

**ELECTROSYNTHESIS AND CHARACTERIZATION OF Zn-Se-Hg ALLOY FILMS****A.K. Tiwari¹, Md. Rashid Tanveer², and Deepak Mishra^{1,2}**¹Department of Chemistry, DDU Gorakhpur University, Gorakhpur UP 273001²Electrochemistry Research Lab, Department of Chemistry, St Andrew's College, Gorakhpur UP 273001**ABSTRACT**

Zinc selenide and Zn-Se-Hg alloy films have been prepared at optimal deposition potential -0.70V versus saturated calomel electrode on titanium substrate at room temperature. The preparation of these films has been carried out by electrochemical codeposition method under potentiostatic control. The photoelectrochemical characteristics of two types of alloy films have been compared. Electrochemical methods based on Tafel plots were used to study the corrosion characteristics of these films. The effect of mercury inclusion in the deposited films is evident from increase in the deposition current, decrease in the corrosion rate as well as increase in the photoresponse of Zn-Se-Hg alloy films.

KEYWORDS: Electrosynthesis, electrochemical codeposition, Alloy films, Tafel plot.**INTRODUCTION**

Variously formed semiconductor electrodes have been extensively studied for the development of photoelectrochemical cells for the sustained and efficient capture and conversion of solar energy¹⁻⁶. The band gap energy of zinc selenide is wide and not very suitable and compatible with the solar spectrum. This is because its photoexcitability is confined only to high frequency range in the solar spectrum. On the other hand, mercury

selenide is semimetal and it has very low band gap energy. Zn-Se-Hg alloy is expected to have relatively low band gap energy than zinc selenide and may be suitable for enhanced absorption of solar spectrum. Incorporation of Hg in zinc selenide enhances the open circuit voltage and short circuit current in heterojunction devices which results the decrease in the window absorption losses^{7,8}. Although, zinc selenide is not very unstable but

the inclusion of Hg is expected to stabilize the film further against impairment.

In the present investigation, we have explored the possibility of preparation of Zn-Se-Hg alloy films by electrochemical process to assess their suitability for accomplishing optoelectronic conversion. We have examined the electrochemical corrosion behavior to verify their ability to withstand against impairment in structural and functional intactness.

EXPERIMENTAL

The alloy films were synthesized by electrochemical technique using three electrode cells. A titanium plate was polished with diamond lapping compound of specification S-1 and S-2 and Hifin fluid 'OS' (Madras Metallurgical Services Pvt Ltd.). It is then cleaned successively with emery polishing paper of grade 1/0, 2/0, 3/0 and 4/0 (Kohinoor Products, India). This plate is then washed with acetone and finally with deionised water. The plate was then kept in electroplating solution for about one hour for equilibration. The deposition was carried out by adjustment of the potential of the titanium plate, with respect to saturated calomel electrode to a desired value using a titanium counter electrode. For the photoelectrochemical study, the alloy films were combined with titanium counter electrode to form a cell. The deposited films were illuminated with the help of 1000 watt halogen lamp. Photopotential produced, was measured using a digital multimeter (MASTECH^R, MAS830L). All the characterizations were

carried out in testing solution consisting of 1M ZnSO₄, 0.1 M KI and 50 MMI₂.

RESULTS AND DISCUSSION

Synthesis of titanium supported photoelectroactive semiconductor alloy films was carried out using electrochemical codeposition technique. The deposition potential of an ion is given by the equation $E_i = E_i^0 + 2.303 (RT/nF) \log a_i$ (1)

Where, E_i^0 is standard deposition potential of the ion i ; n , the number of electrons involved in deposition process; and a_i , the activity of the ion.

For electrochemical codeposition to occur, it is essential that the deposition potentials of the ions to be discharged must brought to identical value⁹⁻¹². This is usually accomplished by suitable adjustment of ionic activities. It is, however, possible only if the normal deposition potentials of ions do not differ much. It is clear from equation (1) that a tenfold change in concentration of a divalent ion can alter its potential only by about 30 mV. In many cases, therefore, electrochemical codeposition cannot be carried out by adjustment of ionic activities. In such situations simultaneous discharge of ions can be brought about by using deposition potentials in excess of that for most electropositive ion¹³. To identify such domain, current-voltage behavior is studied in the electroplating solution containing ZnSO₄ and SeO₂ as well as the solution containing ZnSO₄, SeO₂ along with HgCl₂ of appropriate

concentration. The result is presented in Fig 1. The result shows that the relevant electrochemical activity is found to be between

-0.45 V to -0.80 V versus saturated calomel electrode.

