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Preparation and characterization of chemically deposited lead sulphide thin films

P. K. BASU, T. K. CHAUDHURI, K. C. NANDI, R. S. SARASWAT, H. N. ACHARYA
Department of Physics and Meteorology, Indian Institute of Technology, Kharagpur 721 302, India

A chemical method for the deposition of PbS thin films has been developed using appropriate amounts of lead acetate, thioacetamide and triethanolamine. The thickness of the films are in the range 0.3 to 1 μm. The films are polycrystalline and p-type. The dependence of the film thickness as a function of the bath parameters has also been studied and explained on the basis of ion–ion condensation theory.

1. Introduction

Thin films of PbS has been studied extensively due to their application as near infrared detectors [1] and in infrared photography [2]. Even though they have been prepared by vacuum evaporation [3–5], electrochemically [6], the dip dry process [7], and reactive evaporation [8], those prepared by the solution growth technique [9–12] are found to be most suitable for these technical applications. It has been found that triethanolamine (TEA) can be used as a complexing agent for chemical deposition of Bi_2S_3 [13], Bi_2Se_3 [14], CdS [15], CdSe [15], CuSe [16], ZnS [17], ZnSe [18], NiS [19], NiSe [19], $Cu_{1.8}S$ [20], $Co_{1.035}S$ [21], CoSe [22], MnS [23] and SnS [24] thin films. This paper reports a new method for the deposition of PbS thin films utilizing TEA as a complexing agent and a base. The method also incorporates thioacetamide as a sulphur-releasing agent instead of thiourea as used by earlier workers [9–12].

2. Experimental procedure

2.1. Preparation

10 ml freshly prepared 0.3 M lead acetate solution was taken in a 100 ml beaker to which 15 ml 7.4 M triethanolamine (TEA) and 10 ml 0.3 M thioacetamide (TAA) (AR grade) were added successively and the volume was made up to about 100 ml with distilled water. The solution was stirred for a few seconds and then poured into another beaker containing a scrupulously cleaned glass substrate clamped vertically. The solution gradually turned deep brown. After about 3 h the slide was covered with a shiny deep brown deposit. The glass slide was removed, washed with distilled water, dried and stored in a desiccator.

The thickness of the films was studied as a function of deposition time with (i) temperature, (ii) TEA concentration, and (iii) concentration of thioacetamide solution. The thicknesses were measured with Surfometer (SF 101, Plane Products). The film thicknesses were found to be in the range 0.3 to 1 μm.

2.2. Characterization

The composition of the films prepared by the present method was determined by X-ray studies; films on glass substrates were used and their diffraction profiles were recorded using nickel-filtered Cu*Kα* radiation (Philips PW 1729).

Electrical conductivity of the films was measured by making gap cells with graphite contacts (Aquadag). The gap was 1 cm and the field applied was $10\,V\,cm^{-1}$. To determine the type of conduction and the carrier concentration, the thermoelectric power of the films was also measured.

The surface morphology of the films was studied by scanning electron microscopy (Camscan, Series - 2DV).

3. Results and discussion

3.1. X-ray characterization

An X-ray diffractogram of a typical PbS film on glass is shown in Fig. 1. The presence of well-defined peaks indicates that the films are polycrystalline in nature. The *d* values of the lines obtained were calculated and compared with standard *d* values for PbS taken from the ASTM diffraction data file as given in Table I. The observed *d* values are in good agreement with the standard ASTM values, confirming that the material of the film is PbS.

3.2. Effect of bath parameters on the thickness of PbS films

Fig. 2 shows the growth of PbS films with deposition time at 27 and 50° C. The effect of the concentration of TEA and TAA on the thickness of PbS films is shown in Figs 3 and 4, respectively. It can be seen that, generally, in the initial stages of growth the thickness increases at a faster rate. Then the rate decreases until a terminal thickness (TT) is approached. For an optimum solution, at 27° C, the growth rate is $4\,nm\,h^{-1}$ and a TT of about 1 μm is attained after 3 h (Fig. 2). The rate of growth, at 50° C, is faster and TT of about 0.5 μm is reached much earlier (after 1 h). When the

