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Effect of pH enhancer on Some Physical Properties of CB Deposited MNS Thin Films

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Abstract

Physical and optical properties of chemical bath deposited MnS thin films were studied. The physical properties such as variation of thickness, variation of transmittance and variation of optical band gap have been investigated. The concentration of pH enhancer of the precursor effectively tuned the physical and optical properties of the deposited MnS thin films. The film prepared using 12 ml of 7M (NH_3OH) exhibits maximum band gap 3.75 eV. Thickness of the MnS films was observed decreased with increasing concentration of 7M (NH_3OH). It was found that increasing pH enhancer concentration the blue shifting of absorption edge increased.

Key Words: Chemical bath deposition; MnS thin films; Optical Properties

Introduction

Manganese sulphide (MnS) thin films have been used in variety of applications such as solar cells, sensor, photoconductors, optical mass memories and solar selective coatings. Manganese containing Diluted Magnetic Semiconductors (DMS) have recently attracted much attention due to their potential applications in solar selective coatings, solar cells, sensors, photoconductors etc. Among the available DMSs, Manganese Sulphide (MnS) was broadly studied because of its magneto-optical properties and wide band gap nature.

Thin films of metal chalcogenide can be deposited on glass, metal and other substrates by a variety of techniques, such as SILAR [1], solvothermal [2], hydrothermal [3], RF-sputtering [4], MBE [5], solid solid reaction [6] and chemical bath deposition (CBD) [7]. Metal chalcogenide thin preparation by chemical bath deposition (CBD), is currently attracting considerable attention as it is relatively inexpensive, simple and convenient for large area deposition. CBD is a technique in which thin films are deposited on substrates immersed in dilute solutions containing metal ions of either sulfide or selenide. This process usually uses a chelating agent to control the release of metal ions and sulfide ions to produce the controlled homogeneous precipitation of the film on the solid substrate. CBD is well suited for producing large-area thin films and has many other advantages [8,9,10].

In present study, MnS thin films were deposited onto glass substrates by CBD technique using the precursor solutions of manganese chloride (MnCl2.4H2O) and thiourea $(SC(NH)_2)_2$ at different concentrations of complexing agent (NH_3OH) at a temperature of 45°C. The physical properties such as film thickness and optical properties were investigated.

Material and Methods

The synthesis of MnS thin films was carried out using CBD technique. The glass substrates used was previously cleaned. Initially the substrates were degreased in HCl over a night, ultrasonically washed with detergent, rinsed with distilled water and dried in air. High purity AR grade chemicals (Thomas Baker) were used for synthesis of MnS thin films. The precursor solutions 1M, MnC_{l2} (Manganese Chloride), 1M, (NH_2CSNH_2) (thiourea) and 7M NH_3OH (Amonium hydroxide) were prepared previously.

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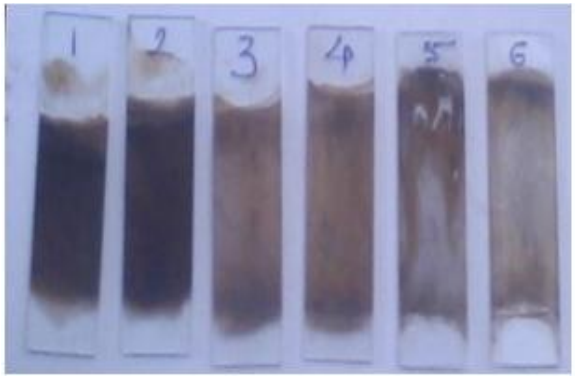

Fig. 1. MnS thin film deposited for different molar concentrations of complex agent.

Six chemical baths were prepared containing, 5ml of 1 M MnC_{l2}, 5ml of 1M, NH_2CSNH_2 to which 30 ml of deionised water was added with continuously stirring. Baths were numbered as 1 through 6. To these baths 7 M NH_3OH (6ml , 9ml, 12 ml, 15ml, 18ml, 21ml,) was added in baths 1 through 6 respectively as pH enhancer. The prepared baths were kept in water bath maintained at 45 0C. The cleaned glass substrates were immersed in each bath vertically. After 48 hours the deposited substrates were removed from chemical baths, washed twice with double distilled water. The uniform pinkish black MnS thin films were deposited on the glass substrates as shown in figure 1.

