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Chemical bath deposition of mercury(II) sulfide thin layers

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Thin layers of mercury(II) sulfide have been prepared by a newly developed chemical bath deposition technique. The layers were grown on glass substrates previously coated with a very thin layer of lead sulfide (thickness <10 nm). The deposition was performed in alkaline media at 65 °C from thiosulfate complexes of mercury. X-Ray investigation indicates that the deposited material is a mercury(II) sulfide mixture of two phases, α-HgS and γ-HgS, with α-HgS dominant. The optical bandgap, E_g, was evaluated from VIS absorption spectra and found to have a value of 3.1 eV.

1 Introduction

Mercury(II) sulfide crystallizes in three different structures. Trigonal (α-HgS) and zincblende β-HgS have been most explored. Thin layers of mercury(II) sulfide have been prepared by evaporation[1] and sputtering[2–6] methods. They are useful in ultrasonic transducers,[2,6] image sensors,[3] electrostatic imaging materials,[3] and photoelectric conversion devices.[2,3,6] Formation of ternary alloys between HgS and PbS has also been established and well investigated. A chemical bath deposition of $Pb_{1-x}Hg_xS$ thin films has been reported by Sharma *et al.*[7–11] Owing to its wide compositional range, the band gap can be varied from 0.42 to 0.1 eV. This opens possibilities for fabrication of IR detectors with extended spectral response.

Metal sulfide thin layers fabricated by chemical bath deposition techniques (electroless deposition) are an interesting category of materials which are attracting attention as inexpensive, easy to make, and important materials for various photoelectric and other applications. Among the deposition techniques, chemical bath deposition is the most economical and the simplest. A thiosulfate bath has been successfully adapted for thin layer deposition of copper sulfides (Cu_xS),[12–14] Ag_2S,[15] Cu_2Se,[16] Sb_2S_3[17] and Bi_2S_3.[18]

2 Experimental

Mercury(II) sulfide thin layers were grown on substrates previously coated with a thin layer of lead sulfide. Chemical bath deposition from two solutions has been used previously to produce thin layers of lead sulfide.[19] Thin layers of lead sulfide were deposited on planar glass (75 × 25 × 1 mm). Then, they were immersed in a 250 cm^3 chemical bath containing 64 cm^3 $Hg(NO_3)_2$ (0.25 mol dm^{-3}), 8 cm^3 25% $NH_3(aq)$ and 40 cm^3 $Na_2S_2O_3$ (1 mol dm^{-3}); deionized water was then added to make a total volume of 200 cm^3. If the pH of the chemical bath differed from 11, additional $NH_3(aq)$ was added to adjust it (this can happen if the ammonia solution is not freshly prepared).

When $Hg(NO_3)_2$ and NH_3 solutions were mixed, a white solid precipitated. Then an aqueous solution of $Na_2S_2O_3$ was added and the precipitate turned to yellow as it dissolved. Finally, a colorless solution was obtained as all of the precipitate dissolved. Upon heating, HgS began to precipitate within the beaker, while at the same time thin layers grew on both sides of the substrates.

The depositions were carried out in alkaline media and the bath temperature was kept at 65 °C. Stirring was necessary to obtain uniform layers.

2.1 Characterization of the films

The deposited films as well as the bulk precipitates were studied by X-ray diffraction, using a JEOL Model JDX diffractometer and nickel filtered Cu-Kα radiation. The mass of each deposited film was determined gravimetrically in terms of the difference in mass between the blank and coated substrate. Its thickness was then calculated, taking into consideration the covered area, assuming the same density as in the bulk material. The sheet resistance of the films was measured between two silver-pasted electrodes, 1 cm in length and 1 cm apart. Optical studies were carried out on a (Hewlett Packard) HP 8452 A UV–VIS spectrophotometer.

3 Results and discussion

3.1 Chemical considerations

To the best of our knowledge no chemical bath deposition technique for mercury(II) sulfide from aqueous thiosulfate has yet been reported. Owing to hydrolysis, aqueous solutions of mercury(II) salts are usually very acidic and if these are mixed with an aqueous solution of sodium thiosulfate, a black precipitate is immediately formed as a result of the following reactions:

$$2S_2O_3^{2-} + H^+ \rightarrow S + HSO_3^- \tag{1}$$

$$2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e^- \tag{2}$$

$$S + 2e^- \rightarrow S^{2-} \tag{3}$$

$$Hg^{2+} + S^{2-} \rightarrow HgS \tag{4}$$

We found that whenever an immediate precipitate forms in a reaction, it does not favor film growth on substrates. However, if a solution of NH_3 is added to a solution of mercury(II) nitrate, a white precipitate begins to form by the following reaction:

$$Hg(NO_3)_2 + 2NH_3(aq) \rightarrow [NH_2Hg]NO_3 + NH_4NO_3 + 2H_2O \tag{5}$$

If at this point, an aqueous solution of sodium thiosulfate is introduced into the beaker, dissolution can be observed as a result of thiosulfate complex formation. Upon heating, the

