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Electrosynthesis and Characterization of CdSeHgTl Thin Films

Pathak R.K.
Department of Chemistry, Government MLB College, Indore, MP, INDIA

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Abstract

Tl containing CdSeHg films have been electrosynthesised at – 0.600 V vs SCE on titanium substrate from the aqueous solution. Electrochemical properties of the films were investigated in $1/_2I$- redox solution. Films were found to be p-type conductivity with charge carrier level 10^{25}. The carrier concentration and flat band potential of the film were determined from capacitance measurements. The films were characterized with scanning election microscopy (SEM) combined with energy dispersive X-ray analysis (EDAX) system. The corrosion characteristics of the films have been studied by polarization technique. The inhibitor inhibits corrosion even in trace amount. This is the study to investigate the effect of thallium concentration on the composition, capacitance, photo activity, morphology and corrosion parameters of the CdHgSeTl films electrosyntesised by electrodeposition.

Keywords: Electrodepostion, SEM, EDAX.

Introduction

Group-II-IV compounds semiconductor are used in a wide range of electrochemical applications including solar energy conversion and photovoltaic devices[1-3]. CdSe is one of the most promising materials for solar energy conversion because it has low energy gap and direct optical transition takes place[4,5]. Several methods have been used to prepare the thin films. Electrochemical method is a useful tool for preparing polycrystalline materials[6,7]. It has some advantage over the other means of preparation and find advantages in lowering the cost and environmental stress of the film processing, because material can be obtained under very mild condition at atmospheric pressure and room temperature. The electrochemical formation of solid films is widely used in surface coating in industries. The cathodic deposition route involving the co-reduction of chalcogenides has been extensively studied, particularly in the case of II-IV compound semiconductor. I have reported the electrosyntesis of Tl containing CdHgSe films and their characterization on the basis of electrochemical, corrosion, compositional and morphological analysis.

Material and Methods

CdSe films were electrodeposited potentiostatically from aqueous solution on the Titanium sheet (1x 1cm). Electrosyntesis was carried out from the solution containing 0.1 M $CdSO_4$ and 0.001 M SeO_2. The deposition potential was maintained at -0.600 V vs saturated calomel electrode (SCE). Various concentrations of Hg and Thallium were added to be solution of CdSe during deposition. The chemicals $CdSO_4$ (CDH), SeO_2 (CDH), $TlNO_3$ (AR) and $HgNO_3$ were used without pretreatment. Water was purified by distillation. A three electrode cell was used for electrodeposition. A titanium plate and SCE were used as counter electrode and reference electrode respectively. For the preparation of working electrode, the titanium plates were subjected to cleaning process, by using emery paper, acetone and distilled water. The power supply (Systronics) was used for application of the potential for deposition. Digital multimeters were used for current and potential measurements. Electrochemical deposition was carried out at room temperature and the electrodes were kept in electroplating solution for about one hour for equilibration. The morphology and composition of the films were investigated with using SEM (JOEL) equipped with EXAX (JOEL). The CdSe, Hg and Tl containing CdSe films are used for measurement of electrical properties. The photoelectroactivity studies were carried out in the redox system containing 1 M $(CH_3COO)_2Cd$, KI and I_2. The capacitance measurements was done by using a digital LCR meter (Systronics). For corrosion behaviors, the electrodeposits were used as working, titanium as counter and SCE as reference electrode. The electrodes were kept in the electrolyte. The working electrode exposed to corrosive media. Anodic and cathodic polarization was carried out for the purpose of construction of tafel plots. The anodic and cathodic slopes are to be used for the estimation of corrosion parameters.

Results and Discussion

Concentration of Tl in the electrolytic solution containing CdHgSe is an important variable governing the composition of the electrodeposited films. The ratio of the ions in the electrolyte can be varied by either changing the relative concentration of the ions while keeping the total content the same or by varying the concentration of one of the ion while keeping the other constant. In the present study, we have followed the latter technique and changed the composition by varying the Tl concentration in the electrolyte. Electrochemical

deposition[8-10] of CdSeHg and Tl containing CdSeHg films of variable composition were carried out are summarized in table 1. Figure 1 shows the concentration of Tl inclusion in the films as a function of initial and steady state current density. The Tl content in the electroplating solution increases from 2 to 10 ml with an increase in current density from -1.700 to -3.400 mA. During deposition, deposition current decreases very fast initially to a plateau. The relative speed with which the current decreases during deposition is expected to depend on quality of the deposits in terms of effective coverage of the substrate. The thickness values (table 1) of the films are estimated from the quantity of charge passed through the electrolyte. Variation of current with time during deposition is shown in figure 2. Diffusion coefficient value obtained with the help of the curve between I vs $t_{1/2}$ (figure 3)[11].

