

Preparation and structural characterisation of chemically deposited $Pb_{1-x}Cd_xS$ films

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Abstract. Alloy films of $Pb_{1-x}Cd_xS$ have been prepared on glass substrates by electroless deposition from a chemical bath. Structural characterisation of the alloy was carried out by x-ray powder diffraction technique using Debye-Scherrer camera. The study shows that $Pb_{1-x}Cd_xS$ exists in cubic phase and the lattice constants are found to be greater than individual CdS and PbS value. This expansion of lattice is possibly due to interstitials. The lattice constants have been found to vary linearly with atomic percent of cadmium sulphide. The SEM micrographs show that particle size increases with increase in atomic percent of cadmium sulphide in the alloy.

Keywords. Electroless deposition; $Pb_{1-x}Cd_xS$; lattice constants; x-ray powder diffraction.

1. Introduction

The recent energy crisis has compelled the search for non-conventional sources of energy. Solar energy can play a promising role in the coming decades, if suitably harnessed, particularly in a tropical country like India. Against this backdrop, efforts are being made to find new and low cost materials for photovoltaic solar energy conversion. It was suggested by Loferski (1973) that newer materials like Bi_2S_3 , $Pb_{1-x}Cd_xS$, $CuInS_2$ and $CuInSe_2$ could be used for better efficiency. In the present case $Pb_{1-x}Cd_xS$ was chosen as it could have a variable band gap which could match the solar spectrum. In this compound, the ideal band gap for solar energy conversion can be achieved if the percentages of the components are properly adjusted. Attempts to prepare $Pb_{1-x}Cd_xS$ film have so far been limited to thermal evaporation techniques (Sood *et al* 1978; Jensen and Schoolar 1978). Material in the bulk form has been prepared among others by [Harman *et al* (1971)], Calwa *et al* (1972) and Steitu (1973). It was therefore considered worthwhile to prepare the said films by a chemical method which could be simple and inexpensive and which could be used to deposit polycrystalline films in large areas.

2. Preparation of films

Aqueous solution of lead acetate (400g/litre), thiourea (100g/litre) and cadmium acetate (300g/litre) are taken in a beaker and mixed thoroughly by stirring for about 5 min. Ammonium hydroxide is then added to it to maintain a pH of 10 in the solution. Thoroughly cleaned glass substrates are dipped in the beaker. Films gradually start depositing on the substrates and also on the wall of the beaker. A good quality film takes about 45 min to deposit at room temperature. The quality of the film mainly depends on the pH and the temperature of the solution bath. As temperature increases, for a given thickness, the time of deposition decreases. For uniform deposition, a compromise has to be made among temperature, pH and time.

3. Determination of chemical composition

The films are dissolved in dilute nitric acid and the composition of the solution is then polarographically determined to get the value of x in the $Pb_{1-x}Cd_xS$ alloy. The results have been shown in table 1.

3.1 Structure

The photographic x-ray powder diffraction technique has been used to identify the phases present and to characterize the solid solution. The films are scrapped from the substrates and ground properly to make a powder of suitable size. A Debye-Scherrer type of diffraction is taken using a Philips (11.46 cm) camera and Cu-K α radiation. The values of d and those of a in pure PbS (precipitated by lead acetate and thiourea in an alkaline medium of ammonium hydroxide), CdS (precipitated by cadmium acetate and thiourea in an alkaline medium of ammonium hydroxide), and $Pb_{1-x}Cd_xS$ for different values of x are determined by this method. It has been found that $Pb_{1-x}Cd_xS$ prepared by the present method exists in the cubic phase. A typical Debye-Scherrer diffraction is shown in figure 1 for $x = 0.5$.

The variation of lattice constant $Pb_{1-x}Cd_xS$ as a function of x has been plotted in figure 2. The lattice constant a_0 varies as $a_0 = (6.005) + (0.5 \times 10^{-2})x$. The

Table 1. Polarographic determination of cadmium in $Pb_{1-x}Cd_xS$ as a function of cadmium acetate solution.

