CHAPTER - 4
CHAPTER 4
PREPARATION AND CHARACTERIZATION OF
NANOCRYSTALLINE HgS THIN FILMS

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CHAPTER 4
PREPARATION AND CHARACTERIZATION OF
NANOCRYSTALLINE HgS THIN FILMS

4 Introduction

Nanotechnology forms bridge that links single element with single crystal bulk structure. Usually large-scale structures are made of polyatomic or molecular assemblies of matter, where the multiplicity of such unit blocks, whether ordered or statistically distributed. Due to this macroscale properties effectively extended down to the microscale, traditional manufacturing techniques have been miniaturized for fabrication of microstructure as in microelectronics, in a top down approach atom by atom manufacturing synthesis. Nanoparticles, therefore, with their oligo-atomic or molecular composition comprising a countable number of such units, represent a scale of matter where radically different phenomena are manifested and dominated its behavior [1-4].

Mercury sulfide (HgS) belongs to group II–VI compounds material. HgS with its direct band gap of 2 eV and its absorption coefficient continuously increasing from the infrared through the visible region has been used in infrared detectors. The HgS thin films have been used in solid-state solar cells, photoelectrochemical cells and photoconductors [5]. Many workers have deposited HgS thin films by chemical bath deposition (CBD) method [6-8]. The potential of chemical bath deposition (CBD) has been shown by a number of workers [9-13]. In the present investigation, section 4A deals with preparation of nanocrystalline HgS thin films by chemical bath deposition method and its characterization. From literature survey, it is seen that no reports are available on the deposition of HgS thin film by modified chemical bath deposition (M-CBD) method. Section 4B reports the preparation of nanocrystalline HgS thin films by M-CBD method and its characterization.
SECTION A

4A Preparation of nanocrystalline HgS thin films by chemical bath deposition (CBD) method

4A.1 Introduction

In the present section, we report on the preparation of mercury sulphide thin films by chemical bath deposition using aqueous alkaline medium. The preparative parameters such as concentration of Hg$^{2+}$ ion source and deposition time are optimized in order to get good quality HgS thin films. Thin films are characterized for structural, surface morphological, optical and electrical properties.

4A.2 Deposition of nanocrystalline HgS thin films

The experimental set up for the thin film deposition by chemical bath deposition (CBD) method is shown in Fig. 3.1. Mercury acetate [(CH$_3$COO)$_2$Hg], thiourea [CH$_4$N$_2$S] and 30 % aqueous ammonia are used as starting chemicals. All chemicals are A. R. grade, supplied by Loba chemie Mumbai. Double distilled water is used for preparing solutions.

The HgS thin films were prepared from aqueous alkaline bath using mercury acetate as Hg$^{2+}$ ion source, thiourea as S$^{2-}$ ion source and ammonia as a complexing agent. The effect of various parameters such as concentration of Hg$^{2+}$ ions, deposition times etc. on film thickness has been carried out.

For the deposition of HgS thin films, 20 ml (0.1 M) mercury acetate solution was taken in glass beaker of 100 ml capacity (deposition bath) to this, 30 % ammonia solution was slowly added with constant stirring. To this mixture, 20 ml (0.1 M) thiourea solution was added slowly with constant stirring. The pH of the bath was adjusted to 9. The ultrasonically cleaned glass substrates were fitted in the bakelite holder having the slots for substrate and the holder is fixed in a beaker containing the precursor solution. The depositions were allowed to proceed without stirring the solution at room temperature (300 K). The substrates coated with HgS thin film were removed
from the bath at suitable intervals (1 to 6 h), washed with double distilled water, dried in air and preserved in a plastic container. Films prepared by this method were uniform and well adherent to the substrates and grayish in color. Fig 4.1 shows photographs of HgS thin films at different thickness.

Fig 4.1 Photographs of HgS thin films deposited by CBD method at different thickness.

4A.3 Characterization of nanocrystalline HgS thin films

The nanocrystalline HgS thin films prepared at optimised preparative parameters were characterized using techniques discussed in section 3A.3.

