JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 9, No. 7, July 2007, p. 2019 - 2022

Annealing effect on physical properties of thermally evaporated MnS nanocrystalline films

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MnS nano-crystalline films were formed on glass substrates by thermal evaporation technique at room temperature (300 K) and the films were annealed at 573 K. The films were characterized for composition, structure and surface morphology by using EDAX, XRD, SEM and AFM. The optical properties were studied by spectrophotometer. AFM studies showed that all the films were in nanocrystalline form with the grain size varying in the range between 30 - 32 nm and exhibited wurtzite structure. The lattice parameter and band gaps (3.842 – 3.916 eV) increase with increasing annealing temperature.

(Received April 17, 2007; accepted June 27, 2007)

Keywords: Magnetic Semiconductors, MnS nanocrystalline films, Wurtzite structure, Optical properties

1. Introduction

Materials containing manganese are interesting because their applications are possible in many areas of modern technology. Recently metal chalcogenide thin film materials have opened a new area in the field of electronic applications. Their properties can be changed by changing the crystallite size and thickness of the film. Depending upon the deposition conditions, the structural and optical properties of these materials can be controlled in many ways [1 - 5]. The diluted magnetic semiconductors (DMS), which have an interesting combination of magnetism and semiconductivity, have attractive considerable attention in recent years. Manganese sulphide (MnS) is a magnetic semiconductor material (E_g= 3.1 eV) that is of potential interest in short wavelength optoelectronic applications such as in solar selective coatings, solar cells, sensors, photoconductors, optical mass memories [6 - 9]. MnS thin films or powders can be found in several polymorphic forms: the rock salt type structure (α-MnS) which is the most common form, by low growing techniques it crystallizes into the zincblende (β-MnS) or wurtzite (γ-MnS) structure [10-11]. The properties of thin films prepared by different methods are critically dependent on the nature of preparation technique. Thermal evaporation technique is a relatively inexpensive, simple and convenient method for large area deposition and a variety of substrates can be used to grow thin films. Number of workers has not thermally prepared MnS thin films. However, most of the workers have been prepared chemically deposited MnS thin films and the deposition of γ-MnS is not achieved at room temperature [9, 12 - 14]. In order to get good quality of MnS thin films, the preparation parameters such as concentration of manganese, deposition rate and temperature were optimized.

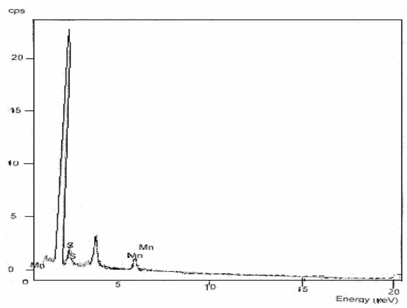
2. Experimental procedure

MnS nanocrystalline films were deposited by simple thermal evaporation technique. The films were prepared on glass substrates at room temperature (300 K) and the films were annealed at 573 K. Fixed quantity of high pure MnS powder (Sigma Aldrich, Germany) was taken into crucible. The source to substrate distance was maintained at ~14 cm to get deposition rate of ~15 Å/s. Every time, known fixed quantity of material was loaded in the boat and was completely evaporated. The thicknesses of the films was ~ 0.5 μm. Coatings were carried out in the pressure range of 2×10^{-6} m bar. Radiant heater was used to heat the substrate and the thickness of the films was monitored using a quartz crystal thickness monitor (Model QTM101). These films were annealed at 573 K and then allowed to cool to room temperature naturally.

The prepared MnS nanocrystalline films were subjected to various characterization studies. The composition of the films was estimated using Energy Dispersive Analysis of X-rays (EDAX) attached to Scanning Electron Microscopy (SEM, Model: JSM 840A). The grain size and RMS surface roughness of the films were obtained by Atomic Force Microscopy (AFM, Model: Veeco CP 2). The structure of the films was studied using powder X-ray diffractometer (XRD, Model: Phillip's X'Pert Pro) in the scanning range of 2θ = 10 - 70°. Optical properties of the films were investigated by JASCO V-570 UV/VIS/NIR Spectrophotometer.