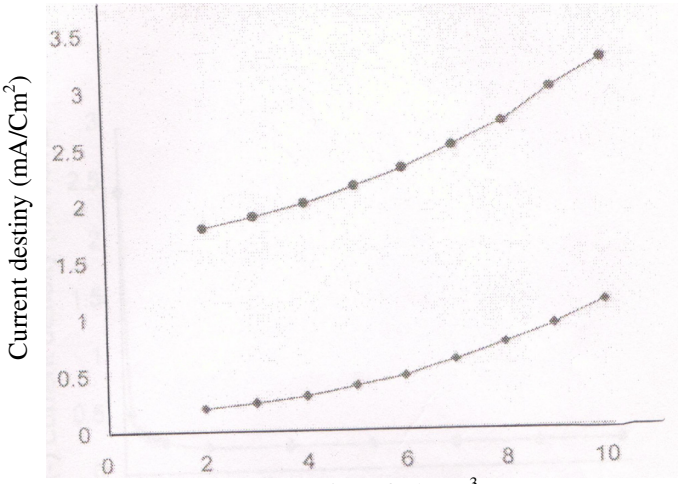

Figure-1
Variation of deposition current

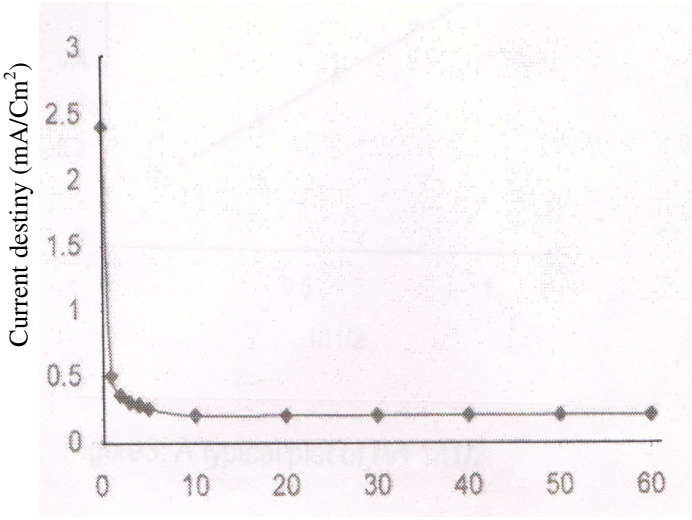

Figure-2
Variation of current with time during deposition of CdSeHg thin film

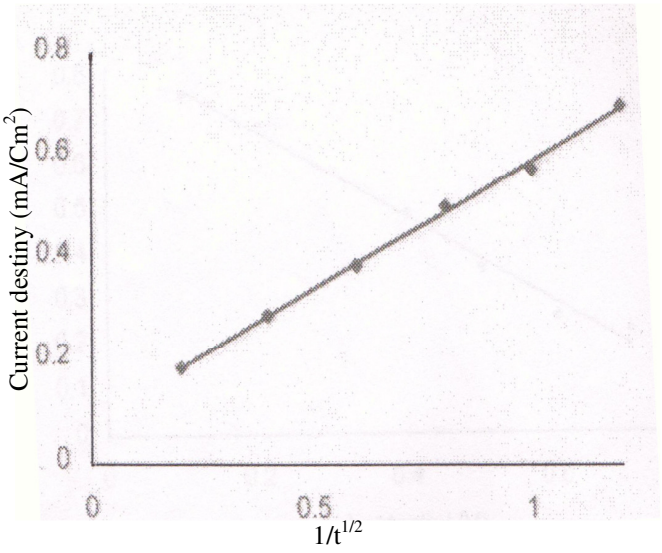

Figure-3
A typical plot of l vs $1/t^{1/2}$

The films obtained using various concentration of Tl in CdSeHg were studied for their photo activity using I_2/I-redox solution. The result are given in table 1. The electrodeposits containing Tl shows improved photoactivity up to 0.0006 M concentration. The slopes from linear portion of Mott-Schottky plot[12,13] dC_2/dE decreases as the concentration of Tl was increased. The slopes are used to evaluate charge carrier density . Flat band potential also comes from the intersection of curve at potential axis. Figure 4 shows a typical plot for variation of capacitance with applied potential.

