

A study of nano crystalline $Cd_{1-x}Co_xS$ thin composite films deposited by a liquid phase chemical bath deposition

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ABSTRACT

A modified liquid phase chemical bath deposition (LPCBD) process set for its deposition conditions was used to synthesize CdS and $Cd_{1-x}Co_xS$ ternary thin films. The deposition was carried out from a complex liquid phase formed by equimolar volumes of cadmium sulphate, triethanolamine, thiourea and cobalt sulphate. With the appropriate concentration and volume (x) of cobalt sulphate the initial film deposition compositions ($0 \leq x \leq 0.5$) were chosen. The growth kinetics was studied for various deposition time, temperature, resulting bath pH and speed of the substrate rotation and the reaction mechanism is suggested. It has been found that good quality samples (thin, uniform, tightly adherent, smooth, and diffusely reflecting) with colour changing from orange red to dark chocolate are obtained at $56^\circ C$, 80 minutes deposition time, 70 rpm and pH equal to 11. The film thicknesses were measured by an interference technique. The chemical composition of the deposits was determined by an EDS analysis technique and it revealed that the films are Cd-rich. The XRD analysis of the as-grown CdS ($2\theta = 20^\circ - 80^\circ$) showed hexagonal wurtzite structure with a good match of d -values, intensities of reflections and the lattice parameters with the JCPD data. With the introduction of Co^{+2} in the lattice of CdS, the interplanar distances and the lattice parameters (a and c) have been found to be decreased continuously with the increase in x up to a value of $x=0.1$. The ratio c/a is almost constant. The average crystallite size, as-determined using FWHM method, is in the nano-range and increases typically from 11.77 nm to 17.37 nm upto $x=0.1$, then decreases for higher values x . A homogeneous solid solution of the $Cd_{1-x}Co_xS$ type has been observed for these composites up to a value of x equal to 0.1. Spectral studies were performed on these films in the range of wavelengths between 500 nm to 1300 nm. Absorption by the film material is high ($10^4 - 10^5 cm^{-1}$) and the estimated bandgap decreased from 2.42 eV to 1.94 eV as x was varied from 0 to 0.5. Electronic transitions are of the direct type ($m \approx 0.5$).

Keywords: $Cd_{1-x}Co_xS$, EDS, hexagonal wurtzite, solid solution, nano crystalline.

INTRODUCTION

In the recent years, metal chalcogenide thin film materials have been intensively studied [1-5]. Owing to their efficient energy conversion ratio, they are the potential candidates of high performance and low production cost for optoelectronic and energy conversion devices including photo-electrochemical solar cell fabrication [1, 2, 5-8]. One of the main challenges in solar energy research is to search and fabricate a new method that yields high quality thin films at low production cost and should be easily scalable. Attempts were therefore made to deposit a variety of alloyed /mixed metal chalcogenide thin films employing various deposition technologies individually, [1, 2, 5, 9-12] and with a combinatorial approach very recently[13, 14, 26]. The device grade thin films can be usually obtained by chemical bath deposition, electrodeposition, vacuum depositions, spray pyrolysis etc. [1, 2, 9-14]. Deposition using chemical bath in an aqueous medium is more advantageous than other methods[1,2,5,8,10-14,25-27]; because it is the conventional method with the advantages of economy, convenience, ease of scaling up to large area deposition and high degree of direct composition control[1,2,5,8,10-14]. Different working conditions and preparation parameters, (e.g. the sources of metal and chalcogen ions, concentration of metal and chalcogen ions, pH of the resulting solution, deposition time, temperature, etc.) can easily be optimized without use of the sophisticated instrumentation and with almost no consumption of the electrical power [1, 2, 5, 8, 10-14].

