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RESEARCH ARTICLE

GROWTH AND CHARACTERIZATION OF CHEMICALLY SYNTHESIZED CdS, FeS AND CdFeS THIN FILMS

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Abstract

A Simple and cost-effective chemical bath deposition process has been employed for the preparation of CdS, FeS and $Cd_{0.5}Fe_{0.5}S$ thin films. Cadmium Sulphate, Iron Sulphate and thiourea were used as the basic source materials. The effect of various preparative parameters on growth process is studied and they are optimized for good quality films. The film thickness is measured by gravimetric weight difference method. The X-ray diffraction (XRD) studies revealed that films are polycrystalline in nature and exhibit hexagonal structure for pure CdS, FeS and CdFeS films. The energy dispersive analysis by X-rays (EDAX) studies revealed that films are sulpher deficit.

Keywords: Chemical bath deposition, CdFeS Thin films, XRD. EDAX.

Introduction

The ternary semiconductor thin films are considered to be an important technological material due to its prime applications in various optical and electronic devices. The II-VI and IV-VI group compound materials having specific physical properties like high efficiency, high optical absorbance and direct band gap, are considered to be potential materials in respect for a wide spectrum of optoelectronic applications such as photo detectors, photovoltaic devices, photo-electrochemical cells (Barreau et al., 2002; Al Kuhaimi and Tulbah 2000; Chen 1998; Sankagal and Lokhande 2002), lasers, IR devices, solar control coatings, (Rakesh K.doshi et al., 2002; Gutierrez 1991) solar cells (Nair and Nair 1993). These materials can be deposited in thin film form by various methods, such as electro-deposition (Masumdar 2003) spray pyrolysis (Shahane 1997), vacuum deposition (Henry 1980) and chemical bath deposition (Taskar 1990; Kahle and Berger 1970). Among them the chemical bath deposition method is very simple, convenient for large area deposition on substrates of different materials, size and shape and it is inexpensive. Especially, one of the attractive features of the chemical bath deposition process is the ease with the alloys can be generated without the use of any sophisticated instrumentation and process control (Buckley and Woods1973).

The objective of present work is to synthesize the CdS, FeS and ternary CdFeS thin films by chemical bath deposition method to understand growth mechanism. Further, films will be characterized through XRD and EDAX techniques to know thin film structure and composition in order to make them suitable candidate for various optoelectronic and nanodevice application.

Experimental procedure

Substrate preparation

The microscopic glass substrates of dimensions 75 X 25 X 1.3 mm (Blue Labels Scientific Pvt. Ltd. Mumbai) were cleaned with detergent several times and then boiled in chromic acid (2M) for 30 minutes. Then these substrates were washed with double distilled water and stored in dark desiccators and then used for the deposition.

Deposition of pure CdS film

Pure CdS thin film has been deposited onto well processed glass substrate from a reaction mixture consisting of equimolar cadmium sulphate and thiourea. A 10 ml cadmium sulphate solution was taken in a reaction container and complexed with an appropriate quantity of triethanolamine to obtain a stable Cd-TEA complex. Liquid ammonia and sodium hydroxide were added to adjust pH of the solution. Then 10 ml thiourea was added to reaction mixture. The reaction mixture was kept hot plate at a suitable temperature in which thoroughly cleaned glass substrates were positioned vertically to specially designed substrate holder kept it rotated. For good quality CdS film the various preparative parameters like speed of rotation, deposition time and temperature of bath and pH of the reaction mixture have optimized.

Deposition of pure FeS film

Pure FeS films have been deposited onto glass substrates by taking equimolar solutions of Iron sulphate and thiourea instead of cadmium sulphate. The rest of procedure that followed was as that of in case of pure CdS.

Deposition of $Cd_{0.5}Fe_{0.5}S$ films

For CdFeS composite films the volume stoichiometric quantities of cadmium sulphate and Iron sulphate were added into the reaction container in the ration 1:1. An appropriate quantity of triethenolamine and sodium hydroxide were added to form stable complex. Then liquid ammonia was added into the reaction solution. The rest of the procedure was same as that for the CdS.

Characterization technique

The thickness of CdS FeS and CdFeS thin film was estimated by using the gravimetric weight difference method. The X-ray diffractograms were recorded by using a Philips PW-3710 X-ray diffractometer (XRD) with Cu k_α line (λ = 1.54056A^0) in the 2θ range from 20^0 to 80^0. The compositions of samples were determined by energy dispersive x-ray spectroscopy (EDAX) using JEOL JSM 5600.

