Electrochemical synthesis and characterization of Zn-Se-Hg Thin film

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Abstract

The electrochemical deposition and characterization on Hg containing ZnSe thin films are reported. Electrodeposition of ZnSeHg alloy coating onto aluminum substrates in a useful form from acid bath. The study of the electrochemical deposited alloys using electrochemical impedance spectral (EIS) and corrosion characteristics. The composition and structure of these alloys were investigated. The corrosion parameters determined from the polarization curves recorded in 0.5M NaCl solution at room temperature. The impedance spectra recorded at the ocp showed in all cases, which may be explained by the development of corrosion products on the electrode surface. The surface morphology of deposited films was investigated by scanning electron microscopy (SEM). The compositional analysis of electrodeposited films was investigated by Energy dispersive X-ray spectroscopy (EDAX).

Keywords: ZnSeHg thin films, Corrosion, Electrochemical impedance spectroscopy (EIS), SEM, EDAX.

Introduction

ZnSe is an II-IV compound with a direct optical band gap of 2.7 eV at room temperature[1], which makes it suitable material for a variety of the optoelectronic applications in the blue green wave length region, including light emitting diodes[2]. It is also used as window material in high efficiency solar cells, because its large band gap permits a large number of photon to reach the absorbed layer[3,4]. Different methods have been used for the synthesis of ternary compounds including vaccum techniques, chemical bath deposition and electrodeposition[5-10]. In particular, electrode position is a simple and cost-effective approach, which can conveniently modulate the composition of the thin films using electrolyte composition and deposition potentials[5]. Alloy electrode position is widely used in the production of new materials that require specific mechanical, chemical, and physical properties [11-12]. Even through many techniques are used for the preparation of ZnSeHg thin films, electrochemical deposition from aqueous solution attracts much attention in recent years, due to its low cost and ability to control the film properties by varying the deposition parameters. The structural properties of Hg containing ZnSe layers are deeply influenced by the bath parameters in the electrochemical deposition. The effect of bath compositions, current density, deposition potential, pH and corrosion resistance of deposits were studied and discussed.

The electrochemical behaviors of electrodeposited ZnSeHg alloys were studied using electrochemical impedance spectroscopy. Tafel extrapolation and linear polarization resistance methods were used to determine the corrosion rate of the deposited materials. The structural morphology and composition of the film was studied by SEM and EDAX technique.

Experimental

The chemicals used for the deposition of ZnSe films were of analytical reagent grade. Hg containing Zinc selenide films were deposited onto aluminum oxide substrates from an aqueous solution bath containing 0.1 M $ZnSO_4$, 0.01 M SeO_2, and 0.001M, 0.003M, 0.005M $HgCl_2$. The substrates were cleaned prior to deposition with methanol and rinsed in distilled water. Deposition was carried out cathodically using a scanning potentiostate. A standard three-electrode system comprising of substrate, counter electrode and reference electrode i.e. saturated calomel electrode (SCE) was used for the deposition of the films. The electrolyte solution was taken in a beaker; the reference electrode was introduced into the solution with a capillary arrangement. Deposition was carried out at 19 V at 50°C. The pH of the electrolyte was kept between 3 to 4. To adjust the pH value of the solution dilute H_2SO_4 was used. After film formation, the samples were rinsed with distilled water and stored in desiccators for further studies.

Surface morphological and compositional analysis was carried out using a scanning electron microscope (SEM) and energy dispersive X-ray analysis (EDAX). For corrosion studies, current –voltage behavior of the electrodeposited films was investigated to construct Tafel plots for the estimation of corrosion currents. The electrochemical behaviors of electrodeposited ZnSeHg alloys were studied using impedance spectroscopy. ZnSeHg alloy were obtained by electrodeposition from the solutions shown in table 1.

Results and Discussion

Corrosion characteristics of compositionally modulated ZnSeHg deposits were evaluated using Tafel polarization techniques.