3. Results and discussion

The deposited MnS nanocrystalline films were pinhole free and strongly adherent to the surface of the substrate. Chemical compositions of the constituents in the coatings, obtained from EDAX did not deviate much from the original composition it is within ± 5 %. The EDAX spectra for the as-deposited and annealed MnS films were shown in Fig. 1.



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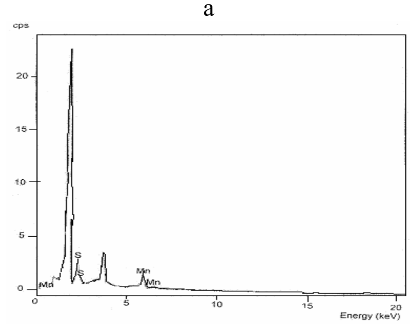

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Fig.1.EDAX spectra of (a) MnS films deposited at 300 K and (b) MnS films annealed at 573 K.

The chemical analysis data for the as-deposited and films annealed at 573 K are given in Table.1.

Table 1. EDAX data of MnS films deposited at 300 K and of the films annealed at 573 K.

Deposited at 300 K		Annealed at 573 K	
Mn at. %	S at. %	Mn at. %	S at. %
48.23	51.77	49.15	50.85

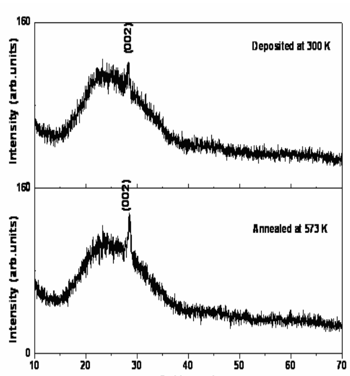
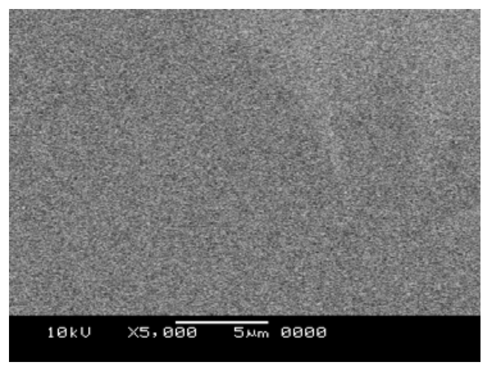


Fig. 2.Comparative XRD spectra of MnS films deposited at 300 K and the films annealed at 573 K.

An obvious change in the peak intensity of MnS films is observed with increasing annealing temperature. It can be seen that annealed temperature is also an important parameter in obtaining crystalline films. MnS films grown at room temperature exhibited a dominant peak at $2\theta = 28.53^0$ (d = 0.31262 nm) which corresponds to (002) plane and annealed MnS films exhibited a dominant peak at $2\theta = 28.25^o$ (d = 0.31562 nm) which can be attributed to the (002) plane of the hexagonal γ - MnS wurtzite phase. The deposited MnS nano-crystalline film grows preferentially along the c – axes. As determined lattice parameter to be 0.626 – 0.632 nm for as-deposited and annealed films, this is consistent with the standard value of 0.6447 nm. Lokhande et al [9] have been reported that chemical bath deposition of MnS thin films on glass substrates at 313 K is of poor crystallinity however the deposition on fluorine doped tin oxide coated glass substrate results in mixed phase crystalline MnS films. In the present study the grain size of as-deposited and annealed films was estimated from XRD peaks using Debye Scherer formula and was found to lies in the range 30 – 32 nm. Similar variation in grain size was also observed in AFM and SEM studies. No data on the dependence of grain size on annealing temperature of MnS films is available in literature for comparison.



