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OPTICAL AND MICROSTRUCTURAL PROPERTIES OF CHEMICALLY DEPOSITED MERCURY CADMIUM SULPHIDE THIN FILMS

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1. Introduction

The II – VI semiconductor compounds, especially the cadmium chalcogenides, are of technically and potentially important class of materials and have been extensively studied owing to the fact that their physical and materials characteristics can be altered to cope up with the desired application potential. In the real sense, they are the materials of only the applied interest and possess key role in the optoelectronic and electro-optic devices such as photoelectric, photovoltaic and photoconductive cells [1–10]. In addition Cd-rich compounds have been reported to be reasonably efficient in photovoltaic solar cell applications [6, 7, 10–12] and in an effect to do so mercury can be incorporated into Cd-based chalcogenides to reduce the materials band gap and enhance the electrical conductivity significantly [12–15]. Both CdS and HgS exhibit similar crystallographic features and therefore there is a scope for engineering of their properties to the desirable limits. In an attempt to achieve the above goals, we tried to deposit CdS and $Cd_{1-x}Hg_xS$ thin films using our idegeneously developed chemical deposition process [7, 11, 13–16]. The working parameter, x, was varied in the limit $0 \leq x \leq 0.25$. The growth mechanism, reaction kinetics and few of the spectro-optical characteristics of series of materials have been examined.

2. Experimental

2.1. Synthesis of the $Hg_xCd_{1-x}S$ thin films

$Hg_xCd_{1-x}S$ thin films of varying composition ($0 \leq x \leq 0.25$) were deposited onto the optically plane glasses by a chemical deposition process [7, 11, 13–18]. Equimolar solutions of cadmium sulphate, mercury chloride and thiourea were mixed into their stoichiometric proportion to obtain x from 0 to 0.25. Initially, aqueous solutions of Cd^{2+} and Hg^{2+} ions were mixed together in a glass beaker 250 ml in capacity and complexed with sufficient quantities of ammonia and triethanolamine. The sulphur ion source (thiourea) was provided at a constant rate from outside. The chemo mechanically and ultrasonically cleaned glass substrates were assembled on a specially designed substrate holder and were rotated in reaction container with a constant speed of 72 ± 2 rpm. Thus a constant, automatic, and uniform mechanical stirring of the reaction mixture was made feasible. The deposition was carried out at a pH value of 10.8 ± 0.2. The deposition temperature was optimized as 60 ^{0}C .

2.2. The techniques of characterization

The layer thicknesses of various samples were measured using an interference technique. The optical absorption spectra for these samples were recorded in the 300–1000 nm wavelength range. A spectronic 20-D spectrophotometer was used for this purpose. The surface morphology was observed through a scanning electron microscope, stereoscan 250 MK III, (Cambridge, Instruments, UK). The X-ray diffractograms were obtained to determine the crystal structure of the as-deposited films. The range of 2θ values was from 10^o to 80^o (CuKα = 1.5406 Å).

3. Results and discussion

3.1. Kinetic studies

The thin film layers of CdS and $Hg_xCd_{1-x}S$ were deposited in an aqueous alkaline medium having pH value 10.8 ± 0.2. The substrates used were spectroscopic grade glass microslides. First, the CdS films were synthesized as follows: 10 ml (1M) $CdSO_4$ solution was taken in a 250 ml beaker and a sufficient quantity of hydrolyzed ammonia and triethanolamine solutions were added to it to form a complex. The temperature of the reaction mixture was then raised to 60^o C. The glass substrates mounted on a specially designed substrate holder were kept rotating with a constant 72 ± 2 rpm speed in the reaction vessel containing the complex compound. A special arrangement was made for simultaneous addition of 10 ml (1M) thiourea into the bath during deposition. The period of deposition was 90 mins. The films were then detached from the system and

