

STUDIES ON LEAD CONTAINING ZINC SELENIDE PHOTOACTIVE FILMS

Deepak Mishra^{*1,2}, A. K. Tiwari¹ and Md. Rashid Tanveer²

¹Department of Chemistry, DDU Gorakhpur University, Gorakhpur -273001 (UP), India

²Electrochemistry Research Lab, Department of Chemistry, St Andrew's College, Gorakhpur -273001 (UP), India

ABSTRACT: *Synthesis of lead containing zinc selenide semiconducting films has been carried out through electrochemical codeposition technique and compared with the photoelectrochemical characteristics of zinc selenide synthesized and tested under similar experimental conditions. The inclusion of lead affects significantly the characteristics of zinc selenide. Photoaction spectral studies have been carried out for the measurement of the band gap of zinc selenide and lead containing zinc selenide films. Capacitance measurements and current-voltage behavior in dark and under illumination have also been used for their characterization. The lead containing zinc selenide films exhibit relatively improved quality in terms of enhanced photoresponse but inclusion of higher concentration of lead cause decrease in the stability of deposited films. However addition of cetyl pyridinium chloride in small concentration stabilizes these deposited films and decreases their corrosion rate.*

Key words: *Electrochemical codeposition, photoresponse, photoaction spectral studies, capacitance, band gap, corrosion rate.*

Introduction

Development of alternative sources of energy [1-3] is an important issue which has attracted attention over the past decade. A major step towards the realization of this goal has been achieved by the photoelectrochemical [4,5] and voltaic cells [6-8]. Photoelectrochemical process at the semiconductor - electrolyte interface then became much important with a view of their possible applications in the conversions of solar energy into electrical energy and especially in the case of water splitting to generate environmental friendly fuels. Choice of materials plays an important role for the fabrication of any photoelectrochemical cell. Such material may be polycrystalline, single crystal etc. Many workers are using nanostructured thin films [9] for semiconducting devices due to their exceptional properties, which are remarkably different from those of bulk materials. They are believed to be the result of surface and quantum confinement effects. They are thus suitable for short wavelength optoelectronic devices including blue UV light emitting and room temperature UV lasing diodes. In recent past, researches on wide band gap semiconductor materials such as selenide, sulphide and oxide films e.g., ZnSe, CdS, ZnS, ZnO, TiO₂, SnO₂, WO₃ and Nb₂O₃ etc. [10-12] has received significant attention because of their minutely structured crystalline size with an enormous internal surface area. Further metal chalcogenides, especially zinc, cadmium and lead, have a lot of potential as efficient absorbers of electromagnetic radiation [13-15]. In recent years, there has been considerable interest in lead chalcogenides and their alloys due to their demanding applications as detectors of infrared radiation, photoresistors, lasers, solar cells, optoelectronic devices, thermoelectric devices, and more recently, as infrared emitters and solar control coatings [16-18]. A lot of work has also been focused on the fundamental issues of these materials possessing interesting physical properties including high refractive index [19-20]. There have been many theoretical and experimental studies on lead chalcogenides such as PbS, PbSe and PbTe [21-22]. These chalcogenides are narrow and direct band gap semiconductors (IV-VI groups). They crystallized at ambient condition in the cubic NaCl structure. They possess ten valence electrons instead of eight for common zinc blend and wurtzite III-V and II-VI compounds. They also exhibit some unusual physical properties, such as anomalous order of band gaps, high carrier mobility and high dielectric constants. All these unique properties of these semiconductors have inculcated great interest in the fundamental studies of these materials. Thin film semiconductor compounds, especially lead chalcogenides and their alloys have drawn a lot of attention due to their technological importance and future prospects in various electronic and optoelectronic devices [23-26].

Among various metal chalcogenides zinc selenide itself has large band gap and considered useful only for the formation of p-n liquid junction solar cells [27-28]. The present investigation deals with the possibility of lowering down the band gap and the enhancement of photoelectroactivity of zinc selenide thin film by inclusion of lead. A prior consideration suggests that such films are expected to have enhanced p-type semiconductivity in comparison to zinc selenide films [29]. Photoactivity data in conjunction with capacitance measurements and current voltage behavior in dark and under illumination indeed show that lead containing zinc selenide semiconducting films exhibits enhanced photoresponse.

