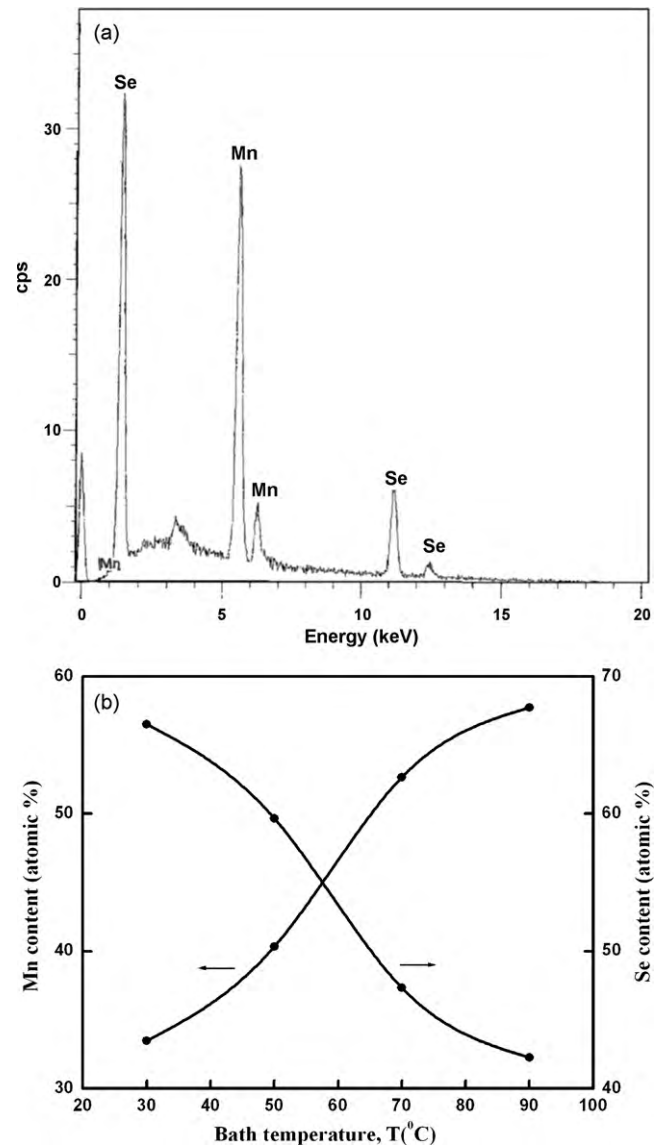


Fig. 7. (a) Typical EDX spectrum of MnSe thin film electrodeposited at bath temperature 70 °C. (b) Variation of Mn and Se content with bath temperature for MnSe thin films deposited at various bath temperatures.

rected by introducing an uncoated ITO substrate in the reference beam. The absorption coefficient (α) rises sharply owing to band-to-band transition and levels off later. An analysis of absorption spectrum in the investigated energy range ($1.0 < h\nu < 3.5$ eV) shows that (α) follows the relation [21,22]:

$$\alpha h\nu = A(h\nu - E_g)^n \quad (7)$$

where A is constant (slope), E_g is band gap of the material and $h\nu$ is photon energy. From the calculated values of absorption coefficient a plot of $h\nu$ versus $(\alpha h\nu)^2$ is drawn for MnSe thin films electrodeposited at bath temperature 70 °C (Fig. 8). The plot is linear indicating the presence of direct transition. Extrapolation of linear portion of the graph to energy axis (X-axis) gives the band gap energy of the material. The intersection point gives the band gap energy of the material and its value is found to be 1.22 eV. It is found that the band gap value of material obtained in the present work is found to be in close agreement with the value reported earlier for MnSe thin films by brush plating method [13].

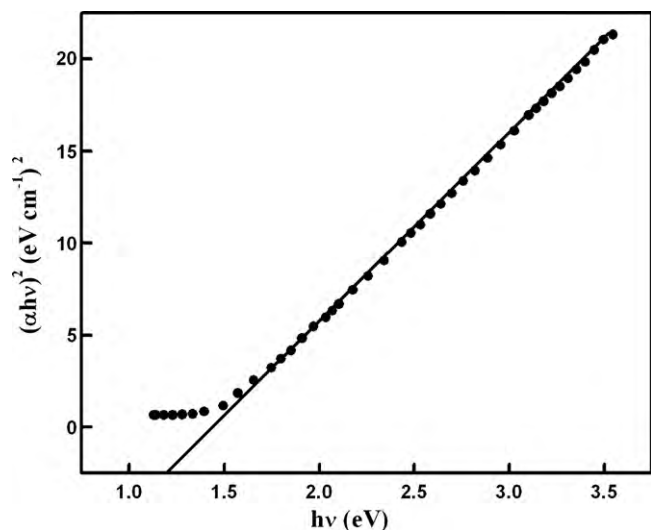


Fig. 8. Plot of $h\nu$ versus $(\alpha h\nu)^2$ for MnSe thin film electrodeposited at bath temperature 70 °C.

4. Conclusions

Thin films of MnSe were deposited on indium doped tin oxide coated conducting glass substrates using potentiostatic electrodeposition technique. A cyclic voltammetric study was used to fix the deposition potential in the range between -1500 and $+1500$ mV versus SCE. X-ray diffraction pattern of the deposited films shows the formation of polycrystalline MnSe thin films with cubic structure with preferential orientation along (2 0 0) plane. No change in crystal structure is observed for films prepared at various bath temperatures. The structural parameters such as crystallite size, strain and dislocation density are evaluated and their dependency with bath temperature is studied. SEM observation shows that smooth surface with spherically shaped grains were obtained at higher bath

temperature. Stoichiometric films with well-defined composition were obtained at bath temperature 70 °C. The band gap value of MnSe thin films obtained in the present work is found to be 1.22 eV which is quite closer to the value reported earlier.

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