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washed with double distilled water, dried and preserved in dark desiccator. The synthesis of $Hg_xCd_{1-x}S$ ($0 \le x \le 0.25$) films was done as follows [17, 18]: The appropriate volumes of $CdSO_4$ and $HgCl_2$, each 1M, were taken in a reaction bath and triethanolamine was added to form a complex compound containing Cd^{2+} and Hg^{2+} ions. To this, ammonia was added to enhance the film adherence. The sulphur source was provided at a constant rate of 0.8 ml / 5 min. Triethanolamine controls the rates of reaction of Cd^{2+}, $Hg^{2+}$and S^{-2} ions to be settled on the substrate surface. The solubility products of metal sulphides are very small and are: K_{sp} (CdS) = 10^{-27} and K_{sp} (HgS) = 10^{-52} . The over all reactions can be formulated as [17, 18]:

$$H_2N\text{-}CS\text{-}NH_2 + OH^- \rightarrow H_2N\text{-}CO\text{-}NH_2 + SH^- \quad (1)$$

$$SH^- + OH^- \rightarrow H_2O + S^{2-} \quad (2)$$

$$CdSO_4 + (CH_2CH_2OH)_3N + OH^- \rightarrow [Cd(CH_2CH_2O)_3N]^{2+} + H_2SO_4 + H_2O \quad (3)$$

$$[Cd(CH_2CH_2O)_3N]^{2+} + S^{2-} + H_2O \rightarrow CdS + (CH_2CH_2OH)_3N \quad (4)$$

$$HgCl_2 + (CH_2CH_2OH)_3N + OH^- \rightarrow [Hg(CH_2CH_2O)_3N]^{2+} + 2HCl + H_2O \quad (5)$$

$$[Hg(CH_2CH_2O)_3N]^{2+} + S^{2-} + H_2O \rightarrow HgS + (CH_2CH_2OH)_3N \quad (6)$$

$$[Cd(CH_2CH_2O)_3N]^{2+} + [Hg(CH_2CH_2O)_3N]^{2+} + 2S^{2-} + H_2O \rightarrow CdHgS + 2\,(CH_2CH_2OH)_3N. \quad (7)$$

The growth of CdS and $Hg_x\,Cd_{1-x}\,S$ films on glass strip surface has been studied as a function of the deposition temperature and time. The growth rate is dependent on the deposition time and is shown in figure 1,*a*. It is seen that initially the films grew almost linearly and tend toward saturation for longer durations. The time dependence of growth could be justified from the following facts. Initially, at shorter deposition times, the number of ions present in the solution, which deposited onto the substrate surface, is large and they have free access to condense on the substrate surface. As the time passes the solution bulk becomes depleted of the ions that decreased the further growth rate. For longer deposition time the solution bulk still becomes depleted of the ions reducing the growth rate to a practically zero value [17, 18].

The temperature dependent growth is shown in figure 1,*b*. It is seen that at low temperature the growth is very slow and the growth rate increases almost linearly with increasing temperature (up to a moderate temperature, typically 60 ^{0}C). Beyond 60 ^{0}C, precipitation results at a faster rate causing decrease in layer thickness. The best conditions for the deposition process for yielding quality deposits are: temperature 60 ^{0}C and growth time 90 mins [17, 18].

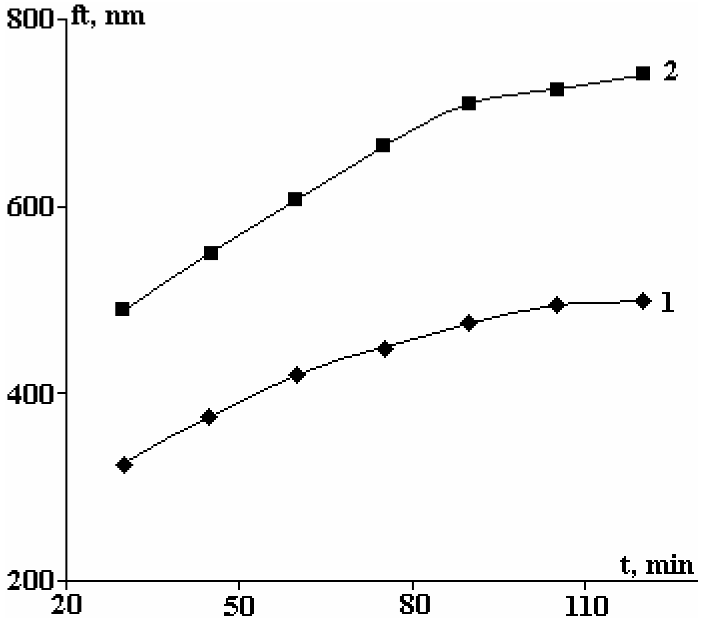


Fig. 1,a. Variation of film thickness with deposition time. 1 – x = 0,01; 2 – x= 0. Conc = 1M; Speed = 72 rpm; Temp = 60 °C; pH = 10.8±0.2