Table 1. Experimental conditions for synthesis of ZnSe and Zn-Se-Hg films

Electroplating Solution	Applied Potential (V)	Initial deposition current (μA)	Final deposition current (μA)	Deposition Time (hours)
0.05 M ZnSO_4	-0.70	0.121	0.016	3
0.01 M SeO_2	-0.70	0.780	0.022	3
0.05 M ZnSO_4	-0.70	0.670	0.024	3
0.01 M SeO_2	-0.70	0.560	0.022	3
10^{-3} M HgCl_2				

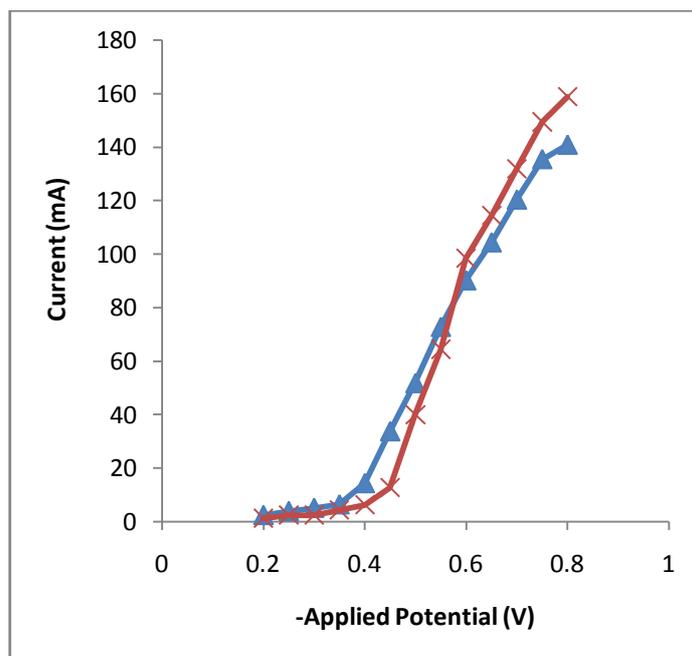


Fig 1. Current-Voltage curve for the deposition of ZnSe ---x--- and Zn-Se-Hg ---<|--- alloy films.

Different ZnSe and Zn-Se-Hg alloy films were then synthesized by electrochemical codeposition method under almost similar conditions. The experimental conditions are listed in Table 1. This table shows a large difference between initial deposition current and final deposition current in the deposition of two types of alloy films. This indicates the

inclusion of mercury in the film during deposition. It is observed in almost every case that during deposition the initial current is very high but with start of formation of semiconductor film on the titanium substrate, the deposition current suddenly falls down till a very low and constant value is attained. A

representative result is given in Fig. 2 for ZnSe and Zn-Se-Hg alloy films.

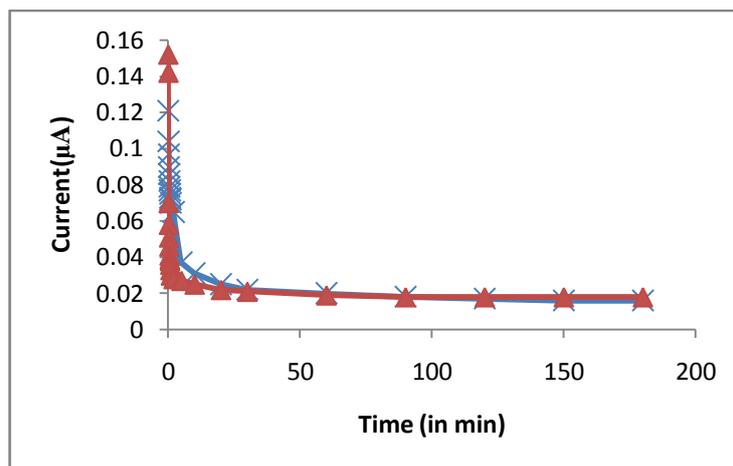


Fig 2. Current- time graph of ZnSe and Zn-Se-Hg alloy films.