Cadmium sulfide and cobalt sulfide have the direct band gaps of 2.42 eV and 1.10 eV, respectively, and high coefficients of optical absorption and excellent stability [15-19, 21]. Therefore, these materials are of extremely importance for efficient use in the optronic devices, especially in solar cell applications [2, 11, 12, 15-20, 24]. In the present work, we have deposited CdS (as a reference) and $Cd_{1-x}Co_xS$ ($0 \leq x \leq 0.5$) thin films using a liquid phase chemical bath deposition (LPCBD) method. The influence of growth conditions, e.g. concentrations of basic precursors, deposition time and temperature, pH of the reaction bath, speed of the mechanical churning, etc on film quality has been examined. Compositional, structural and optical characteristics of these composites have been studied and highlighted.

MATERIALS AND METHODS

Chemicals

The precursor chemicals used were of the analytical grade cadmium sulphate, cobalt sulphate, thiourea, liquid ammonia and triethanolamine. Equimolar volumes of cadmium sulphate, cobalt sulphate and thiourea(in proportion with x value) were taken in a reaction bath and allowed to react in an alkaline medium to produce CdS and $Cd_{1-x}Co_xS$ thin film deposits.

Deposition Method

CdS and $Cd_{1-x}Co_xS$ ($0 \leq x \leq 0.5$) thin films were obtained onto the glass substrates using a liquid phase chemical bath deposition (LPBCD) method set by us[19,21]. For deposition of CdS films; 10 ml (1M) cadmium sulphate solution was taken in a glass beaker 250 ml in capacity. Triethanolamine (TEA) and liquid ammonia were added drop wise to increase the pH of reacting solution. To this 10 ml (1M) thiourea was added. The pH of the final reaction mixture was 11. For deposition of the $Cd_{1-x}Co_xS$ composite films, an appropriate quantity of 1M $CoSO_4$ solution was used. For each of the materials out of this series, the film deposition stoichiometry was

maintained by adjusting the ion concentration volumes of the cadmium sulphate and cobalt sulphate. The end volume of the reaction bath was made 180 ml by adding doubled distilled water. The reaction container was then transferred to a constant temperature oil bath whose temperature was maintained at 56⁰C. Thoroughly cleaned glass substrates of the suitable dimension were mounted on a specially designed substrate holder and were attached to a constant speed gear motor to set them in rotation at 70±2 rpm. The deposition was continued for 80 minutes and the samples were taken off the reaction bath and detached from the substrate holder, washed with double distilled water, dried and then preserved in dark desiccator.

Characterization of the samples

The films so obtained were then characterized through the composition, structure and optical properties to reveal the effects due to the deposition parameters and Co²⁺ concentration. The thicknesses of the as-deposited layers were measured by an interference technique and the film composition was determined by an energy dispersive spectroscopy method. The analysis was carried out using a KEVEX 7000-77 EDS spectrometer at the operating voltage of 20 kV. The X-ray diffraction technique was used to examine the structure of the as-deposited samples. An X-ray diffractometer, Philips PW-3710 with Cu K_α line ($\lambda=1.5406\text{\AA}$) in the 2 θ range from 20⁰ to 80⁰, was used for this purpose. The diffractograms were further analyzed to determine the crystal dimensions and hence the structure. The optical constants such as an absorption coefficient (α), optical gap (E_g) and the type of transition in these films were then determined from the measurement of the optical absorbance spectra. A spectrophotometer, Shimadzu UV-3600 was used for this purpose and the incident wavelength was varied from 500 nm to 1300 nm. The optical absorbance was recorded for each of the wavelengths in steps.

RESULTS AND DISCUSSION

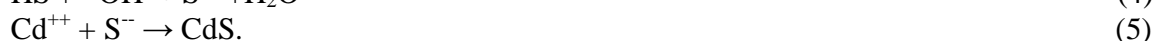
Film formation, reaction kinetics and physical observations