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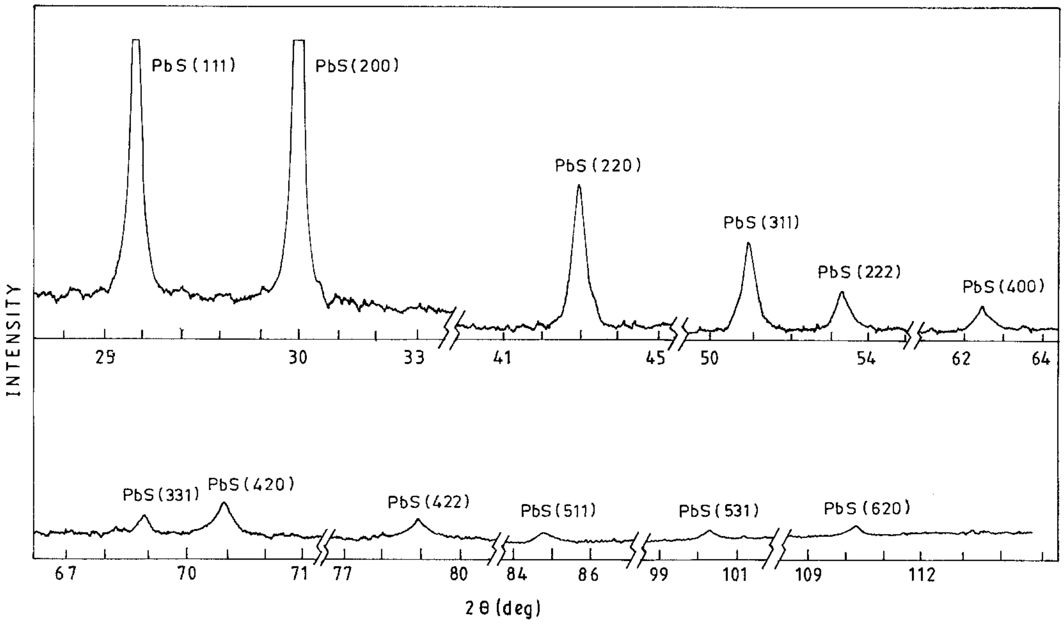

Figure 1 X-ray diffractograph of PbS film on glass.

concentration of TEA is varied (Fig. 3), at 27° C, the TTs for 112.8 and 225.6 g l^{-1} are ~0.9 and ~0.8 μm, respectively. These are less than the TT ~ 1 μm obtained for the 169.2 g l^{-1} (optimum). The TTs for TAA concentrations of 1.8, 2.25 and 2.7 g l^{-1} are 0.9, 1 and 0.85 μm, respectively (Fig. 3).

The above results can be explained on the basis of ion–ion condensation [15]. The formation of PbS is governed by the equation

$$\mathrm{Pb\,(TEA)^{2+} + CH_3CSNH_2 + H_2O \rightarrow}$$
$$\mathrm{PbS + CH_3CONH_2 + TEA}$$

However, at a particular temperature PbS will be deposited if the ionic product of Pb^{2+} and S^{2-} exceeds