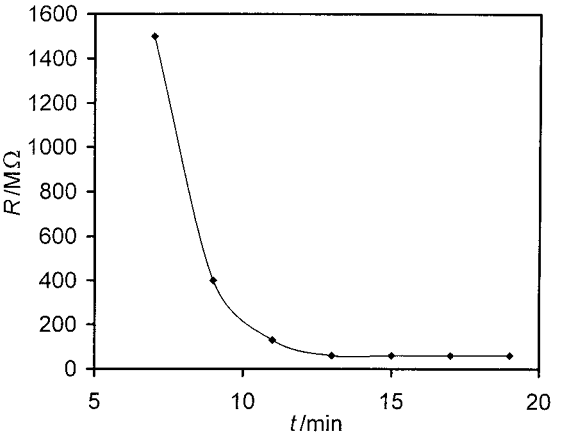

Fig. 1 Sheet resistance of Ag^+ doped HgS layer *vs.* doping time, at room temperature by $[Ag(NH_3)_2]^+$ solution with $c = 0.001$ mol dm^{-3}.

following reactions occur:

$$S_2O_3^{2-} + OH^- \rightarrow HS^- + SO_4^{2-} \quad (6)$$

$$HS^- + OH^- \rightarrow S^{2-} + H_2O \quad (7)$$

$$Hg^{2+} + S^{2-} \rightarrow HgS \quad (8)$$

The mercury(II) ions are released from the thiosulfate complexes, due to hydrolysis, while sulfide ions are released from thiosulfate ions in alkaline media. The thin films of mercury(II) sulfide prepared by this method with thickness of *ca.* 100 nm are golden–yellow, while thicker films (*ca.* 500 nm) are red. Also, thinner films exhibit a mirroring surface, unlike thicker films. A terminal thickness of about 80–90 nm was achieved in *ca.* 20 min. Thicker films for X-ray determination were obtained by re-inserting the initially deposited HgS layers.

The sheet resistances of the HgS layers were >1 GΩ. A substantial decrease of the resistance was achieved by Ag^+ doping, when thin layers of HgS were immersed in a solution of 0.001 mol dm^{-3} $[Ag(NH_3)_2]^+$ for an appropriate time.

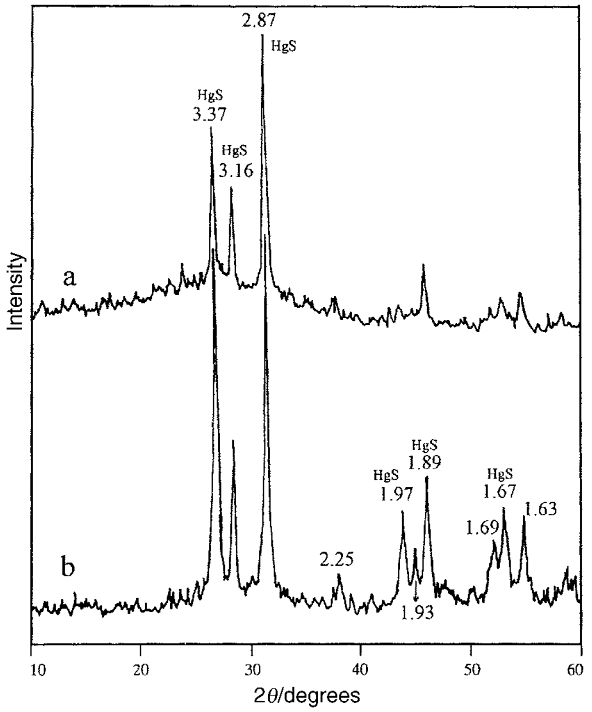

Fig. 2 XRD patterns of a, HgS layer; b, bulk precipitate from the chemical bath.

Table 1 Comparison of observed and literature *d* values with corresponding relative intensities

d_{lit}/Å	Relative intensity (%)	d_{obs}/Å	Relative intensity (%)
3.36	83	3.37	93
3.16	27	3.16	46
2.85	100	2.87	100
1.97	33	1.97	27
1.89	1	1.89	35
1.68	27	1.67	27

Sheet resistance as a function of the doping time is shown in Fig. 1.

3.2 X-Ray investigations

X-Ray diffractograms of the bulk precipitate removed from the bath and a thin layer sample are shown in Fig. 2. Comparison of the observed diffraction peaks with standards[20–22] confirmed that most of the deposited material is mercury(II) sulfide, *i.e.*, a mixture of the γ and dominant α modification (cinnabar). No PbS diffraction peaks were observed indicating that the PbS content in the ultrathin films was below the detection limit of the diffractometer. The *d* values of our diffractograms were compared with available literature data[23] and Table 1 summarizes the relevant literature and observed *d* values and their corresponding intensities. Some of the discrepancies in the intensities may be due to preferred orientation.