Experimental

Synthesis of zinc selenide and lead containing zinc selenide films were carried out by electrochemical codeposition method using three electrode cell. 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). Finally it was washed successively with acetone and deionised water. The plate was then kept in electroplating solution for about one hour for soaking. Electrodeposition was carried out by adjustment of the potential of the titanium plate, with respect to saturated calomel electrode, to a desired value. For the measurement of photoactivity, the deposited films were combined with a titanium counter electrode to form a cell and illumination was done with the help of 1000 watt tungsten lamp. Photopotential thus generated, was measured using a digital multimeter. Capacitance measurements were carried out using LCR meter (Systronics, Model 925). All the characterizations were carried out in testing solution consisting of 1M ZnSO₄, 0.1 M KI and 50 mM I₂. For spectral studies monochromator was used. All the characterizations were done in the redox solutions consist of 1M ZnSO₄ solution containing 0.1M KI and 50 mM I₂.

Results and Discussion

In the synthesis of zinc selenide the electroplating solution used consist of $ZnSO_4$ and SeO_2 . In the synthesis of lead containing zinc selenide, addition of salt of lead in the electroplating solution gives precipitate of $PbSO_4$. To overcome this problem we have replaced $ZnSO_4$ by $ZnCl_2$ in the synthesis of lead containing zinc selenide. Further for the deposition of zinc selenide the suitable composition electroplating solution is 0.05 M $ZnCl_2$ and 0.01M SeO_2 . But on addition of $PbCl_2$ in higher concentration causes increase in the deposition current and hence the deposited films were incoherent with low photoresponse. Thus we reduced the concentration of $ZnCl_2$ in the electroplating solution. Then various zinc selenide and lead containing zinc selenide films were synthesized by electrochemical codeposition method using electroplating solution containing 0.02 M $ZnCl_2$ and 0.01M SeO_2 . For lead containing zinc selenide we added 10^{-3} M $PbCl_2$ in the electroplating solution and prepared various films under almost identical experimental conditions. The experimental conditions of electrosynthesis are summarized in Table 1. During electrochemical synthesis, the initial current was much higher. But due to the resistance of deposited film the current falls rapidly and after some time almost constant value is obtained. It is however observed that in the synthesis of lead containing zinc selenide films, the steady current is much higher than that observed in the case when the electroplating solution does not contain lead chloride. This clearly shows the deposited material consist of lead containing zinc selenide. The deposited films were tested for their photoactivity in I_3^-/I_2 redox couple. The results are presented in Table 2. Both types of films i.e., zinc selenide and lead containing zinc selenide films become anodic upon illumination indicating their p-type semiconducting nature [30-31]. Lead containing zinc selenide, found to exhibit much improved functional activity as expected [32]. Variation of the photoeffect with light intensity is shown in Fig. 1. In both cases of zinc selenide and lead containing zinc selenide films, E_p are found to increase with increase in light intensity but at higher light intensity a condition of saturation is observed. However, the graph between \log (light intensity) and E_p exhibit straight line. This result is presented in Fig.2. The occurrence of the straight line shows the formation of a good Schottky barrier [33-34].

For the determination of band gap photoaction spectral studies were carried out. A comparison of the photoaction spectral studies of zinc selenide and lead containing zinc selenide films is presented in Fig.3. For higher wavelength region of these curves, λ vs E_p^2 plots were obtained which is presented in Fig.4. From the intercept of straight line on λ -axis the value of threshold frequency is determined. The threshold wavelength values in the case of zinc selenide and the lead containing zinc selenide films are 542 nm and 583 nm respectively corresponding to band gap equal to 2.17eV for zinc selenide and it is 2.04 eV for lead containing zinc selenide films. Thus, incorporation of lead in zinc selenide is evident which results in lowering of the band gap of the material. This causes enhancement of the capture and conversion of light energy into photoeffect.

For the determination of flat band potential and donor density, capacitance measurements were carried out. The results are presented in the form of Mott-Schottky plots in Fig.5. These results support the inference derived on the basis of photoactivity measurements that lead containing zinc selenide film, prepared by electrochemical codeposition, exhibits p-type semiconductivity. The donor density and the flat band potential values derived from the slopes of the Mott-Schottky plots are compared in Table 3. While flat band potential values are comparable in the two cases, the donor density is substantially higher in the case of lead containing zinc selenide, again indicating the possibility of enhanced photoresponse. The nature of semiconductivity of zinc selenide and lead containing zinc selenide films were further confirmed by examination of their current voltage behavior in dark and under illumination. The result is presented in Fig.6. This study again shows p-type semiconductivity of deposited films.