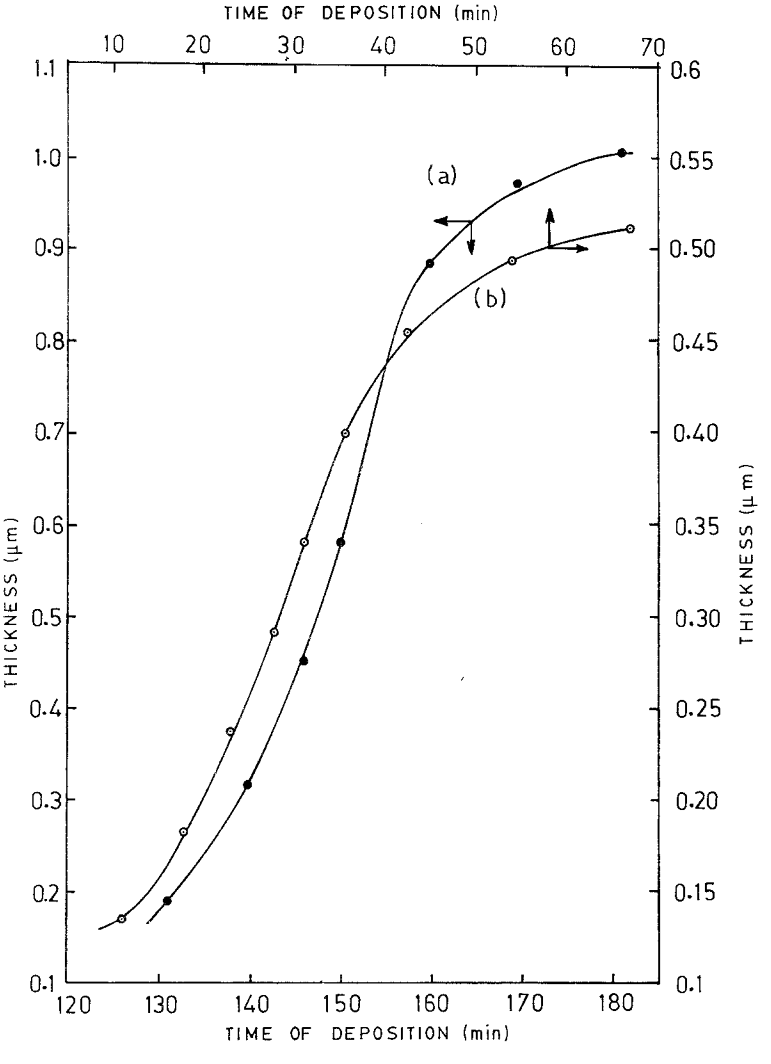

Figure 2 Thicknesses of PbS films as a function of the deposition time at (a) 27° C, and (b) 50° C.

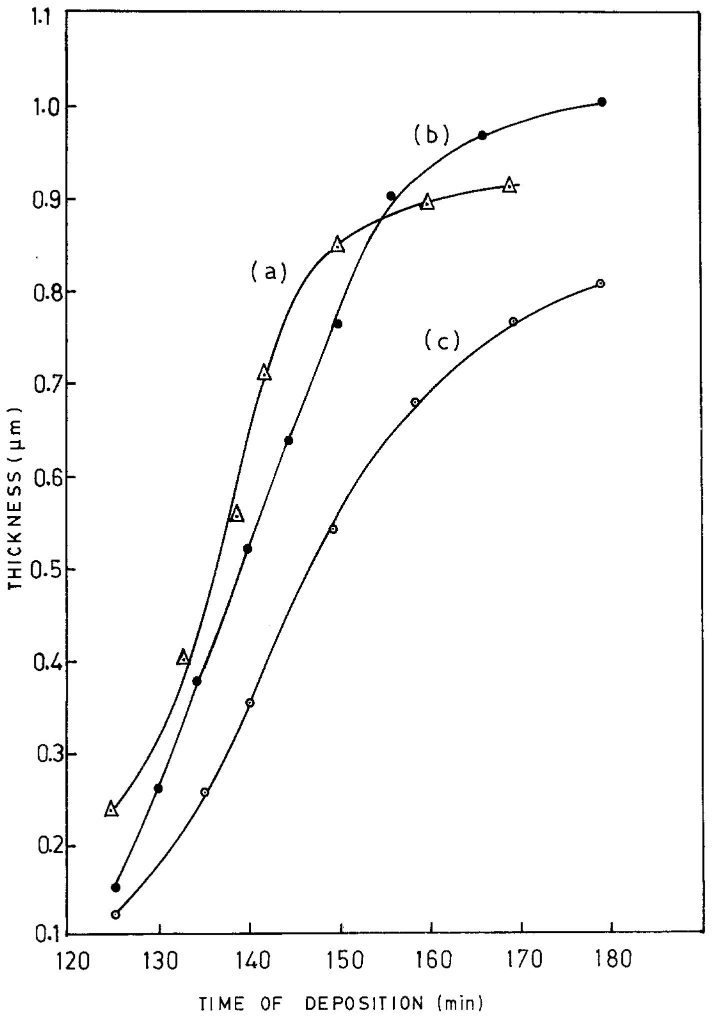

Figure 3 Variation of PbS film thicknesses with deposition time for different concentrations of TEA. (a) 112.8 g l^{-1}, (b) 169.2 g l^{-1}, (c) 225.6 g l^{-1}.

