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Studies and Characterization of Nanostructured MnS thin film prepared by Chemical Bath Deposition Technique

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Abstract

MnS thin films were deposited by chemical bath deposition method at 60^{o}C for 2 hours. The MnS thin films were characterized by X- ray diffraction (XRD), scanning electron microscopy (SEM). The scanning electron microscope images showed the formation of a fairly uniform surface with fine flower like structure, Energy dispersive X-ray analysis (EDAX) and optical absorption spectroscopy. XRD measurements show that the films are crystallized in the wurtzite (γ-MnS) and zincblende (β-MnS) phases . The deposited MnS thin films on glass substrates consist of nanocrystalline grains. EDAX analysis shows that average ratio of atomic percentage of Mn:S can conclude that the films are in good stoichiometric ratio. The optical band gap of thin film was estimated to be 3.33 eV. The electrical properties of these films were studied by I –V measurement in dark and illumination (100 mW/cm^2) condition.

Keywords: Nanostructured, CBD, hexagonal, chalcogenide….. etc.

1. INTRODUCTION

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 or thickness of the film. Depending upon the deposition conditions, the structural, electrical and optical properties of these materials can be controlled in many ways [1–5]. Materials containing manganese are interesting because their applications are possible in many areas of modern technology. Manganese sulfide (MnS) is a magnetic semiconductor material (Eg =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 temperature growing techniques it crystallizes into the zincblend (β-MnS) or wurtzite (γ-MnS) structure[10,11] . MnS is extensively studied in the literature, preparation of its thin films has been carried out by different methods such as radio-frequency sputtering [12,13] , hydrothermal [14–16] , molecular beam epitaxy [17] and chemical bath deposition (CBD) [9,18–20] . The properties of thin films prepared by different methods are critically dependent on the nature of preparation technique. Chemical bath deposition is a relatively inexpensive, simple and convenient method for large area deposition and a variety of substrates can be used to grow thin films. It does not require complicated instrumentation [21] .

In the present investigation, we report the chemical deposition of MnS thin films from an aqueous alkaline medium. In order to get good quality MnS thin films, the preparation parameters such as concentration of manganese, deposition time, temperature and pH were optimized. Well-crystallized MnS thin films were deposited by CBD method at 60^{o} C. The MnS thin films were characterized by scanning electron microscopy (SEM),(XRD), (EDAX) and optical absorption spectra.

2. EXPERIMENTAL PROCEDURE

2.1. Preparation of MnS films

MnS thin films were deposited on glass substrates using CBD technique at (60^{o} C). The substrate used for the deposition of MnS thin films were commercial glass slides . Substrate cleaning plays an important role in the deposition of thin films. Before the deposition the substrate was etched with diluted chromic acid solution, and cleaned in deionized water and finally dried in air. Aqueous solutions of manganese sulphate ($MnSO_4.H_2O$) was used as manganese source, Thioacetamide ($SC(NH_2)_2$) as sulphur source, ammonia (NH_3) , triethanolamine [N(CH2CH2OH)3] as complexing agents for depositing MnS thin films were purchased from Merck chemical (India) Pvt. Ltd. Double deionized water was used through out the experiment. Deposition of MnS thin films is based on the release of Mn^{2+} ions and S^{2-} ions in the solution.10 ml (0.3M) Manganese sulphate solution, 0.5 ml ammonia and 15 ml (0.6M) Thiourea solution were placed in 50 ml beaker. Deionised water was added to make the volume up to 40 ml. The pH of the resulting solution is measured about 10 after the mixture of chemical components . The prepared solution was mixed with a magnetic stirrer; after obtaining a clear homogenized solution the stirrer was turned off and glass slides were placed in the bath vertically for 2 hours.

2.2 Characterization

The XRD pattern was recorded using X-ray diffractrometer Bruker AXS, Germany (Model D8 Advanced). The Energy Dispersive analysis of X-rays (EDAX) and Field Emission Scanning Electron Micrographs (FE-SEM) were taken by using Bruker and

S-4800 hitachi respectively. UV-Vis spectrophotometer (Perkin Lembda-25) in the range from 300-800 nm was used to measure its optical properties. I-V characteristic were calculated by Lab-equipped model 24 (2004) computer interfaces measurement unit.