4A.4 Results and discussion

4A.4.1 Optimization of preparative parameters

For the optimization of the concentration of Hg$^{2+}$ ions, 20 ml volume of (0.1 M) thiourea [CH$_4$N$_2$S] solution was taken in each beaker containing glass substrate and 20 ml volume of mercury acetate [(CH$_3$COO)$_2$Hg] of various concentrations (0.025 to 0.15 M) was added in each beaker. The reactant beakers were kept at room temperature (300 K) for deposition time of 6 h. Then the films were taken out, washed with distilled water and then dried. Fig. 4.2 (a) shows variation of HgS film thickness as a function of concentration of mercury acetate at constant concentration of thiourea (0.1 M) and deposition time of 4 hours. It is observed that film thickness is highest (133 nm) when concentration of mercury acetate is 0.1 M. After this due to the peeling off film material, film thickness decreases for further increase in concentration of mercury acetate.
Fig. 4.2 (b) shows the variation of HgS film thickness as a function of deposition time. Initially film thickness increases linearly and then shows a slight declination for further deposition time. Such behaviour can be understood by the film formation and continuous precipitation, which are taking place in the deposition bath. Thickness of films was found to vary between 37 and 133 nm with deposition time of 1-6 hours.

**Fig. 4.2 Variation of HgS film thickness with (a) mercury acetate concentration and (b) deposition time.**

4A.4.2 Reaction mechanism

Nanocrystalline HgS film can be prepared by hydrolysis of thiourea in an alkaline medium containing a Hg$^{2+}$ salt and a suitable complexing agent which allows for obtaining a soluble species, Hg$^{2+}$ in this medium. The decomposition of Hg$^{2+}$ occurs when ionic product of Hg$^{2+}$ and S$^{2-}$ exceeds the solubility product of HgS [$K_{sp}$ (HgS) = $1.6 \times 10^{-52}$]. Mercury complex formation of [Hg(NH$_3$)$_4$]$^{2+}$ takes place in the presence of ammonia, at pH ~ 9. This complex is soluble in an alkaline medium.

Thiourea (CH$_4$N$_2$S) hydrolyses in solution to give S$^{2-}$ ions according to reaction proposed in equation 3.1 and 3.2.

Similarly, ammonia hydrolyses in water to give OH$^-$ ions according to the equation,

$$\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$$

(4.1)
When ammonia solution is added to Hg$^{2+}$ salt solution, Hg(OH)$_2$ starts precipitating when solubility product (SP) of Hg(OH)$_2$ is exceeded, i.e.

$$\text{Hg}^{2+} + 2\text{OH}^- \leftrightarrow \text{Hg(OH)}_2 \quad (4.2)$$

The Hg(OH)$_2$ precipitate dissolves in excess ammonia solution to form the complex mercury tetra-amine ions $[\text{Hg (NH}_3)_4]^{2+}$,

$$\text{Hg}^{2+} + 4\text{NH}_3 \leftrightarrow [\text{Hg (NH}_3)_4]^{2+} \quad (4.3)$$

Finally the HgS thin film formation takes place,

$$[\text{Hg (NH}_3)_4]^{2+} + \text{S}^{2-} \rightarrow \text{HgS} + 4\text{NH}_3 \quad (4.4)$$

4A.4.3 X-ray diffraction (XRD)

The XRD pattern of as deposited HgS thin film onto glass substrate is shown in Fig. 4.3. The X-ray diffraction studies show that HgS film is nanocystalline in nature with face centered cubic crystal structure. The central broad hump is due to the amorphous glass substrate. The existence of single peak (200) may imply that the present material is nanocystalline in nature. We tried to determine grain size by using Scherre's formula of half width of central maxima, however, the width of peak is too small we could not broaden it.

