CRYSTALLOGRAPHIC AND MICROSCOPIC INVESTIGATIONS ON CHEMICALLY SYNTHESIZED MERCURY CADMIUM SULPHIDE (MCS) THIN COMPOSITE FILMS

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$Hg_xCd_{1-x}S$ is a technically important class of material owing to its widespread utility in a variety of optoelectronic devices. The structural characteristics and microscopic features of this important composite material obtained using a liquid phase chemical deposition process have been investigated. A series of $Hg_xCd_{1-x}S$ ($0 \leq x \leq 0.25$) composite thin films were therefore fabricated onto the spectroscopic grade glasses. The composites were analyzed by an EDS analysis technique. The analysis showed that Cd^{2+} from the lattice of CdS has been replaced by Hg^{2+}. The X- ray diffraction studies in the 2θ range from 10^0 to 80^0 showed that the composite films consist of polycrystals of hexagonal wurtzite type with dominant reflections at d = 3.367 A^0 (002), 3.160 A^0 (101), 2.068 A^0 (110) and 1.761 A^0 (112). The interplanar distances (d) and intensities of reflections (I / I_{max}) for (002) and (101) change with the composition parameter x. These changes are continuous up to a value of x equal to 0.08. The variations in the lattice parameters a and c with x are analogous to the variations in the interplanar distances, d. The crystallite size is in the nano range and varied from 13.4 nm to 18.0 nm for the range studied. The SEM observations on these composite structures revealed that the deposits appeared to be a network of randomly oriented polycrystals of elongated rhomboids of irregular shapes and sizes with size decreased with increasing Hg- content in the composite.

1. Introduction

In recent years, thin film science has grown world wide into a major research area and the importance of coatings and synthesis of new materials for industry have resulted in a tremendous potential for innovative thin film processing technologies. Currently, this development goes hand-in- hand with the explosion of scientific and technological break through in microelectronics, optics and nanotechnology [1-3]. In this respect, CdS and its alloyed / mixed composites have received key impact due to their very important role in the photovoltaic technology and optoelectronic devices such as solar cells, photoconductors, radiation detectors, thin film transistor, etc. [4-7].

There exists a huge variety of thin film deposition processes and technologies which originate from purely physical or purely chemical processes. The structural and electronic properties as well as the primary particle size distribution are strongly dependent on the preparation method. The more important thin film processes are based on liquid phase chemical techniques, gas phase chemical processes, glow discharge processes, and evaporation methods [1,8-13]. Among the various deposition technologies available in the literature, chemical growth

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process, commonly known as liquid phase deposition (LPD), has several over-riding advantages over the other conventional methods and is conceptually ranked as more reliable, less expensive, and capable of producing films with new or improved properties [1,8-13]. It is a process to achieve high quality films, which are obtained by optimizing minimum deposition conditions and preparative parameters [9-13]. Therefore, through these investigations, we are aimed at the synthesis of excellent quality CdS and $Hg_xCd_{1-x}S$ thin composite films via our well established liquid phase chemical deposition technique [11,12] set for its deposition conditions and Preparation parameters and to analyze these composites compositionally, structurally and surface morphologically to obtain rigid information's on the composition dependent scenario of these composites in terms of materials characteristic properties.

2. Experimental techniques

CdS and $Hg_xCd_{1-x}S$ thin composite films with $0 \leq x \leq 0.25$ were deposited on the commercial glass plates using a chemical liquid phase growth process [14-17]. The glass plates were degreased and cleaned thoroughly using mechanical and ultrasonic cleaning processes. For obtaining CdS thin films by a liquid phase chemical growth process, the following procedure was followed [14-17]. First, 10 ml, 1M $CdSO_4$ ($5H_2O$) aqueous solution was taken in a beaker 250 ml in capacity. To this, 10 ml (17 N, AR grade) ammonia was added so as to obtain a white precipitate of $Cd(OH)_2$ which was just redissolved in excess ammonia and then 3 ml TEA (AR grade) was added so as to form Cd(TEA) complex. The total volume of the resulting mixture in the beaker was then made 200 ml by adding appropriate volume of double distilled water. The beaker was then transferred to the constant temperature oil bath whose temperature was controlled to $60 \pm 0.1\ ^0C$. The well cleaned glass substrates were attached to the substrate holder and the substrate holder was then fixed to a constant speed AC / DC gear motor. The speed of the rotation of these substrates was maintained to 70 ± 2 rpm. To this reaction mixture, 10 ml, 1M thiourea was added at a constant rate of 0.8 ml / 5 min with a special arrangement provided to the system. The reaction was then allowed to take place for 90 mins. The resulting pH of the reaction mixture was 10.8 ± 0.2.