The CdS and (Cd, Co)S thin composite films were obtained from a sufficiently high alkaline medium (pH=11) on glass substrates which were previously degreased in concentrated nitric acid for 24 hours, washed with detergent solution and rinsed with double distilled water and dried ultrasonically[19,21]. The reaction bath for deposition of CdS was composed of 10 ml (1M) CdSO₄, 2 ml TEA, 16 ml ammonia, 10 ml (1M) thiourea and 150 ml double distilled water, which were added chronologically[19, 21]. The effect of ammonia quantity (in ml) on growth of the film was examined. The quantity of ammonia in the bath was varied from 5 ml to 25 ml. For lower ammonia concentration (<14 ml); thick, porous, rough, diffusely reflecting and non sticky films were obtained. Comparatively thin, uniform, smooth, tightly adherent and diffusely reflecting films were obtained in the mid range quantity (14ml to 18ml) of ammonia. An average quantity of ammonia (16 ml) was found to be suitable for good quality deposition. At higher ammonia concentration(>20 ml), physical nature of the samples is more or less the same however layer thickness is found to be decreased further with a faint colour appearance. Effect of ammonia concentration on film growth is shown in fig.1 (a). The quantity of triethanolamine (TEA) was also varied from 0.5 ml to 5 ml and resulting pH of the solution bath was measured. For a good film growth, quantity of TEA optimized was 2 ml. During deposition cations and anions react each other to form neutral molecules, which either precipitate spontaneously or very slowly in high alkaline medium. Fast precipitation implies no film formation on the substrate surface. On the other hand, if the precipitation action is controlled slow (with reaction additives

like TEA or NH₃), then neutral molecules could get sufficient time and chance to stabilize on the substrate surface that initiate the film formation process, which is favored energetically and enhanced by the reaction temperature and speed of the substrate rotation. The reaction steps involved in the chemical deposition of CdS thin films are given below[21];



Where R=H/CH₂CH₂CH₂OH



The Cd⁺⁺ ions are released slowly from the cadmium sulphate-NR₃ complex (where R=H/CH₂CH₂OH) due to hydrolysis while sulfide ions are provided by dissociation of thiourea in alkaline medium. The Cd⁺⁺ and S²⁻ then condense on the surface of the substrate and get deposited as CdS. The formation of CdS occurs when the ionic product of Cd⁺⁺ and S²⁻ exceeds the solubility product under the control of deposition conditions.

The Cd_{1-x}Co_xS thin composite films with various x values (0 ≤ x ≤ 0.5) were obtained by the codeposition of Cd²⁺, Co²⁺, S²⁻ ions from the reaction mixture consisting of triethanolamine complex of cadmium and cobalt ions under the same conditions of deposition. The Cd(TEA) and Co(TEA) complexed ions adsorb on the glass surface offering Co⁺⁺ heterogeneous nucleation phase and growth takes place by ionic exchange and in turn by an ion by ion condensation or by adsorption of the colloidal particles on the substrate surface. The reaction mechanism can be proposed as follows[19, 21,27]:



Where, R=H/CH₂CH₂OH



As far as Cd_{1-x}Co_xS thin composite films are considered, this is our first attempt to deposit these films by employing a liquid phase chemical deposition process set by us [8, 12, 18, 19, 21, 25,27]. The quality deposition results only when a number of preparative parameters (such as temperature, time, pH, speed of the substrate rotation, concentration of basic ingredients, etc) are optimized. Therefore, in this preliminary work, the film growth was examined as a function of few of the deposition parameters [19,21,27]. The deposition temperature was therefore varied from 40°C to 70°C and the terminal layer thickness was measured. While doing this, the other parameters such as time (80 mins), pH (≈11) and speed (≈70 rpm) were kept constant at their pre-determined values. It is observed that the terminal layer thickness increased almost linearly with increase in the deposition temperature, maximize at around 56°C and then decreased for

