Mat. Res. Bull., Vol. 24, pp. 945-952, 1989. Printed in the USA. 0025-5408/89 \$3.00 + .00 Copyright (c) 1989 Pergamon Press plc.

DEPOSITION OF AMORPHOUS MERCURY SELENIDE THIN FILMS BY AQUEOUS REACTIVE SOLUTION GROWTH TECHNIQUE

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(Received April 6, 1989; Communicated by J.B. Goodenough)

### ABSTRACT:

A chemical method has been developed for the preparation of Mercury selenide (HgSe) thin films on glass substrate at room temperature. Mercury selenide thin films was prepared by using mercury formamide a novel complex compound and sodium selenosulphate as a selenide releasing agent. The adherence and uniformity of the film was improved by adding polyvinyl pyrollidone as minor additive. X-ray diffraction, optical absorption and electrical measurements were performed to characterize the deposition of Mercury selenide. The films were found to be amorphous, p-type semiconductor with an energy gap of 1.42eV.

MATERIAL INDEX : Selenide, Mercury.

#### INTRODUCTION

Semiconducting chalcogenide thin films have received major attention in recent years due to their application in device fabrication [1]. There are several techniques both physical and chemical e.g., vacuum evaporation, R.F. Sputtering, chemical vapour deposition, spray pyrolysis, electrodeposition, solution growth technique etc. by which thin films can be deposited. However, the cheapest and most convenient way of depositing the thin films is the reactive solution growth technique because it does not involve complex instrumentation and growth rates are easily controllable. We in our laboratory are carrying out research in this field for the last few years and have developed several semiconducting films by this technique e.g.,  $Bi_2S_3$ ,  $Bi_2Se_3$ , CdS, CdSe, ZnS, ZnSe, NiS, NiSe, CuSe,  $CoS_{1.035}$ , CoSe and  $Sb_2Se_3$  [2-11] have been reported. However,

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the deposition of HgSe thin films by a chemical method has not been achieved to date. Mercury selenide displays the Korsunskii effect [14-15] in thin film form. This phenomenon seems to be promising with regard to the development of new types of devices. In this paper we report a chemical method for a deposition of HgSe thin films at 300K onto glass substrate and its characterization through x-ray diffraction and studies of optical and electrical properties.

#### EXPERIMENTAL DETAILS

Preparation of a 0.2M Sodium Selenosulphate Solution

5 gms selenium powder was mixed with 12 gms of anhydrous sodium sulphite in 100 ml of distilled water. The mixture was then refluxed for 7-8 hrs. It was cooled and kept overnight so that a little selenium separated out from the solution. It was then filtered to obtain a clear solution and made up to 200 ml with distilled water.

Preparation of Hg<sup>+2</sup> Solution

5 gms of HgO (yellow) was dissolved in 25 ml of (98%) formamide solution with constant stirring for about  $1\frac{1}{2}$  hrs. Then it forms a clear solution. The resulting solution was made up to 250 ml with distilled water.

### Deposition of HgSe Thin Films at 300K

8 ml of freshly prepared  $Hg^{+2}$  solution was taken in a beaker to which 6.5 ml of 2 M NaOH solution and 1.5 ml of 0.5% polyvinyl pyrollidone solution were added with constant stirring followed by 2.2 ml of 0.2M sodium selenosulphate solution. The resulting solution was made up to 25 ml with distilled water. The resulting mixture was stirred for a few seconds and then poured into another beaker containing a scrupulously cleaned glass substrate, clamped vertically. The solution gradually turned black. After about  $4\frac{1}{2}$  hrs both sides of the glass slide were covered with a brownish black deposit. The glass was taken out, washed with distilled water and dried in a desiccator. The thickness of the deposited mercury selenide films were measured by Taylor Hobson Talystep instrument. The film was uniform and strongly adherent.

The composition of the films prepared by the present method was determined by x-ray powder diffraction with an 11.46 cm Debye Scherrer Camera and nickel-filtered  $CuK_{\infty}$  radiation.

The optical absorption measurements were taken with a Cary 17-D spectrophotometer.

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The intrinsic activation energy of the films were determined by measuring the dark conductivity from 300K to 500K by a four probe method.

The sample housing consisted of a heavy brass chamber which was evacuated by a combination of oil diffusion pump. The samples were heated electrically. The e.m.f developed across the copper constantan thermocouple was measured by a D.C. micro-voltmenter (Philips pp 9004).