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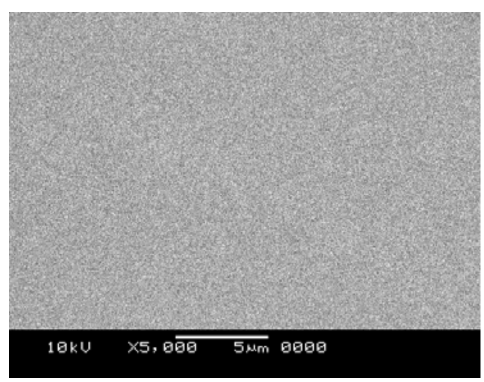

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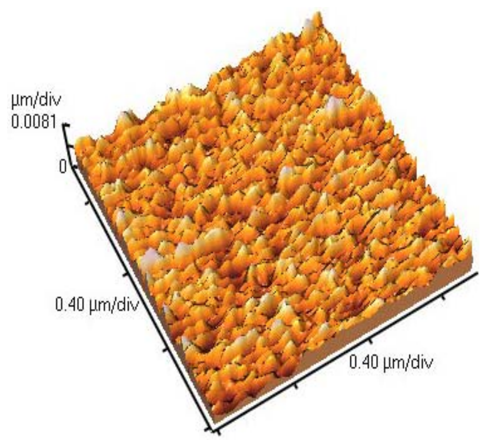
Fig.3. SEM image of (a) MnS films deposited at 300 K and (d) MnS films annealed at 573 K.

The surface topology of the MnS films carried out by SEM reveals appreciable difference for as-deposited and annealed films. All the as-deposited films of all compositions had a smooth surface structure, whereas the annealed films exhibited small granular surface structure. This indicates the increase in crystallinity of the films on annealing. The SEM micro graphs are shown in Fig. 3.



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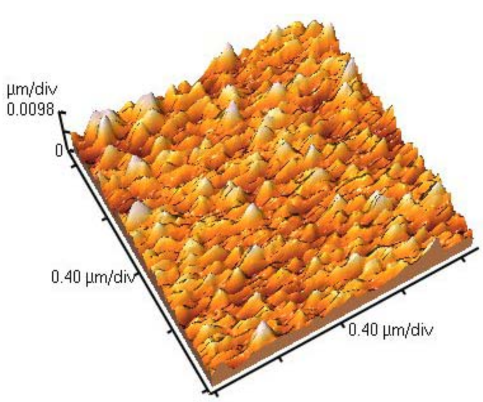

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Fig. 4. AFM pictures of (a) MnS films deposited at 300 K and (b) MnS films annealed at 573 K.

The surface morphology of all the as-deposited films was studied using AFM. The AFM images for as-deposited and annealed films were shown in Fig. 4. The images were taken in an area of 2 × 2 μm^2. The surface morphology of MnS films changes with annealing temperature. The grain size (30 – 32 nm) evaluated from this study is comparable with the data obtained from XRD studies. The surface roughness (1 – 1.4 nm) increased with increasing annealing temperature.

The optical transmittance (T) of the films was studied in the wavelength range 300 - 900 nm at room temperature with unpolarised light at normal incidence. Fig. 5 shows the optical transmittance as a function of wavelength for the as-deposited and for the films annealed at 573 K.

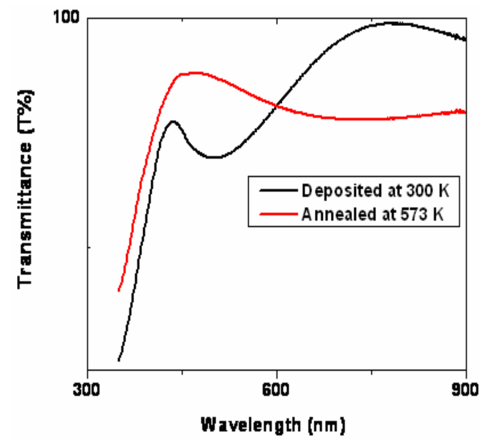

Fig.5.Variation of transmittance with wavelength for MnS films deposited at 300 K and the films annealed at 573 K.

The films were highly transparent in the visible range of the electromagnetic spectrum with in the average transmittance reaching to values upto 80 – 95% over 400 nm. The optical spectra of the MnS films exhibited interference pattern with a sharp fall in transmittance at the fundamental absorption edge. The absorption edge lies in the range 323 – 317 nm (about 3.842 – 3.916 eV) in the present films and also agreed with the previous results [14, 15]. The absorption edge primarily shifted from higher wavelength to lower wavelength region. The absorption edge in general shifted towards lower wavelength with increase of annealing temperature.