3. RESULTS AND DISCUSSIONS

3.1 Structural Studies

Figure (1) shows XRD diffraction of MnS thin film . It is evident that the low intensity peaks suggest that the MnS thin film may be either nanocrystalline nature. From the XRD pattern the peak was identified as origination from the (200),(102) and (201) planes of the hexagonal and cubic phases of Nanocrystalline MnS thin film, which is in agreement with earlier reports . The low-intensity and broad diffraction peak indicated that the as-deposited films consist of coarsely fine grains and/or nanocrystalline in nature.

The calculated amounts of composition for hexagonal and cubic phases are 66.6% and 33.3%, respectively. Further, it is evident from the XRD analysis that no peak corresponding to the oxide and/or hydroxide phases of manganese was observed.

The lattice parameter values are a=b=c=5.26 Å. It is observed from Fig. 1 that the hig hest peak obtained corresponds to (200) plane .

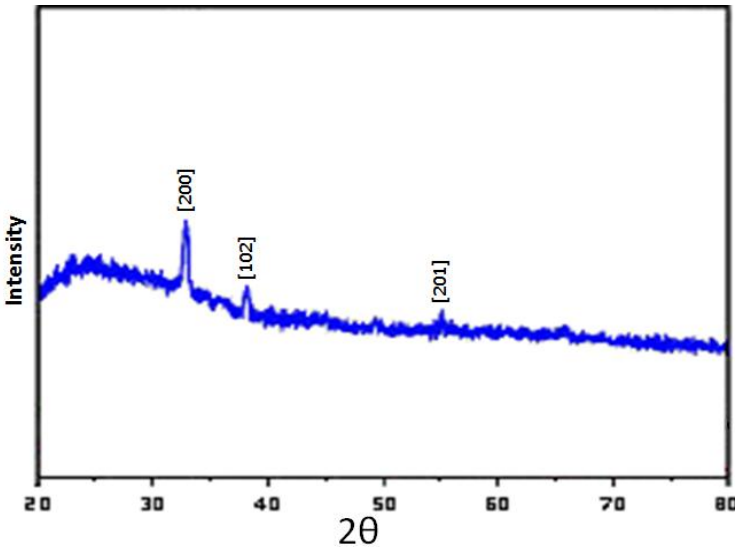


Fig.1. Shows the XRD pattern of Nanostrctured MnS thin film

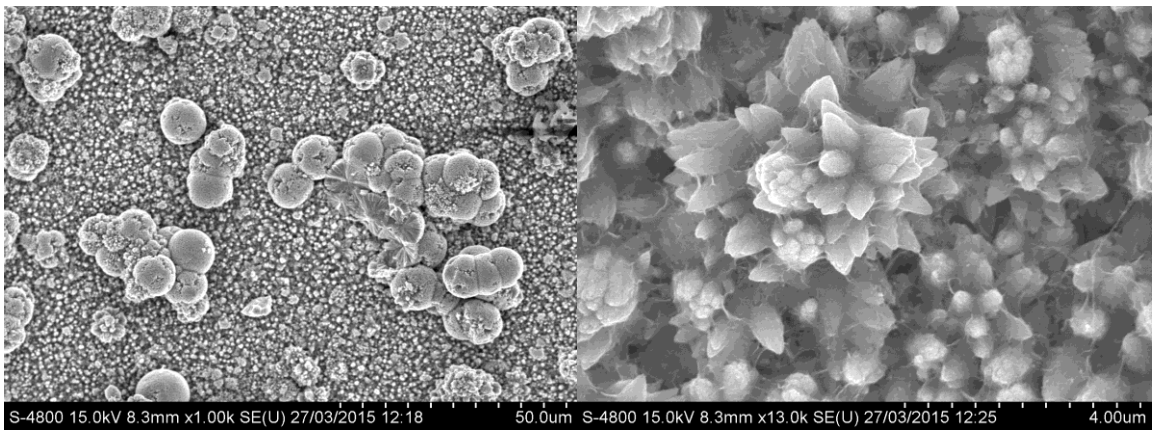
The crystallite size was calculated by using Scherrer's formula,

$$D = \frac{K\lambda}{\beta Cos\theta} \text{.....(1)}$$

Where D is crystallite size, 'λ' is the X-ray wavelength used, β is the angular line width of half maximum intensity, θ is Bragg's diffraction angle and K is constant.

