

SOME STUDIES ON CHEMICALLY DEPOSITED CD1-XFE_xS THIN FILMS.

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ABSTRACT The Cd_{1-x}Fe_xS (0 ≤ x ≤ 1) thin films have been deposited by simple and inexpensive chemical bath deposition technique. For good quality deposits the various preparative parameters such as deposition temperature, time, speed of substrate rotation, pH of the reaction mixture and molar concentration has been optimized. Triethanolamine (TEA) was used as a complexing agent. The 'as-grown' thin films have been characterized for structural, compositional, surface morphological and optical studies by XRD, EDAX, SEM and UV-VIS-IR spectrophotometer respectively. The X-ray diffraction patterns of the sample showed that all the films are polycrystalline in nature. Pure CdS and FeS exhibits hexagonal structures. The energy dispersive analysis by X-ray revealed that films are sulphur deficient. The optical study at room temperature revealed that films have absorption coefficient (10⁴ cm⁻¹) with a direct allowed type transition. The optical band gap energy decreased continuously from 2.48 eV to 0.89 eV as the composition parameter 'x' increased from 0 to 1.

KEYWORDS : Chemical bath deposition, Cd_{1-x}Fe_xS thin films, XRD, EDAX, SEM.

INTRODUCTION

The II^{VI}-VI^A group semiconductor materials are becoming interesting and important because of their major contribution to opto-electronic devices [1-2], and solar cells [3]. Among II^{VI}-VI^A group CdS is very important wide band gap semiconductor which is widely used in non-linear optics, visible light emitting diodes and lasers [4]. Also, FeS is a prominent material with a direct band gap having absorption coefficient continuously increasing from the infrared through visible region [5-6] and has been used as selective surfaces for photo thermal conversion applications. FeS thin films have been widely studied for their structural, optical and photoelectrochemical properties [7-11].

These films can be prepared by variety of methods such as electrodeposition [12-13], spray pyrolysis [14], vacuum deposition [15] and chemical bath deposition (CBD) method [16-18]. Among these methods the chemical bath deposition method is very popular due to its low cost, ease of handling, reliable, simplest and useful for large area industrial applications.

In the present study, considering the advantages laid down by ternary compounds, the chemical bath deposition technique was used for the deposition of Cd_{1-x}Fe_xS thin films with 0 ≤ x ≤ 1. The growth, structural, compositional, surface morphological and optical properties have been studied over entire range of composition.

Experimental Details

The Cd_{1-x}Fe_xS thin films with 0 ≤ x ≤ 1 were deposited onto optically plane glass substrates by a chemical bath deposition method. For the deposition, equimolar solutions of cadmium sulphate, Iron sulphate and thiourea (all AR grade) were mixed in stoichiometric proportions to obtain x from 0 to 1. Triethanolamine was used as a complexing agent and pH of the reaction mixture was adjusted to optimized value 8 ± 0.1. Thoroughly, cleaned glass substrates were mounted vertically on a specially designed substrate holder and were rotated in reaction mixture to achieve uniform churning. To obtain good quality samples, the temperature, time of the deposition and speed of the substrate rotation were optimized. These optimized parameters were 70 °C, 60 min. and 60 rpm respectively.

The thickness of 'as-deposited' samples was measured by weight-difference density method using sensitive microbalance. The structural properties of these film samples were studied using Philips PW-3710 X-ray diffractometer with CuK_α line (λ = 1.54056 Å) in the 2θ range from 20° to 80°. The film surface morphology and composition were investigated using scanning electron microscopy (SEM) and energy dispersive analysis by X-ray with JEOL-JSM 5600 respectively. The optical absorption studies were carried out using UV-VIS-IR spectrophotometer (Hitachi-330) in the 350-3000 nm wavelength range. The absorption coefficient, energy band gap and type of transition were determined from these studies.

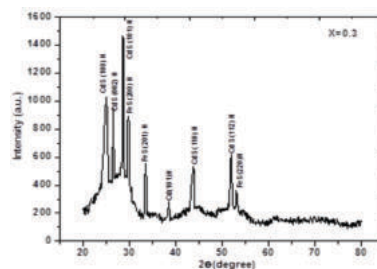
RESULTS AND DISCUSSION

Kinetic Studies

The deposition of thin film depends on various preparative parameters such as deposition temperature, time, speed of substrate rotation and pH of the reaction mixture. We tried the deposition Cd_{1-x}Fe_xS (x=0) thin films at various temperatures from 40 °C to 75 °C. It was found that no film formation take place at 40 °C, although the reaction mixture was kept for a long time. Above 40 °C the rate of deposition was found to be increased significantly. At about 70°C, the thickness of film found to be maximum and above it the thickness decreases. This can be explained on the basis that, at low temperature most of the ions are not free for the reaction to take place. At increasingly higher temperatures the rate of release of Cd²⁺, Fe²⁺ and S²⁻ ions are higher, that enhances the rate of film growth and increases the film thickness up to 70°C. Above this temperature, more and more ions will come out of the bound complex state at a relatively faster rate and therefore the ions may not have sufficient time to condense on the substrate surface, consequently they settle down at the bottom, thus decreasing the layer thickness [19]. The time dependence of film growth is also studied. It is found that, initially the layer thickness increases with the deposition time and later on it saturates. This may be explained as for smaller deposition time up to 60 min. more and more ions will get deposited on the substrate showing the layer thickness to increase almost linearly. For higher deposition time (>60 min.) the process of depletion of number of ions in the solution causes growth rate to decrease, resulting into saturation of the layer thickness [20]. The other parameters namely pH of reaction mixture and speed substrate rotation was optimized and found to be 8 ± 0.1 and 60 rpm respectively. By choosing appropriate composition parameter x = 0.5 and x = 1, the optimization of the mentioned parameter was confirmed. Then the Cd_{1-x}Fe_xS (x = 0 to 1) thin film sample series was deposited onto the well processed glass substrates at the optimized deposition conditions. The terminal thickness of the as-deposited layers increased up to 0.3 and then decreased with further increase in 'x' up to 1.