Result and Discussion

Film Kinetics:

CdS film Kinetics

The rate of CdS thin film growth is mostly dependent on the rate of release of Cd^{2+} and S^{2-} ions from the complex state which condense on an ion by ion basis on the glass substrate. Generally, the metal chalcogenides MX (where X = S, Se, Te) is formed when the ionic product (IP) of M^{2+} and X^{2-} exceeds its solubility product (SP). The ratio IP/SP=S gives the super saturation of the ions over MX. S can be changed by changing appropriate initial concentrations of the reactants. When S>1, the ions combine on the substrate and in the solution to form MX nuclei which they grow with time to give a film and precipitate. So, the concentration of Cd^{2+} and S^{2-} ions have to be controlled very carefully during the film growth (Norian and Edington 1981). This can be achieved by using a high stability complexant and other parameters such as pH of the reaction mixture, deposition time and temperature and speed of substrate rotation in reaction bath and initial concentrations of ions. The mechanism of film formation can be understood from the following reaction.

$Cd\,[N(CH_2CH_2OH)_3]^{+2}$ + $(NH_2)_2CS$ + $2OH^-$ ---------> CdS + Waste product.

FeS film Kinetics

The formation of FeS film depends on the rate of release of Fe^{2+} and S^{2-} ions from the bound state. The film grew by a nucleation process involving an energetic-atomistic condensation of the ions on the substrate to form FeS nuclei, which then grew in size by adsorbing more and more ions from the reaction bulk. The controlled rate of arrival of Fe^{2+} and S^{2-} ions on the substrate surface from the solution controls the rate of film formation and its growth rate.

$Cd_{0.5}Fe_{0.5}S$ film kinetics

Similarly, the formation of CdFeS film depends on the rate of release of Cd^{2+}, Fe^{2+} and S^{2-} from the bound state. Experimentally, we found that at low temperature there is no film formation. At room temperature most of the ions are in bound complex state and the ionic product of the Cd^{2+} and S^{2-} does not exceed the solubility product CdS. When temperature is increased, more of ions will get free for film formation. At these temperatures, free ions get sufficient time to condense on the substrate surface shows maximum layer thickness. At higher temperature more and more ions will be released. All these released ions will not get chance to adsorb very few of them will adsorb on the substrate surface. The ions which were not adsorbed will settle down at the bottom of the reaction container decreasing the film thickness (Akkad 1989). The average terminal thickness for the different films according to the composition parameter x is listed in table 1. The color of the deposits changed from orange to black as the composition parameter x has increased from 0 to 1.

Effect of preparative parameters

Composition of reaction solution

The film growth can be affected by changing the preparative parameters. The change in bath composition can alter the processes of homogeneous nucleation and heterogeneous nucleation and ultimately the growth of thin films (Berry 1968). The hydroxide species plays an important role in film formation and acts as nucleation centers on the substrates. The proper amount of hydroxy species in bath solution enhances the film growth and gives good quality film. The good quality CdS, FeS and CdFeS thin film is associated with supersaturated bath, cadmium and Iron hydroxide species. If the bath contains low concentration of bath ingredients generally favors the nucleation in early stage. By many more trial and error method, 1 molar concentration has been optimized. It is well known that the bath concentration plays an important role, when bath contains high concentration the films formed were thicker and for low concentration films too thin and non-uniform and non-homogeneous. This indicates that there is lack of required number of ionic species for better quality film. Above certain concentration when rate of reaction becomes high and precipitation also becomes important leading to lesser amount CdS/FeS on the substrate and hence lowers the thickness (Cameron et al., 1979; Dawar et al., 1990)

Role of complexing agent

The deposition of thin film on glass surface is an adsorption phenomenon. Film formation occurs by combination of released metal ions from complex metal ion source and chalcogen source. In the present study trietnanolamine is used as the complexing agent. With the help of triethanolamine complexed metal ion can be made free in alkaline medium of pH value 8 ± 0.1. It helps to limit the hydrolysis of the metal ion and impart some stability to bath otherwise it undergoes rapid hydrolysis and precipitation. If less amount of triethanolamine is used fast precipitation occurs, when excess triethanolamine is used a smaller number of ions are available for film formation, so thinner films formed (Dawar 1990; Croitoru and Jakobson 1979) So, in this case pH of is optimized at 8 ± 0.1for good quality films

XRD analysis

The X-ray diffractograms of 'as-deposited' CdS, FeS and CdFeS films prepared by chemical bath deposition is shown in Fig. (1-3). The presence of large number of peaks indicates that the films are polycrystalline in nature with hexagonal structure [31-37]. The reflection from the (1 0 0), (0 0 2), (1 0 1), (1 1 0) and (1 1 2) are for CdS thin film while (1 0 1) (0 0 2), (2 0 1), (2 0 2), (2 1 2), (2 2 0) and (4 0 2) are for FeS thin film which coincide well with the JCPDS data (#06-0314 and #80-01028). The observed 2θ-values correspond to hexagonal structure. The (h k l) indices are given in the table 1.