higher deposition temperatures. This is shown in fig.1 (b). It has been seen that deposition of CdS and $Cd_{1-x}Co_xS$ films at low temperature (≤ 40 °C) is much delayed and the rate of deposition is found to enhance significantly as the deposition temperature was increased. At the increasing deposition temperature up to 56 °C, thermal energy releases the Cd^{2+} , Co^{2+} and S^{2-} ions from the bound complex state at an increasing rate and more and more ions are made free to condense on the surface of the glass substrate increasing the layer thickness. At 56°C, excellent quality film layers exhibiting uniformity, tight adherency, spectral reflectivity and maximal thickness were obtained. This can be explained as usual. Above this deposition temperature Cd^{+2} , Co^{+2} and S^{2-} ions are released at a relatively faster rate, the rate of reaction now shift towards the precipitation and consequently layer thickness decreased. Fig.1(c) shows time dependence of the film growth. The time of the film growth was varied from 30 minutes to 100 minutes and the terminal layer thickness was measured. The temperature of the reaction bath (56°C), pH (≈ 11), and the speed of the substrate rotation (70 ± 2 rpm) were kept constant. The layer thickness was then measured and is plotted against time as shown in fig1(c). It is seen that the film growth rate is time dependent and is initially linear and then it becomes quasi-linear; the reason being that, at smaller deposition times, number of available species of Cd^{2+} , Co^{2+} and S^{2-} ions condensing on the substrate surface are very large contributing to the higher growth rate whereas at higher deposition durations, the number of Cd^{2+} , Co^{2+} and S^{2-} ions species went on continuously depleting from the reaction bulk that causes layer thickness to saturate. A deposition time of 80 minutes was therefore found to be suitable at our experimental conditions.

The effects due to pH of the reaction mixture and speed of the substrate rotation (rate of mechanical churning) on film growth were also studied. The resulting pH of the reaction mixture was varied from 8 to 12 by adding ammonia solution appropriately. The terminal layer thickness was measured and its variation with pH is shown in fig.1 (d). It appeared that at low pH values (< 10), the layer thickness increased almost linearly with pH value. The films were thick, porous, non-reflecting and weakly adhered to the substrate. At the intermediate pH values ($10 \leq pH \leq 11.5$), the films are uniform, smooth, nonporous, reflecting and tightly adherent to the substrate support. The variation of the film thickness with pH value in this region seems to be quasi-linear. We attribute the constancy of layer thickness in this region to the controlled rate of release of ions species. At still higher pH values ($11 \leq pH \leq 12.5$), layer thickness decreased considerably. Films are more or less similar to that obtained from the mid-range pH values however layer thickness is decreased significantly. A pH value of 11 was selected for good growth of the films. The speed of the substrate rotation was also optimized to 70 ± 2 rpm. At low speeds (≤ 50 rpm) thick, porous and less adherent films were obtained. On the other hand at higher speeds (> 80 rpm), very thin, smooth, tightly adherent and reflecting films were obtained. Therefore, a moderate speed of the substrate rotation (70 rpm) was selected for the deposition. The speed-thickness variation is shown in fig.1 (e). The film thicknesses of the various $Cd_{1-x}Co_xS$ composites were measured. It is found that the film thickness increased initially with increasing Co content up to 0.2 and thereafter decreased with further increase of Co concentrations in CdS. This behavior can be understood first, from role of the cobalt atom as a nucleation centre that enhances the growth process and therefore the thickness. Secondly at higher concentrations (> 0.2), cobalt may occupy interstitial sites causing an impurity scattering and thereby preventing the further film growth. The variation of film thickness with Co^{+2} concentration is shown in fig.1 (f).

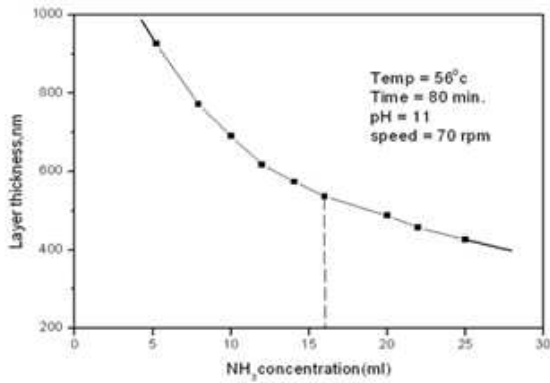


Fig.1 (a).Variation in Cd $_{1-x}Co_xS$ layer thickness with ammonia concentration