The photoelectrochemical study of these alloy films were carried out in I_3^-/I_2^- redox solution. The results are listed in Table 2. The result presented in this table clearly shows that on illumination, ZnSe film becomes anodic indicating its p-type semiconducting behavior. Zn-Se-Hg alloy films upon illumination also showed p-type nature under the respective concentration and experimental conditions. However, inclusion of mercury leads to much improved functional activity. The current-voltage behavior of these alloy films examined in dark and under illumination also confirmed it. Variation of the photoeffect with light intensity is shown in Fig. 3. In both the cases of

ZnSe and Zn-Se-Hg alloy, E_p inclusion of mercury leads to much improved functional activity. The current-voltage behavior of these alloy films examined in dark and under illumination also confirmed it. Variation of the photoeffect with light intensity is shown in Fig. 3. In both the cases of ZnSe and Zn-Se-Hg alloy, E_p increases with increase in light intensity but at higher light intensity a condition of saturation is observed. However, the graph between $\log(\text{light intensity})$ and E_p exhibit straight line. The results is shown in Fig.4. The occurrence of the straight line shows the formation of a good Schottky barrier.

Table 2. Photoelectrochemical behavior exhibited by ZnSe and Zn-Se-Hg alloy films.

alloy Films	Deposition Potential (V)	E_D (mV)	E_L (mV)	E_P (mV)
0.05 M ZnSO ₄ 0.01 M SeO ₂	-0.70	-30.7	76.8	107.5
	-0.70	-29.1	78.1	107.2

0.05 M ZnSO ₄	-0.70	10.8	141.3	130.5
0.01 M SeO ₂	-0.70	56.2	187.5	131.3
5x10 ⁻³				

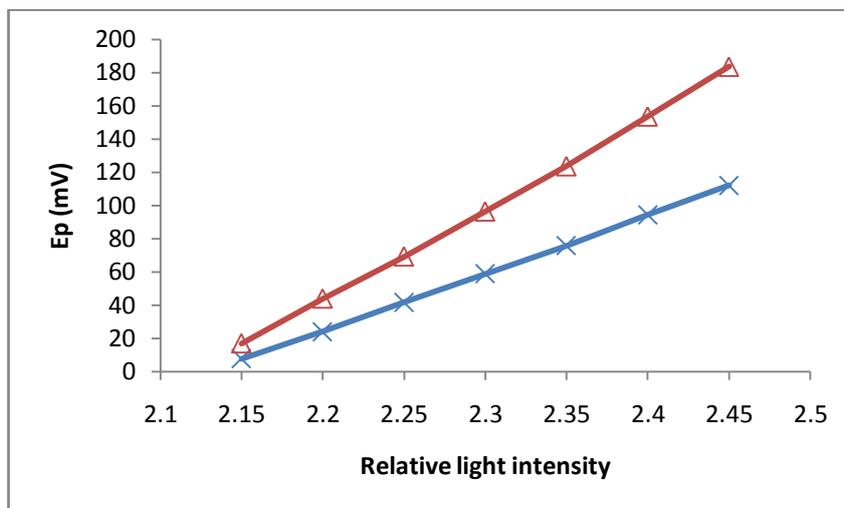


Fig. 3. Ep vs light Intensity for the deposition of ZnSe ---×--- and Zn-Se-Hg ---<|--- alloy films.

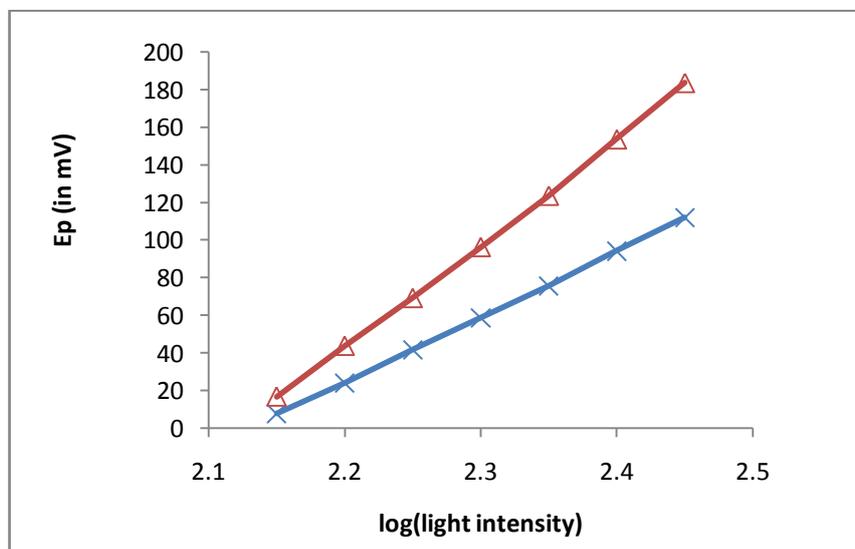


Fig. 4. Ep vs log(light intensity) curves for ZnSe ---×--- and Zn-Se-Hg ---<|--- alloy films.