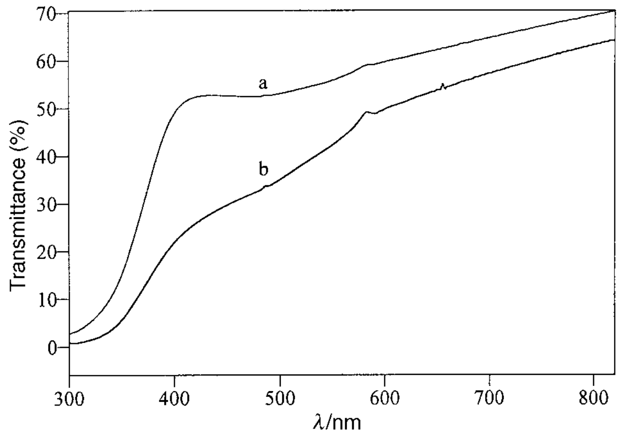

Fig. 3 VIS transmission spectra of the HgS layers: a, 30 nm thick; b, 60 nm thick.

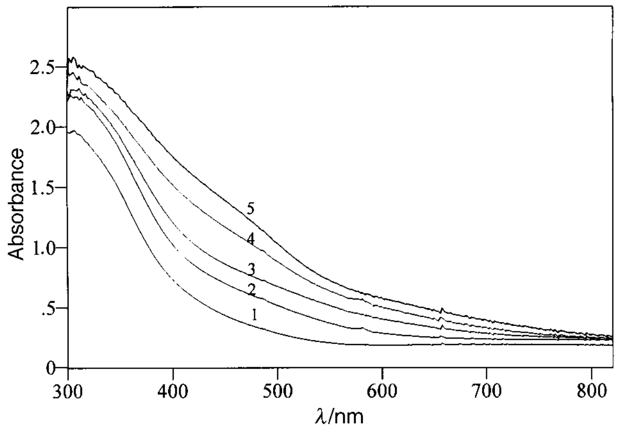

Fig. 4 VIS transmission spectra of HgS layers doped by $[Ag(NH_3)_2]^+$ solution with $c = 0.001$ mol dm^{-3} at room temperature: 1, 0 min; 2, 1 min; 3, 3 min; 4, 9 min; 5, 15 min.

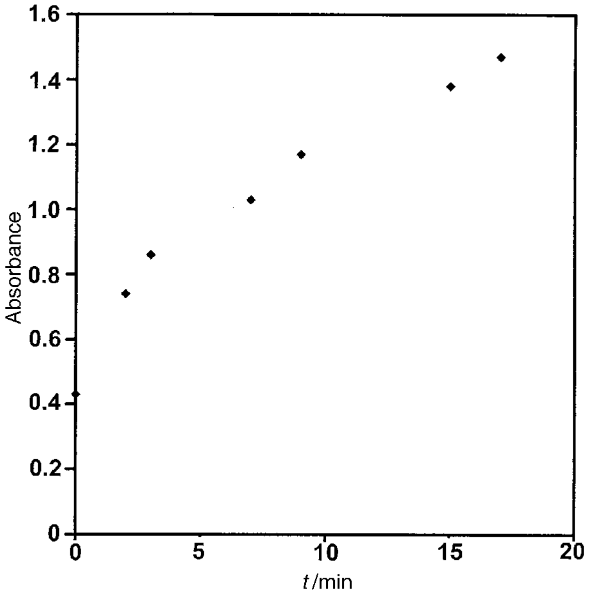

Fig. 5 Absorbance of an Ag^+ doped HgS layer at 500 nm *vs.* doping time.

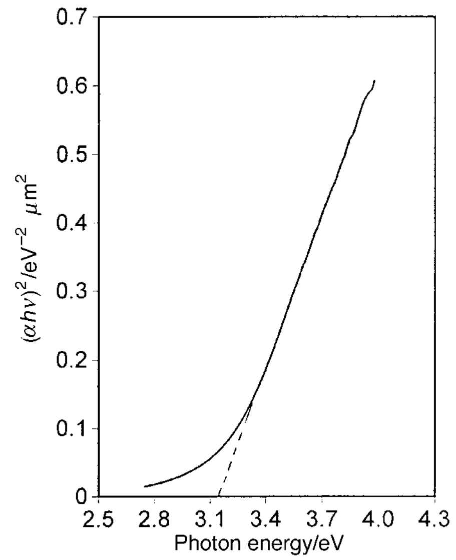

Fig. 6 Optical band gap determination with extrapolation of the linear plot $(\alpha h\nu)^2$ *vs.* *E*.

3.3 Optical investigations

Optical absorption and transmission spectra in the VIS region were recorded for mercury(II) sulfide thin films and also of films doped with Ag^+. Optical transmission spectra for mercury(II) sulfide layers in the spectral region 300–820 nm are shown in Fig. 3.

In order to investigate the expected optical changes as a result of Ag^+ doping, absorption spectra of Ag^+ doped HgS films were recorded and are shown in Fig. 4. A gradual shift in the absorption edge is observed as the amount of Ag_2S increases. Absorption changes at 500 nm after 20 min of Ag^+ doping are shown in Fig. 5. Using the optical transmission data in the region between 290 and 450 nm, the room temperature optical bandgap was determined from a plot of $(\alpha h\nu)^2$ *vs.* *E* (Fig. 6). The extrapolation of the linear plot[24] gave a bandgap energy of 3.1 eV.

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