The electrodeposited zinc selenide and lead containing zinc selenide films were quite stable against corrosion. But when the concentration of $PbCl_2$ in the electroplating solution was kept higher, the photoresponse of deposited films were found to be sufficiently high. But it leads to instability in the deposited films. Thus, it is necessary to control their corrosion rates. The lowering of corrosion rate may be achieved by many ways. Incorporation of non-metals like boron, phosphorous etc., is often used to improve corrosion resistance. Many workers have used primary amine, mercaptan, amide like urea thiourea etc. But these compounds cause increase in the particle size of the depositing material and thus lower the photoresponse. In the present investigation we have used a surface active agent, cetyl pyridinium chloride for this purpose. A surface active agent causes reduction in the potential of discharging metal ions and hence expected to reduce corrosion rate. We have introduced cetyl pyridinium chloride in the electroplating solution in different concentrations and synthesized lead containing zinc selenide films by maintaining other conditions of deposition identical. The deposited films were then tested for corrosion behavior by polarization method. The result presented in the Fig.7 in the form of anodic polarization curves. Further, R_p , polarization resistance may be given as [35].

$$R_p = \frac{\Delta E}{\Delta i}$$

Thus the reciprocal of slope of the straight lines of anodic polarization curves gives the values of R_p

$$R_p = \frac{1}{\text{Slope}}$$

The polarization resistance is related to corrosion current density i_{corr} by the relationship [36]

$$i_{\text{corr}} = \frac{RT}{F R_p}$$

From the values of corrosion current density, corrosion rate R_{corr} is then determined by the relationship

$$R_{\text{corr}} = i_{\text{corr}} \times \frac{E}{F}$$

Here E is the equivalent weight of the depositing film. The values of corrosion parameters calculated using above relationships are presented in Table 4. The values of E_{corr} , included in the first column of the table is the value of equilibrium potential, i.e., the potential with respect to the saturated calomel electrode when $i = 0$. The result shows a sharp drop in the corrosion rate is observed with increasing concentration of cetyl pyridinium chloride. This decrease in the corrosion rate may be attributed to the adsorption of surfactant molecules on the electroactive sites of the electrode surface.

Conclusion:

The above studies illustrate the possibility of inclusion of lead in the zinc selenide lattice. This inclusion causes the lowering of band gap and improves the quality of the deposited films in terms of their photoresponse. But its higher concentration cause decrease in its stability of

deposited films. However, addition of cetyl pyridinium chloride in electroplating solution in small concentration stabilizes these deposited films and decreases their corrosion rate.

Acknowledgment:

The authors are grateful to the Principal, St. Andrew's College, Gorakhpur, for providing necessary laboratory facilities. The authors are also grateful to the Head, Department of Chemistry, DDU Gorakhpur University, Gorakhpur, for his encouragement and help.

References:

