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# Deposition and characterization of nanocrystalline thin film of MnS from chemical route

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**ABSTRACT**

We have synthesis manganese sulfide nano-crystalline (n-MnS) powder using manganese acetate and thiourea, trisodium citrate, from chemical route at different pH. The formation of MnS has been confirmed with help of infrared (IR) spectroscopy by observing bands corresponding to the multi phonon absorption. We have also observed the IR bands at 1403 and 1560 $cm^{-1}$ due to symmetric and asymmetric stretching of COO of the capped sodium citrate at MnS nano-crystalline particles. The Size of crystal is determined as 3-5 nm with the help of X-ray diffraction. We also deposited the thin film of MnS on glass substrate from the solution using self- aggregation approach. The film thickness is measured as 366 nm with profile meter. The optical band gap is calculated as 3.1-3.5 eV. Its value is found to depend on pH. We also measured dark and photo- conductivity at different temperatures.



## Introduction

Synthesis of semiconductor nano-particles or quantum dots has been at the focus of intense research due to their enormous application for optical and optoelectronic devices. In addition, their study provides an opportunity to observe the evolution of collective behavior of the bulk from the discrete nature of molecular properties [1,2]. In particular, II-VI and III-V compound semiconductors have been extensively investigated due to the their strong quantum confinement effects resulting in significant variation in their electrical and optical properties with size, non linear optical properties, reactive and selective photo-catalysis and enhancement in fluorescence efficiency [3,5]. This has resulted in the development of many viable routes for their synthesis in liquids and at solid interfaces [6-8]. II-VI semiconductor materials are synthesized generally by wet chemical methods. Thin films now occupy a prominent place in basic research and solid state technology. The use of thin film semiconductors has attracted much interest in an expanding variety of applications in various electronic and optoelectronic devices due to their low production costs. MnS has a direct band gap and can be used as window material in photovoltaic solar cells. Direct energy gap materials result in large optical absorption which in turn permits the use of thin layers of active material. The semiconducting nature of MnS films is found to be p-type. [9-10], piezo-electronic [11,12] and semiconducting devices. Recently, manganese sulfide (MnS) has been the subject of intense researches for its potential applications in optoelectronic devices. [13].

Nano-crystalline thin films are also polycrystalline in nature but with sizes of crystallites of the order of a few nanometers. Many properties of nano-crystalline materials are found to deviate from those of coarse grained polycrystalline materials with the same average chemical composition. These deviations result from dimensionality of nanometer sized grains and numerous interfaces between adjacent crystallites [14-16]. A major research goal of recent years is to understand the size dependent properties of nano-crystalline materials and as a result considerable amount of work on synthesis and characterization of nano-crystalline thin films are being carried out [17-18]. Out of several methods for deposition of nano-crystalline thin films, chemical bath deposition (CBD) technique suitable for deposition of film on large area substrate.

In the present work, we report the preparation of n-MnS particles and thin films on glass substrate by CBD method. These have been characterized by infrared (IR), UV-Vis, XRD spectroscopic techniques and electrical conductivity measurements.

## Experimental

Nano-crystalline thin films are deposited on glass substrates by CBD technique. In order to prepare adherent and uniform films, we carefully clean the surface of the substrates used within the deposition experiments. We have synthesized n-MnS powder at different pH (pH=9,12) in the presence of capping agent (tri-sodium citrate). Aqueous solution of MnS has been prepared by dissolving a nominal amount of Manganese-acetate, capping agent (tri-sodium citrate) and thiourea for sulfide ion source in 50 ml deionized water and the resultant mixture has been stirred at elevated temperature. The solid phase is isolated by filtration and finally dried in hot bath, from the residue solution. This solid phase consists of MnS nano-crystals. Thin films have been deposited on cleaned glass, quartz substrates for the optical, electrical and structural measurements. Crystallographic study has been carried out using a Phillips PW-1610 X-ray diffractometer with $CuK_{\alpha}$ radiation in the 2θ range from $10^{\circ}$ to $70^{\circ}$. The IR spectrum is determined on a Perkin-Elmer PE-Rx 1 FTIR spectrophotometer. The spectral resolution of the IR spectrophotometer was 1 $cm^{-1}$ throughout the experiment. To study the optical properties of n-MnS thin films, the transmission spectra are recorded using a double beam UV/VIS/NIR spectrometer [Hitachi-330] in the transmission range 300-1000 nm for all samples. The electrical measurements of these thin films were carried out in a specially designed metallic sample holder. A vacuum of about $10^{-3}$ mbar is maintained throughout these measurements. Planar geometry of

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the films (length ~ 1.0 cm; electrode gap ~ $8\times10^{-2}$ cm) is used for the electrical measurements. Thick In electrodes are used for the electrical contacts. Thickness of the film is measured as ~ 465 nm with a profile meter. The electrical conductivity is noted manually from a digital picoammeter (DPM-11Model).The accuracy in current measurements is typically 1 pA.

