Optical, electrical and morphological studies of βHgS thin film prepared by improved chemical bath deposition technique

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Abstract. Polycrystalline mercury sulphide (HgS) thin film at room temperature and in acidic condition was deposited on amorphous glass substrate by using improved chemical bath deposition technique. The structural and morphological analysis of as-deposited and annealed films was carried out by X-ray diffraction and scanning electronic microscopic technique. Ultraviolet and d.c. electrical resistivity measurement were made to study electrical and optical properties of the thin films. The outcome indicates formation of well-crystallized pure βHgS thin films having good electrical and optical properties. For this reason, HgS thin film in acidic medium was deposited properly by using chemical bath deposition technique.

Keywords. HgS thin film; crystal structure; SEM; semiconductor.

1. Introduction

In current years, chalcogenide semiconductors have been successfully applied as absorber layer for thin film solar cells [1]. At present an important matter in Materials science is the solar energy conversion, an escalating number of studies mainly related to materials structured on the nanometre length scale can be found in journalism in the last decade [2]. Polycrystalline materials have diverse properties and frequently better to those of predictable coarse-grained materials [3]. In the middle of the binary semiconductor compound, HgS belongs to II–VI compound material. Due to big absorption coefficient and composition, its bandgap varies among 1.8 and 2.70 eV. It is one of the most hopeful optical absorbers for high efficiency thin film solar cells [4,5]. The HgS thin films are used in infrared detectors, photo-electrochemical cells, storage cells and photoconductors [6,7].

As we know variety of techniques are used for the preparation of HgS thin films, e.g., successive ionic layer adsorption and reaction (SILAR) trend [8], rf-sputtered HgS films [9], sonochemical methods [10,11]. The chemical bath deposition process for metal chalcogenide thin film preparation draws significant interest, as it is relatively less expensive, simple and appropriate for huge area deposition. Bhushan *et al* [12], Lokhande *et al* [13], Kale and Lokhande [14], Najdoski *et al* [15] and Gadave *et al* [16] prepared HgS thin films by chemical bath deposition technique. They prepared HgS thin films in acidic as well as in basic conditions by using ethylenediamine and triethanolamine as a complexing agent. Due to toxicity of ethylenediamine and tri-ethanolamine, it is not environment friendly and they have also high affinity for complexation and produces precipitate quickly, which affects thickness and uniformity of films. The film in alkali conditions also provoke the deposition of Hg (OH) Xs, which roughly affect the conversation efficiency of the solar cells. We prepared uniform single-phase βHgS thin films by using tartaric acid as a caping agent in acidic condition, which should be advantageous to get enhanced HgS thin film.

This study reports the unbeaten deposition of HgS thin films at 32°C at pH 5 using improved chemical bath deposition method and the deposition conditions were optimized to get good quality, well adherent films on the top of glass substrate. The electrical resistivity, optical absorption, X-ray diffraction (XRD) and scanning electron microscopic (SEM) studies are reported for characterization of the prepared films.

2.   Experimental

2.1   *Substrate cleaning*

The deposition was completed on commercially available glass slides of $75 \times 25 \times 2$ mm dimensions. This substrate were cleaned by chromic acid and water, followed by rinsing in alcohol and lastly stored in double distilled water before use.
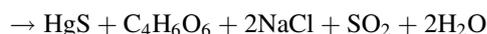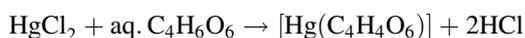
2.2   *Reagents and preparation of solutions*

Analytical grade chemicals mercury chloride, tartaric acid and sodium thiosulphate were used. The solutions were prepared in double distilled water.

2.3   *Synthesis of mercury sulphide thin film*

The deposition of mercury sulphide thin film was done in a reactive solution. Mercury chloride solution, 20 ml (0.025 M), complexed with 15 ml of (0.25 M) tartaric acid were mixed with 20 ml of (0.125 M) sodium thiosulphate solutions in 100 ml capacity beaker at room temperature 32°C. The total volume of the reaction mixture was made to 80 ml by adding double distilled water. The reaction mixture was reserved in an oil bath. The substrate was mounted on a particularly planned substrate holder and rotated in reaction mixture with a rate of $45 + 2$ rpm at room temperature. After 5 h, the slides covered with films were removed, washed with distilled water, dried naturally and kept in dark desiccator.