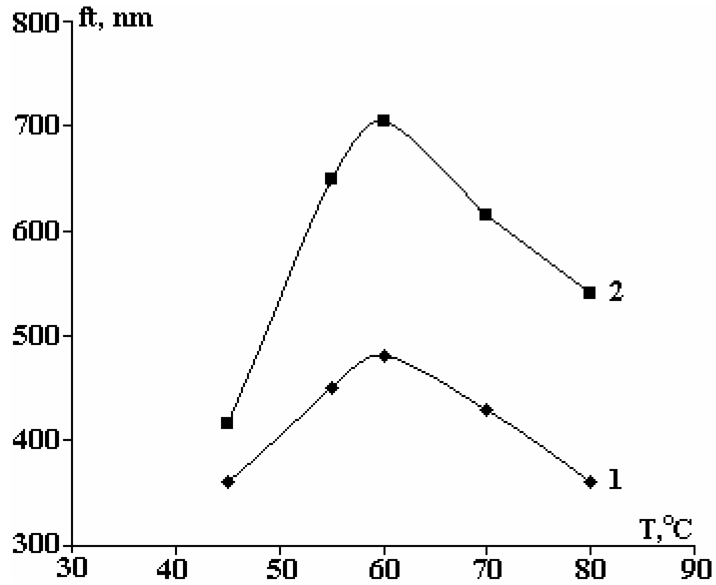


Fig. 1,b. Variation of film thickness with deposition temperature. 1 – x = 0,01; 2 – x= 0. Conc = 1M; Speed = 72 rpm; Time = 90 min; pH = 10.8±0.2

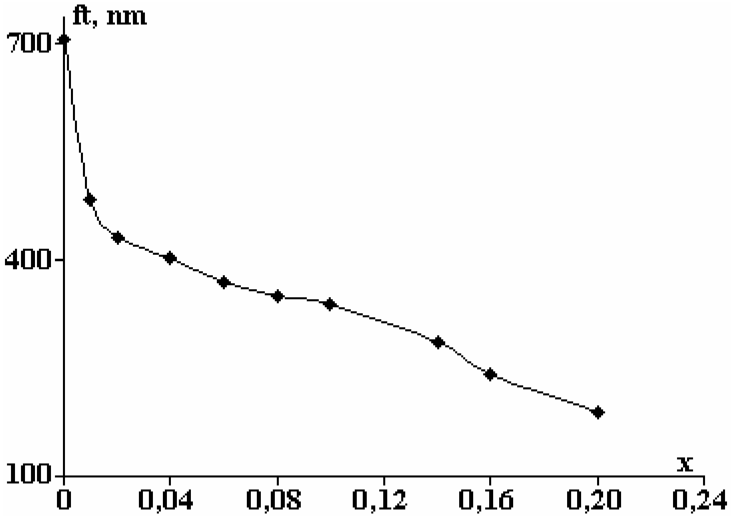


Fig. 1,c. Composition dependence o film thickness

As one of the physical parameters, the effect of film composition (*x*) on the film thickness was also studied. It is found to be decreased with x as shown in figure 1,*c*. The as-grown films were tightly adherent to the substrate support, relatively uniform and smooth, and diffusely reflecting with colour changing from yellowish red to pale yellow and finally yellowish black as *x* was changed from 0 to 0.25.