![Fig. 4.3 The XRD pattern of HgS thin film.](image-url)
4A.4.4 Scanning electron microscopy (SEM)

HgS thin film deposited on to glass substrate with 133 nm thickness was used for study of surface morphology using Scanning electron microscope. Fig. 4.4 shows a scanning electron micrograph of HgS thin film deposited onto a glass substrate at 30,000 X magnification. The scale bar length is 100 nm. From SEM, we draw two conclusions. First the film seems to be composed of large number of nanosized spherical particles. It is also worth to note that, particles are spherical in shape, confirm the cubic phase of HgS. Hence it clearly shows that the growth of HgS films takes place via cluster-by-cluster deposition i.e. aggregation of colloidal particles formed in the solution, rather than ion by ion deposition that agrees well with the observation previously reported by number of researchers [16, 17]. From SEM, It is observed that the film is smooth, homogeneous, fine grained and well covered to the substrate.

![SEM image of HgS film](image_url)

Fig. 4.4 The SEM of HgS film at magnification 30,000 X.

4A.4.5 Transmission electron microscopy (TEM)

Fig.4.5 shows transmission electron micrograph of as-deposited HgS thin film. A TEM micrograph of HgS film deposited onto glass substrate shows agglomeration of very fine particles, which is a feature usually observed when
chemical synthesis is used. The scale bar length is 100 nm. It is clearly seen that the film has been composed of small particles of aggregate size ~ 30 to 35 nm.

Fig. 4.5 Transmission electron micrograph of HgS thin film.

4A.4.6 Optical absorption

Optical properties of HgS thin film were calculated with the help of optical absorption. Fig. 4.6 shows the variation of absorbance coefficient ($\alpha$) with wavelength ($\lambda$) for HgS film. It is observed that absorption coefficient ‘$\alpha$’ is of the order of $10^4$ cm$^{-1}$. The variations of $(\alpha \lambda )^2$ verses $\lambda$ (Fig. 4.7), is a linear at the absorption edge confirms that the HgS is a semiconductor with direct band gap. Extrapolation the straight line portion of the plot $(\alpha \lambda )^2$ verses $\lambda$ for zero energy gives the optical band gap energy of nanocrystalline HgS thin film ($E_g$ = 2.7 eV), which is greater than the value reported earlier for polycrystalline HgS films [18].
4: Preparation and characterization of nanocrystalline HgS thin films

Fig. 4.6 Variation of ($\alpha$) against $\lambda$

Fig. 4.7 Variation of ($\alpha h\nu$)$^2$ against $h\nu$

4A.4.7 Electrical resistivity

The dark dc electrical resistance of the HgS film was measured in 300-600 K temperature range. The electrical resistivity was found to be of the order of $10^3$ Ω cm. Fig. 4.8 shows variation of ln $\rho$ with inverse of absolute temperature for mercury sulfide thin film. The electrical resistivity of HgS film decreases with increase in temperature indicating the semiconducting nature. The nature of the plot indicated the presence of two types of conduction mechanism [15].

It is observed that the ln $\rho$ versus $1000 / T$ curve for HgS film shows two linear portions. The first is at lower temperature region characterized by small slope while second in the higher temperature region characterized by high slope. The activation energy ‘Ea’ obtained using equation 2.22, is 0.08 eV for low temperature (300-363K) and 0.28 eV and high temperature (363-473 K) regions. This clearly indicates that different scattering mechanisms are operative in two regions.
Fig. 4.8 The variation of \( \log \rho \) with inverse of absolute temperature.

4A.4.8 Thermoemf

The type of electrical conductivity exhibited by HgS thin film is determined by thermo-emf measurement. The polarity of thermally generated voltage at the cold end was positive indicating that HgS is p-type semiconductor [20].
SECTION B

4B Preparation of nanocrystalline HgS thin films by modified chemical bath deposition (M-CBD) method

4B.1 Introduction

In this section we report on the deposition of nanocrystalline mercury sulphide thin films by M-CBD method. The preparative parameters such as concentration, immersion cycles, immersion time and rinsing times are optimized in order to get good quality HgS thin films. The HgS films are characterized.

