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# Temperature Dependance of the Energy Band Gap and Absorption Coefficient of Thin Films of Chemically Deposited Zinc Sulfide, Manganese Sulfide and Multilayer Zinc Sulfide-Manganese Sulfide

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Zinc sulfide (ZnS) and manganese sulfide (MnS) single layer thin films are deposited on glass substrates by chemical bath deposition technique. Multilayer ZnS-MnS thin films are also obtained by using MnS films as substrates for the deposition of ZnS films. These films are annealed in air at different temperatures. Optical studies are separately done on ZnS, MnS and multilayer ZnS-MnS films. Optical properties are studied (between 300-900 nm) in a UV-VIS-spectro photometer and the absorbance recorded as a function of photon energy. The optical band gap and maximum absorption coefficient of the as deposited and annealed samples are determined. Optical band gap and absorption coefficient decreases with annealing.

**Key Words: Thin films, Multi layer film, Zinc sulfide, Manganese sulfide.**

## INTRODUCTION

Chemical bath deposition is a technique in which thin semiconductor films are deposited on substrates immersed in dilute solutions containing metal ions and a source of hydroxide, sulphide or selenide ions[1-9]. The number of possible materials to be produced through this technique is bound to multiply in subsequent years. This is due to the feasibility of producing multilayer films by this technique- the annealing of which promotes interfacial diffusion of metal ions and the production of new materials with improved thermal stabilities[10,11].

Zinc sulphide and manganese sulphide are materials being tested in thin film devices and photovoltaic cells. Zinc sulfide 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 ZnS and MnS films are found to be *p*-type[12,13]. In this paper we report the feasibility of ZnS-MnS junction based on MnS films grown on glass substrates by chemical bath deposition technique, which is used as the substrate for depositing ZnS over it by chemical bath deposition technique. The optical band gap, absorption coefficient and the effect of annealing on ZnS, MnS and multilayer ZnS-MnS thin films are studied.

## EXPERIMENTAL

**Preparation of ZnS thin films:** Chemical bath deposition is a technique for controlling the homogeneous precipitation of water insoluble compounds and their solid solution[14,15]. In this paper we describe the chemical deposition of ZnS thin films on pyrex glass substrates by the decomposition of thioacetamide in an alkaline solution containing a zinc salt[16,17]. The chemical process consists of the slow release of $Zn^{2+}$ and $S^{2-}$ ions in solution which subsequently condenses on an ion-ion basis on to the glass substrate[18].

Stock solutions of 1M zinc sulfate and 1M thioacetamide are prepared in tridistilled water[19,20]. A 100 mL deposition bath is prepared by the sequential addition of the following. 15 mL of 1M zinc sulfate, 4.4 mL of $NH_3/NH_4Cl$ (pH 10), 5.4 mL of 50 % triethanolamine, 15 mL of 1M thioacetamide and the rest deionized water to make upto 100 mL by volume. The glass slides are washed with detergent solution, then with chromic acid and finally rinsed with deionized water prior to the deposition of the films. Cleaned glass slides are kept vertically on the walls of the container with the deposition mixture. Depositions are done at room temperature for 24 h. The films are dried in air.

**Preparation of MnS thin films by chemical bath deposition technique:** Stock solutions of 1M manganese sulfate

and 1M of thioacetamide are prepared in tridistilled water. A 100 mL deposition bath is prepared by the sequential addition of the following. 15 mL of 1M manganese sulfate, 4 mL of $NH_3/NH_4Cl$ (pH 10), 5 mL of 50 % triethanolamine, 15 mL of 1M thioacetamide and the rest deionized water to make upto 100 mL by volume. The glass slides are washed with detergent solution, then with chromic acid and finally rinsed with de ionised water prior to the deposition of the films. Cleaned glass slides are kept vertically on the walls of the container with the deposition mixture. Depositions are done at room temperature for 24 h. The films are dried in air.

**Preparation of multilayer ZnS-MnS thin films:** MnS films are deposited onto glass subtrates by chemical bath deposition technique. These films are used as substrates for the deposition of multilayer ZnS-MnS films. Manganese sulfide films are kept vertically on the walls of the container with the deposition mixture for ZnS. Depositions are done at room temperature for 12 h. The multilayer ZnS-MnS films are dried in air.

