

## Electrodeposition and characterization of HgSe thin films

T. Mahalingam<sup>a,d,\*</sup>, A. Kathalingam<sup>a</sup>, C. Sanjeeviraja<sup>a</sup>, R. Chandramohan<sup>b</sup>, J.P. Chu<sup>c</sup>,  
Yong Deak Kim<sup>d</sup>, S. Velumani<sup>e</sup>

<sup>a</sup> Department of Physics, Alagappa University, Karaikudi — 630 003, India

<sup>b</sup> Physics Department, National Chang-Hua University of Education, Chang-Hua 50058, Taiwan

<sup>c</sup> Institute of Materials Engineering, National Taiwan Ocean University, Keelung 202, Taiwan

<sup>d</sup> Department of Electrical and Computer Engineering, College of Information Technology, Ajou University, Suwon 443–749, Korea

<sup>e</sup> Departamento de Fisica, ITESM — Campus Monterrey, Nuevo Leon, C.P.64849, Mexico

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### Abstract

In this article we present the results on the electrochemical synthesis of mercury selenide (HgSe), an interesting II–VI material. HgSe thin films were deposited potentiostatically on conducting glass substrates from an aqueous bath containing HgCl<sub>2</sub> and SeO<sub>2</sub>. The prepared films were characterized by X-ray diffraction (XRD), energy dispersive X-ray analysis (EDX), scanning electron microscope (SEM) and optical absorption techniques. Stoichiometric polycrystalline HgSe films were obtained at a deposition potential around –0.7 V vs SCE, at a temperature 60 °C and a pH value of 3.5. The as-grown films exhibited a direct optical band gap of 0.78 eV. This report deals with the growth mechanism and a study related to the influence of electrolyte bath composition, deposition potential, temperature and pH on the properties of HgSe thin films.

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### 1. Introduction

Mercury selenide (HgSe) is one of the very interesting II–VI materials to be investigated for its applications in IR emitters, IR detectors and tunable lasers [1]. HgSe has a unique combination of properties; it is a semimetal, characterized by high electron mobility, large electron concentration and a variation of band gap with temperature [2]. To get low-resistance ohmic contacts has been a major problem in the technology of optical devices based on ZnSe. But the recent studies have proved the

possibility of an ohmic contact between HgSe and ZnSe comparable to the case of HgTe on CdTe. There has also been a great interest towards ternary alloy thin films containing HgSe as a host material in optoelectronic devices. Enfeldt et al.[3] have reported the molecular beam epitaxial growth of HgSe for ohmic contacts to P-ZnSe; they have also studied MBE growth parameters on the structural properties of HgSe and on its different electrical properties compared with bulk HgSe. Anh et al. [4] have demonstrated self-organization of HgSe quantum wires. MBE growth of HgSe thin films and its effects has been reported by Becker et al. [5]. A huge amount of literature is available on bulk HgSe, but only a small amount of information is available on the thin films of HgSe. Most studies in II–VI compounds have been focused on zinc and cadmium chalcogenides, but the

\* Corresponding author. Permanent address: Department of Physics, Alagappa University, Karaikudi — 630 003, India. Tel.: +82 31 219 1847; fax: +82 31 212 9531.

E-mail address: maha51@rediffmail.com (T. Mahalingam).

studies of on mercury chalcogenide are less, owing to the toxicity problem of mercury. To our knowledge, electro-deposition of HgSe has not been reported in the literature. Hence, we have attempted in the present study to deposit an HgSe thin film by electrodeposition, a convenient, room temperature root for the deposition of films.

