Structural And Microscopic Studies On Mercury Zinc Sulfide Thin Films

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Abstract. Thin films of (Hg, Zn) S of varying composition were deposited on clean glass substrates using a chemical bath deposition technique. The precursors and complex agent were used to obtain quality samples. Optimization of preparatory parameters such as deposition time, temperature and pH of the reaction mixture has been obtained. The as-deposited thin films were then characterized by using X-ray diffraction and SEM techniques for their structural and microscopic studies. From these studies, it has been observed that these samples are polycrystalline in nature and slow separate phases of both cubic and hexagonal structures, whereas the solid solution has been taken place only for cubic structure. The crystallite size went on increasing with the composition parameter; x up to1 .The scanning electron microscope (SEM) was used to determine the surface morphology.

Keywords: CBD, MZS, structural, microscopic studies.

INTRODUCTION

In the recent years, much importance has been given to group II-VI compounds because of their important application in catalysis, optical devices, and magnetic fields and so on. ZnS and HgS are important semiconducting compounds of II-VI groups with excellent physical properties and wide band-gap energy ranging from 3.7 to 1.98 eV, respectively have attracted great attention [1, 2]. It has been extensively investigated due to their potential application for devices such as window layers for solar cells, production of hydrogen, blue- light diodes, electro-luminescent displays, anti reflection coatings for infrared and other non-linear optical devices [3].
Several techniques have been used for the deposition, of II-VI and IV-VI group compound thin films, such as molecular beam epitaxy, H_2 plasma chemical sputtering, MOCVD, MOVPE and liquid phase techniques (electrochemical deposition, chemical bath deposition)[4]. Among these techniques, chemical bath deposition (CBD) is the low cost, scalable, simple, convenient and low temperature technique by which a variety of substrates can be coated and desired orientations can be achieved. However, the attempts were made to make the system more systematic, accurate and easy to handle [5] . $Hg_xZn_{1-x}S$ thin films are deposited optimizing for different preparative parameters and their structural and surface morphological studies are reported in this paper.

EXPERIMENTAL DETAILS

The amorphous glass substrates were used to deposit (Hg, Zn) S thin films. The key precaution taken before deposition of the thin films is the careful cleaning of the substrates. The glass substrates were boiled in chromic acid for 20 minutes and washed several times with double distilled water. They were further dipped in a medium concentrated detergent solution and again washed with double distilled water and then an ultrasonic cleaner. All the substrates were kept immersed in double distilled water before used. Initially, the preparation parameters such as time and temperature of deposition, pH, and morality of reaction mixture, speed of mechanical churning etc were optimized. 1M zinc sulphate ($ZnSO_4.7H_2O$), thiourea ($CS(NH_2)_2$), mercuric chloride ($HgCl_2$) (all AR grade) were used to deposit these thin films. Appropriate volumes (in stoichiometric ratio) of the reacting compounds were taken in 200 ml beaker (reaction bath) and triethylamine (TEA) is used as a complexing agent. Sodium hydroxide and aqueous ammonia were added to adjust the pH of the reaction mixture and film adherence respectively. Thoroughly cleaned glass substrates were vertically immersed into the reaction mixture and mechanically churned to deposit these thin films of different compositions ($0 \leq x \leq 1$).

The structure and crystalline nature of all the samples were examined by an X-ray diffraction technique. The diffractograms (XRD patterns) of these as-deposited thin films were obtained by an X-ray diffractometer (Rigaku Denki Co. Ltd. Japan / MDI

JADE 5.0 X-ray diffractometer) using Cu-kα line (λ = 1.5406 A.U.) working at 40kV and 20mA. Diffractograms were obtained in the step scanning mode with a step of 2θ = 0.02°and speed at 3°/min. for the range of 20-60°.

The surface morphologies of these samples were observed through a scanning electron microscope, model - JSM-7001F (Thermal Field Emission). The specimen chamber pressure was up to 50Pa at resolution of 3.0nm at 30 kV. Dry nitrogen and gun pressure at $5x10^{-7}$ were used.

RESULTS AND DISCUSSION

Structural studies

The structural investigations on these as-deposited $Hg_xZn_{1-x}S$ thin films of varying composition parameter, x are shown in figure 1. The diffractograms clearly showed that the as-deposited films are polycrystalline in nature. Both ZnS and HgS exhibit cubic zinc blend and hexagonal wurtzite structures [6-9]. The dominant peaks (111), (200) and (220) shift towards the lower 2θ side, thereby increasing their d-values: from 3.108 A^o to 3.147 A^o for (111) plane, from 2.689 A^o to 2.723 A^o for (200) plane and from 1.894 A^o to 1.937 A^o for (220) plane. Thus, there must be the formation of solid solution of the kind $Hg_xZn_{1-x}S$ for cubical phase only.