- [1] Joyce J. Chen and Mark M. Pitt, *Energy Economics*, 61 (2017)147.
- [2] Venkataramanaiah, Y. Suresh, A. K. Panda, *Renewable and Sustainable Energy Reviews*, 76, (2017)788.
- [3] F. Cebulla Haas, K. Cao, W. Nowak, R. Palma-Behnke, C. Rahmann and P. Mancarella, *Renewable and Sustainable Energy Reviews*, 80 (2017) 603.
- [4] Ruwini D. Rajapaksha, Mahinda I. Ranasinghe, *Journal of Luminescence*, 192 (2017) 860.
- [5] G. L. T. Filho, C. A.Rosa, R. M. Barros, I.F. S. D. Santos and F. das G. B.da Silva
- [6] *Sol. Energy Mater. and Solar Cells*, 144 (2016) 383.
- [7] L. Hu, G. Zeng, G. Chen, Z. Huang and Lei Qin, *Colloids and Surfaces B: Biointerfaces*, 159(2017) 303.
- [8] B. Chen, H. Choi, Lawrence J. Hirsch, A. Katz and K. Detyniecki, *Epilepsy & Behavior*, 76 (2017) 24.
- [9] J. Qiu, B.Weng, W. Ge, L. L. McDowell, Z. Shi, *Sol. Energy Mater. Sol. Cells*,172 (2017)117.
- [10] M. Afzaal and P. O'Brien in "Reference Module in Chemistry, Molecular Sciences and Chemical Engineering, from Comprehensive Inorganic Chemistry II" (Second Edition), Vol 1 (2013) p1001.
- [11] N. Hernandez-Como, V. Martinez-Landeros, I. Mejia, F.S. Aguirre-Tostado, C.D. Nascimento, G. de M. Azevedo, C. Krug and M.A. Quevedo-Lopez *Thin Solid Films*, 550(2014) 665.
- [12] Natalia Maticiu, Jaan Hiie, Valdek Mikli, Tamara Potlog and Vello Valdna, *Materials Science in Semiconductor Processing*, 26(2014) 169.
- [13] Jongmin Kim, C. Park, S.M. Pawar, Akbar I. Inamdar, Yongcheol Jo, J. Han, Jin Pyo Hong, Young S. Park, D.Y. Kim, W. Jung, Hyungsang Kim and Hyunsik Im, *Thin Solid Films*, 566(2014) 88.
- [14] P. K. Mahapatra, C. B. Roy, *Electrochem Acta*, 29 (1984) 1435.
- [15] M. A. Kenaway, H A Zayed, A M Ibrahim, *Indian J Pure & Appl Phys*29 (1991) 624.
- [16] L. P. Deshmukh, B M More and S G Holikatti, *Bull Mater Sci*, 17 (1994) 455.
- [17] A. A. Al-Ghamdi, S Al- Heniti, S A Khan, *J. Luminescence*, 135 (2013) 295.
- [18] P K Nair, V M Garcia, A B Hernandez, *J Phys D: Appl Phys* 24 (1991) 1466.
- [19] M. Schluter, G Martinez Cohen, *Phys Rev B* 12(1975) 650.
- [20] S. Yuan, H Krenn, G Springholz, G Bauer: *Phys Rev B* 47 (1993) 7213.
- [21] Alvi and Khan, *Nanoscale Research Letters*8: 148 (2013) 9.
- [22] G. Nimtz, B Schlicht: *In Narrow-Gap Semiconductors*, New York: Springer-Verlag; (1983) 98.
- [23] D. B. Chesnokova, VA Moshnikov, AE Gamarts, EV Maraeva, OA Aleksandrova, VV Kuznetsov: *J Non-Crystt Solids* 356 (2010) 2010
- [24] Y. Bencherif, A Boukra, A Zaouli, M Ferhat: *Infrared Phys Tech* 54 (2011) 39.
- [25] M. Henini, PJ Rodgers, PA Crump, BL Gallagher, G Hill, *Appl Phys Lett* 2054, (1994) 65.
- [26] H. Zogg, K Alchalabi, D Zimin, K Kellermann: *Infrared Phys Technol*, 43 (2002) 251.
- [27] S. Kumar, B. Lal, P Aghamkar, M Hussain: *J Alloys Compd*, 488 (2009) 334.
- [28] 27. P. Lemasson, A. Etchebessy and J. Gautson, *Ber. Bunsenges Phys. Che.*, **86**(1982)283.
- [29] 28. P. Lemasson, and J. Gautson, *J. Electroanal. Chem.* **119**(1981)289.
- [30] 29. L. L. Kazmerski in "Polycrystalline and Amorphous Thin Films and Devices", Academic Press, New York, (1980) 219.
- [31] A. Aruchamy, G. Aravamudan and G. V. Subbarao, *Bull. Mater. Sci.*, **4**(1982)483.
- [32] A. J. Nozik, *Annu. Rev. Phys. Chem.*, **29**(1978)189.
- [33] P. J. Holmes, *The Electrochemistry of Semiconductores*, Academic Press, New York (1962) 20
- [34] R. S. Davidson, H. R. Mech and R. M. Slater, *J. Chem. Soc. Faraday trans I*, 75(1979) 2507.
- [35] T. V. Reddy, V. Ramakrishnan and J. C. Kuriacose, *Indian J. Chem.*, 22A(1983) 74.
- [36] K. Singh and R. K. Pathak, *Ind. J. Chem.* 30A (1991)674.
- [37] J. O'M Bokris and A. K. N. Reddy in "Modern Electrochemistry" volume 2 (Plenum Press, New York) 1970 p 893.

Table 1. Experimental conditions for synthesis of three samples each of zinc selenide and lead containing zinc selenide films.

Deposition potential: -0.70 V

Deposition period: Three hours

Electroplating solution	Initial current (mA)	Final current (mA)
0.02 M ZnSO ₄ and 0.01M SeO ₂	0.761	0.18
	0.594	0.13
	0.783	0.17
0.02 M ZnCl ₂ , 0.01 M SeO ₂ and 10 ⁻³ M PbCl ₂	1.132	0.89
	1.147	1.03
	1.164	0.99

Table 2. Photoactivity exhibited by zinc selenide and lead containing zinc selenide films.

Photoactive films	E_D (mV)	E_L (mV)	E_P (mV)
zinc selenide films	-97	42	139
	-117	34	151
	-116	29	145
lead containing zinc selenide films.	-163	145	308
	-173	123	296
	-114	118	232

Here E_D is the dark potential; E_L , the potential on illumination; and E_P , the photopotential.

Table 3. Flat band potential and donor density values of zinc selenide and lead containing zinc selenide films.

Photoactive films	E_{fb} vs SCE (V)	N_D (10^{16} cm^{-3})
zinc selenide films	0.66	2.91
	0.24	3.63
	0.39	3.18
lead containing zinc selenide films	0.76	9.35
	0.81	9.12
	0.73	6.74

Table 4. Variation in the corrosion parameters of lead containing zinc selenide films on addition of cetyl pyridinium chloride in the electroplating solution.