## 2. Experimental details

The electrolyte bath was prepared by dissolving the chemicals in de-ionized water. All the chemicals used in this work were of analytical reagent grade (99% purity, E-Merck). Mercuric selenide thin films were deposited onto fluorine-doped tin oxide-coated glass substrates (approximately  $1 \text{ cm}^2$  area and  $25 \text{ } \Omega/\text{cm}^2$ ) from an aqueous solution bath containing 0.5 to 2.0 mM  $\text{HgCl}_2$  and 1 to 5 mM  $\text{SeO}_2$  in the pH range between 2 and 4. The substrates were cleaned with acetone, methanol and rinsed in distilled water prior to deposition. After cleaning, the substrate showed a resistance of  $20 \text{ } \Omega/\text{cm}^2$ . Films were deposited cathodically using a scanning potentiostat (Model 362, EG&G, Princeton Applied Research, USA) at different potentials ranging from  $-0.2 \text{ V}$  to  $-1.2 \text{ V}$  versus SCE (Saturated Calomel Electrode) with different bath temperatures. A standard three-electrode system comprising a graphite rod and a saturated calomel electrode were used as counter and reference electrodes for the depositions. The electrolyte solution was taken in a beaker; the reference electrode was introduced into the solution with a luggin capillary arrangement. During deposition, the bath solution was stirred slowly using a magnetic stirrer with a hot plate. After film formation, the slides coated with the film were removed, rinsed with distilled water, dried and stored in a desiccator for further studies. Multiple beam interferometry and microbalance techniques were used to measure the thickness of the film. X-ray traces of grown films were recorded using a Bruker Discover D8 diffractometer in  $2\theta$  ranges between  $20^\circ$  and  $80^\circ$  with  $\text{CuK}_\alpha$  radiation ( $\lambda=0.1542 \text{ nm}$ ). Surface morphological and compositional analysis were carried out using a scanning electron microscope (SEM) and an energy dispersive X-ray analysis set up (EDAX) attached with SEM (Philips, Model XL 30). Optical measurements were carried out using a JASCO V-570 spectrophotometer.

## 3. Result and discussion

### 3.1. Growth and physical properties

In the electrochemical deposition of HgSe thin films, the growth rate was found to depend on temperature, pH and concentration of the electrolyte. Fig. 1 shows the

variation of film thickness with deposition time and temperature of HgSe thin film growth. The film thickness increases with deposition time and reaches a maximum value of 90 nm in 2h for the deposition temperature of  $60 \text{ } ^\circ\text{C}$ . For temperatures above  $60 \text{ } ^\circ\text{C}$  only precipitation was observed, this might be due to the faster release of ions. The thickness of the film was also found to increase linearly with both  $\text{HgCl}_2$  and  $\text{SeO}_2$  concentrations. However, the increase is restricted to a very low concentration range and it becomes saturated for higher concentrations of both precursors (above  $1.5 \text{ mM HgCl}_2$  and  $2 \text{ mM SeO}_2$ ). The Hg content in the film increases linearly with bath concentration up to  $1.2 \text{ mM HgCl}_2$  and afterwards saturation was observed. As shown in Fig. 2, there is a major change in Hg/Se ratio for the films deposited at potentials between  $-0.2 \text{ V}$  and  $-1.2 \text{ V}$  versus SCE. Good stoichiometry of the film was obtained at around  $-0.7 \text{ V}$  vs SCE as revealed by compositional analysis. Deposited films usually appear to be a shiny grayish color, but when the concentration of the bath is high it turns into a blackish color. The more blackish color of the films deposited from baths with more than  $1.5 \text{ mM Hg}$  could be ascribed to an excess of unbound mercury. The films deposited at a potential of  $-0.7 \text{ V}$  vs SCE with precursor concentrations of  $1 \text{ mM (HgCl}_2)$  and  $2 \text{ mM (SeO}_2)$ , a pH value of 3.5 and a temperature around  $60 \text{ } ^\circ\text{C}$  were found to be uniform and strongly adhering to the substrates. When the films are deposited with precursor concentrations

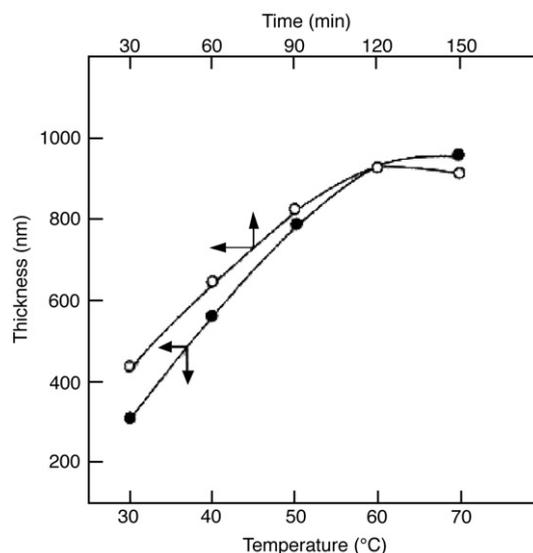


Fig. 1. Variation of film thickness with time and bath temperature (bath composition:  $1 \text{ mM HgCl}_2$ ,  $2 \text{ mM SeO}_2$ , pH 3.5, deposition potential  $-0.7 \text{ V}$  vs SCE, temperature  $60 \text{ } ^\circ\text{C}$ ).