For the deposition of $Hg_xCd_{1-x}S$ composites, appropriate volume of $HgCl_2$ was added so as to determine the value of x between 0.01 and 0.25. The samples were then taken off the reaction container after the deposition time and were preserved in a dark desiccator.

The contents of Hg, Cd, and S in the composite films were determined by the EDS technique. A Philips - XL – 30 energy dispersive spectrometer was used for this purpose. The crystallographic informations on these composites were obtained using a Philips –X - ray diffractometer [PW – 1710, anode – Cu, 40 kV/ 30 mA, Int. ratio 0.5, step size : 0.02, time per step 0.4, etc.] with Cuk_α line (1.5406 A^0). The 2θ range was from 10^0 to 80^0. The surface features were observed through a stereoscan, scanning electron microscope, [250 MK III, Cambridge, Instruments, UK)] at the magnification of 5000. The accelerating voltage was 25 kV and a thin layer of gold was sputter coated over the samples to enhance the electrical conductivity.

3. Results and discussion

3.1 Crystallographic investigations

The film growth kinetics and physical observations on $Hg_xCd_{1-x}S$ thin Composite films have been reported earlier [15,16]. It has been seen that excellent quality deposits are obtained with this technique at our experimental conditions. The pure CdS samples are yellowish – red in colour whereas colour of the $Hg_xCd_{1-x}S$ went on faint yellow and finally grayish -black as Hg content (x) in the deposit was varied from 0.01 to 0.25. This indicated strong possibility of substitution of Cd^{+2} by Hg^{+2} atoms in the CdS lattice. An EDS analysis was therefore conducted on these samples to determine the quantitative measure of the contents of the composites. This is shown in table- I. The analysis showed that Cd^{+2} from the CdS lattice has been