3.2 Morphological and Compositional studies

Scanning electron microscopy is a convenient method for studying thin films. Figure 2 (a, b) show scanning electron micrograph for deposited nanostructured MnS thin film in different resolution images. Surface morphological studies play an important role to observe smoothness and nature of the film. Film indicates that MnS vertical flower like structure cover on the substrate, as resolution increases morphology also increases [21-22].



(a) (b)

Fig.2. (a, b) Show the different resolution images of Nanostructured MnS thin film

Composition of the nanocrystalline MnS thin film was studied by Energy dispersive X-ray analysis (EDAX).EDAX indicated the presence of manganese and sulfur for the substrate fig (3).

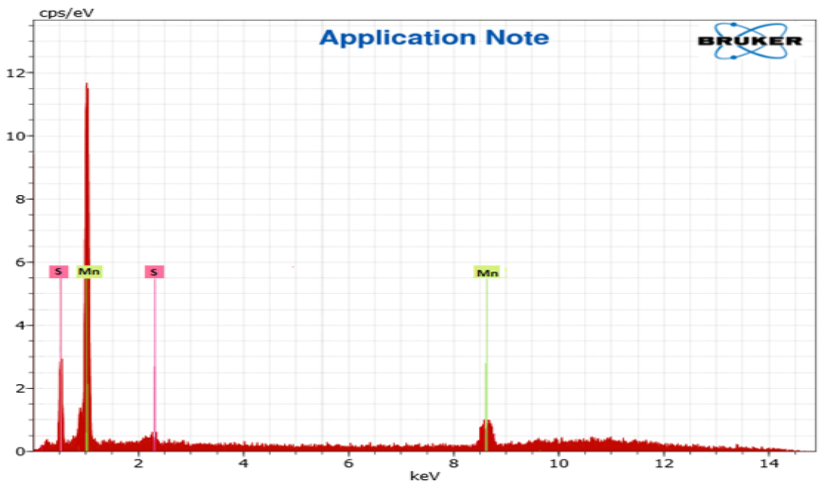


Fig.3. Show the EDAX spectra Nanostructured MnS thin film

3.3 Optical study of MnS thin film

The optical absorbance Of MnS thin film is determined from the range 300-800nm**.** Fig 4 shows absorbance as-deposited nanostructured MnS thin film.

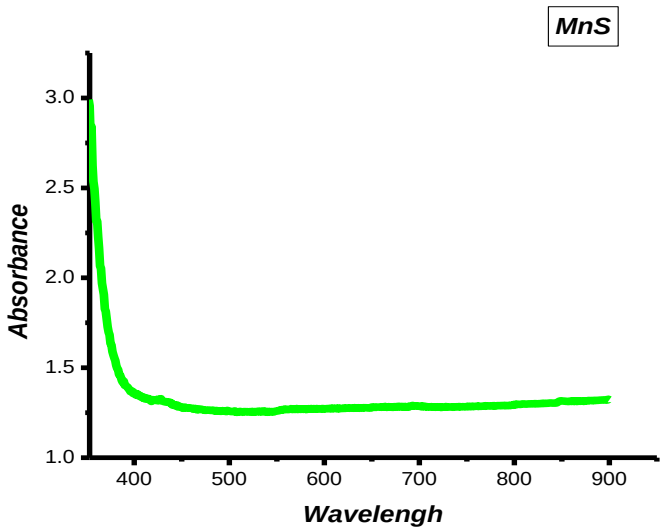


Fig.4. Shows absorption spectra of Nanostructured MnS thin film

$$\alpha = \frac{A(h\nu - E_g)^n}{h\nu} \text{.....(2)}$$

Fig 5 shows band gap of nanostructured MnS thin film obtained from absorption spectra. The relation between the absorption coefficient α and the incident photon energy (hν) is given by relation:-

In this relation n= ½ is taken for direct allowed transition and 'Eg' is optical band material. Absorption coefficient (α) is associated with the strong absorption region of thin films was calculated from absorbance (A). Eg is the separation between the valence and conduction bands and n is a constant that is equal to 1 for direct band gap semiconductors. These band gap values are higher than the bulk value of hexagonal MnS because of quantum confinement in MnS nanocrystals. The band gap energy could be obtained from the plot of ($\alpha\, h\, \nu^2$) as a function of ($h\, \nu$) (Figure 5). A sharp cut off is obtained from absorption spectra at ~380 nm which corresponds to band gap energy of 3.33 eV [21-22]. The observed value is greater than the standard band gap (3.1 eV) of MnS material, showing a `blue shift' of 0.23 eV. This is attributed to size quantization in nanocrystalline semiconductors. This size quantization

occurs due to localization of electrons and holes in a confined volume of the semiconductor nanocrystallites.