The Tafel polarization was performed to evaluate the kinetic parameters of the potential of ZnSeHg deposits by ± 200 mV from the open circuit potential at a scan rate of 10 mV/s and resulting Tafel plots are shown in figure 1-4. The electrochemical characteristics such as, polarization resistance (R_p), corrosion rate (mpy) and corrosion potential (E_{corr}) obtained are summarized in Table II.Electroplated specimens were subjected to corrosion study in aerated 5% NaCl solution and experimental data are given in table 2. Corrosion rates of the deposits were determined by Tafel's extrapolation method. The Tafel plots were used for the estimation of corrosion current using the relationship:

$$\acute{\eta}=\beta \log \frac{i}{i_{corr}}$$

Where ή is the overpotential, i the current at the applied voltage, i_{corr} the corrosion current and β the symmetry factor. Corrosion rates were then obtained on the basis of the relationship:

$$R_{corr}=\frac{i_{corr}\,(EW)}{P}$$

The corrosion rates estimated using these relationships is included in table 2. The results show that inclusion of Hg results in improvement of the corrosion resistance of the ZnSe electrodeposits.

Table-1
The Solution composition and operating parameters for ZnSeHg Alloy

Composition of solution	I	II	III	IV
$ZnSO_4.7H_2O$	0.1 M	0.1M	0.1M	0.1M
	2.8754 g	2.8754 g	2.8754 g	2.8754 g
SeO_2	0.01M	0.01 M	0.01 M	0.01 M
	0.1109 g	0.1109 g	0.1109 g	0.1109 g
$HgCl_2$	-	0.001M	0.003M	0.005M
	-	0.02715 g	0.08145g	0.1357g
Solution pH	4.5	4.5	4.5	4.5
Temperature (^{0}C)	50	50	50	50
Time (sec)	30	30	30	30
Frequency (Hz)	200	200	200	200
Voltage (V)	19	19	19	19

Table-2
Corrosion parameter of ZnSeHg alloy deposit in different concentration

Constitute	Wt. % in deposite	E_{corr} (V v/s SCE)	(V v/s SCE)	B_c	B_a	I_{corr}	R_p	Corrosion Rate
		Obs	Cal	(V/dec)	(V/dec)	(A/cm^2)	(Ohm)	(mm/yr)
ZnSe	Zn-0.1 M Se-0.01 M	-.584 V	-.597 V	.089	.121	1.261e-6	4.724e+3	2.456e-2
ZnSeHg	Zn- 0.1 M Se- 0.01M Hg-0.001M	-.559 V	-.563 V	.035	.053	1.596e-6	6.492e+3	3.107e-2
ZnSeHg	Zn-0.1 M Se- 0.01 M Hg- 0.003M	-.678 V	-.678 V	.106	.176	1.932e-6	5.304e+2	3.762e-2
ZnSeHg	Zn-0.1 M Se- 0.01 M Hg- 0.005M	-.641 V	-.655 V	.144	.128	1.507e-8	5.368e+5	2.934e-4
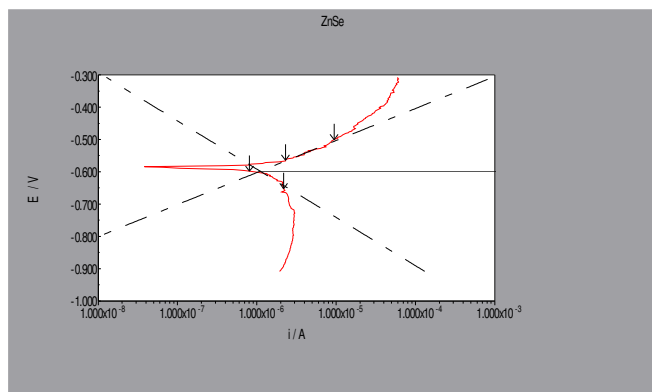
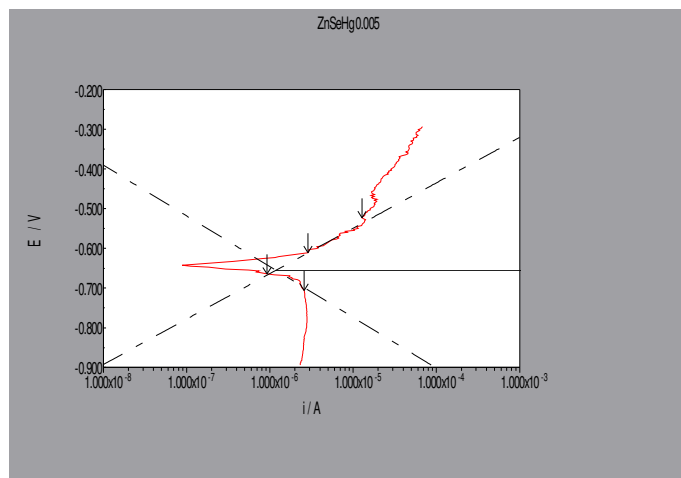**Figure-1**
Tafelplot of ZnSe
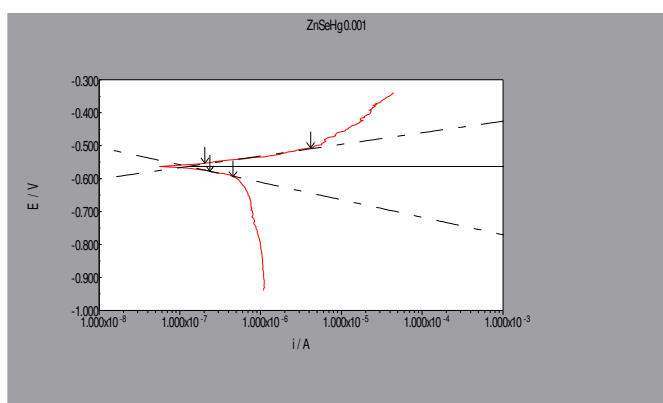
Figure-2
Tafelplot for 0.001 M Hgcontaining ZnSe
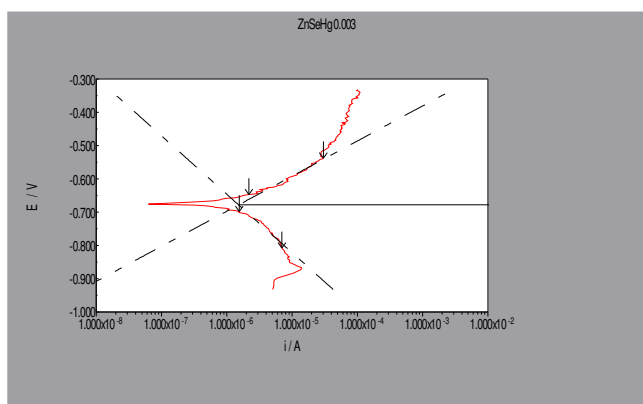
Figure-3
Tafelplot for 0.003 M Hg containing ZnSe