No. of sample	Volume of lead acetate (400 g/litre) in c. c. in the bath	Volume of cadmium acetate (300 g/litre) added in c. c. in the bath	Atomic percent of Cd as determined by polarographic technique
1	10	1	14.363
2	10	2	27.731
3	10	3	39.388
4	10	4	50.561

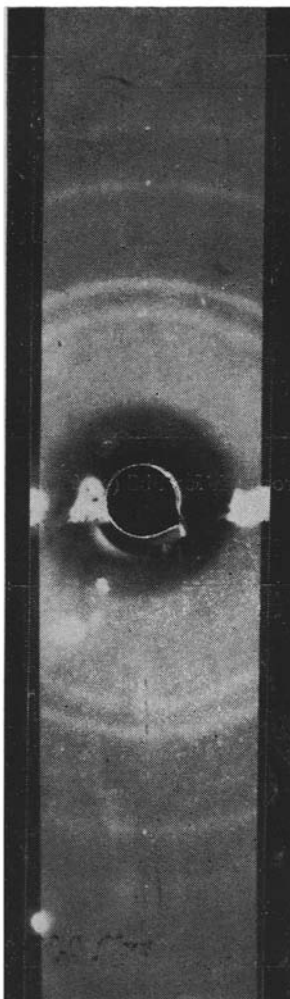


Figure 1. X-ray powder photograph of $Pb_{1-x}Cd_xS$ for $x=0.5$

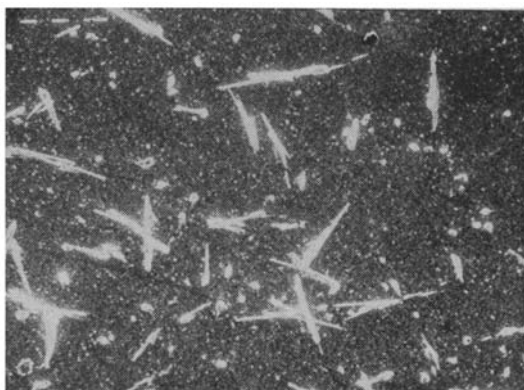


Figure 3. SEM micrograph for PbS ($\times 620$)

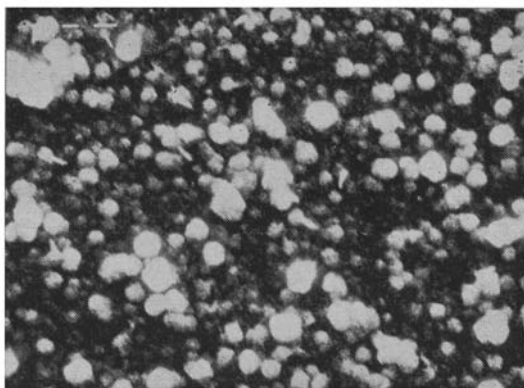


Figure 4. SEM micrograph for Pb_{1-x}Cd_xS for $x=0.5$ ($\times 5400$)

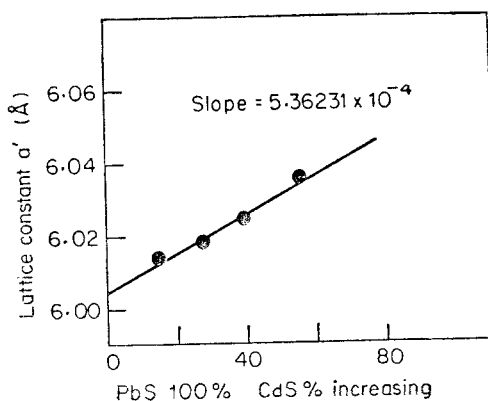


Figure 2. Variation of lattice constant as a function of x

a values are obtained using the Taylor-Sinclair extrapolation technique using available reflections which are always in the low angle range $\theta < 60^\circ$.

3.2. Surface topology of the films

The surface structure of the films was observed using scanning electron microscopic technique. It has been found that with increase in the cadmium percentage, the particle size increases. The micrographs were at first taken for pure PbS and then for $Pb_{1-x}Cd_xS$. The nature of change is as shown in figures 3 and 4.