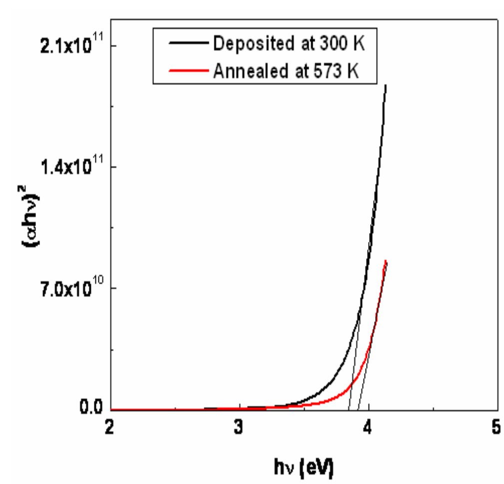

Fig. 6. $(\alpha h\upsilon)^2$ as a function of hυ for MnS films prepared at 300 K and the films annealed at 573 K.

The absorption coefficient (α) of the films was obtained from the optical transmittance data and is found to be greater than 10^4 cm^{-1} above the fundamental absorption edge. The variation of absorption coefficient α, with photon energy hυ, was linear indicating that the absorption near fundamental edge is direct and allowed.

The energy band gap (E_g) has been estimated using the standard equation, $(\alpha E)^2 = E - E_g$, where E is the incident photon energy. Fig. 6 shows $(\alpha h\upsilon)^2$ vs. $h\upsilon$ plots for the as-deposited and the films annealed at 573 K. The E_g value increased from 3.842 – 3.916 eV with increase of annealing temperature, which is consistent with the previously reported values [9, 12].

The extinction coefficient of the MnS films was estimated using the relation

$$k = \alpha\lambda/4\pi \quad (1)$$

Where λ is the wavelength of incident light. The evaluated extinction coefficient, 'k' changed from 0.134 to 0.108 with the annealing temperature. The value of critical wavelength (λ_c) is higher for the as-deposited films compared to the annealed films.

The refractive index of the MnS films was estimated from the optical data using the standard relation,

$$N= [N+ (N^2 - n_1^2 n_2^2)^{1/2}]^{1/2} \quad (2)$$

where

$$N= [(n_1^2+n_2^2)/2+2n_1n_2 (T_{max}-T_{min})/T_{max} T_{min}] \quad (3)$$

Where n_1 is the refractive index of air, n_2 the refractive index of the substrate, T_{max} and T_{min} are the transmittance maxima and minima at a given wavelength. In general the as-deposited films have high refractive index compared to annealed films, and the refractive index lies in the range 2.145 – 2.022 for as-deposited and the annealed films.

4. Conclusions

MnS nano-crystalline films have been prepared by resistive thermal evaporation at room temperature and the films were annealed at 573 K. The XRD studies showed that all the films exhibited wurtzite structure. SEM micrographs of the samples indicated that the samples had smooth surfaces. AFM studies showed that the films were nano-crystalline in nature with grain size lying in the range 30 - 32 nm. Both the grain size and the rms surface roughness increased with increasing annealing temperature. Optical behaviour of the films was investigated at room temperature. It has been found that all the films showed higher absorption coefficient, $>10^4$ cm^{-1} and exhibited direct allowed transitions. The optical band gap of the films increased with annealing temperature. The band gap varied from 3.842 - 3.916 eV for all the films. The material parameters such as refractive index and extinction coefficient were also obtained and their dependences on annealing temperatures are reported.

Acknowledgments

The authors are grateful to Dr. K. Ramesh Dept of Physics, for help in the XRD analysis; Gurulinga, Department of Metallurgy, for help in the EDAX and SEM and Prof S. Sampath, Inorganic Physical Chemistry, Indian Institute of Science, Bangalore for the help with the AFM studies. The authors are grateful to Prof J. Lakshmana Rao and to Mr. Omkar, Dept. of Physics, S.V. University, Tirupati, for the help with the optical studies.

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