Figure-4
Tafalplot for 0.005 M Hg containing ZnSe

EIS was used to determine the polarization resistance and the corrosion rates without modifying the surface. The solution resistance remains same for all deposits. This is to be expected since the studies were done under similar conditions. Polarization resistance values can be approximately determined by fitting the response to a simple equivalent circuit consisting of Ohmic resistance, double layer capacitance, and polarization resistance. Figure 5 shows the bode response of impedance analysis for ZnSe film.
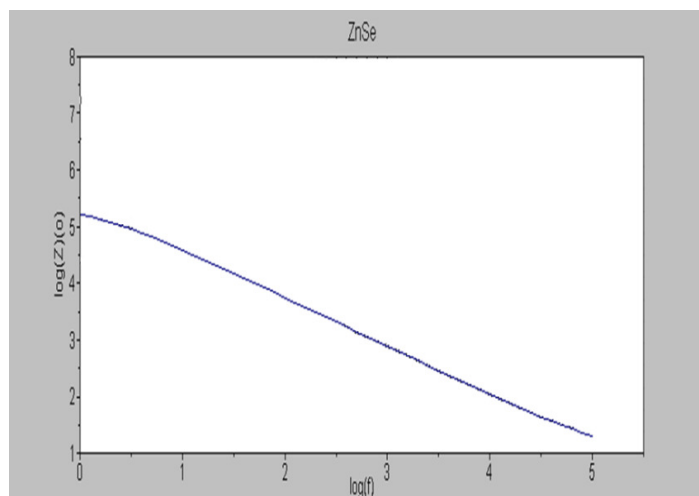

Figure-5
EIS for ZnSe

The electrochemical behaviors of electrodeposited ZnSeHg alloys were studied using impedance spectroscopy. Nyquist plots are found to be not perfect semicircles as expected from the theory of EIS for the assumed equivalent circuit, and this difference can be explained as follows. The plots obtained in the real system represent a general behavior where the double layer as a real on the interface of the metal does not behave as a real capacitor.