4. Results and discussion

As seen from tables 2 and 3 for PbS and CdS, it is found that in the case of PbS at lower angles the d values vary appreciably from the ASTM values which are taken for natural galena crystal. At higher angles, they approach the ASTM values. Both random and systematic errors are responsible for changing the d values. (Klug and Alexander 1974). While random errors decrease in magnitude as θ increases, the effect is negligibly small as θ approaches 90° since $\Delta d/d = -\cot \theta \cdot \Delta \theta$ tends to zero at $\theta = 90^\circ$. Systematic errors like radius errors film shrinkage, eccentricity of the specimen, absorption of the x-ray beam by specimen, radial (horizontal) divergence of the beam, axial (vertical) divergence of the beam tend to minima as θ approaches 90° . In the extrapolation method for correcting the systematic errors Bradley and Jay's extrapolation against $\cos^2 \theta$ (Klug and Alexander 1974) is valid only when $\theta > 60^\circ$. The Taylor-Sinclair correction (Klug and Alexander 1974) although valid for all angles for practical purposes, is employed when absorption is the principal error. It ignores eccentricity and other systematic errors. The least square extrapolation method (Klug and Alexander 1974) is also valid when $\theta > 60^\circ$. Therefore, from all these considerations it is advisable to take lines between 60° and 90° for d values determination. But in the case of PbS the highest angle never reaches

Table 2. Lattice parameters of PbS precipitated by the chemical method.

d values in Å determined	d values in Å from ASTM	Plane of reflec- tion	a in Å determined
3.391	3.429	(111)	5.875
2.943	2.969	(200)	5.886
2.083	2.099	(220)	5.894
1.783	1.790	(311)	5.916
1.711	1.714	(222)	5.930
1.482	1.484	(400)	5.929
1.361	1.362	(331)	5.933
1.327	1.327	(420)	5.936
1.212	1.212	(422)	5.939
1.143	1.142	(511)	5.940

Table 3. Lattice parameters of CdS precipitated by the chemical method.

d values in Å determined	Various possible reflection planes and d values from ASTM chart			
3.381	α -CdS (002),	3.357 Å	or β -CdS (111),	3.360 Å
2.072	α -CdS (110),	2.068 Å	or β -CdS (220),	2.058 Å
1.769	α -CdS (112),	1.761 Å	or β -CdS (311),	1.753 Å
1.346	α -CdS (210),	1.353 Å	or β CdS (331),	1.337 Å
1.313	β -CdS (420),	1.298 Å		
1.199	α -CdS (300),	1.194 Å	or β -CdS (422),	1.186 Å

Table 4. Lattice parameters of $Pb_{1-x}Cd_xS$ prepared by the chemical method.

Sample	Atomic percent of CdS in the sample	Lattice parameter a calculated
1	14.363	6.014
2	27.731	6.018
3	39.388	6.024
4	50.561	6.036

60° (as seen from the ASTM chart). Hence we have considered the d values at higher angles out of the available angles of reflection.

In the case of CdS and $Pb_{1-x}Cd_xS$ the same arguments apply. In CdS, as seen from table 3 the d values are always higher than the ASTM values.

In the case of $Pb_{1-x}Cd_xS$ as seen from table 4 the lattice parameters are more than the respective CdS and PbS values. This agrees with the observations of Sharma *et al* (1977) for chemically-deposited alloy films of $Pb_{1-x}Hg_xS$. The possible explanation for this lattice expansion, is due to the accommodation of α -HgS through a stacking rearrangement in the f. c. c. PbS lattice. This

contention is not accompanied by any confirmatory evidence like line profile analysis, stability of the stacked lattice from energy consideration, density determination, etc. to substantiate the point. Electron diffraction, a technique inherent with much inaccuracy, cannot lead to draw such an unusual conclusion.

On the other hand we are led to the conclusion that this phenomenon is due to the interstitial alloy, PbS entering as interstitial into the CdS lattice and causing lattice expansion.

References

- Calwa A R, Mroczowski J A and Harman T C 1972 *J. Electron Mater.* **1** 191
Jensen J D and Schoolar R B 1978 *J. Electron. Mater.* **7** 237
Klug H P and Alexander L E 1974 *X-ray diffraction procedures* (II edn) (New York : John Wiley), pp 567, 591, 594
Loferski J J 1973 *Proc. Workshop photovoltaic conversion of solar energy for terrestrial application* **1** 27 sponsored by the National Science Foundation, USA
Sharma N C, Pandya D K, Sehgal H K and Chopra K L 1977 *Thin Solid Films* **42** 383
Sood A K, Wu K and Zemel J N 1978 *Thin Solid Films* **48** 73
Stetiu P 1973 *Phys. Status Solidi A* **15** K 19