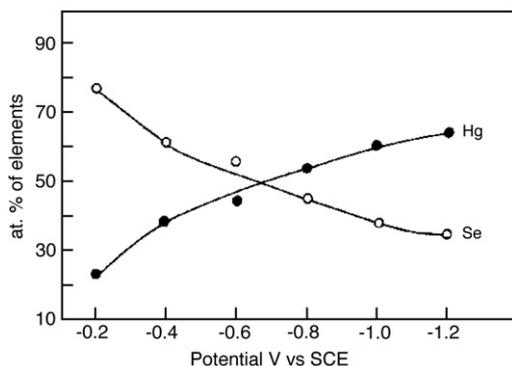


Fig. 2. Variation of Hg and Se content in the film with deposition potential (bath composition: 1 mM  $\text{HgCl}_2$ , 2 mM  $\text{SeO}_2$ , pH 3.5, temperature 60 °C).

higher than 1.5 mM of  $\text{HgCl}_2$  and 2 mM of  $\text{SeO}_2$ , the resultant films are found to be less adherent with the substrates.

### 3.2. Structural studies

X-ray diffraction patterns of HgSe thin films deposited at different conditions were obtained. Fig. 3 shows the X-ray diffraction pattern of HgSe film deposited at different potentials and at a bath temperature of 60 °C. The diffraction peaks obtained at 25.36°, 29.35°, 41.96°, 49.62°, 51.95°, 60.82° and 66.88° are

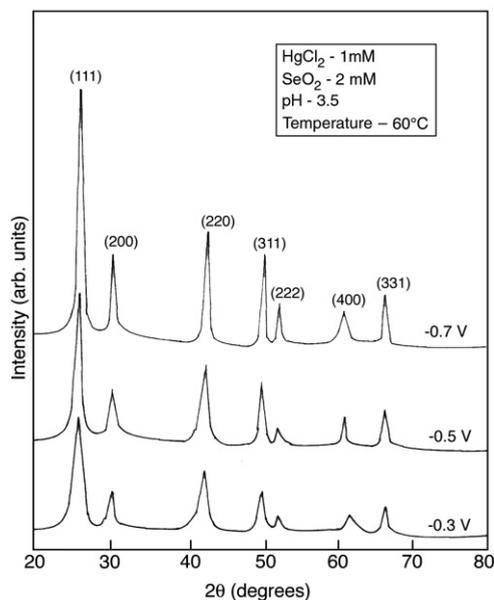


Fig. 3. XRD patterns of films deposited at the deposition potentials of  $-0.3$  V,  $-0.5$  V and  $-0.7$  V vs SCE (bath composition: 1 mM  $\text{HgCl}_2$ , 2 mM  $\text{SeO}_2$ , pH 3.5; temperature 60 °C).

attributed to the reflections of the (111), (200), (220), (311), (222), (400) and (331) planes, respectively. These  $2\theta$  values of the peak positions match well with the standard X-ray powder diffraction patterns of the ASTM data [6]. The X-ray diffraction patterns with a large number of peaks confirmed that polycrystalline HgSe films with a cubic zinc blende structure were deposited. Li et al. [7] have reported a cubic zinc blende structure for a HgSe powder synthesized through a room temperature conversion route. Hankare et al. [8] and Mathe and Cox [1] have also reported a cubic zinc blende structure for HgSe thin films prepared by both a chemical bath and electrochemical atomic layer epitaxy methods. All the peak intensities are found to increase with a decreasing deposition potential down to  $-0.7$  V vs SCE. These results indicate that the polycrystalline morphology of the best quality films are formed at  $-0.7$  V vs SCE.