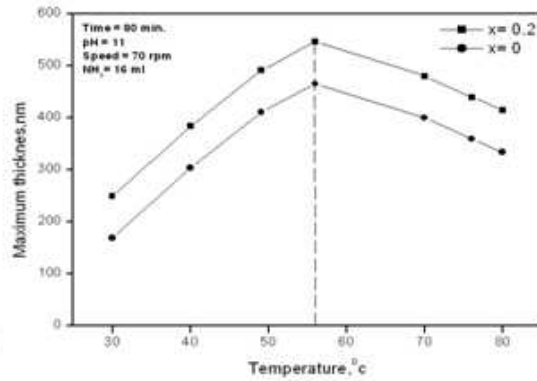


Fig.1 (b).Variation in Cd $_{1-x}Co_xS$ layer thickness with deposition temperature for $x=0$ and $x=0.2$.

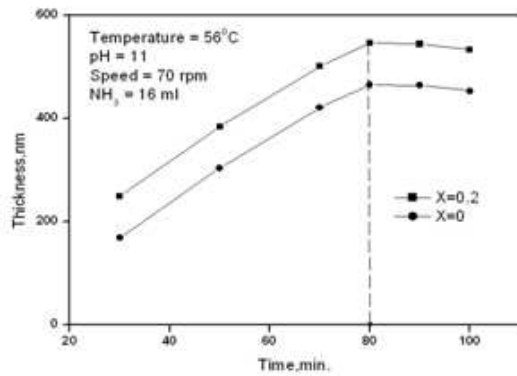


Fig.1(c). Variation in Cd $_{1-x}Co_xS$ layer thickness with deposition Time for $x=0$ and $x=0.2$.

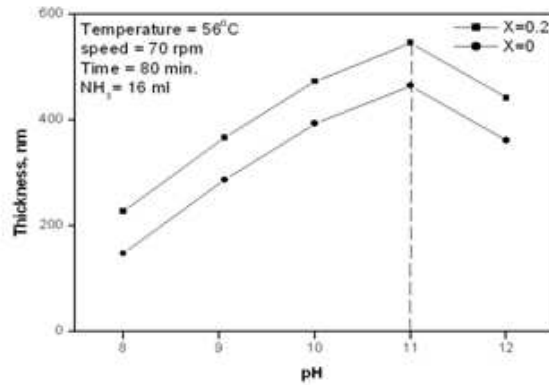


Fig.1(d). Variation in Cd $_{1-x}Co_xS$ layer thickness with pH for $x=0$ and $x=0.2$.

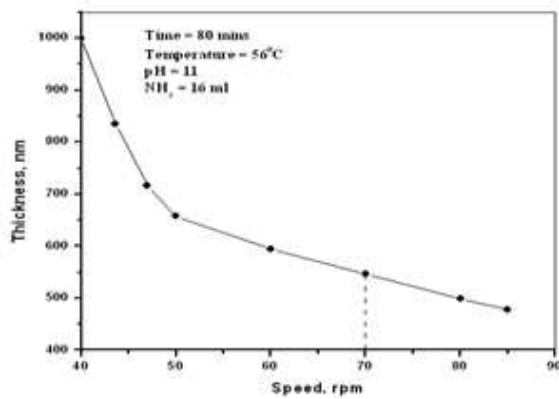


Fig.1(e). Variation in Cd $_{1-x}Co_xS$ layer thickness with rpm $x=0.2$.