**Measurements:** The films are annealed in air for different temperatures. Thickness of the films are accurately determined by Tolanskys multiple beam interference technique[21]. UV-visible absorption spectra are obtained from a Shimadzu 240 UV-VIS spectrophotometer. The absorption edge is analyzed to obtain the optical band gap of ZnS, MnS and multi layer ZnS-MnS thin films.

## RESULTS AND DISCUSSION

Optical studies are done to determine the band gap, maximum absorption coefficient and the effect of annealing on band gap. The optical absorption spectrum in the range 300 nm to 900 nm is recorded using the Shimadzu UV-visible spectro photometer. To obtain information about the absorption, the fundamental absorption edge is analyzed within the one electron theory of Bardeen *et al.*[22].

The absorption coefficient $\alpha^2$ is calculated and it is reated to the band gap $E_g$ and photon energy hν according to the relation, $\alpha = \alpha_o (h\nu - E_g)^n$ where n = 1/2, for direct allowed transition. Graph of $\alpha^2$ *versus* hν is plotted and is shown in Figs. 1-3 for as deposited and annealed ZnS, MnS and multi layer ZnS-MnS films, respectively. The absorption coefficient $\alpha$ is calculated using the relation, $\alpha$ = 2.303 A/t, A is the absorbance of the film, t is the thickness. Extra polation of this plot to $\alpha^2 = 0$ gives the optical band gap. The optical band gap and maximum absorption coefficient of as deposited and annealed ZnS, MnS and multilayer ZnS-MnS thin films are given in Tables 1-3, respectively. The band gap energy is found to decrease with annealing. The estimated accuracy in the measurement of the energy gap is + or -0.02 eV. The energy band gap measurements provide a measure of the trapping levels. It has been reported that the removal of oxygen causes a redistribution of traps and hence a drop in band gap energy[23]. Sussman has reported that the distribution of trapping sites is altered by annealing[24]. Shirai *et al.*[25] reported that the as deposited films usually have poor crystallinity and thermal annealing is needed to improve the quality[25]. Therefore the annealing process is of critical importance in the solar cell fabrication[26].