The chemical reactions during the formation of HgS thin films are as:

$$HgCl_2 + aq. \, C_4H_6O_6 \rightarrow [Hg(C_4H_4O_6)] + 2HCl$$

$$[Hg(C_4H_4O_6)] + 2HCl + aq. \, Na_2S_2O_3$$
$$\rightarrow HgS + C_4H_6O_6 + 2NaCl + SO_2 + 2H_2O$$

2.4   *Characterization of HgS thin films*

Philips PW-3710 in the 2θ range from 10–100 with a CrK, line (2.2897 Å) was used to study XRD of HgS film. The layer thickness of the films was estimated by using a weight difference method. The electrical resistance capacity was done on Zintek-502BC mill ohmmetre in temperature series of 300–500 K by the two-probe method. Rapid drying silver glue was applied for ohmic contact purpose. Calibrated thermocouple (Chromel alumel, 24 gauge) B was used to sense the working temperature. In the wavelength range 400 to 1200 nm, the optical absorption measurements were carried out by using a Hitachi-330 (Japan) UV–VIS NIR double beam spectrophotometer at room temperature, placing similar, uncoated glass substrate in the reference

beam made a substrate absorption improvement. The investigation of the spectrum was carried out by computing the values of absorption at each step of 2 nm. The microscopic observation of film was carried out by SEM JEOL JSM-6360.

3.   Results and discussion

HgS films were deposited by reacting mercury chloride with tartaric acid as complexing agent, which was working to manage the reaction in an appropriate medium as indicated by the pH to achieve the crystal growth. Otherwise spontaneous reaction and sedimentation of material will be obtained. The condition for the compound to be deposited from a solution posture of its ions is that, its ionic product (I.P) should be larger than the solubility product (ksp). The complexing agent of a metal in solution forms a moderately constant complex ions of the metal and provides a forbidden liberate of free ions and these ions reacted with sodium thiosulphate to provide HgS thin films.

3.1   *Structural analysis*

Figure 1 shows two characteristic XRD spectra of HgS film deposited using improved chemical bath deposition: (a) as-deposited and (b) annealed state. The film was annealed at 300°C for 2 h. The as-deposited film, figure 1a, shows amorphous nature with some sharp diffraction lines, which have been investigated by resulting diffraction pattern. XRD pattern showed peak broadening indicating small size
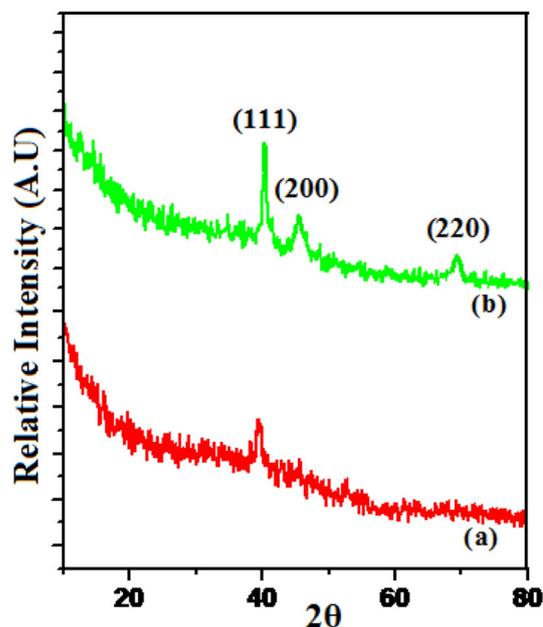

Figure 1. XRD patterns of (**a**) as-deposited and (**b**) annealed HgS thin films.