4B.2 Deposition of nanocrystalline HgS thin films

The photograph of microprocessor-based operating system of M-CBD is shown in figure 3.11. An analytical grade (AR) mercury acetate \([(\text{CH}_3\text{COO})_2\text{Hg}]\), sodium sulfide (Na\textsubscript{2}S) and triethalaoamine were used for the deposition of mercury sulfide thin films. For the deposition of nanocrystalline HgS thin films 0.1 M of mercury acetate solution complexed with triethalaoamine and ammonia (with pH ~ 8) was taken as cationic precursor for mercury ions (Hg\textsuperscript{2+}). The source for anionic precursor was 0.1 M sodium sulfide solution at pH ~ 12 for sulfide ions (S\textsuperscript{2-}). For rinsing purpose, double distilled water was used. One M-CBD growth cycle consisted of four steps a) adsorption of mercury ions from mercury acetate solution for 20 s, b) rinsing with double distilled water for 20 s, c) reaction with sulfide precursor solution for 20 s and d) rinsing with double distilled water for 20 s. This growth cycle was repeated to get desired HgS film thickness. Fig 4.9 shows photographs of HgS thin films deposited by M-CBD at different thickness.
4B.3 Characterization of HgS thin films

The nanocrystalline HgS thin films prepared at optimized preparative parameters were characterized using techniques discussed in section 3A.3.

4B.4 Results and discussion

4B.4.1 Optimization of preparative parameters

In the present study, for the concentration of anionic precursor (sodium sulfide) was arbitrarily kept constant as 0.1 M (pH ~ 12) and the concentration of cationic precursor (mercury acetate) was optimized. For cationic precursor, initially 20 ml mercury acetate solution was taken in a 50 ml capacity beaker, and Triethanolamine (TEA) solution was added to it, which acts as a complexing agent. The pH of the cationic precursor solution was maintained at 8 by adding ammonia solution.

Making several trials for different concentration, immersion cycle, and immersion time, preparative conditions for HgS thin films were optimized. Table. 4.1 shows optimized preparative parameters for HgS thin films on glass substrate. The variation of film thickness against concentration of mercury acetate (sodium sulfide, 0.1 M) for 100 deposition cycles is shown in Fig.4.10 (a). The HgS film formation was started from concentration 0.025 M of mercury acetate. After this HgS film thickness was decreased, this may be due to formation of outer porous layer as film peeled off from the glass substrate. Fig.4.10 (b) shows variation of HgS film thickness with number of immersion.
cycles for optimised concentration of mercury acetate (0.1M) and sodium sulfide (0.1M). The HgS film had a maximum terminal thickness of 104 nm at 100 immersion cycles; afterwards, HgS film thickness was decreased due to the peeling off the outer powdery layer.

![Graph (a)](image1.png)

![Graph (b)](image2.png)

**Fig. 4.10** Variation of HgS film thickness with (a) Hg$^{2+}$ ion concentration for 100 immersion cycles and (b) deposition cycle for optimized Hg$^{2+}$ (0.1 M) concentration

**Table-4.1: Optimized preparative parameters for HgS thin films deposited on glass substrate.**

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Parameters</th>
<th>Precursors</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Concentration (M)</td>
<td>Mercury acetate</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sodium sulfide</td>
</tr>
<tr>
<td>2</td>
<td>Complexing agent</td>
<td>TEA and Ammonia</td>
</tr>
<tr>
<td>3</td>
<td>pH</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12</td>
</tr>
<tr>
<td>4</td>
<td>Immersion time (sec)</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20</td>
</tr>
<tr>
<td>5</td>
<td>Number of immersion cycles</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100</td>
</tr>
<tr>
<td>6</td>
<td>Deposition temperature (K)</td>
<td>300</td>
</tr>
<tr>
<td></td>
<td></td>
<td>300</td>
</tr>
</tbody>
</table>
4B.4.2 Reaction mechanism