**Results and discussion**

Fig. 1 shows the XRD pattern of n-MnS film deposited on the glass substrates (pH = 12). The spectrum in Fig. 1 shows the diffraction peaks at 2θ values of 26.4°, 43.7° and 51.5° on the film deposited at pH = 12. The highest intensity of reflection peak is at 2θ = 26.4° [111], with two another small intensity peaks at 2θ = 43.7° [220] and 51.5° [311] indicating that [111] is the preferred direction. The intensity of these peaks increases as the pH value decreases (figures not shown here). Information of the strain and the particle size are obtained from the full width at half maximum (FWHMs) of the diffraction peaks. The FWHMs (β) can be expressed as a linear combination of the contributions from the strain (ε) and particle size (L) through the following relation [19]

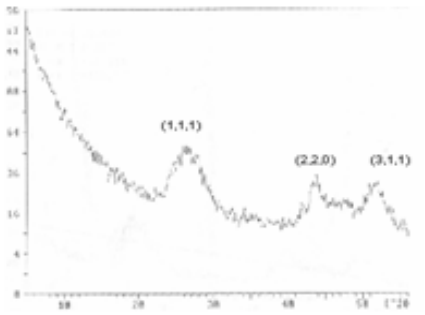


**Fig. 1. XRD spectrum of n-MnS**

$$\frac{\beta\cos\theta}{\lambda}=\frac{1}{L}+\frac{\varepsilon\sin\theta}{\lambda} \qquad (1)$$

Fig. 2 shows the plot of (βcosθ)/λ versus (sin θ)/λ for n-MnS film at (pH = 12) which is a straight line. The reciprocal of intercept on the (βcosθ)/λ axis gives the average particle size as ~ 4 nm. The particle size increases (4.6 nm to 5.4 nm) as the pH value decreases from 10 to 12.

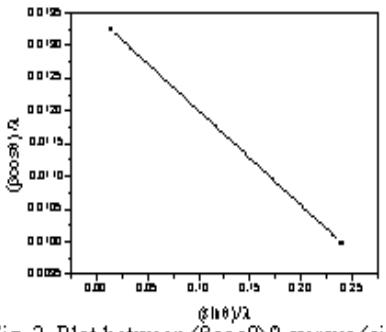


Fig. 2. Plot between (βcosθ)/λ versus (sin θ)/λ.

Further, the formation of n-MnS has been confirmed with help of IR spectroscopy by observing a band at 652 $cm^{-1}$ corresponding to the multi phonon absorption of MnS. We have also observed the IR bands at 1403 and 1560 $cm^{-1}$due to symmetric and asymmetric stretching of $COO^{-}$ of the capped sodium citrate at n-MnS particles as shown in Fig. 3.

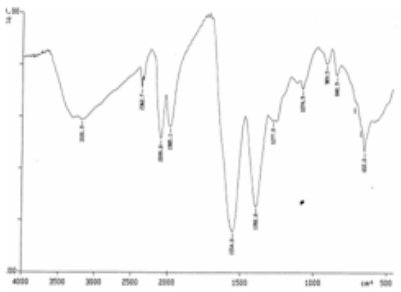

**Fig. 3. IR spectrum of n-MnS Electrical Properties**

Fig.4 shows the temperature dependence of dark conductivity ($\sigma_d$) and photoconductivity ($\sigma_{ph}$) of n-MnS thin films deposited at pH 12 and 80° C. Similar behavior have been found for the films deposited at different pH and temperatures. The electrical conductivity shows typical Arrhenius type of activation

$$\sigma_d=\sigma_o\exp\left(\frac{-\Delta E}{kT}\right) \qquad (2)$$

where ΔE is the activation energy for dc conduction; k is the Boltzmann's constant.

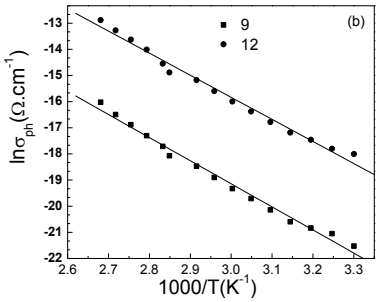


**Fig. 4. Temperature dependence of dark conductivity of n-MnS thin films**

The values of $\sigma_d$ and $\sigma_{ph}$, calculated using Eq. (2), are (4.1 ± 0.02)$\times10^{-8}$ $\Omega^{-1}cm^{-1}$ and (1.6 ± 0.02)$\times10^{-7}$ $\Omega^{-1}cm^{-1}$ for n-MnS film respectively. The value of $\sigma_d$ increases as the particle size of n-MnS increases at different pH. The increase in electrical conductivity and decrease in the activation energies as the value of pH decreases may be due to the change in structural parameters, improvement in crystallite and grain size, decrease in inter-crystallite boundaries (grain boundary domains) and removal of some impurities (adsorbed and absorbed gases).

Fig. 5 shows the plot between $(\alpha h\nu)^2$ vs. hν for n-MnS films deposited at different pH (9 & 12). Form the intercept of the x-axis, we have obtained the values of optical gap ($E_g$) which are 3.1 and 3.5 eV respectively. The increase in the optical gap from the bulk value (3.0 eV) can be explained on the basis of the quantum confinement effect.

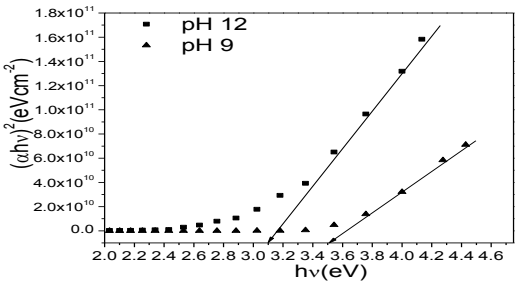


**Fig. 5. Plot of $(\alpha h\nu)^2$ vs. hν for n-MnS films deposited at different pH (9 & 12).**

**Conclusions**

n-MnS powder as well as thin films have been deposited at different pH values of the deposition bath solution. The particle size has been calculated using XRD data and found to be 3-5 nm. IR data confirms the formation of MnS nano-particles. The optical band gap has been calculated using optical data and it is found that the band gap increases from the bulk value which is due to the quantum confinement effect.

The particle size decreases as the value of pH increases. Electrical conductivity measurements show that the value of dark conductivity increases and activation energy decreases as the particle size increases.

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