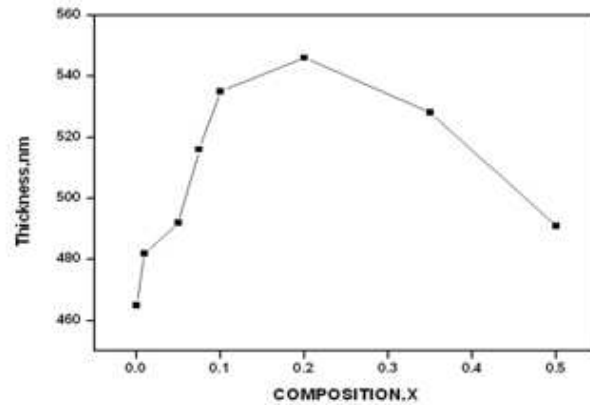


Fig.1(f).Variation of film thickness with composition x .

The as-grown CdS thin films were orange red in colour. When the Co^{2+} content is increased from 0 to 0.5 there is a change in colour from orange red to dark chocolate. The change in colour may be the indication of substitution of Co in the host CdS lattice. The compositional studies may strengthen these observations.

Compositional analysis

The as-grown samples were analyzed by an energy dispersive spectroscopy (EDS) technique. The contents of Cd^{2+} , Co^{2+} and S^{2-} in CdS and $\text{Cd}_{1-x}\text{Co}_x\text{S}$ film structures were determined and are listed in table-I. It appears that the composites are Cd rich and Co^{2+} replaces Cd^{2+} from the lattice. A marginal S-replacement is also noticed[21].

TABLE NO. I: Chemical composition and the optical m values for the various $\text{Cd}_{1-x}\text{Co}_x\text{S}$ thin composite films ($0 \leq x \leq 0.5$)

| Composition, (x) | Cd AT% | Co AT% | S AT% | m |
|---------------------|-----------|-----------|----------|------|
| 0 | 55.13 | ----- | 44.87 | 0.56 |
| 0.01 | 54.40 | 0.65 | 44.95 | 0.54 |
| 0.05 | 53.98 | 1.12 | 44.90 | 0.50 |
| 0.075 | 53.71 | 1.35 | 44.94 | 0.48 |
| 0.1 | 52.73 | 1.46 | 45.81 | 0.48 |
| 0.2 | 52.20 | 3.23 | 44.57 | 0.49 |
| 0.35 | 49.74 | 6.91 | 43.35 | 0.48 |
| 0.5 | 44.96 | 10.72 | 44.32 | 0.50 |

XRD studies

The structure of these composite films was then investigated using XRD analysis. The X-ray diffractograms were obtained on the as-grown CdS and $\text{Cd}_{1-x}\text{Co}_x\text{S}$ samples in the 2θ range from 20° to 80° ($\lambda=1.5406 \text{ \AA}$). These are shown in fig.2 for six representative film compositions. The analysis of diffractograms clearly showed that the as-deposited films are polycrystals of CdS, $\text{Cd}_{1-x}\text{Co}_x\text{S}$ and CoS depending upon the range of the film composition, x . It has been further revealed that as-deposited CdS exhibited hexagonal wurtzite structure [22,23]. There are four dominant reflections at the d values equal to 3.353 \AA , 2.962 \AA , 2.070 \AA , and 1.765 \AA those correspond to the (002), (101), (110) and (112) reflections, respectively. Further the above major peaks shift towards higher 2θ side and the shift is continuous (d -decreased) up to $x=0.1$. Above $x=0.1$, d -values change randomly and irregularly but tend to the original values of the host material. This indicated that both CdS and $\text{Cd}_{1-x}\text{Co}_x\text{S}$ films are hexagonal wurtzite in structure[21,22]. As far as intensities of reflections (I/I_{max}) for these peaks are considered, the reflected intensity (I/I_{max}) for the (101) strongest diffraction peak is 100 and is constant throughout the range studied. The reflected intensities for (002), (110), and (112) planes increase with x up to 0.1 and remained more or less constant (around their JCPD values) for higher values of x . The separate phases of CoS have also been detected at higher values of x . With the incorporation of Co in the lattice of CdS, the lattice parameters a and c decreased with increasing concentration of Co up to $x=0.1$. Typically a decreased from 4.132 \AA to 4.110 \AA and c from 6.707 \AA to 6.658 \AA . For higher values of x , changes in a and c are unsystematic. The values of the lattice parameters a and c are presented in table-II. The changes in a and c can be correlated to the ionic radii of Cd (0.148 nm) and Co (0.058 nm) [9,21]. The ratio c/a is almost constant in the range of interest. Thus incorporation of Co in CdS lattice caused changes in interplanar