The variations of film thickness and optical properties of deposited deposited MnS thin films were investigated.

Result and discussion

All the films deposited appeared radish blackes in colors. Film thickness is an important parameter in the study of the film properties (1, 2), the weight difference method employed to estimate the film thickness. The thickness was estimated by using the relation

$$t = \frac{m}{A\rho} \qquad (1)$$

where m is the mass of the film deposited on area *A*, ρ is the density of the material. The variation of the film thickness v/s concentration of pH enhancer was plotted in fig. 2.

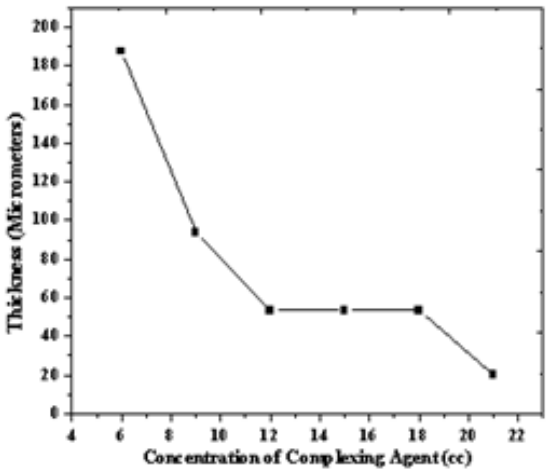

Fig. 2. Plot of thickness of thin film verses complex agent.

Initially film thickness was found maximum for 6ml of 7 M NH_4OH and linearly decreased and become constant up to 18 ml of NH_4OH and then decreased. The film deposited for 12ml of 7 M NH_4OH is thin uniform and transparent show high percentage transmittance as compared to other films. It was concluded that the 12ml of 7M ammonia water is the optimum value to slow down the reaction and better formation of the MnS thin film.

The deposited films were characterized by using systronics double beam 2201 spectrophotometer, the percentage absorption was plotted against wavelength in nm as shown in fig. 3.

All the films show that absorption decreases with increase in wavelength. Films 1and 2 for 6 and 9 ml 7M NH_4OH show no significant change of absorption. All the films prepared for 12 to 21ml of 7M NH_4OH ammonia-water show blue shifting. The film sample deposited for 18 ml of 7M NH_4OH exhibit significant blue shift. It was reported that blue shifting of absorption edge indicates that the prepared film exhibit low absorption in the blue region which is the advantage for solar cell application.

The optical band gap was obtained by using the following relation, $\frac{A(h\nu - Eg)^n}{h\nu}$.

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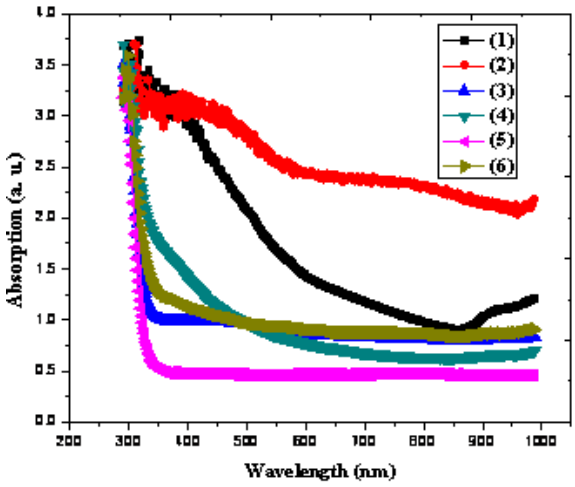

Fig. 3. Plot of percentage absorption verses wavelength for MnS thin films.