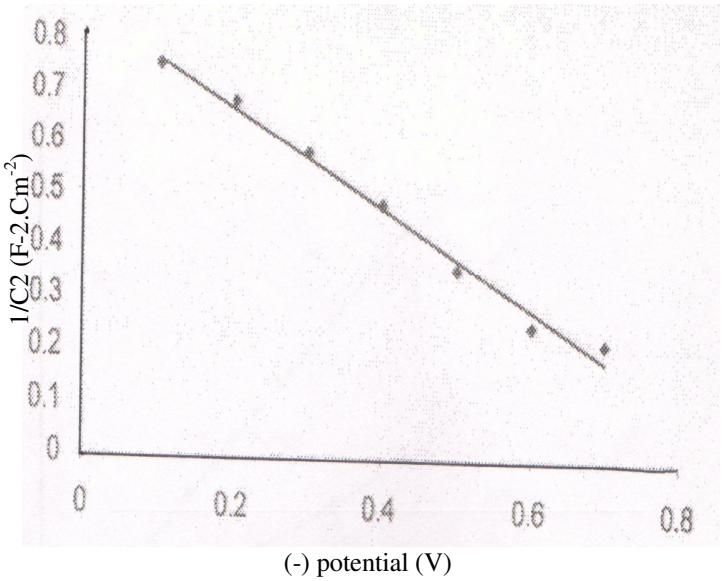

Figure-4
A typical Mott-Schottky plot of CdSeHg thin film containing 0.0002 M Tl

Table-1
Electrochemical and corrosion characteristics of CdSeHgTl

Composition of electroplating solution				(-) deposition current (mA/cm^2)		Film thickness (10^{-5} cm)	Photo-potential	Charge Carrier	Corrosion MPY
Cd	Se	Hg	Tl	Initial	Final				
0.1	0.01	0.0005	0.0000	1.50	0.20	2.50	150	0.95	2.85
0.1	0.01	0.0005	0.0002	1.75	0.24	5.62	170	1.23	1.24
0.1	0.01	0.0005	0.0004	1.95	0.26	6.91	230	6.15	1.10
0.1	0.01	0.0005	0.0006	2.16	0.32	9.50	325	9.33	0.85
0.1	0.01	0.0005	0.0008	2.85	0.38	12.35	215	7.31	1.35
0.1	0.01	0.0005	0.0010	3.40	0.62	15.55	205	4.58	2.12

Figure 5 shows that the composition relation of Tl between electroplating and deposited films. The ratio of the metals in the film is usually different from that in the electrolyte[14]. It may be noted from the figure 5 that the Tl concentration in the films is always less than in the electroplating solution for all concentration of Tl employed in this study. This indicates that the more noble metal is preferentially depositing in the film. When the Tl in the electrolyte is increased from 2 ml to 10 ml, the Tl in the films increase from 1 to 8 atomic percentage, implying that, at higher concentration of Tl more of it is deposited than at its lower concentration in the solution. The broken line in the figure 5 is a reference line along which Tl concentration is plotted to be same in the film and in the electroplating solution as well.

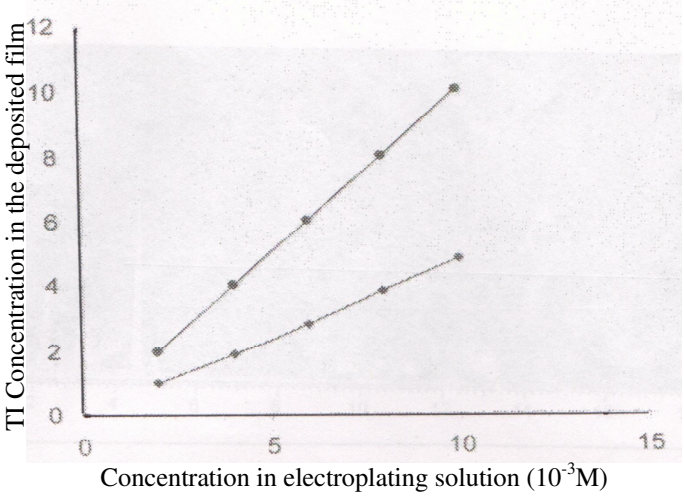

Figure-5
Composition relation of Tl between electroplating solution and deposited films

The surface morphology of the electrodeposited films were studied by scanning electron micrograph images. Figure 6 shows the SEM of electrodeposit (a) CdHgSe and (b) 0.0002 M Tl containing CdSeHg films. From these micrographs, we can draw some conclusion i.e. i. The films are continuous and homogenous, ii. The films appear to be polycrystalline in nature and densely packed. iii. The morphology of the films is affected by Tl incorporation. iv. The grains of the deposits at increased Tl content appeared clearer and larger than that of CdSeHg.