[CPC] (10^{-3} M)	E_{corr} ($i = 0$) (mV)	R_p ($k\Omega$)	i_{corr} (10^{-6} A)	R_{corr} (10^{-10} gs^{-1})
0.00	-317	3.22	7.95	5.93
0.20	-295	4.76	5.38	4.02
0.40	-279	6.25	4.10	3.06
0.60	-261	8.33	3.07	2.29
0.80	-234	1.25	2.05	1.53

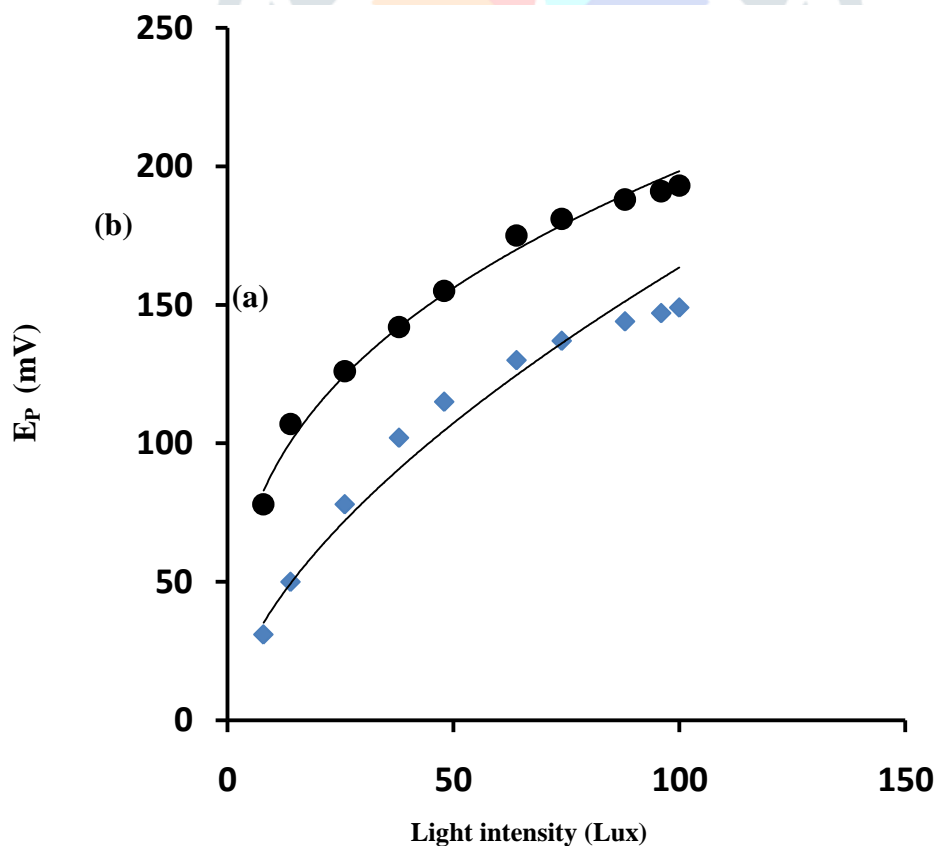


Fig.1. Dependence of photopotential on light intensity (a) for zinc selenide and (b) for lead containing zinc selenide films.