All the films show high absorption coefficient. The values of direct band gap (Eg) were determined by plotting $(\alpha h\nu)^2$ v/s. photon energy as shown in fig. 4 and extrapolating the straight line curve to zero absorption. The band gap was observed increase for increasing PH values up to certain limit. The film prepared by using 12 ml complexion agent solution exhibit maximum band gap of 3.75 eV. Other composition show the band gap was found in the range 1.97, 2.5,3, 3.5 eV etc.

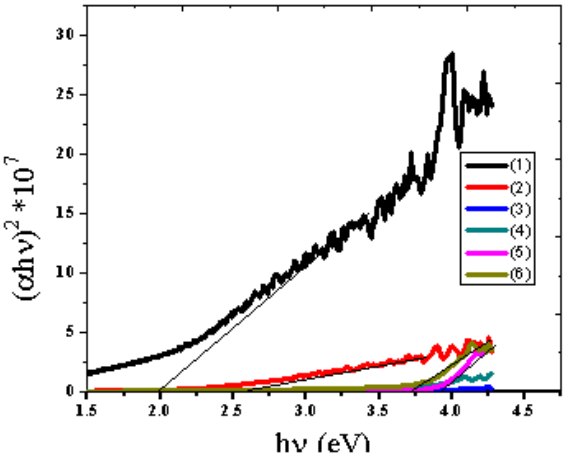

Fig. 4. Plot of $(\alpha h\nu)^2$ verses energy.

The transmittance spectra were shown in fig. 6. The figure show the film prepared by using 12 ml of 7M NH_4OH exhibit maximum transmittance of 39%. From the transmittance spectra we concluded the complexing agent play a vital synthesis of MnS thin films.

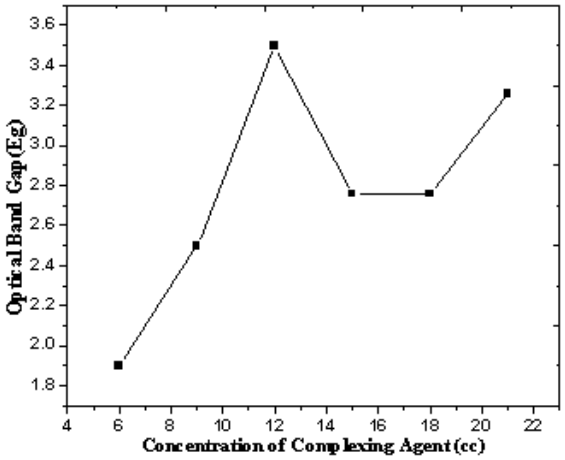

Fig. 5. Plot of Band gap Eg verses Complexing agent.

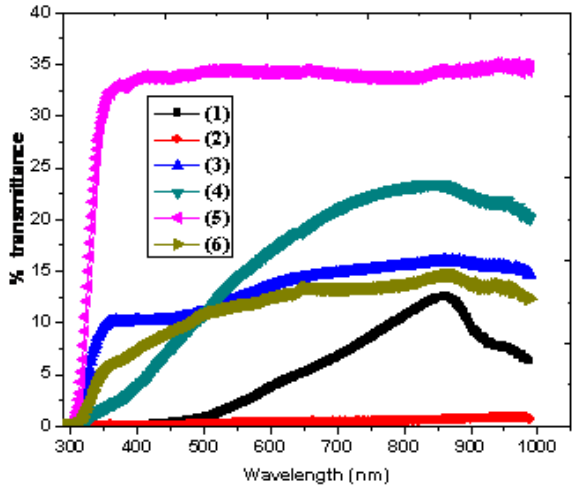

Fig. 6. Plot of Percentage transmittance verses wavelength.

Conclusion

Manganese supplied (MnS) thin films successfully deposited by using CBD technique. The optical band gap energy was found depend upon the concentration of pH enhancer. The film deposited using 12ml of 7M NH3OH exhibits the maximum band gap 3.75 eV and maximum transmittance. It was therefore concluded that either PH of the precursor or concentration of complexing agent play a vital role in adhering the MnS thin film on substrates. Study show that the concentration of 7M NH3OH may vary from 12 to 18ml for better deposition of MnS thin films.

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