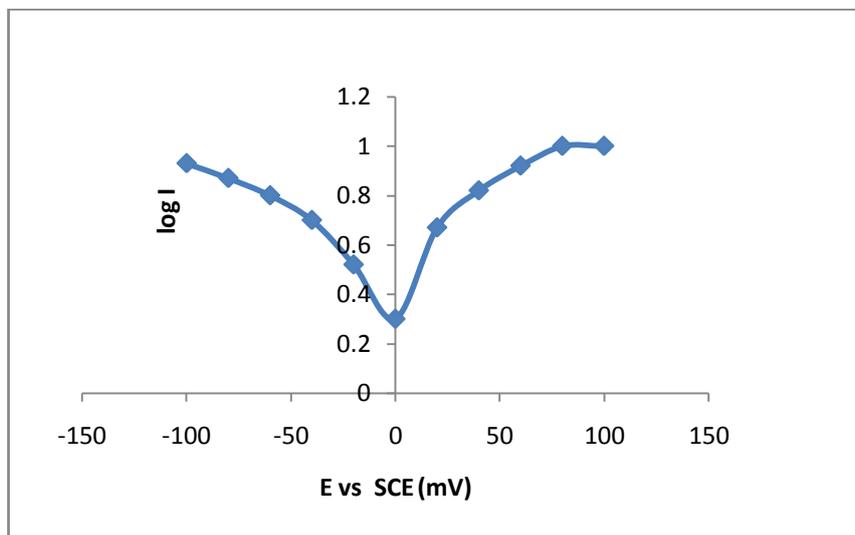


Fig. 5(a). Tafel plot for ZnSe alloy film.

In order to investigate electrochemical behavior of the alloy films, variation of current with potential was studied to obtain Tafel plots of different alloys films. The anodic and cathodic Tafel plots are described by equation

$$\eta = \beta \log(i/i_{\text{corr}}) \dots (2)$$

Where η is overvoltage potential of the alloy electrode with respect to its value at

equilibrium, so called corrosion potential E_{corr} ; i , the current at the applied voltage and i_{corr} , the corrosion current. The anodic and cathodic Tafel slopes are β_A and β_C . They are said to be anodic and cathodic Tafel respectively. E_{corr} and i_{corr} were obtained using Paralac Data Analysis Technique. The corrosion rate is expressed in Milli-inches per year as

$$\text{Corrosion rate} = 0.13 \times i_{\text{corr}} \times (\text{EW})/dA \dots (3)$$

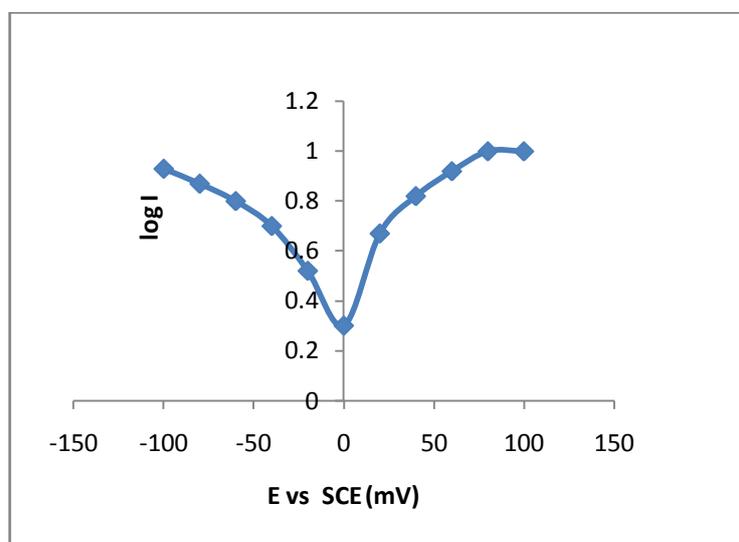


Fig. 5(a). Tafel plot for ZnSe alloy film.