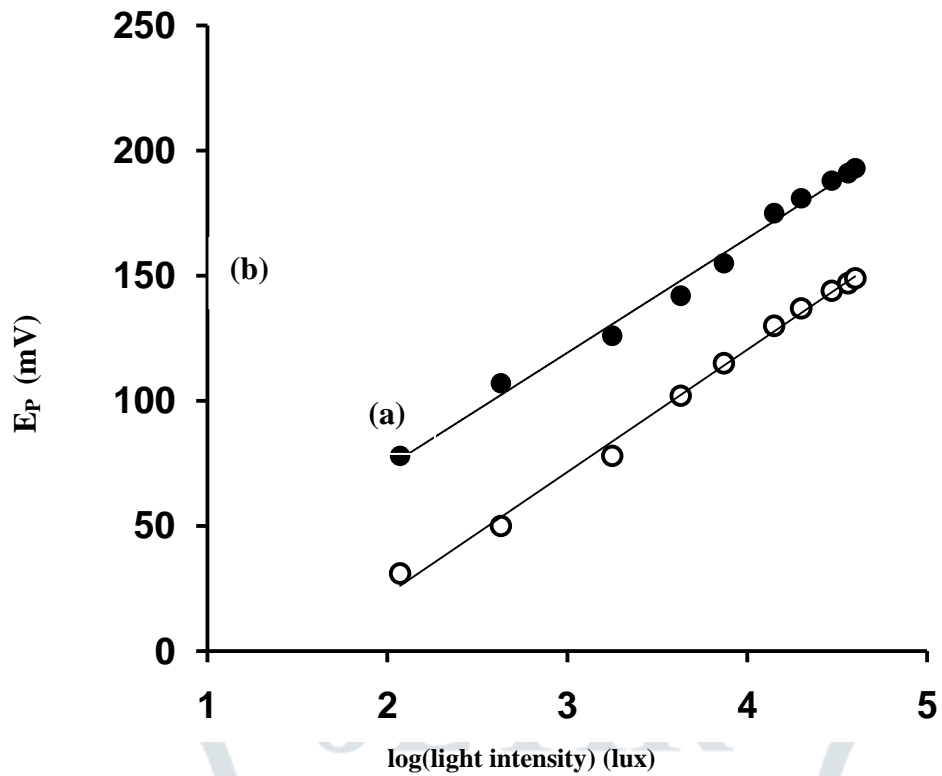


Fig. 2. Variation of photopotential E_p with $\log(\text{light intensity})$ (a) for zinc selenide and (b) for lead containing zinc selenide films.

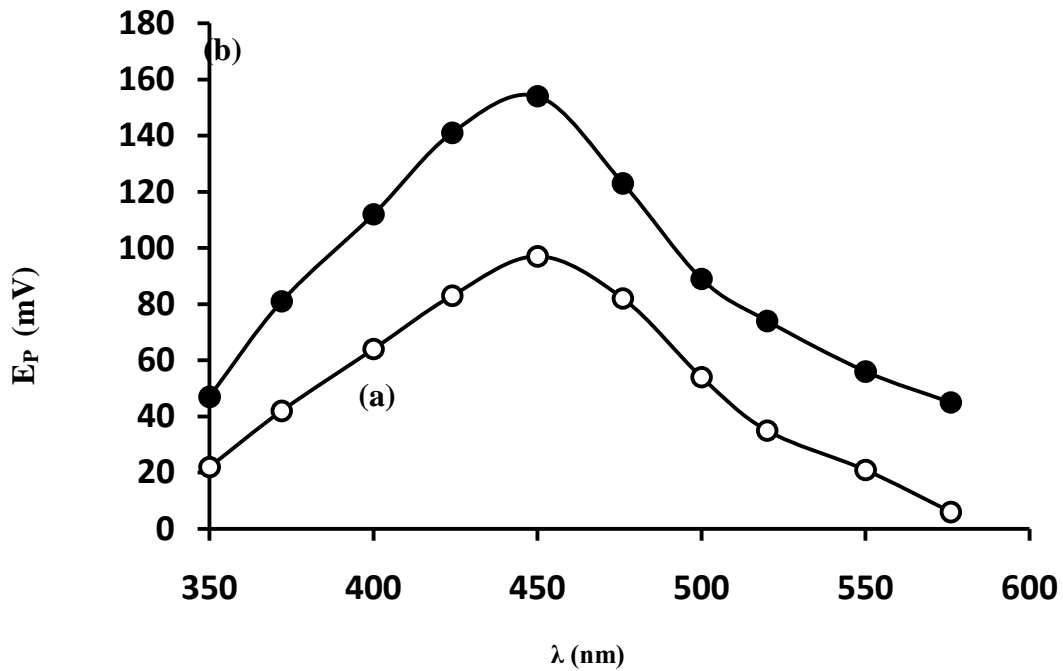


Fig. 3. Photoaction spectrum of (a) for zinc selenide and (b) for lead containing zinc selenide films.