The grain size was calculated by using Scherer's equation

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

Where λ is the wavelength of X-ray used, β is the full width at half maximum in radian, and θ is the Bragg's diffraction angle.

The average grain sizes are in the range 18-25 nm and listed in table 1.

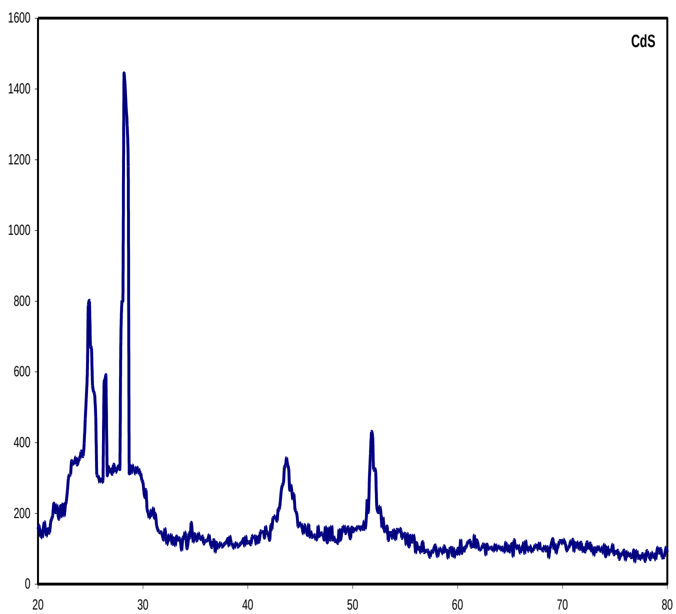

Fig.1: X-ray diffractogram of as deposited CdS thin film

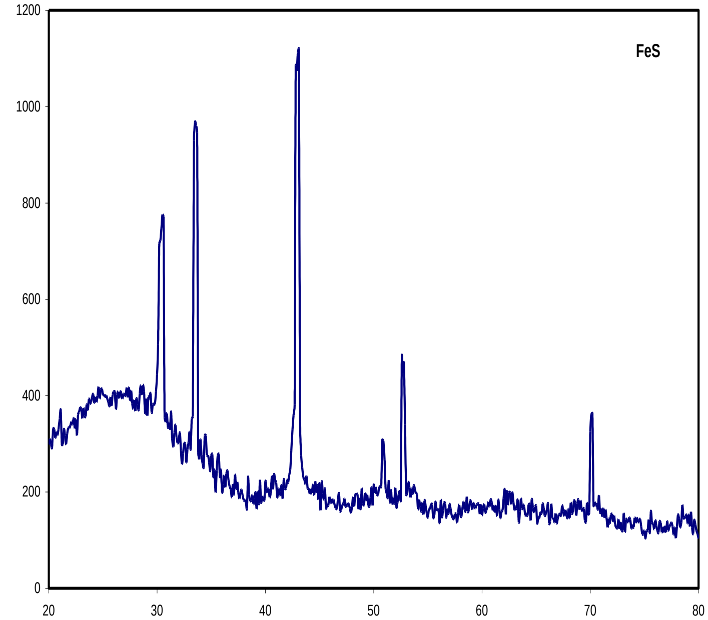

Fig. 2: X-ray diffractogram of as deposited FeS thin film

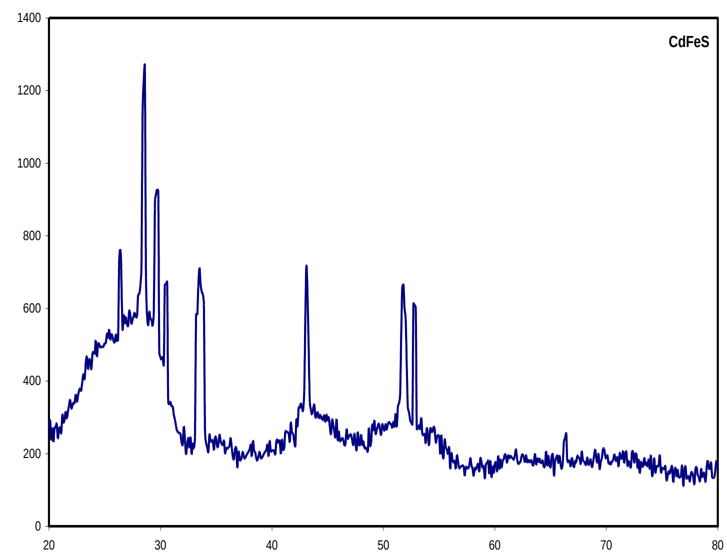

Fig. 3: X-ray diffractogram of as deposited $Cd_{0.5}Fe_{0.5}S$ thin film

Composition	2θ Observed	2θ Standard	hkl planes			Crystallite Size, D (nm)
			CdS (H)	FeS (H)	Oxide / elemental phase	
CdS	24.90	24.828	1 0 0	---	---	21.0
	26.47	26.449	0 0 2	---	---	
	28.22	28.216	1 0 1	---	---	
	43.72	43.735	1 1 0	---	---	
	51.86	51.875	1 1 2	---	---	
CdFeS	26.44	26.449	0 0 2	---	---	24.1
	28.22	28.216	1 0 1	---	---	
	29.74	29.626	---	2 0 0	---	
	30.66	30.678	--	0 0 2	---	
	33.48	33.459	---	2 0 1	---	
	43.74	43.735	1 1 0	---	---	
	51.86	51.875	1 1 2	---	---	
	52.66	52.569	---	2 2 0	---	
	66.52	66.544	---	---	0 0 4 Cd (H)	
X=1	21.18	21.199	---	1 0 1	---	18.3
	30.66	30.678	---	0 0 2	---	
	33.50	33.459	---	2 0 1	---	
	43.18	43.171	---	2 0 2	---	
	50.90	50.856	---	2 1 2	---	
	52.60	52.569	---	2 2 0	---	
	70.20	70.298	---	4 0 2	---	

EDAX analysis