replaced by Hg^{+2} and that the content of Hg went on increasing when Hg- content in the chemical bath was increased [15,16]. Correspondingly Cd- content decreased. The X-ray diffractograms were obtained for all these composites within 2θ range from 10^0 to 80^0 and are shown in fig.1. The diffractograms were further analyzed to determine the interplanar distances (d), hkl planes, and intensities of reflections (I / I_{max}). Table – II shows analysis of these composites. These are then compared with the JCPD data [18, 19]. It appeared that the deposits are crystalline throughout the composition range studied and both CdS and $Hg_xCd_{1-x}S$ deposits are hexagonal wurtzite with d and I / I_{max} values in close agreement with that of the JCPD values. As - deposited CdS has five prominent reflections at the d - values equal to 3.347 A^0 , 3.046 A^0, 2.416 A^0, 2.056 A^0 and 1.774 A^0 that correspond respectively to the (002), (101), (102), (110) and (112) reflections. It has also been seen that the major peaks, (002) and (101) shift towards lower 2θ side and the shift is continuous upto x = 0.08. The d - values for these planes vary typically from 3.347 A^0 to 3.376 A^0 and 3.046 A^0 to 3.076 A^0, respectively. A continuous increase in d value up to x = 0.08 and then it falls to its original value for further increase in x have been observed. In our case the dominant reflection is (112) and the changes in 2θ and d values are comparatively small. This is shown in fig. 2. As far as intensities of reflections (I / I_{max}) for these peaks are considered, the reflected intensities for (002) and (101) peaks increased continuously and maximized up to x = 0.08 or even before. For higher x values I / I_{max} have no systematic variation however it tends to decrease (figure 3). The variations in d and I / I_{max} values for (102) and (110) reflections are insignificant and unsystematic. Another important feature of these studies, which is not fully understood, is the reflection from a (112) plane. It is observed that, for CdS, this reflection occurred at d = 1.774 A^0 with I / I_{max} equal to 100. The variation in d with x is more or less constant throughout the range, however, I / I_{max} remained more or less the same up to a value of x equal to 0.08 and then decreased thereafter for higher values of x. We correlate this decrease in intensity to in homogeneity of the material for $0.08 < x \leq 0.2$ wherein crystallite sizes have been reduced considerably. The variations of d and I / I_{max} with x for (112) plane are shown respectively in figures 2 and 3. The lattice parameters of these film structures were then determined. The variations of a and c with x are shown in table II. It has been observed that variations in a and c with x are analogous to variations in interplanar distances, d. Further, our earlier observations have shown continuous variation of optical gap with the film composition, x [15, 16]. This is true upto a value of x equal to 0.08. The ratio c/a is almost constant in the range of interest. Therefore, it can be inferred from the above studies coupled with the change in colour of the samples that there is a formation of homogeneous solid solution of the hexagonal $Hg_xCd_{1-x}S$ type for $0.01 \leq x \leq 0.08$. For higher concentration of Hg^{2+} in CdS ($0.08 < x \leq 0.25$), the interplanar distance (d) and lattice parameters (a & c) falls to their initial values of the pure components indicating separate phase formation. It has been further seen that the values of lattice parameters for CdS are in close agreement with that of the JCPD data [18] whereas these parameters very smoothly (as shown in table – II) with the film composition (upto x= 0.08). Similar variations have been reported by others [20 – 23]. In this range of x – values, the intensities of reflections are also reduced. The average crystallite size ($\dot{D}$) of the crystallites was then determined for (112) reflection using Scherrer's relation. The crystallite size is found to be enhanced from 13.4 nm to 18 nm as x was increased. Not much change in the crystallite size has been observed up on addition of Hg^{+2} in CdS. The enhancement in grain size can be co- rrelated, at this moment, to the decrease in band gap due to the incorporation of Hg^{+2} in CdS [24 – 26]. This can be explained as usual [24 – 26]: The incorporated Hg^{2+} segregates along the grain boundaries resulting in improved grain structure that causes band gap to decrease. Also an excess Hg^{2+} in the lattice makes the donor levels degenerate and finally merge into the conduction band of CdS, which causes band gap to decrease.

Fig. 1. X-ray diffractograms for: (a) x = 0, (b) x = 0.01, (c) x = 0.02, (d) x = 0.04, (e) x = 0.06, (f) x = 0.08, (g) x = 0.1, (h) x = 0.14, (i) x = 0.16, and (j) x = 0.2.

Table: I. Determination of contents of Hg, Cd, and S in the CdS and   Hgx Cd1-xS composites by the EDS technique.

Composition (x)	Hg (LA) AT%	Cd (L A) AT %	S (L A) AT %
0.0	----	54.06	45.94
0.01	0.24	53.79	45.97
0.02	0.53	53.44	46.03
0.04	0.87	53.20	45.93
0.06	1.08	53.05	45.87
0.08	2.77	51.18	46.05
0.1	4.46	49.76	45.78
0.16	6.68	47.71	45.61
0.2	7.83	46.41	45.76

Table: II. Some crystallographic characteristics of the Cd1-xHgxS composite thin films (0 ≤ x ≤ 0.2).