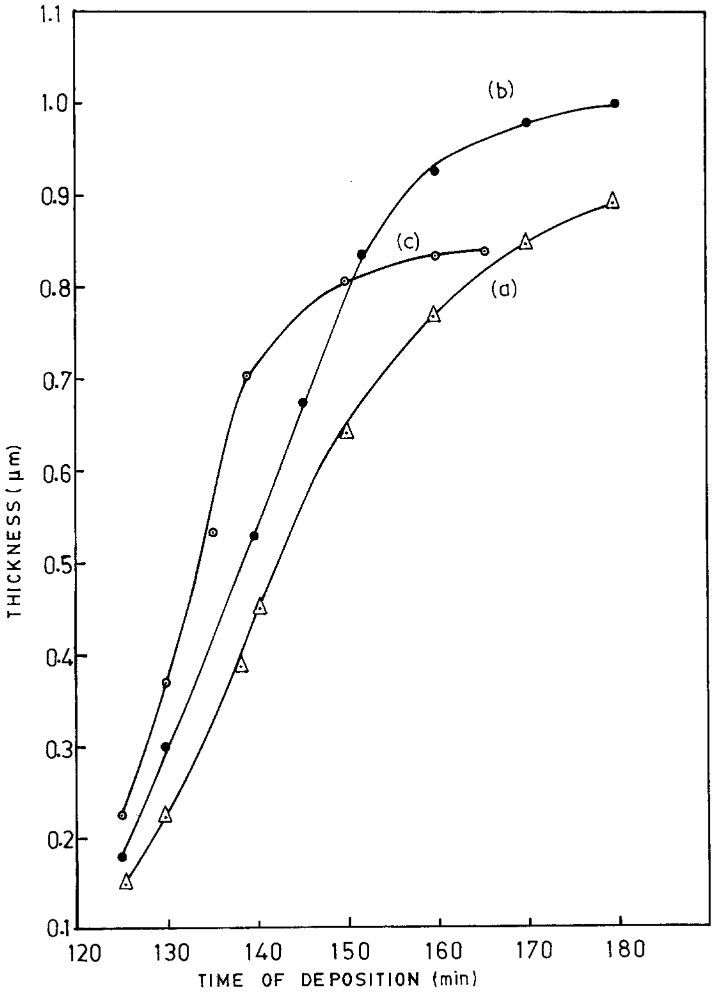

Figure 4 Variation of PbS film thicknesses with deposition time for different concentrations of thioacetamide solution. (a) 1.8 g l^{-1}, (b) 2.25 g l^{-1}, (c) 2.7 g l^{-1}.

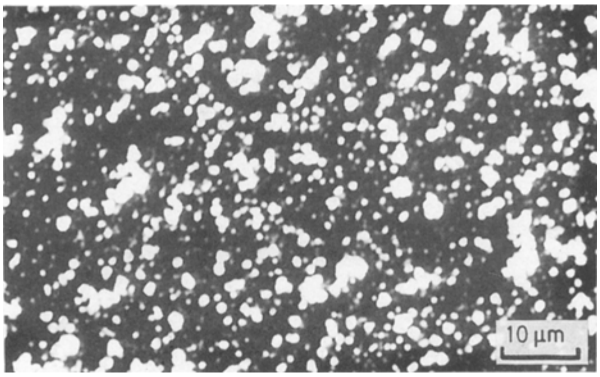

Figure 5 Surface morphology of a typical PbS film on glass.

the solubility product. The Pb^{2+} released by the TEA complex and S^{2-} released by TAA combine at the nucleation centres on the substrate to produce PbS. The quantity of ions utilized for film formation depends on the rate of formation of PbS on the substrate surface, which in turn, depends not only on the ratio of the nucleation centres available at the surface of the substrate to those in the volume of the solution, but also on the rate of release of Pb^{2+} and S^{2-} ions.

3.3. Surface morphology

A scanning electron micrograph of PbS film on glass is shown in Fig. 5. It can be seen that the films are, in general, aggregates of grains of size $\sim 1\ \mu m$.

3.4. Electrical measurements

The films were found to be p-type with a thermoelectric power of $500\ \mu V\ K^{-1}$. The conductivity and carrier concentration of the films are $\sim 10^{-2}\ mho\ cm^{-1}$ and $\sim 10^{17}\ cm^{-3}$, respectively.

TABLE I X-ray diffraction lines of PbS film prepared by this chemical method

Line no.	Observed		Identification	Standard* d (nm)
	2θ (deg)	d (nm)		
1	25.9	0.3437	PbS (1 1 1)	0.3429
2	30.0	0.2976	PbS (2 0 0)	0.2969
3	43.0	0.210	PbS (2 2 0)	0.2099
4	50.9	0.1792	PbS (3 1 1)	0.1790
5	53.3	0.1717	PbS (2 2 2)	0.1714
6	62.5	0.1485	PbS (4 0 0)	0.1484
7	68.8	0.1363	PbS (3 3 1)	0.1362
8	70.9	0.1328	PbS (4 2 0)	0.1327
9	79.0	0.1211	PbS (4 2 2)	0.1212
10	84.9	0.11412	PbS (5 1 1)	0.11424
12	100.4	0.10026	PbS (5 3 1)	0.10034
12	110.2	0.09391	PbS (6 2 0)	0.09386

*ASTM Powder Diffraction File, Card No. 5-0592.

4. Conclusion

The chemical method described above yields PbS thin films at room temperature. The films are p-type with a carrier concentration of $\sim 10^{17}\ cm^{-3}$.

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