The morphology of the electrodeposited ZnSe and ZnSeHg composite coating is presented in figure 6-9. Scanning Electron Microscopy was used for the microstructural characterization and the composition analysis. The presence of microcrackes is probably due to the growth of internal stress during the electrodeposition process. Differences in terms of chemical composition are also observed in the morphology of the electrodeposited films.
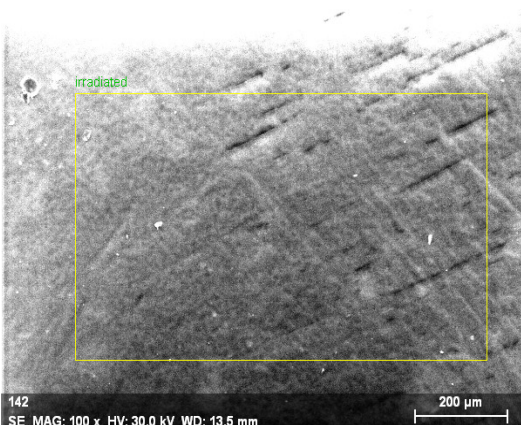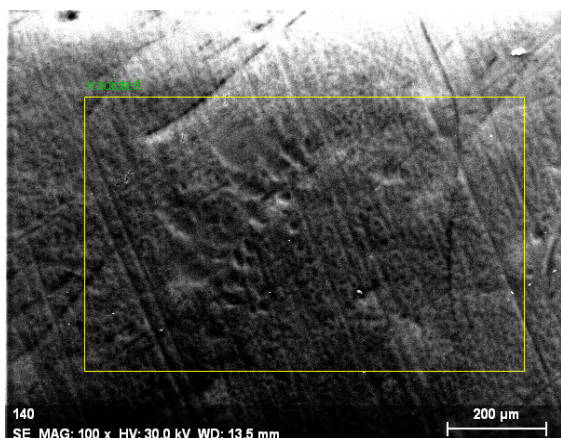
Figure-6
SEM image for ZnSe

Figure-7
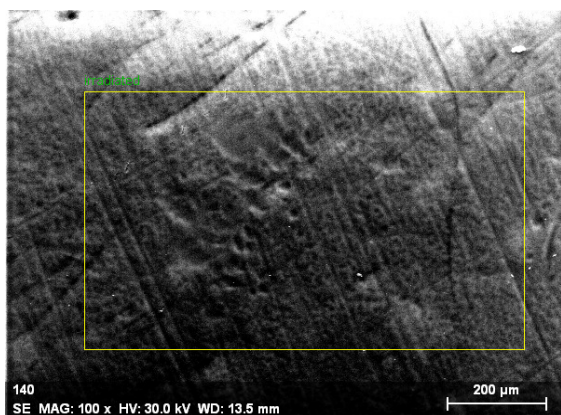**SEM image for 0.001 M Hg containing ZnSe**

Figure-8
SEM image for 0.003 M Hg containing ZnSe

Energy dispersive analysis using X-rays (EDAX) was used to analyze the distribution of the elements in the deposit. The concentration of the elements was determined by comparing the intensities of the X-ray spectrum to the standard intensities of

the pure element. These composition values of ZnSeHg alloys deposited from the plating bath containing different concentrations of Hg containing ZnSe alloy are given in table 3. The data indicates that addition of Hg during electrodeposition also increases in electroplated films.
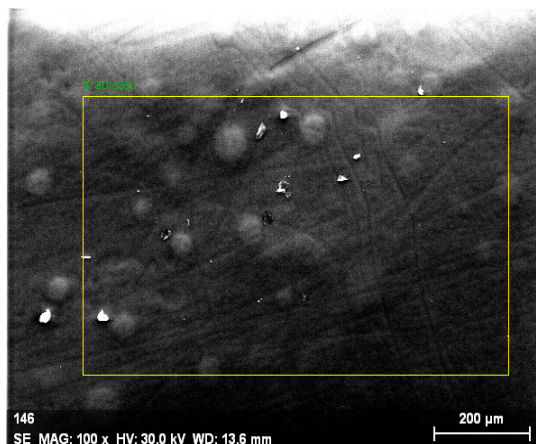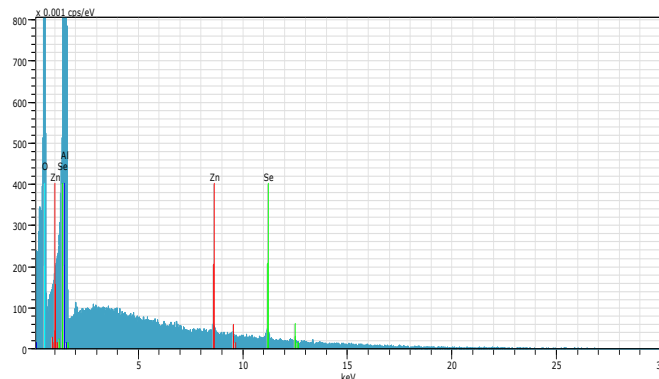