Fig. (4) Shows the EDAX pattern for representative $Cd_{0.5}Fe_{0.5}S$ thin film. The pattern confirms the presence of cadmium, Iron and sulpher. The proportion of these elements measured as Cd = 47.78 %, Fe= 8.20 % and S= 44.02 %. The result indicates that the deposited films are non-stoichiometric in composition. EDAX analysis shows that the films are sulpher deficit and cadmium reach. It may be due to the fact that the reactivity of cadmium is more than sulpher ions (Yufit *et al.*, 2004; Reisner et al., 1990). The deviation in the composition can be adjusted by changing the volume or concentration or both of the individual ion sources in the reaction mixture.

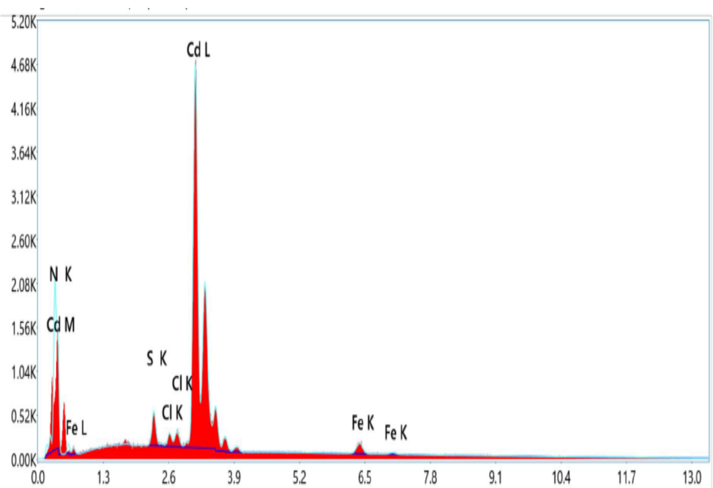

Fig. 4: EDAX pattern of $Cd_{0.5}Fe_{0.5}S$ thin film

Conclusion

From above study it is concluded that thin, uniform and adherent cadmium lead sulphide thin films with different composition parameter $0 \leq x \leq 1$ can be deposited successfully by simple chemical bath deposition technique. The effect of various preparative parameters such as composition of bath, pH of the reaction solution, deposition temperature, and deposition time, speed of substrate rotation and nature of complexing agent on growth process is studied. XRD studies reveal that the 'as deposited' thin films are polycrystalline in nature with hexagonal phases. EDAX spectra confirmed that the films are sulphur deficit.

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