Thermoelectric measurements were performed to determine the type of majority carrier. For the electrical measurements silver paint was used as an electrical contact. Four equidistant strips of 2mm breadth were then made on the film by using silver paint and a musk. The continuity of the contacts were checked from current-voltage characteristic of the film.

#### RESULT AND DISCUSSION

The main principle for the formation of chaleogenide thin films is a slow release of metal ions from a complex. This will react with sulphide or selenide from a sulphide or selenide releasing agent. By following this principle earlier workers have deposited several chalcogenide thin films by using different complexing agents like triethanolamine, ammonia, cyanide etc. Since the solubility product of mercury selenide is very low hence all these complexing agents as mentioned above which was previously used in chemical deposition of other metal chalcogenide failed to deposite mercury chalcogenide thin films. Only Ias complexing agent showed some promise, though the reagent is only successful for HgS [16] but posed difficulties to reproduce the film of good quality. In this investigation it has been observed that mercury-formamide is a suitable compound which release Hg+2 slowly and the compound is water soluble so that non-aqueous is not needed. This complex is moderately stable which causes slow release of mercury ion and forms mercury selenide thin films. Hence mercury formamide complex is unique for this chemical deposition of mercury selenide thin films.

An x-ray diffractograph of the powder scraped off the substrate did not show any sharp peaks, indicating that the films are amorphous. Hence for x-ray analysis the powder was crystallized by heating at 473K for 6-7 hrs in an inert atmosphere. The d values of the lines obtained in the x-ray diffraction pattern of the crystallized sample were calculated and compared with the standard d values for HgSe. The observed d values are in good agreement with the standard ASTM values, confirming that the material of the film is HgSe.

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### TABLE I

X-ray Powder Diffraction Lines of Crystalline HqSe Prepared

Observed d value (Å)	d values from ref 13 (Å)	Relative Intensity	
3.51	3.515	50	
2.95	2.93	100	
2.15	2.16	30	
2.06	2 <b>• 02</b>	100	
1.82	1.83	10	
1.71	1.713	20	
1.62	1.615	20	

A plot of  $(\alpha, h\gamma)^{1/2}$  vs h) is shown in Fig.1. Extrapolation of the linear portion of the curve gives the optical gap of the semiconductor, which is 1.42eV. Though crystalline HgSe (Wurtzite) is semimetal. The higher value of band gap may be the outcome of stabilized amorphous structure. The thermoelectric conductor measurement inferred that the present films are p-type.

The variation in dark conductivity with temperature from 300 -500K for an HgSe film is represented in Fig.3. The plot reveals that there are two regions, one below 380K where the conductivity varies very slowly and the other above 4000K. The activation energy in the high-temperature zone is 0.71eV, which is half of the optical band gap. This is the characteristic of an intrinsic semiconductor. The basic chemical reaction that leads to the formation of HgSe is as follows :

by the Present Method.



Fig 2(a) shows the growth of HgSe films with time of deposition at 300K. In the initial stage of growth, the thickness increases rapidly. Then the rate decreases resulting in a terminal thickness of about 500 nm. The growth of a HgSe film without adding polyvinyl pyrollidone is shown in Fig 2(b). It has been found that the rate of deposition of the film increases and the terminal thickness is less than that of the thickness of the films deposited by adding polyvinyl pyrollidone.



Time (hours)

### FIG 2

- (a) Thickness of HgSe films as a function of deposition time at room temperature (300K) with polyvinyl pyrollidone.
- (b) Thickness of HgSe films as a function of deposition time at room temperature (300K) without polyvinyl pyrollidone.

All these measurements have been carried out several times and the result obtained are more or less repeatable. The specimens are not damaged during various measurements which indicate the stability of the materials upto 700K in amorphous form.

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Variation in the dark conductivity with temperature for HgSe film.

# <u>Conclusion</u>

A method for the chemical deposition of HgSe has been developed using mercury formamide as a complex compound which is an unique compound for the deposition of mercury selenide thin films. A trace amount of polyvinyl pyrollidone improves the quality of the film such as uniformity, adherence and thickness by lowering the deposition rate. The films were found to be amorphous prype semiconductor instead of semimetallic phase with an optical band gap of 1.42eV.

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