| Composition x	Lattice parameters				Crystallite Size A^0	c /a	
	CdS(H)		HgS(H)			CdS(H)	HgS(H)
	a (A^0)	c (A^0)	a (A^0)	c (A^0)			
0	4.103	6.694	-	-	134	1.631	-
0.01	4.108	6.702	-	-	145	1.631	-
0.02	4.116	6.716	-	-	154	1.632	-
0.04	4.122	6.734	-	-	156	1.633	-
0.06	4.128	6.743	-	-	161	1.633	-
0.08	4.132	6.762	-	-	180	1.636	-
0.1	4.117	6.733	4.142	9.468	111	1.635	2.286
0.14	4.124	6.741	4.159	9.477	119	1.634	2.278
0.16	4.111	6.717	4.147	9.423	147	1.634	2.272
0.2	4.116	6.718	4.136	9.435	149	1.632	2.281
ASTM	4.136	6.713	4.149	9.495		1.623	2.288
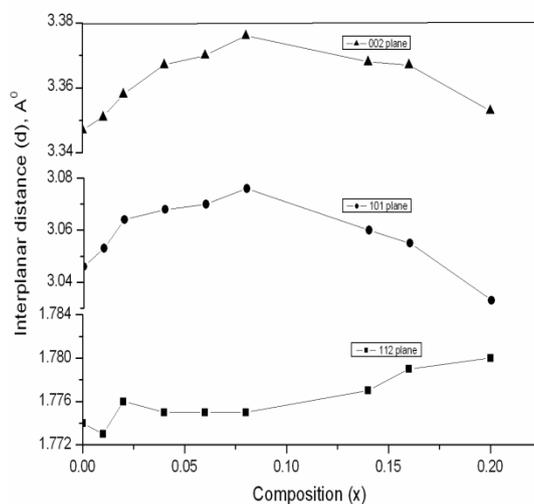
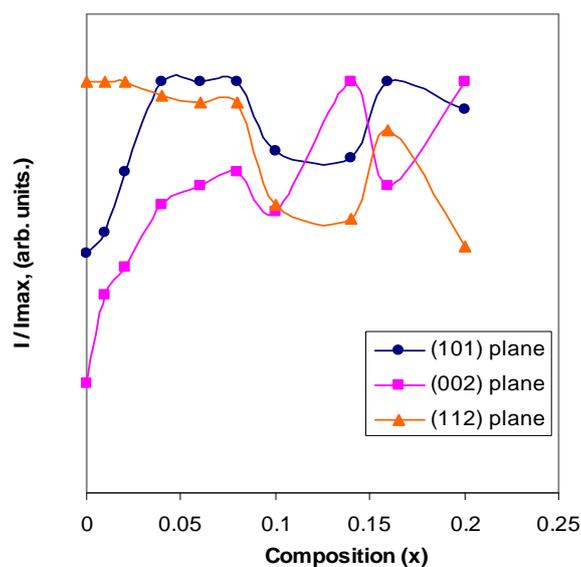*Fig. 2. Variation of interplanar distance (d) with composition (x).*

Fig. 3. Variation of I / I$_{max}$ with composition (x).