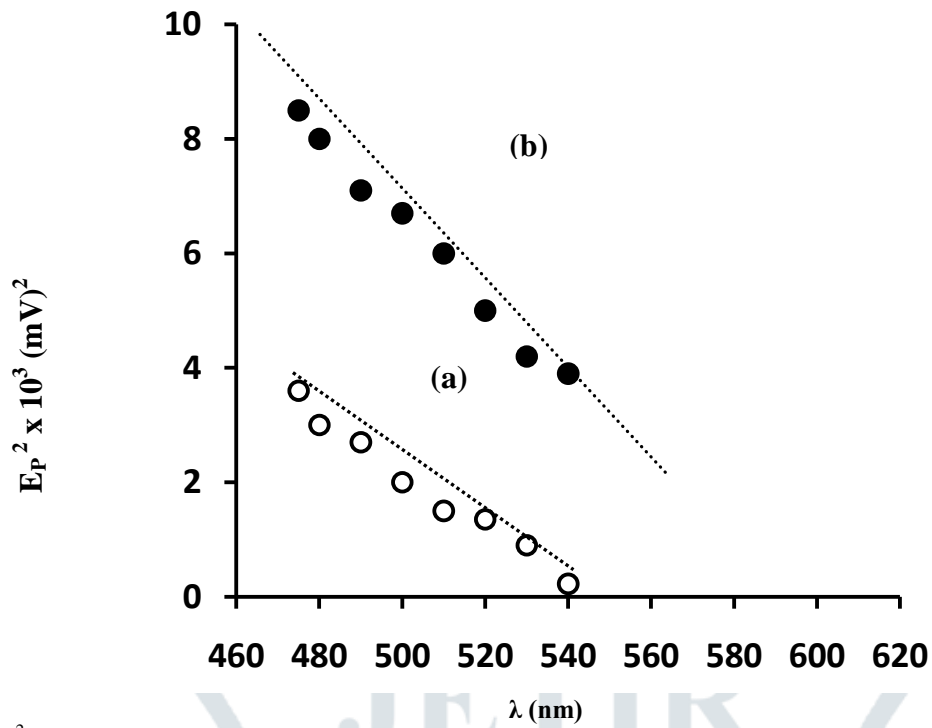


Fig. 4. λ vs E_p^2 plots for determination of threshold wavelength (a) for zinc selenide and (b) for lead containing zinc selenide films.

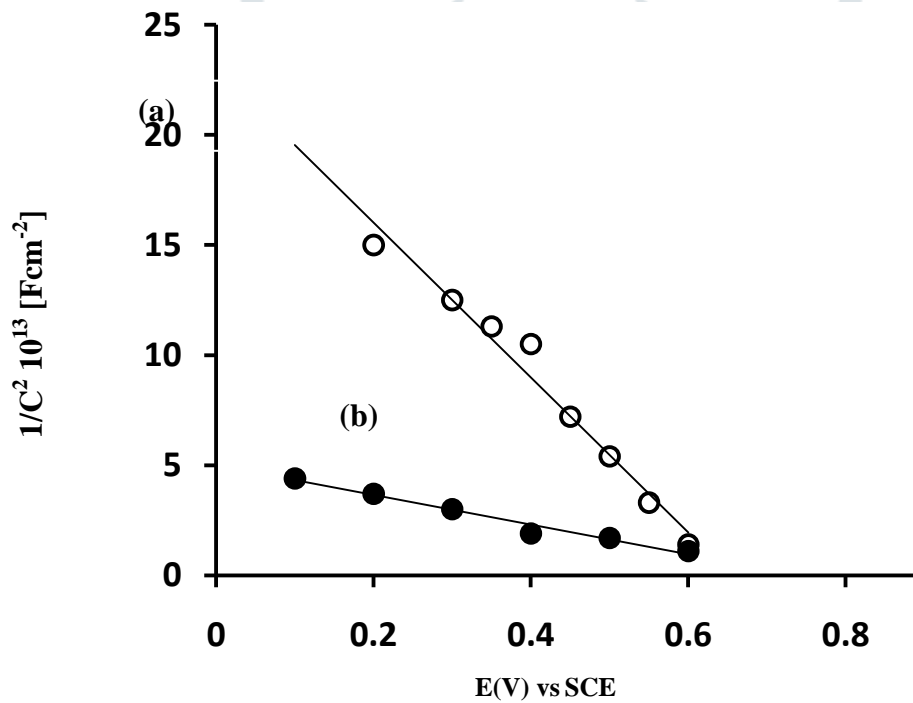


Fig. 5. Mott-Schottky plots (a) for zinc selenide and (b) for lead containing zinc selenide films.