The X-ray diffractograms (figure 2) of these samples were obtained within the range of 2θ angles between 10^0 to 80^0 (CuK_α radiation) to obtain the structural informations. The peaks were identified by comparing interplanar distance (d) and relative intensities (I / I_{max}) obtained from the XRD patterns with the standard JCPD data. The diffractograms showed that the as-deposited films are polycrystalline in nature over the $0 \leq x \leq 0.25$ range and both CdS and HgS exhibited hexagonal wurtzite structure [19, 20]. The dominant reflections, (101) and (002), shifted towards lower 2θ side with increasing *d* values from 3.046 to 3.076 Å for (101) plane and $3.347A^0$ to 3.376 Å for (002) plane, respectively, for the change of x value from 0 to 0.08. It has also been observed that the intensities of reflections for (101) and (002) reflections increased continuously up to a value of *x* equal to 0.08. The changes in the intensities of reflections and d values suggest that the crystallite size has been enhanced after incorporation of Hg in the lattice of CdS. It is also surprising to note that the intensities of reflections and corresponding *d* values for the (112) reflection remained more or less the same (showing no appreciable change) for all the x values of $Hg_xCd_{1-x}S$ composites. The calculation of lattice parameters *a* and *c* shows variation with x. The average crystallite size of the composites were determined using FWHM method. The crystallite size seems to be varied from 13.4 to 18 nm. The detailed investigation is under way.

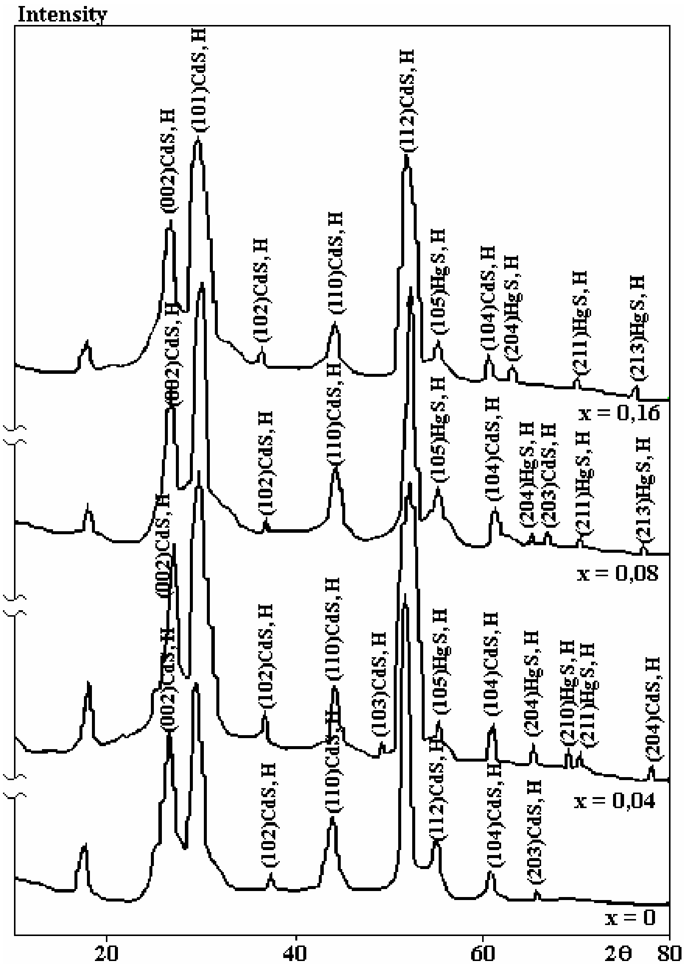


Fig. 2. X-ray diffractrograms for x = 0, 0.04, 0.08 and 0.16

3.2. The optical absorption studies

The optical absorption spectra of the various HgCdS thin films, corrected for glass substrate absorption, were therefore obtained in the range of wavelengths from 300 to 1000 nm for seven representative samples (figure 3,*a*). The spectra were analyzed to evaluate the absorption coefficient (α), optical gap (E_g), and nature of the transitions. The spectra clearly indicated two regions; one for higher wavelengths with practically negligible absorption and other for lower wavelengths that correspond to the maximum absorption. It is found that the absorption coefficient of the pure CdS and CdHgS samples is high; of the order of $10^4 cm^{-1}$. For direct transitions, the absorption coefficient (α) and the photon energy (hν) are related as [17, 21–22]:

$$\alpha h\nu = A(h\nu - E_g)^{1/2}. \tag{8}$$

Thus a plot of $(\alpha\ h\nu)^2$ vs hν should be a straight line whose intercept on the energy axis gives the energy gap, E_g [21, 22]. Figure 3,*b* shows the variation of $(\alpha h\nu)^2$ vs hν for seven film compositions. The straight-line nature of the plots indicates direct type of transitions. The optical gaps were then estimated for all the samples from the extrapolation of the linear regions and are plotted against the Hg concentration as shown in figure 3,*c*. A decrease in band gap, typically from 2.42 to 1.75 eV with increase in Hg concentration from zero to 0.25 mol. % has been observed. The decrease in band gap can be ascribed to the excess Hg that makes the donor levels degenerate and merge into the conduction band of CdS [17]. The transitions are of the direct type.

3.3. Microscopic studies (SEM)

The surface morphologies of the CdS and $Hg_x\ Cd_{1-x}\ S$ thin films were observed through a scanning electron microscope. Figure 4 (*a-h*) shows SEM micrographs of eight representative samples. The micrograph of pure CdS (figure 4,*a*) shows randomly oriented CdS crystallites having leaf-like appearance with sharp and clear edges. This picture becomes more clear for Hg incorporated CdS samples wherein the leafy appearance has been changed to crystallites of the same appearance with some sort of dips or valleys inside (figure 4,*b*). For further addition of Hg in CdS (figure 4 (*c-f*)), the crystallites tend to crystallize in different definite irregular shapes with bit reduced size and fine boundaries. It has also been seen that the morphologies for x = 0.08 and x = 0.1 are little bit coarser than others. At still higher concentration of Hg in CdS (figures *g* and *h*), the micrographs show their interesting appearance. The big crystallites recrystallize into small crystals of more or less same sizes and shapes. Compared to all other micrographs, the micrograph for x =0.2 shows crystallites of more or less same type and orientation. It is difficult to determine the crystallite size both for CdS and CdHgS structures as the crystallites are irregular in shape.

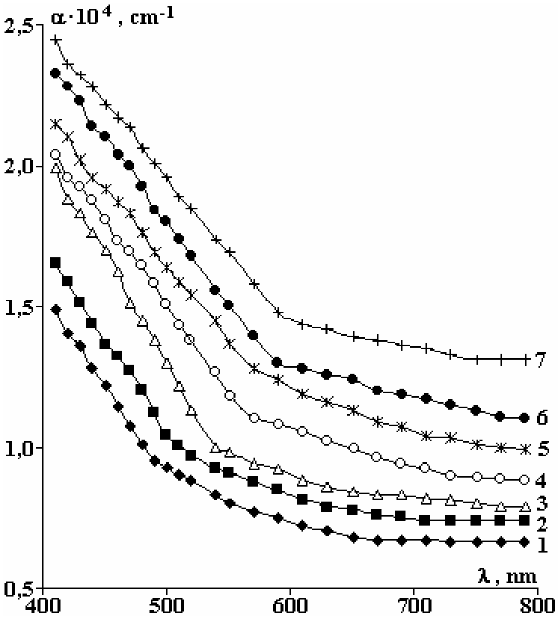


Fig. 3,a. Variation of absorption coefficient vs wavelength for seven representative film compositions. 1 – x = 0; 2 – x = 0,01; 3 – x = 0,04; 4 – x = 0,06; 5 – x = 0,1; 6 – x = 0,16; 7 – x = 0,2