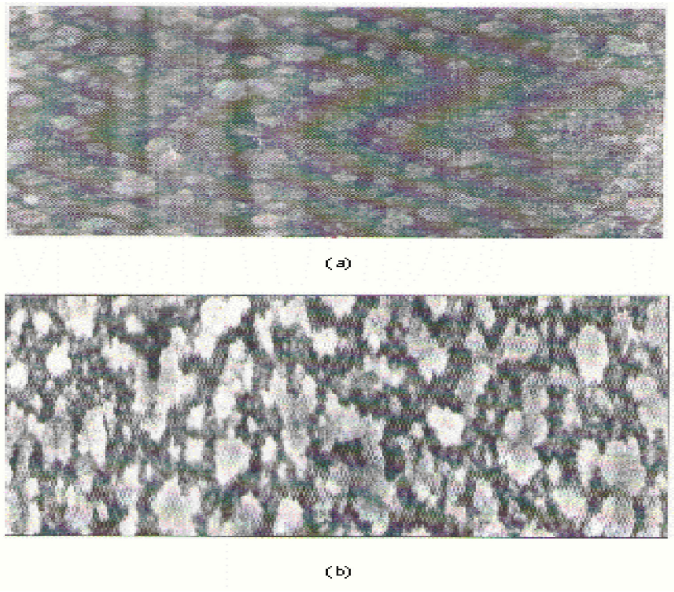

Figure-6
(a) SEM of CdSeHg. (b) SEM of Tl Containing CdSeHg

The comparison of SEM reveals a increase in the grain size with increase in Hg and Tl content. Shape of grain also changes. The typical particle size varies from 50 µm to 5 µm. A larger particles of 10 µm of CdSe is also obvious in the case of 0.0010 M Tl containing CdSe. The energy dispersive X-ray analysis (EDAX) of the deposited films from the same solution under the same condition as in figure 6. The EDAX analysis indicates that the inclusion of Tl in the deposits are as like as in electroplating solution i.e. The inclusion of on increasing concentration of Tl in the electroplating solution, increase the Tl content in deposited films also.

The tafel plots carried at room temperature in I_2/I- redox solution with and without inhibitor. Both anodic and cathodic tafel plots in each case shifted towards higher polarization level in presence of inhibitor[15-16] . From the polarization curve, the corrosion current densities were estimated using the relationship $I_{corr} = b_a . b_c /2.303 (ba+bc). R_p$

Where R_p is the polarization reistance, b_a and b_c are the anodic and cathodic tafel slopes respectively. The corrosion rates of the

electrosynthesized films were calculated with the help of equation

$CR = 0.13. I_{corr.} (EW)/d$

where EW is the equivalent weight and d is the density of the deposited materials. The corrosion current decreases with the addition of Tl and the inhibitor i.e. glycine and benzotriazole also. The corrosion rate values are given in table-1. Figure 7 shows a typical behavior of tafel plot. The corrosion rate values indicates that the inclusion of Tl in CdSeHg films increase the corrosion resistance.

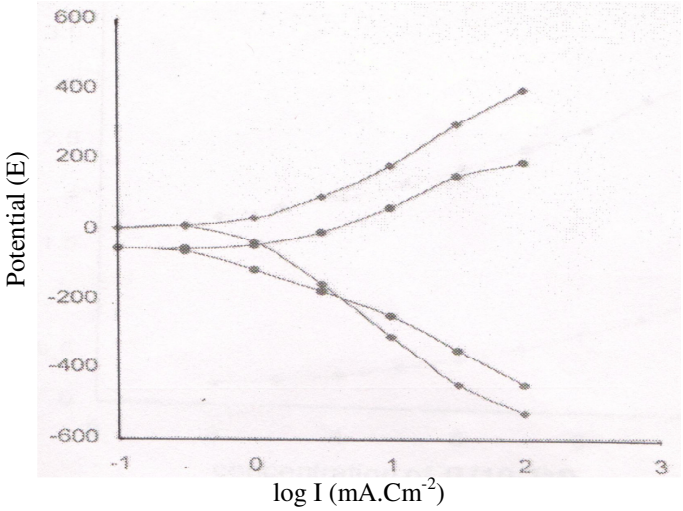

Figure-7
A typical Tafel plot in presence and in absence of inhibitor

Conclusion

Tl containing CdSeHg thin films were deposited by potentiostatic electrodeposition method at the potential -0.60 V vs SCE. The electrodeposits containing Tl shows improved photoactivity. The deposited films are continuous and homogenous. The films appear to be polycrystalline in nature and densely packed. There is a marked improvement observed in the corrosion resistance values when the inclusion of Tl in CdSeHg films.

Acknowledgement

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