Fig. 4 shows the X-ray diffraction pattern of the films deposited at bath temperatures 30 °C, 60 °C and 80 °C. The (111) peak was found to increase up to a bath temperature of 60 °C. This increase of the diffraction peak confirms that the higher temperature leads to the formation of well-crystallized cubic HgSe. However, the XRD pattern of the film deposited at a bath temperature of 80 °C revealed a reduction in the peak heights. At the bath temperature of 80 °C, a high current density was

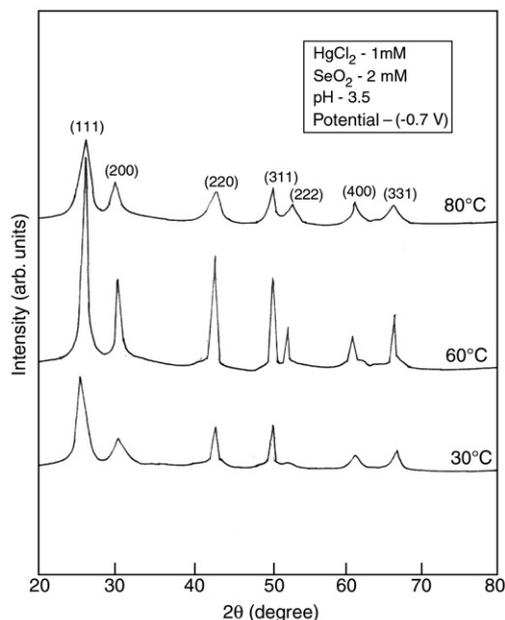


Fig. 4. XRD patterns of films deposited at the bath temperatures of 30 °C, 60 °C and 80 °C (bath composition: 1 mM  $\text{HgCl}_2$ , 2 mM  $\text{SeO}_2$ , pH 3.5; potential  $-0.7$  V vs SCE).

found with a larger mass transfer impeding the growth of crystalline deposits. Also at these high temperatures, due to the bubble formation caused by the large mass transfer, the films deposited were found to poorly adhere with the substrates. The grain size of the deposits was calculated using the Debye–Scherrer equation for the film deposited at  $-0.7$  V vs SCE at a bath temperature of  $60^\circ\text{C}$ . The Debye–Scherrer equation used to calculate the grain size of the deposits is

$$D = K\lambda / B \cos\theta$$

where  $K=0.9$ ,  $\lambda$  is the wavelength of X-rays used,  $B$  is the full width at half maximum of the diffraction peak (FWHM). The average grain size of a typical HgSe film from the (111) peak was estimated to be 78 nm. A scanning electron micrograph of an as-grown HgSe film deposited at optimized condition is shown in Fig. 5. As-grown films do not present well-defined grain edges. The SEM picture reveals few larger grains consisting of the aggregates of a few small crystallites.

### 3.3. Optical studies

The room temperature optical absorption was measured for the as-grown HgSe films in the wavelength region of 500–2000 nm. The spectrum shows an absorption edge at about 1600 nm. The optical band gap of the grown HgSe film is calculated using the relation:

$$h\nu\alpha = k(h\nu - E_g)^{n/2}$$

where  $k$  is a constant,  $E_g$  is the band gap energy,  $\alpha$  is the absorption coefficient of the film and  $h\nu$  is the photon energy. The value of  $n$  is equal to 1 for a direct gap and 4 for an indirect gap. Fig. 6 shows the  $(\alpha h\nu)^2$  vs  $h\nu$  plot of a HgSe film. The linear dependence on  $h\nu$  shown by  $(\alpha h\nu)^2$ , indicates that this transition is direct. The band

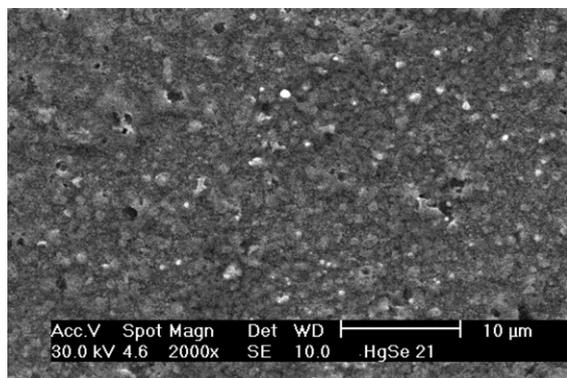


Fig. 5. SEM picture of an as-grown HgSe thin film.