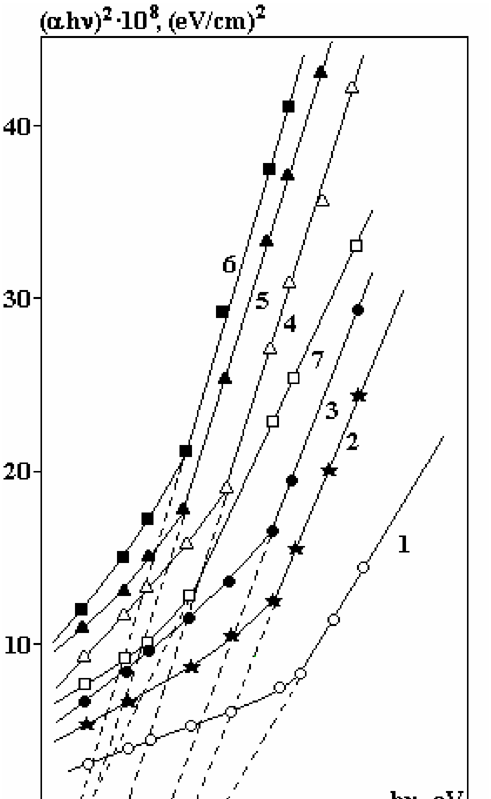


Fig. 3,b. Variation of $(\alpha h\nu)^2$ vs hν for seven film compositions. 1 – 2,42 (x = 0); 2 – 2,28 (x = 0,01); 3 – 2,17 (x = 