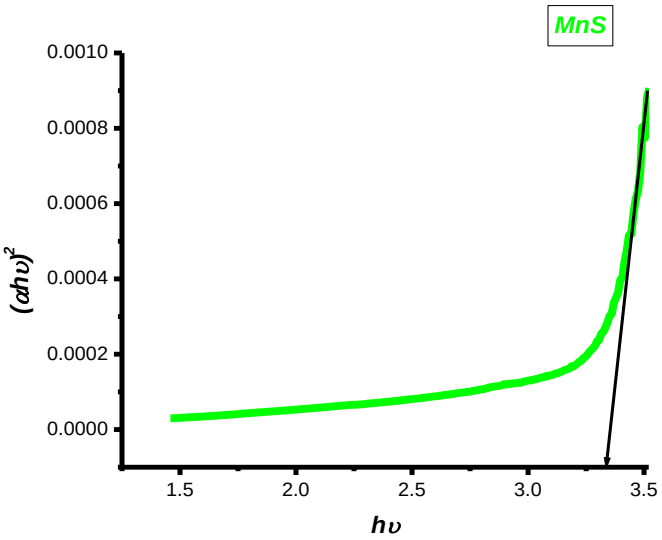


Fig.5. Shows the band gap of nanostructured MnS thin film.

3.4 Electrical Studies

Fig.6 shows I-V characteristic of as deposited in dark & illumination condition (100mw/cm^2).The photogenerated charge carrier's increases with increase in power. The photogenerated current increases due to an increase in conductivity and resistivity decreases. The excitations of valence electrons into the conduction band significantly improve the electrical conductivity of the semiconductors; this phenomenon is known as photoconductivity. Therefore, observing the variation in the I-V plots with respect to the intensity with which the optimized samples were illuminate suggests that Nanocrystalline MnS thin film exhibits photoconductivity.

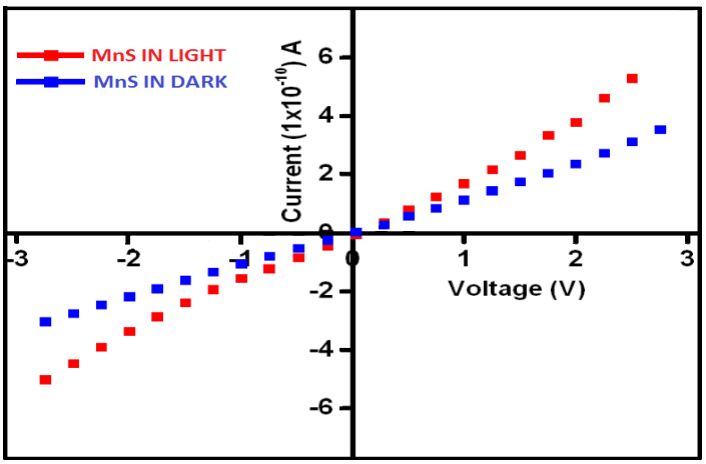


Fig.6. Shows I-V Characteristics in dark and light of nanostructured MnS thin film

Fig.6 shows I-V Characteristics of MnS thin film has increase photocurrent in illumination condition and decrease the resistance, it shows semiconductor behavior.

4. CONCLUSIONS

This work has presented how MnS thin film was grown using Chemical bath deposition techniques. The XRD shows MnS thin film has nanocrystalline structure. The vertical flower like structure was confirmed by Field Emission Scanning Electron Microscopy technique. The Mn and S were available on MnS thin film confirmed by EDAX studies. The absorbance of MnS thin film shifted in blue region and band gap was 3.33 eV. The I-V Characteristics of MnS thin film has increase photocurrent in illumination condition and decrease the resistance, it shows semiconductor behavior.

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