of the particles. The diffraction peak (111) of as-prepared HgS thin film reveals formation of face-centred cubic crystal structure only at room temperature. The existence of low-intensity single peak (111) means that the current material is nanocrystalline. From figure 1b it is observed that, all the diffraction peaks show peak broadening after thermal annealing, which means particles are in smaller size. The existence of strong diffraction peaks corresponds to (111), (200) and (220) planes of cubic βHgS (meta-cinnabar) [17]. The XRD pattern clearly indicates phase transformation after annealing. Crystallite size of as-deposited and annealed HgS thin film were calculated from Scherrer's formula as

$$D = 0.9\lambda/\beta\cos\theta,$$

where D is crystallite size, λ the X-ray wavelength, β the angular line width of half-maximum intensity and θ the Bragg's angle. The crystallite size of as-deposited thin film is 143 Å (14.3 nm), while annealed thin film is 158 Å (15.8 nm). The αHgS (hexagonal) thin films are generally most stable, so any deposited βHgS thin films are easily transformed into αHgS thin films [18,19].

3.2 Surface morphological studies

SEM micrographs of the HgS film (a) as-deposited and (b) annealed states are shown in figure 2. In both the state, the film is very opaque with no apparent voids or pinholes. Many round-shaped grains are observed on the surface of the sample in the as-deposited state. The annealed HgS film surface morphology seems to be uniformly sprinkled in all directions with arrangement of some clusters on the surface. The as-deposited and annealed films show less than 1 μm dimensions indicating nanocrystalline nature of the films, which reveals effectiveness of this technique on particle size distribution. The average grain size of HgS thin film was calculated by Cottrell's method [20] as follows:

$$PL = [n/2\pi r]M,$$

where n is the total number of intercepts, M the magnification and r the radius of the circle. Knowing n, the average grain size of the as-deposited and annealed thin films was calculated. The average grain size for as-deposited and annealed HgS thin films is 13 and 16 nm, respectively, which well agree with XRD data. Due to smaller particle/grain size of HgS thin film, they have larger surface area and hence they have increasing number of active sites.

3.3 Optical studies

In nanomaterial thin films, bandgap energy was obtained from absorption maxima. According to quantum confinement theory, holes from valence band and electrons from conduction band are broadly restricted by the potential barrier of the surface [21]. Owing to detention of electrons and holes, the lowest energy optical transition from the valence to conduction band will boost in energy, which effectively increase bandgap (E_g). Figure 3 shows the study of optical absorption spectra of βHgS thin film, which was carried out in wavelength range of 400 to 1200 nm. No other absorption except the band edge was observed, indicating the absence of any excitonic absorption. Through the intersection of the straight line with the axis of the photon energy, an E_g value is obtained for HgS thin films. The assumption of optical absorption gives the relation among the absorption coefficient α and the photon energy $h\nu$, for direct allowed transition as,

$$\alpha = (K/h\nu)(h\nu - E_g)^{1/2},$$

where K is constant and E_g is the semiconductor bandgap, which gives the bandgap E_g. From figure 3, on further plotting the straight line portion of the curve to the energy axis gives direct bandgap of the material and it is 2.36 eV for annealed HgS thin film. βHgS thin films have small concentration of intrinsic carriers due to high bandgap energy, hence it operates at high temperature.

3.4 Electrical resistivity studies

Figure 4 shows the variation of electrical resistivity with temperature. From figure 4 it is observed that, resistivity of
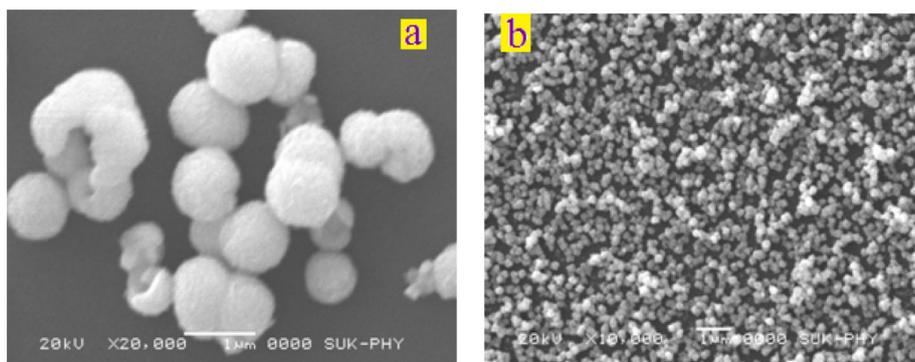