0,02); 4 – 1,98 (x = 0,06); 5 – 1,81 (x = 0,08); 6 – 1,75 (x = 0,10); 7 – 1,80 (x = 0,16)

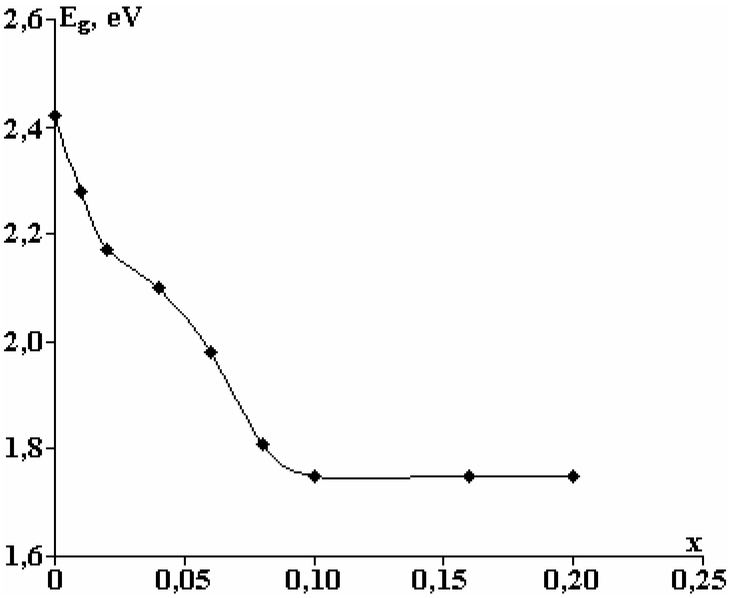
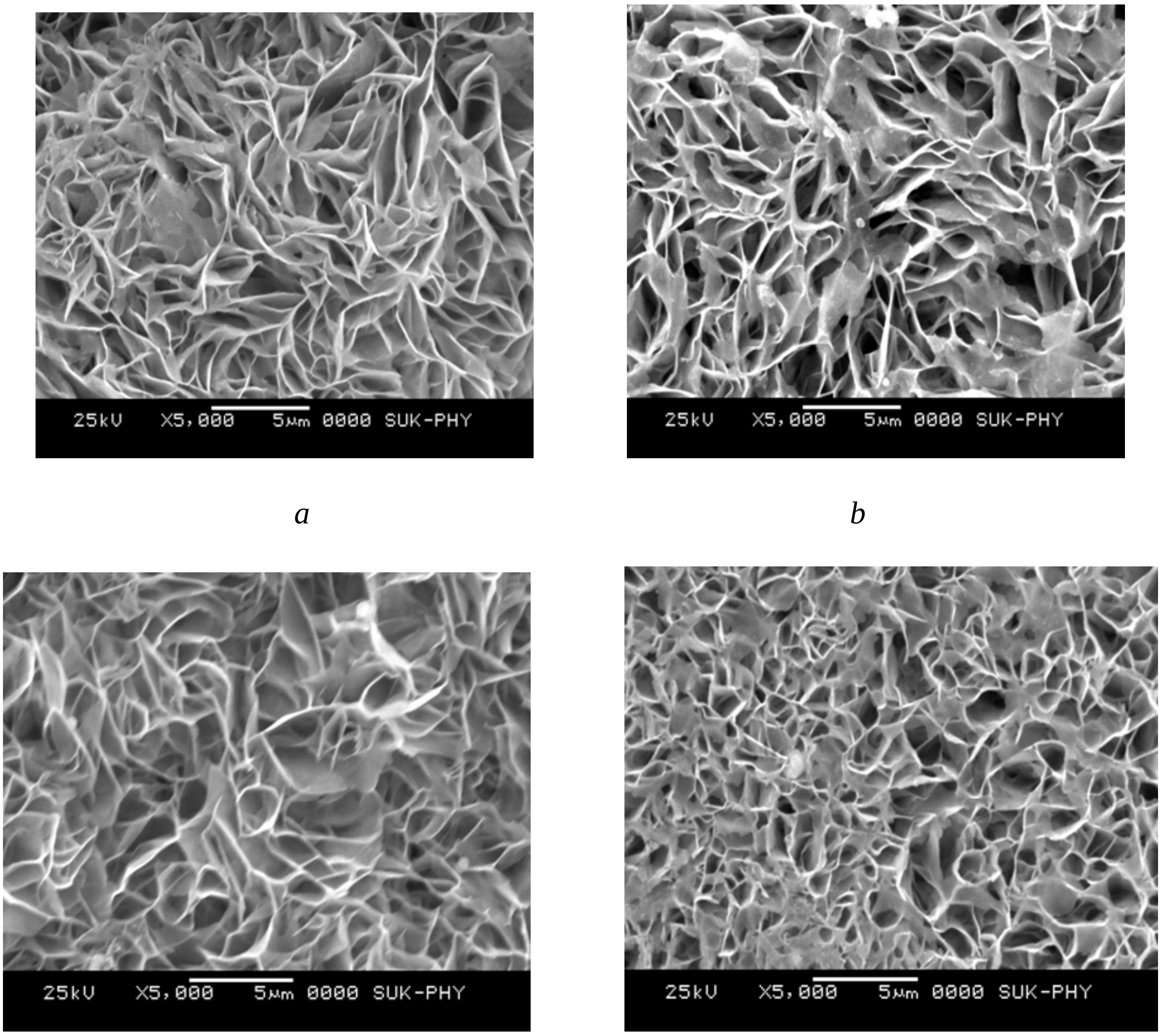