distances (d), intensities of reflections (I/I_{\max}) and the lattice parameters a and c up to a value of x equal to 0.1. These results coupled with continuous change in the energy band gap showed that there is a formation of homogeneous solid solution of the $\text{Cd}_{1-x}\text{Co}_x\text{S}$ kind up to a value of x equal to 0.1. For higher values of x i.e., $x > 0.1$ separate phase formation of CdS and CoS occurred²¹. The average crystallite size (\bar{D}) was then determined for all the composite structures using Scherrer formula. It is found that the average crystallite size for CdS is 11.77 nm. The crystallite size increased upto $x=0.1$ (17.37 nm), then decreases for higher values x.

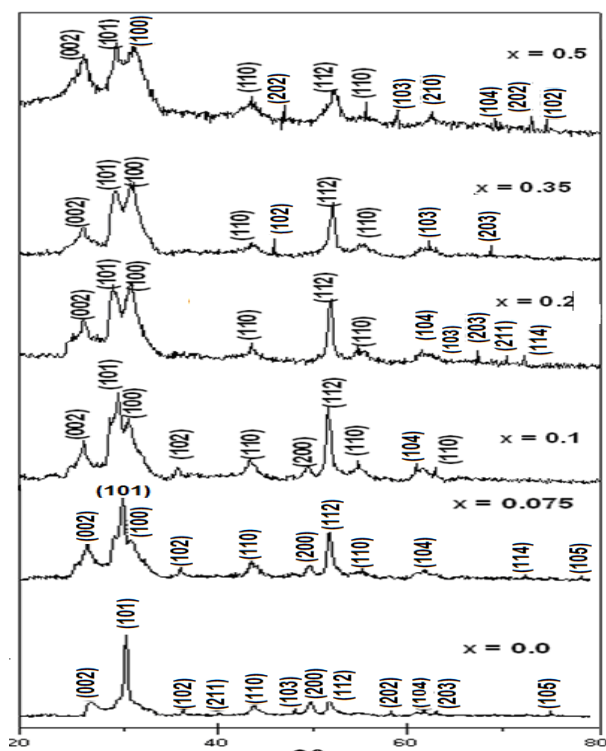


Fig.2.The X-ray diffractograms of the various $\text{Cd}_{1-x}\text{Co}_x\text{S}$ thin composite films ($0 \leq x \leq 0.5$).

TABLE NO. II: Lattice parameters for CdS and $\text{Cd}_{1-x}\text{Co}_x\text{S}$ thin composite films.

| Composition x | Lattice parameters CdS (Hex) | | | Lattice parameters CoS(Hex) | | |
|------------------|---------------------------------|-------------------|-------|--------------------------------|-------------------|-------|
| | a(\AA) | c(\AA) | c/a | a(\AA) | c(\AA) | c/a |
| 0 | 4.132 | 6.707 | 1.664 | ----- | ----- | ----- |
| 0.01 | 4.130 | 6.679 | 1.657 | ----- | ----- | ----- |
| 0.05 | 4.116 | 6.663 | 1.659 | ----- | ----- | ----- |
| 0.075 | 4.111 | 6.659 | 1.660 | ----- | ----- | ----- |
| 0.1 | 4.110 | 6.658 | 1.660 | ----- | ----- | ----- |
| 0.2 | 4.034 | 6.715 | 1.664 | ----- | ----- | ----- |
| 0.35 | 4.006 | 6.683 | 1.668 | 3.389 | 5.118 | 1.510 |
| 0.5 | 3.983 | 6.657 | 1.672 | 3.267 | 5.220 | 1.598 |
| JCPD | 4.136 | 6.713 | 1.623 | 3.370 | 5.140 | 1.525 |