Figure 2. SEM micrographs of (**a**) as-deposited and (**b**) annealed HgS thin films.
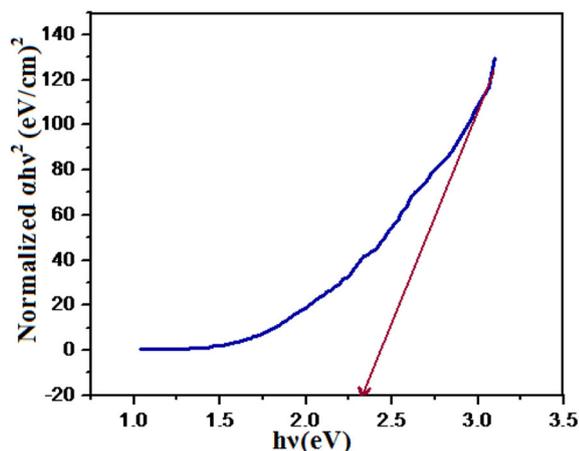
Figure 3.   Optical energy bandgap of HgS thin film.

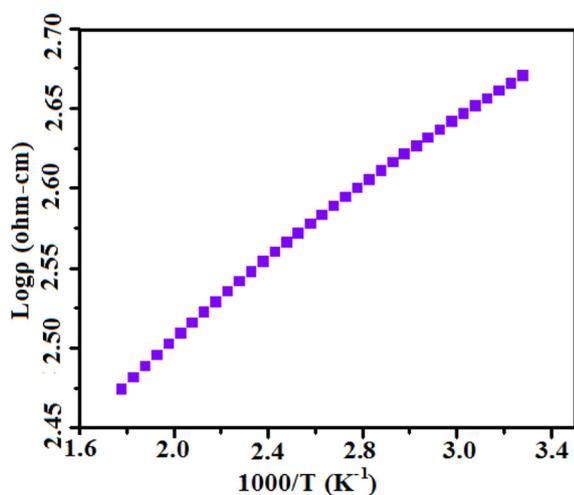**Figure 4.**   The plots of variation of logarithm of electrical resistivity (Log ρ) *vs.* reciprocal of temperature (1000/*T*).

the investigated sample decreases linearly with increase in temperature, reflecting semiconducting behaviour of HgS films [22]. The electrical characterization of βHgS thin films by using hot two-probe method shows p-type semiconducting nature. The conduction mechanism in mercury sulphide thin film is explained on the basis of Wilson's law [23]

$$\rho = \rho_0 \, \exp(E_a/kT),$$

where ρ is the resistivity at temperature T, ρ_0 constant, k the Boltzmann constant and T the absolute temperature. The decrease in resistivity with temperature is due to increase in drift mobility of the charge carrier. The activation energy calculated from resistivity curve by using the above equation is of 0.54 eV. The activation energy represents rate of typical energy of the carriers with respect to fermi energy that they can move only at the bottom or top of the band. This is happening due to electron isolation, which implies potential barrier between them [24].

4.   Conclusion

From the reported result, it can be concluded that a good quality βHgS thin film was prepared by improved chemical bath deposition technique. XRD analysis shows well nano-crystallized single cubic crystal structure of βHgS thin film, having average grain size 15 nm. SEM study shows the formation of uniformly sprinkled morphology with nano-sized grain. Ultraviolet measurement shows 2.36 eV optical bandgap and this value confirms that, it can be used in photo-electrochemical cells, photoconductors and solid-state cells and so on. The electrical resistivity study shows the formation of p-type semiconducting βHgS thin film with activation energy 0.54 eV.

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