Fig. 3,c. Variation of the band gap with film composition



a *b*

c *d*

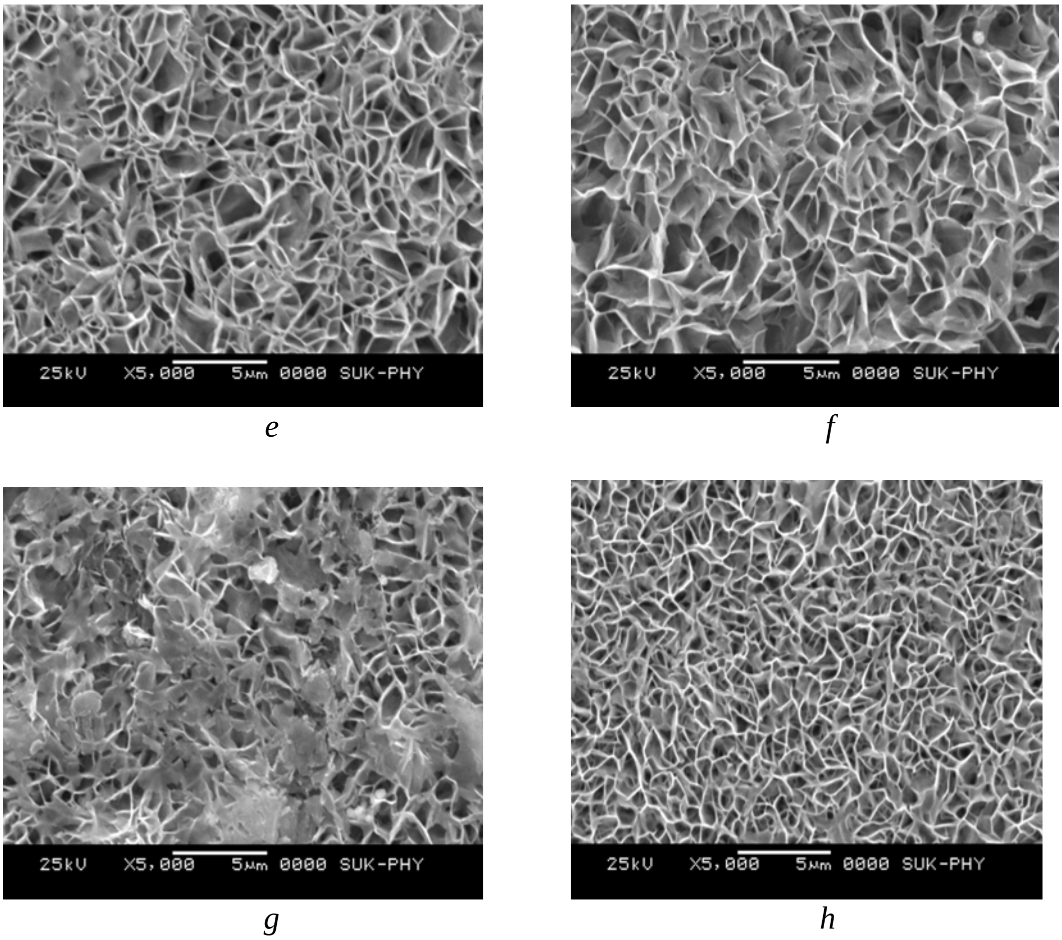


Fig. 4. Surface morphological studies for eight representative films: a) x = 0, b) x = 0.02, c) x = 0.04, d) x = 0.06, e) x = 0.08, f) x = 0.1, g) x =0.14 and h) x = 0.2

4. Conclusions

1. The chemical bath deposition technique is successfully employed to obtain thin semiconductor films of controlled composition and characteristics.

2. The best conditions for yielding quality deposits are: 60 ^{0}C deposition temperature, 90 mins deposition time, and a reaction pH of 10.8 ± 0.2.

3. The as-grown films were tightly adherent to the substrate support, relatively uniform smooth, and diffusely reflecting with colour changing from yellowish red through pale yellow and finally yellowish lead gray.

4. Both CdS and $Hg_xCd_{1-x}S$ deposits are hexagonal wrutzite with d and I/I_{max} values in close consonance with that of the JCPD values.

5. A decrease in band gap, typically from 2.42 to 1.75 eV, with increase in Hg concentration from zero to 0.25 mol. % has been observed.

6. SEM observations show the crystalline nature of the samples.

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Summary

Simple, scalable, extremely convenient and idegeneously developed solution growth technique is used to synthesize a series of $Hg_x Cd_{1-x} S$ thin films for $0 \leq x \leq 0.25$. The basic source materials were cadmium sulphate, mercuric chloride, and thiourea with TEA and ammonia as the complexing agents. The preparation parameters such as growth temperature (60˚ C), growth time (90 mins), reaction pH (10.8 ± 0.2), rate of mechanical churning (70 ± 2), etc., were optimized. The as-grown films were tightly adherent to the substrate support, smooth, relatively uniform and diffusely reflecting with colour changing through yellowish red to yellowish lead-gray. The terminal layer thicknesses were measured for all the deposits and found to be decreased continuously with increase in [x]. The XRD studies ($2\theta = 10^o$ to 80^0) were also carried out to know the structure of these films. It was observed that the samples are polycrystalline in nature and exhibit dominant hexagonal wurtzite type crystal structure. The analysis of the optical absorption data (300 – 1000 nm) showed that the optical band gap is of the direct type and the energy gap , E_g, decreased typically from 2.42 to 1.75 eV as x was increased from 0 to 0.25. Scanning electron microscopy showed that the HgCdS deposits appeared to be a network of polycrystals of mixed, irregular shapes and sizes with size decreased with increasing Hg content in CdS.