3.2. 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. Micrograph a corresponds to pure CdS which shows randomly oriented CdS crystallites of elongated rhomboid shape with sharp and clear edges having leaf like appearance [15]. This is true for micrograph b and to some extent for c also. This picture becomes more clear for micrographs d to h wherein leafy appearance gets continuously transformed into elongated rhomboids [figure 4(d-h)] of considerably reduced size with clear and fine boundaries [15]. Compared with the other micrographs, micrographs e and f are bit more clear and coarser. The micrograph of higher Hg-content; e.g micrograph g, seems to be diffused and having some sort of overgrowth. The micrograph at x = 0.2 is again a clear rhomboid – shaped picture with reduced elongation and crystallite size. The reduction in crystallite size can be correlated to the non stability of the CdHgS system as a result of incorporation of Hg in CdS. When Hg – content in the stable CdS system is increased, internal strain arises due to the structural and chemical disorder and consequently results in an unstable CdHgS solid solution system. For stabilization of unstable CdHgS structure, the grain size is reduced to release the strain as the Hg^{+2} concentration becomes larger [27-28]. Thus at higher concentration of Hg in CdS (figures g & h), the micrographs show its interesting appearance. The big crystallites recrystallize into small crystals of more or less same 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.
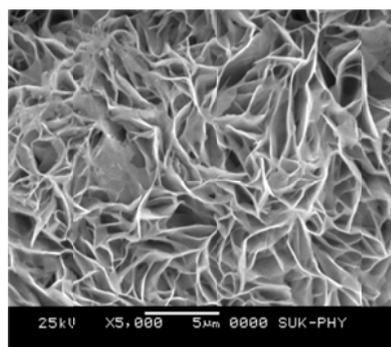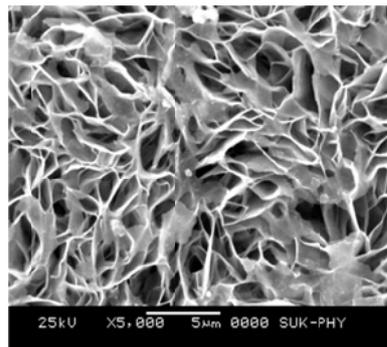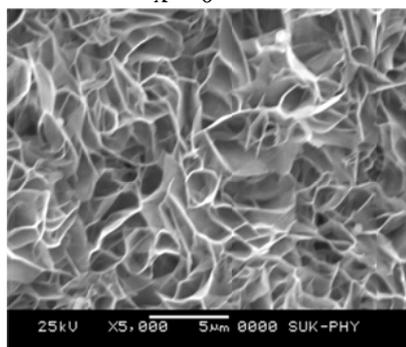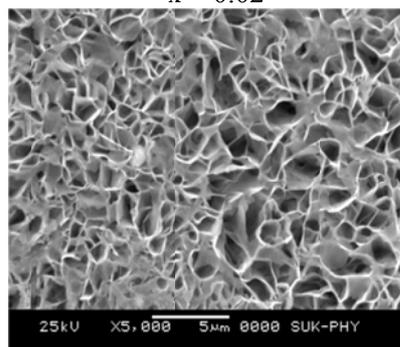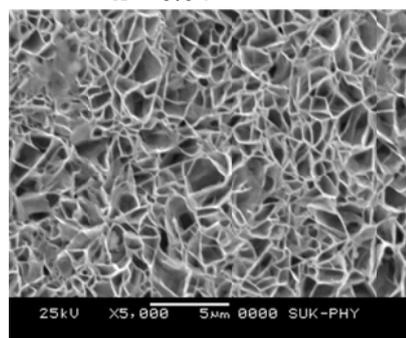
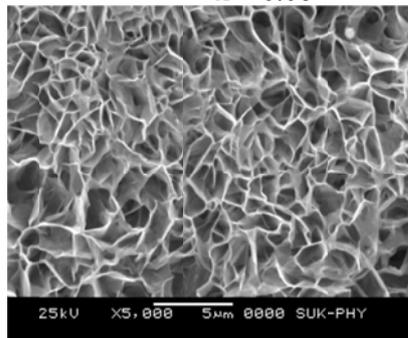*Fig. 4(a-h). Surface morphological studies for eight representative films: a) x = 0,*
b) x = 0.02, c) x = 0.04, d) x = 0.06, e) x = 0.08, f) x = 0.1, g) x =0.14 and h) x = 0.2.

4. Conclusions

The EDS analysis showed replacement of Cd^{2+} by Hg^2 and a solid solution of the type $Hg_xCd_{1-x}S$ has been formed in the process.

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

The major peaks, (002) and (101) shift towards lower 2θ side and the shift is continuous upto x = 0.08.

The reflected intensities for (002) and (101) peaks increased continuously and maximized at x = 0.08 or even before.

There is a formation of homogeneous solid solution of the hexagonal $Hg_xCd_{1-x}S$ type for $0.01 \leq x \leq 0.08$.

The ratio c/a is almost constant in the range of interest.

The crystallite size is found to be enhanced from 13.4 nm to 18 nm as x was increased.

Micrograph of pure CdS shows randomly oriented CdS crystallites of stretched elongated rhomboid shape with sharp and clear edges having leaf like appearance.

For higher concentration of Hg in CdS, the big crystallites recrystallize into small ones of more or less the same shape.

Acknowledgements

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