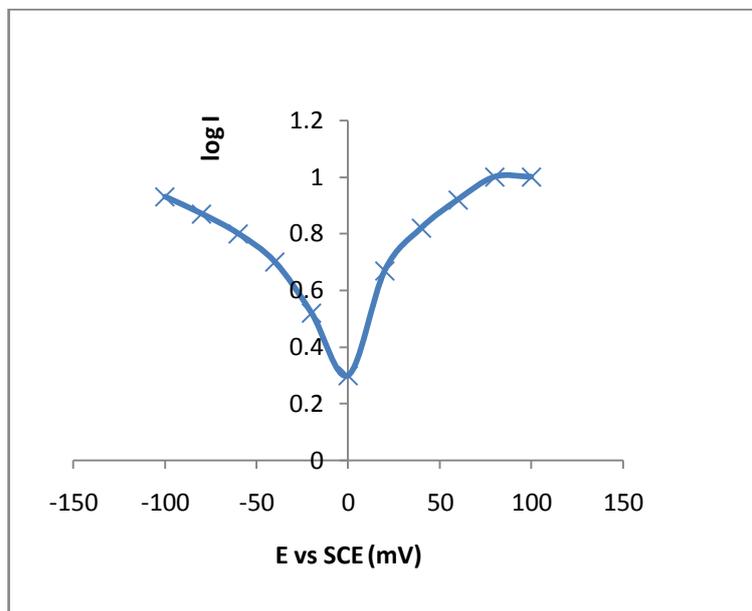


Fig. 5(b). Tafel Plot for Zn-Se-Hg alloy film.

where, (EW) is Equivalent weight of the electroactive material; A, the cross-sectional area of the corroding species and d, its density. Corrosion rates are generally expressed in the unit gs^{-1} by equation

$$\text{Corrosion rate} = i_{\text{corr}} \times (\text{EW})/F \dots\dots (4)$$

The study of the corrosion parameters of these thin films has also been carried out for

both types of films by the Tafel plots. Representative graphs are presented in Fig, 5 (a) and (b). The result of corrosion rate and corrosion current is summarized in table 3. It is found that Zn-Se-Hg alloy films have, indeed, lower corrosion rate in comparison zinc selenide alloy films.

Table 3. Corrosion studies of zinc selenide and Zn-Se-Hg alloy films.

Alloy Films	Resistance of Semiconductor (Ω)	I_{corr} (A)	R_{corr} (gs^{-1})
ZnSe	7.78×10^5	1.73×10^{-6}	1.29×10^{-10}
Zn-Se-Hg	2.08×10^5	1.28×10^{-6}	9.55×10^{-9}

CONCLUSION

The results presented above show the remarkable viability of inclusion of Hg in the

zinc selenide films. The inclusion of Hg improves the quality of zinc selenide films in terms of its photoactivity and corrosion

resistance. Further, both the zinc selenide films and Zn-Se-Hg alloy films exhibit p-type semiconductivity.

ACKNOWLEDGEMENT

The authors are grateful to the Principal, St. Andrew's College, Gorakhpur, for providing necessary laboratory facilities. Thanks are also due to Head, Department of Chemistry, DDU Gorakhpur University for providing facility for some tests.

REFERENCES

1. Laurence M. Peter, *Electrochemistry Communications*, 50, 2015, 88-92.
2. Weishu Liu, Qing Jie, Hee Seok Kim, Zhifeng Ren, *Acta Materialia*, 87, 2015, 357-376.
3. Jiyu Li, Liangxing Jiang, Bo Wang, Fangyang Liu, Jia Yang, Ding Tang, Yanqing Lai, Jie Li, *Electrochimica Acta*, 87, 2013, 153-157.
4. N. Zeiri, S. Abdi-Ben Nasrallah, N. Sfina, M. Said, *Infrared Physics & Technology*, 64, 2014, 33-39.
5. R.K. Nkum, A.A. Adimado, H. Totoe, *Materials Science and Engineering: B*, 55, (1-2), 1998, 102-108.
6. Harishchandra K. Sadekar, AnilVithal Ghule, Ramphal Sharma, *Composites Part B: Engineering*, 44, (1), 2013, 553-557.
7. J. M. Dona, J. Herero, *thin solid films*, 141, 1995 205.
8. T. Yamaguechi, Y. Yamamoto, T. Tanaka, Y. Demizu, A. Yoshida, *thin solid films*, 375, 1996, 281.
9. A.F. Vagramyan and Z.A. Solov'ava, "Technology of Electrochemistry"; 1959, 129.
10. K. Singh and J.P.Rai; *Phys. States Solid*; 99,1987, 257.
11. K. Singh and J.P.Rai; *J. Mater. Sci. Lett.*; 4,1985,1401.
- 12.K. Singh, J.P.Rai and D. N. Upadhyay; *Ind. J. Chem.*; 25A, 1986, 210.
13. S. Glasstone in "An Introduction to Electrochemistry"; 1971, 486.