Figure-9
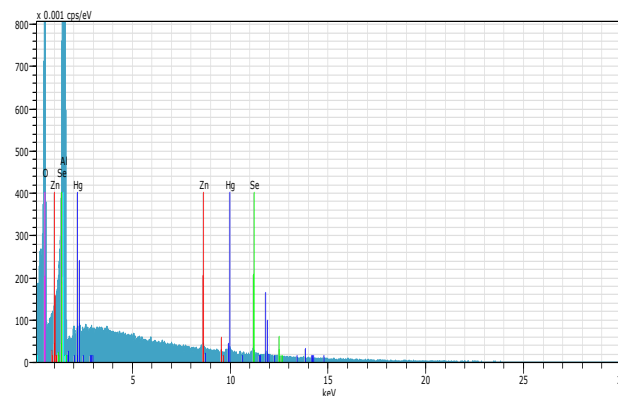**SEM image for0.005 M Hg containing ZnSe**

Figure-10
EDAX image of ZnSe

Figure-11
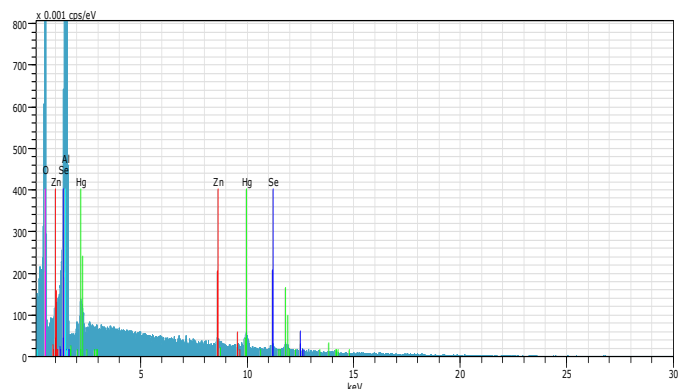**EDAX image of 0.001 M Hg containing ZnSe**

Figure-12
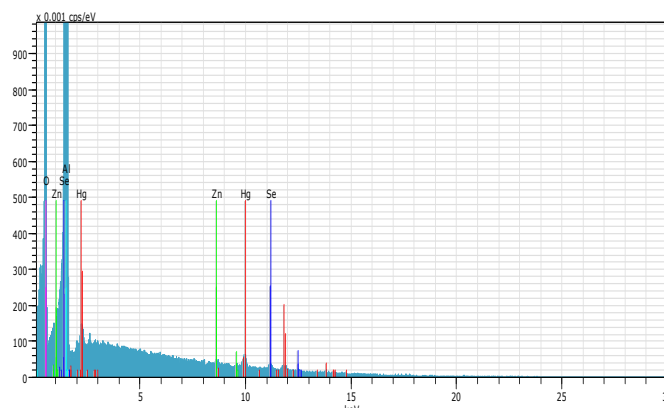**EDAX image of 0.003 M Hg containing ZnSe**

Figure-13
EDAX image of 0.005 m Hg containing ZnSe

Table-3
Dependence of composition on ZnSeHg alloy concentration.

Sample	ZnSeHg alloy	Zn (Atomic Weight %)	Se (Atomic Weight %)	Hg (Atomic Weight %)	Al (Atomic Weight %)
1	ZnSe	0.12	0.27	-	41.97
2	0.001 M Hg in ZnSe	0.10	0.15	0.14	41.50
3	0.003 M Hg in ZnSe	0.11	0.15	0.23	41.01
4	0.005 M Hg in ZnSe	0.17	0.17	0.47	41.43

Conclusion

The corrosion resistance increases on addition of Hg content. The corrosion current decreases with Hg increments. The atomic wt % of Hg increases when the concentration of Hg increased in the electrolyte during deposition. The particle size also decreases with addition of Hg. The bode plots obtained in the real system represent a general behavior where the double layer as a real on the interface of the metal does not behave as a real capacitor.

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