Structural And Morphological Studies

Fig.(1) shows the X-ray diffractogram of optimized 'as-deposited' Cd_{0.7}Fe_{0.3}S film. The presence of large number of peaks indicates the films are polycrystalline in nature over entire range of composition. Also, The analysis showed that pure CdS and FeS exhibit hexagonal wurtzite structure.

Fig.1. XRD Pattern Of Optimized Cd_{0.7}Fe_{0.3}S Thin Film

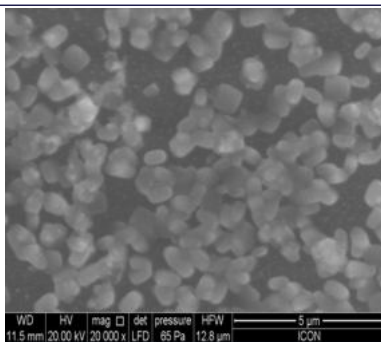


Fig.2. SEM Micrograph Of Optimized $\text{Cd}_{0.7}\text{Fe}_{0.3}\text{S}$ Thin Film

XRD pattern showed the most preferred orientation along (1 0 1) plane. The diffraction peaks at various 2θ values are indexed in fig (1), which is confirmed using the standard JCPDS data card number [06-0314 and 80-1028].

The average grain size 'D' of the film samples was calculated by Scherrer's formula [21]

$$D = 0.94 \lambda / \beta \cos \theta$$

Where λ is the wavelength of the X-ray used, β is the full width at half maximum and θ is the Bragg angle. It is observed that the grain size of the sample increases with increase in 'x' up to 0.3 and further increase in 'x' up to 1 grain size decreased. The SEM micrograph is shown in fig. (2) Supports these observations.

Compositional Analysis

Fig. (3) shows the EDAX pattern of the representative $\text{Cd}_{0.7}\text{Fe}_{0.3}\text{S}$ film sample.

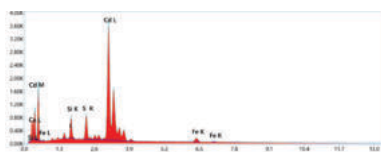


Fig.3. EDAX Pattern Of $\text{Cd}_{0.7}\text{Fe}_{0.3}\text{S}$ Thin Film

The pattern confirms the presence of cadmium, iron and thiourea, and the proportion of these elements measured for $x = 0.15$ is as Cd = 40.78 %, Fe = 16.65 % and S = 42.57 % respectively. This result indicates that the deposited films are sulphur deficient. The elemental composition of $\text{Cd}_{1-x}\text{Fe}_x\text{S}$ thin films as taken and observed by EDAX method is given in table 1.

Optical Analysis

The optical parameters such as absorption coefficient and bandgap are determined from optical absorption measurements. The nature of transition is determined using the following Eq.

$$\alpha h\nu = A(h\nu - E_g)^n$$

E_g is an energy gap, A is energy dependent constant and n is an integer. The value of n determines the type of transition present in the material. In this case, $n = 1/2$ represents that the transition involved in the material is direct allowed.

The energy band gap is varied from 2.48 eV to 0.89 eV as x varied from 0 to 1 it is shown in Fig. 4.

Table1: Elemental Composition And Grain Size By SEM Of 'As-Deposited' $\text{Cd}_{1-x}\text{Fe}_x\text{S}$ ($0.0 \leq x \leq 1.0$) Thin Films.

composition 'x'	Grain sizes by SEM (nm)	As taken atomic percentage in bath solution (%)			As observed atomic percentage in film by EDAX analysis (%)		
		Cd	Fe	S	Cd	Fe	S
0.0	213	50.00	00.00	50.00	56.45	00.00	43.55
0.1	225	45.00	05.00	50.00	51.43	05.12	43.45
0.2	231	40.00	10.00	50.00	52.02	08.30	39.68
0.3	236	35.00	15.00	50.00	40.78	16.65	42.57
0.5	205	25.00	25.00	50.00	28.15	26.22	45.63
0.7	195	15.00	35.00	50.00	18.15	38.50	43.35
1.0	178	00.00	50.00	50.00	00.00	56.40	43.60

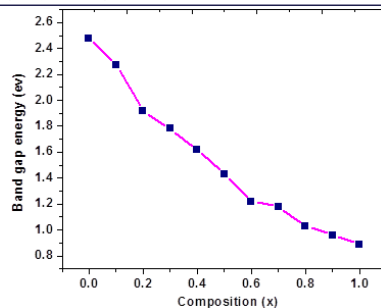


Fig.4 Composition Vs Energy Band Gap For CdFeS Thin Films

CONCLUSION

From the above studies, it is concluded that $\text{Cd}_{1-x}\text{Fe}_x\text{S}$ ternary thin films with different composition range between $0 \leq x \leq 1$ can be deposited by simple, inexpensive chemical bath deposition technique. Structural studies showed polycrystalline nature of deposited films with hexagonal structure. EDAX studies revealed that the films are sulphur deficient. The optical properties showed the band gap engineering could be realized in the $\text{Cd}_{1-x}\text{Fe}_x\text{S}$ thin films with the help of modulating the composition parameter 'x'. It is observed that presence of small amount of iron results in marked changes in the optical band gap of CdS. The wide and fine tunability of the band gap to the ternary $\text{Cd}_{1-x}\text{Fe}_x\text{S}$ thin films have potential applications in various opto-electronic devices and solar cells.

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