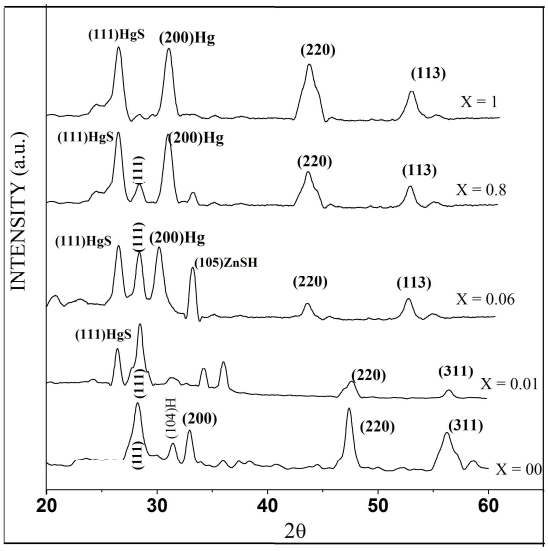

FIGURE 1. X-ray diffractograms of Hg_x Zn_{1-x} S for some of the typical compositions: a) x = 0, b) x = 0.01 c) x = 0.06, d) x = 0.8 and e) x = 1.

The variations in the lattice parameter '**a**' have also been examined. In general, it is seen that the calculated values of the lattice parameters are slightly less than their bulk values. The reason for this discrepancy is the polycrystalline nature of the samples wherein the lattice may be under strain-induced forces. Similar results have been reported by Padam et al [10] for (Cd, Zn) S and by Shahane et al [11] for Cd (S, Se) polycrystalline thin films.

The average crystallite size (D) of the crystallites was then determined by using Scherer's relation [12-14] as:

$$D = \frac{k\lambda}{\beta \cos\theta}$$

Where k = 0.94, λ is the wavelength of incident radiation, β is the full width at half maxima (FWHM) in radian and θ is the diffraction angle. The changes in the intensities of the reflections suggest that the crystallite size has improved after incorporation of Hg in the lattice of ZnS.

Microscopic studies

Figure 2 shows the SEM micrographs of $Hg_xZn_{1-x}S$ thin films of different compositions (x). The micrographs showed a globular structure composed of a single type of small spherical microcrystals. The average crystallite size (D) was then determined for these crystals. It is seen that the average crystallite sizes calculated from the XRD patterns and the SEM micrographs increased with the increasing Hg- content in ZnS up to x = 0.8. However, there is a good agreement between the crystallite sizes calculated from the XRD patterns and the SEM observations.

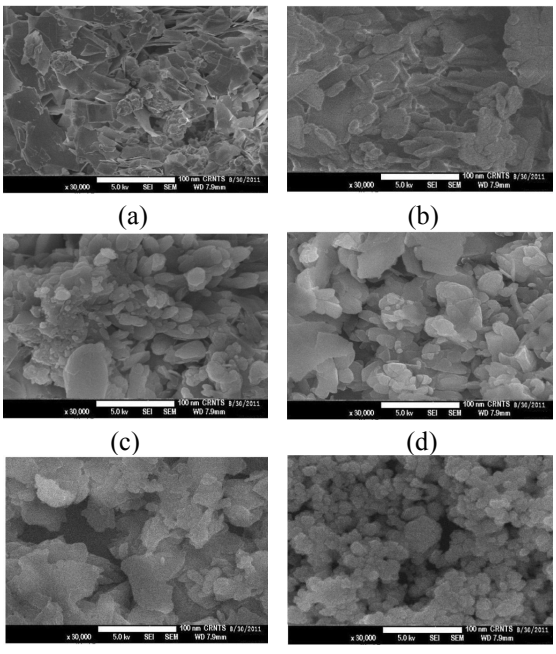

FIGURE 2. SEM micrographs of Hg_x Zn_{1-x} S for some of the typical compositions: a) x = 0, b) x = 0.02 c) x = 0.06, d) x = 0.2, e) x = 0.8 and f) x = 1.

Compositional analysis

The film composition was determined by an energy dispersive analysis by X-ray (EDAX) technique and is cited in table 2. It is found that, as the Hg-content in the solution was increased, the Hg-content in the film increased and the corresponding Zn-content decreased. It means that Hg^{2+} ions replace the Zn^{2+} ions.

TABLE 1 Average crystallite sizes (D- values).

Composition X	D Å XRD	SEM
00	89	110
0.01	98	161
0.04	107	220
0.08	129	272
0.1	143	292
0.4	158	302
0.8	180	321
1	161	304

TABLE 2. Compositional analysis of $Hg_x Zn_{1-x} S$.

Composition x	Zn	Hg	S
00	48.00	00	50.90
0.01	48.20	0.80	49.80
0.06	34.20	14.32	49.80
0.8	03.75	45.82	50.20
1	00	49.20	50.60

CONCLUSIONS

$Hg_xZn_{1-x}S$ thin films of the different compositions ($0 < x < 1$) have been suitably deposited with chemical bath deposition technique which is simple, scalable and easy to handle. The structural studies reveal that these films are polycrystalline in nature with mixed phases of both cubic and hexagonal structures of ZnS and HgS. However the solid solution has taken place only for cubic phase since the dominant peak shifts towards the lower 2θ side. SEM micrographs show somewhat spherical crystallites with some sort of overgrowth which are relatively uniform and diffusely reflecting for higher x-values.

ACKNOWLEDGMENTS

Mr. A. R. Pawar is thankful to Prin. Dr. Arvind Burungale, Secretary, Rayat Shikshan Sanstha, Satara and Prin. Dr. V. S. Shivankar, K.B.P. College, Vashi, Navi Mumbai, and faculty members of KBP College, Vashi and Bhavan's college, Andheri, Mumbai for their generous help and support rendered during these studies.

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