Optical studies

The optical absorption spectra in the wavelength range from 500 nm to 1300 nm were obtained for these films and studied to evaluate the absorption coefficient (α), optical gap (E_g) and the nature of the optical transitions. The energy gaps (E_g 's) were then determined for all the film structures from the variation of $(\alpha h\nu)^2$ vs $h\nu$. The variation of E_g with composition x is shown in fig.3 It is found that E_g decreased continuously, typically from 2.42 eV to 1.94 eV, as Co content in the film was increased from 0 to 0.5. The decrease in optical band gap with Co content can be explained with sp-d exchange interaction between the band electrons in CdS and localized d electrons of Co^{2+} [9,21,24]. The nature of optical transitions was also revealed by plotting $\ln(\alpha h\nu)$ vs $\ln(\alpha h\nu - E_g)$ variations. The plots exhibited linear variation whose slopes are nearly 0.5 (listed in table-I) indicating direct type of transitions. Further $(\alpha h\nu)^2$ vs. $h\nu$ plots show straight line behavior (not shown) at the higher energies. This also supports the fact that band to band direct type of transitions are involved in these films [8, 19, 21,27].

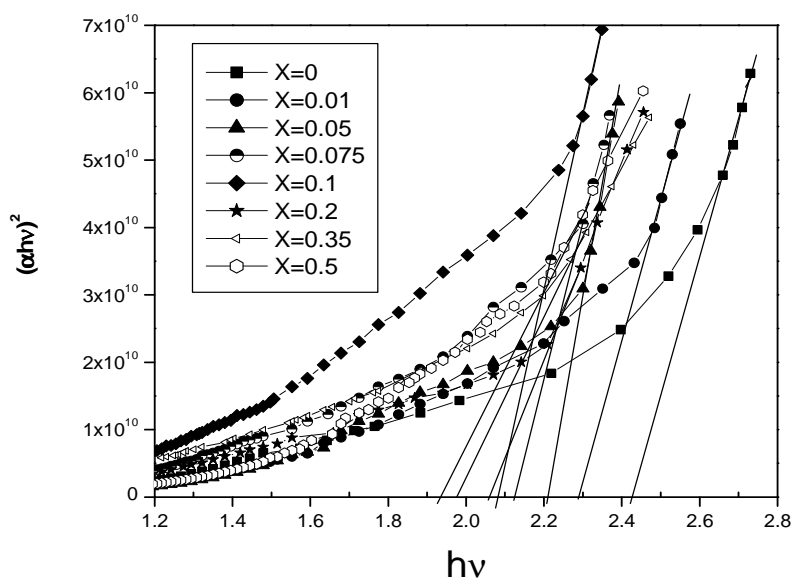


Fig.3. Variation of $(\alpha h\nu)^2$ versus $h\nu$ for the various $\text{Cd}_{1-x}\text{Co}_x\text{S}$ thin composite films ($0 \leq x \leq 0.5$).

CONCLUSION

The synthesis and characterization of CdS and $\text{Cd}_{1-x}\text{Co}_x\text{S}$ thin films deposited on glass substrates by a liquid phase chemical bath deposition technique have been carried out. The film growth is found to depend on the ammonia concentration, deposition temperature, time, substrate rotation and pH of the reaction bath. As deposited samples are thin, uniform, tightly adherent and diffusely reflecting with colour changing from orange red to dark chocolate as x changes from 0 to 0.5. XRD studies showed films to be polycrystalline hexagonal wurtzite with a strong (101) preferred orientation. The EDS analysis indicated that the deposits are Cd rich. The $\text{Cd}_{1-x}\text{Co}_x\text{S}$ thin films are highly absorptive ($\alpha=10^4$ - 10^5cm^{-1}) and the optical band gap E_g decreased from 2.42 eV to 1.94 eV with increasing Co content from $x=0$ to $x=0.5$.

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