Reaction mechanism is similar to proposed reaction in section 3B.4.2. In anionic precursor solution, the hydrolysis of sodium sulfide takes place and sulfide ions are released as per reactions (3.7 and 3.8). The cationic solution releases Hg$^{2+}$ from complexed Hg (TEA)$^{2+}$ as follows,

$$[\text{Hg (TEA)}]^{2+} \rightarrow \text{Hg}^{2+} + \text{TEA} \quad (4.5)$$

Glass substrate is immersed in Hg$^{2+}$ ions containing solution. After immersion of glass substrate in S$^{2-}$ ions containing solution, the following reaction takes place on the glass substrate,

$$\text{Hg}^{2+} + \text{S}^{2-} \rightarrow \text{HgS} \quad (4.6)$$

The overall reaction can be written as,

$$\text{Hg}_{\text{aq}}^{2+} + \text{CH}_3\text{COO}_{\text{aq}}^- + 2 \text{Na}_{\text{aq}}^{2+} + \text{S}_{\text{aq}}^{2-} \rightarrow \text{HgS} + 2\text{Na}_{\text{aq}}^{2+} + \text{CH}_3\text{COO}_{\text{aq}}^- \quad (4.7)$$

Thus HgS film formation takes place on glass substrate.

4B.4.3 X-ray diffraction (XRD)

Fig. 4.11 shows X-ray diffractogram of HgS thin film deposited on glass substrate. The XRD pattern of the as deposited film indicated that the HgS thin film grown on glass substrates is nanocrystalline and cubic [19]. In order to determine average grain size of HgS thin film particles, a slow scan between 36 and 42° was carried out with a step of 0.02°/min. Using the relation 2.17, the average grain size of HgS thin film was found to be about 28 nm [21].

Fig. 4.11 X-ray diffractogram of HgS thin film deposited on glass substrate.
4B.4.4 Scanning electron microscopy (SEM)

Fig. 4.12 shows the Scanning electron micrograph of HgS thin film on to glass substrate at magnification 30,000 X. Films are found to be nanocrystalline. HgS thin film deposited on to glass substrate with 104 nm thickness was used for study of surface morphology. The scale bar length is 100 nm. It is observed that the film is smooth, homogeneous, fine grained and well covered to the substrate.

Fig. 4.12 The Scanning electron micrograph of HgS thin film at 30,000 X magnification.

4B.4.5 Transmission Electron Microscopy (TEM)

Fig. 4.13 shows transmission electron micrograph (TEM) of HgS film deposited on glass substrate. The scale bar length is 100 nm. The random orientations of nanocrystals can be clearly seen. Small nanoparticles with dimensions 30–40Å are identified. The crystallite size observed from TEM is in good agreement with value calculated (28 nm) from XRD.
4B.4.6 Optical absorption

The absorption spectra of HgS thin film on glass substrate was studied in the wavelength range 350–850 nm. Optical absorption spectra of HgS thin film is shown in Fig. 4.14. This spectrum reveals that film has high absorbance ($10^4$ cm$^{-1}$). Fig. 4.15 shows a plot of $(\alpha h\nu)^2$ versus $h\nu$, which is linear at the absorption edge, confirming that the material has a direct band gap. Extrapolation of the curve on energy axis for zero absorption coefficient gives the value of optical band gap energy. The optical band gap energy, $E_g = 2.45$ eV, which is comparable to value reported earlier for nanocrystalline HgS film [21].
4B.4.7 Electrical resistivity

The electrical resistivity at room temperature of HgS thin film onto glass substrate was found to be of the order of $10^3 \ \Omega\text{cm}$ that is well agreed with the value reported earlier [18]. The variation of logarithm of resistivity ($\log \rho$) with the inverse temperature ($1000/T$) is shown in Fig. 4.16. The decrease in electrical resistivity with increase of temperature suggested the semiconducting behavior of HgS thin film. The thermal activation energy ($E_a$) was calculated using equation 2.22. From Fig. 4.16, one can observe two distinct activation energy regimes. The activation energy is low ($0.07 \text{ eV}$) in low temperature regime (300-375 K) where grain boundary scattering is predominant. At high temperatures (375-500 K) activation energy is $0.62 \text{ eV}$. The conduction mechanism in the investigated samples can be explained by applying the models elaborated for the films with polycrystalline (discrete) structure [22, 23].
**4B.4.8 Thermoemf**

In the thermoemf measurement, the polarity of thermally generated voltage at the cold end for HgS thin film is positive indicating HgS is p-type semiconductor [24].
4: Preparation and characterization of nanocrystalline HgS thin films

References:


19. ASTM data File No. 6-261.