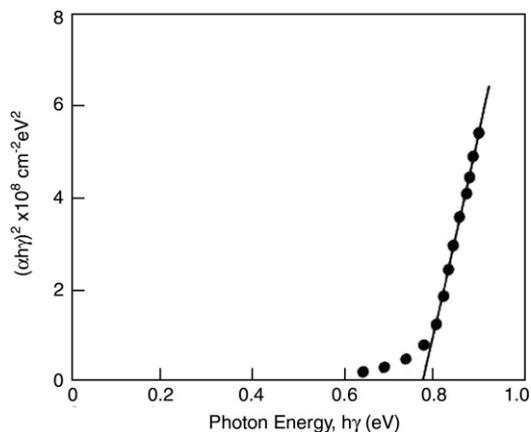


Fig. 6. Plot of  $(\alpha h\nu)^2$  versus  $h\nu$  of HgSe film.

gap value  $E_g$  has been calculated from the linear fit of the  $(\alpha h\nu)^2$  vs  $h\nu$  plot and found to be 0.78 eV. The direct gap is due to the transition between the valence band and conduction band of the spin-orbit split. This value of the band gap is quite close to the value reported by Hankare et al. [9] for HgSe thin films. The HgSe, being a semimetal, it is characterized as a zero band gap material. It is known that the optical band gap of polycrystalline HgSe thin films can be higher than that of bulk HgSe due to quantum size effects, non stoichiometry of the film, large dislocation densities and the presence of ionized impurities [8].

### 3.4. Electrical studies

The electrical resistance measurements were carried out in a temperature range of  $50^\circ\text{C}$  to  $150^\circ\text{C}$  using the two-probe technique. For the electrical measurement studies, a part of the HgSe film was removed from the

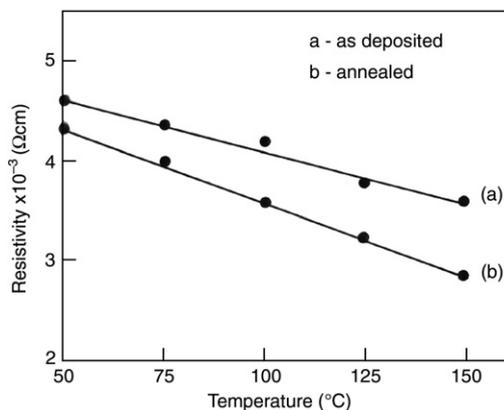


Fig. 7. Variation of resistivity of HgSe films with temperature (a) as-deposited, (b) annealed.

conducting substrate by pressing a non-conducting glass slide over the HgSe film with the use of a non-shrinkable epoxy. Ohmic contacts to the HgSe films were made with silver paste. The conductivity type of the electrodeposited HgSe thin films was studied by the hot probe method. All the electrodeposited HgSe samples were found to be n-type. The electrical resistivity of the as-deposited HgSe film was measured to be  $5 \times 10^{-3} \Omega\text{cm}$  at room temperature. The electrical resistivity of the as-deposited and annealed HgSe films was measured at various temperatures ranging from 50 °C to 150 °C, the change of resistivity with respect to temperature is shown in Fig. 7. The resistivity of the as-deposited HgSe films was found to decrease with temperature and this indicates that the deposited HgSe films are semiconducting. Annealing the deposited films at 200 °C in air reduces the room temperature electrical resistivity of the films from  $5 \times 10^{-3}$  to  $4.6 \times 10^{-3} \Omega\text{cm}$  and this could be attributed to the recrystallization of the as-deposited films, which in turn improves the carrier mobility by reducing the content of grain boundaries.

#### 4. Conclusions

This initial attempt has proved that the growth of polycrystalline HgSe thin films is possible by a simple electrodeposition technique with the proper selection of bath concentration and other growth parameters. The as-grown films present excellent adherence, relatively good morphological and crystalline properties as inferred from SEM and XRD analysis. Our results also show that

the grown films are of a semiconducting nature with n-type conductivity. The band gap energies calculated for the films were quite close to the reported values of HgSe thin films. Further detailed investigations on the electrochemical synthesis of HgSe are under way.

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