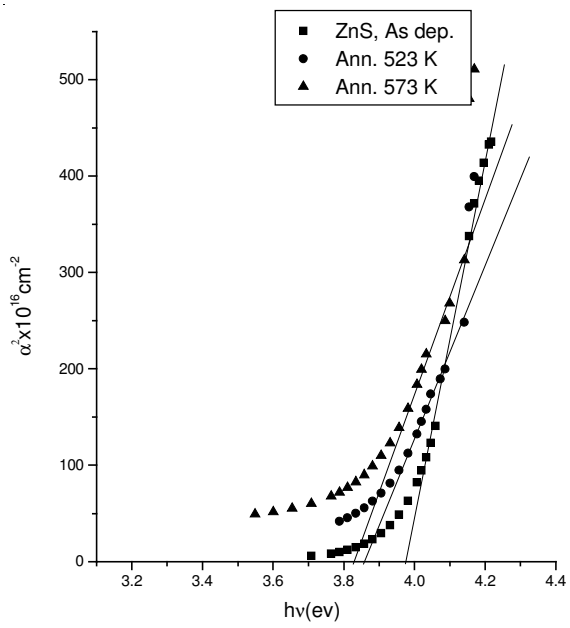


Fig. 1. Plot of $\alpha^2$ *versus* hν for ZnS films of thickness 3215 Å

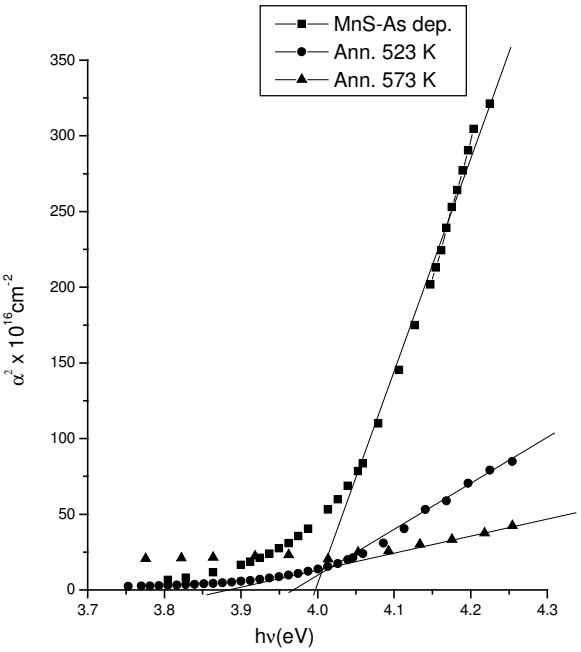


Fig. 2. Plot of $\alpha^2$ *versus* hν for MnS films of thickness 3515 Å

TABLE-1
OPTICAL BAND GAP ENERGY AND ABSORPTION COEFFICIENT OF AS DEPOSITED AND ANNEALED (523 AND 573 K) ZnS THIN FILMS OF THICKNESS 3215 A

| Samples | Optical band gap (eV) | Absorption coefficient $\times 10^8$ cm$^{-1}$ |
|---|---|---|
| ZnS (As deposited) | 3.96 | 28.51 |
| ZnS (Annealed 523 K) | 3.86 | 24.90 |
| ZnS (Annealed 573 K) | 3.82 | 21.52 |

## Conclusion

Zinc sulfide (ZnS) and manganes sulfide (MnS) thin films are deposited on glass substrates by chemical bath deposition technique. Multi layer ZnS-MnS thin films are also obtained by chemical bath deposition technique by using MnS films as

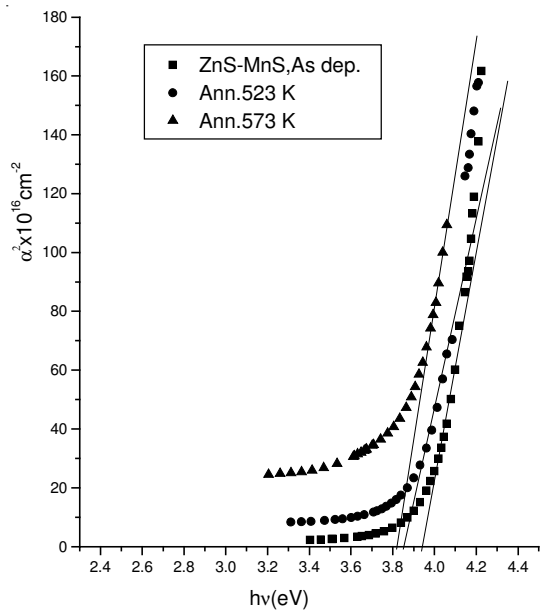


Fig. 3. Plot of $\alpha^2$ *versus* hν multilayer ZnS-MnS films of thickness 6840 Å

TABLE-2
OPTICAL BAND GAP ENERGY AND ABSORPTION COEFFICIENT OF AS DEPOSITED AND ANNEALED (523 AND 573 K) MnS THIN FILMS OF THICKNESS 3515 A

| Samples | Optical band gap (eV) | Absorption coefficient × $10^8$ $cm^{-1}$ |
|---|---|---|
| MnS (As deposited) | 3.98 | 21.18 |
| MnS (Annealed 523 K) | 3.96 | 19.93 |
| MnS (Annealed 573 K) | 3.87 | 17.92 |

TABLE-3
OPTICAL BAND GAP ENERGY AND ABSORPTION COEFFICIENT OF AS DEPOSITED AND ANNEALED (523 AND 573 K) MULTILAYER ZnS-MnS THIN FILMS OF THICKNESS 6840 A

| Samples | Optical band gap (eV) | Absorption coefficient × $10^8$ $cm^{-1}$ |
|---|---|---|
| Multilayer ZnS-MnS (as deposited) | 3.92 | 14.61 |
| Multilayer ZnS-MnS (annealed 523 K) | 3.85 | 12.71 |
| Multilayer ZnS-MnS (annealed 573 K) | 3.80 | 10.45 |

subtrates for the deposition of ZnS films. These films are annealed in air at different temperatures. Optical studies are separately done on ZnS, MnS and multi layer ZnS-MnS films. Optical properties are studied (between 300 nm to 900 nm) in a UV-VIS-spectro photometer and the absorbance recorded as a function of photon energy. The optical band gap and maximum absorption coefficient of the as deposited and annealed samples are determined. Optical band gap and absorption coefficient decreases with annealing.

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