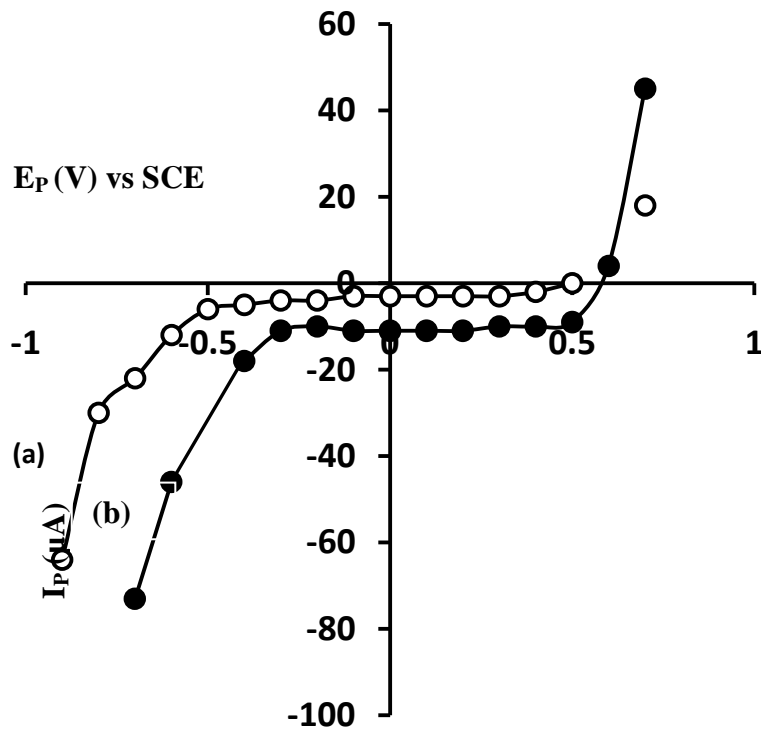


Fig.6. Current voltage behavior (a) for zinc selenide and (b) for lead containing zinc selenide films.

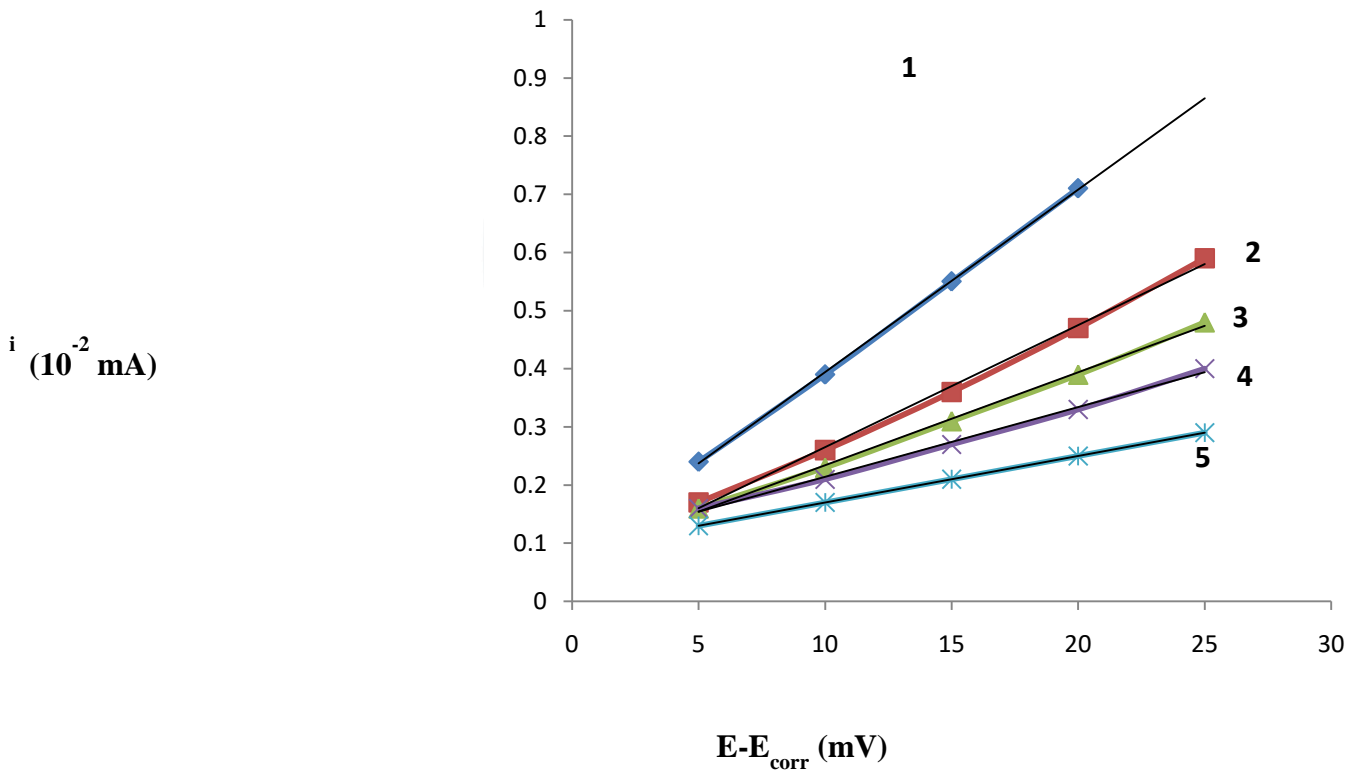


Fig. 7. Polarization curves of lead containing zinc selenide films on addition of cetyl pyridinium chloride in the electroplating solution (1) 0.00 mM, (2) 0.20 mM, (3) 0.40 mM, (4) 0.60 mM and (5) 0.80 mM