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SYNTHESIS AND CHARACTERIZATION OF NANOCRYSTALLINE (CDTL) SE FILMS

Md. Rashid Tanveer, Deepak Mishra and Aradhana Kashyap

Department of Chemistry, St. Andrew's College, Gorakhpur (U.P.) – 273001

ABSTRACT

CdTlSe thin films of different compositions were synthesized on the titanium substrate by electrochemical codeposition technique. In order to study the effect of the inclusion of thallium on the properties of CdSe, these films were characterized for their optical properties and corrosion behavior. The optical properties revealed the presence of direct band gaps with energies in the range of 1.76 – 1.18eV depending upon the concentration of electroplating solution. The corrosion rate decreases sharply with increase in the concentration of $TlNO_3$ in the electroplating solution up to certain limit. This shows the formation of uniform and stable thin films using electroplating solution containing $TlNO_3$ up to 5 x 10^{-3} M concentration. The positive values of photoactivity found in all cases and the study of current voltage behavior in dark and under illumination show that these films are endowed with p- type of semiconductivity.

KEYWORDS*:* (CdTl)Se thin films electrochemical codeposition technique, optical properties, band gap, p- type semiconductor

INTRODUCTION

Thin film technology occupy a prominent place in basic research and the use of thin film semiconductors have attracted much interest in an expanding variety of applications in various electronic and optoelectronic devices due to their low production costs. Nowadays, inorganic thin films with controlled morphology and properties are being fabricated using electrochemical codeposition technique. A variety of substrates such as insulators, semiconductors or metals can be used in this method at which deposition has to be carried out. This technique is relatively less expensive, simple, convenient for large area deposition and ease of application to many compounds such as sulphides and selenides, which include ZnS, CdS, PbS, CdSe, CuS_2, ZnSe and Sb_2S_3 [1-6]. Among these materials CdSe is II-VI binary compound semiconductor. The electronic band gap of CdSe is most important parameter which determines the photosensitivity in visible range of electromagnetic spectrum. The high photosensitivity makes them suitable for thin film photovoltaic device [7]. CdSe is also used in photo conducting, gamma ray detector, optoelectronics, thin film transistor and laser devices [8] due to their excellent electrical, optical and structural properties.

Presently nanocrystalline materials have opened new chapter in the field of electronic application since material properties could be changed by changing the crystallite size of films. Nanocrystalline thin films are also polycrystalline in nature but with sizes of crystallites of the order of a few nanometers. Extensive literature on size reduction effect is available [9-12]. In the present study, we report the synthesis of nanocrystalline films of CdTlSe of variable concentration by electrochemical codeposition technique and their optoelectronic as well as corrosion characteristics.

EXPERIMENTAL

For electrochemical codeposition three electrode cells was used. A flag shaped titanium foil was cleaned with emery paper (John Oakey), polished with diamond lapping paste (METSES diamond lapping 1.0 µm and 0.5 µm size) and METSES lubricating oil. It is then washed successively with acetone and deionized water. This is used as working electrode. Its surface except the portion where material deposition was intended was covered with insulating tape. The electrode was then allowed to soak in an electroplating solution for an hour. Another titanium foil was used as counter electrode. The potential of working electrode was varied with respect to a saturated calomel electrode and the current between working and counter electrodes was measured using a digital multimeter (Scientific Mes-Technik, India). Current voltage studies in appropriate electroplating solution were carried out using indigenously made power supply. For the measurement of photopotential a simple experimental arrangement was used in which when the dark potential between the working and counter electrodes became steady, the work electrode where semiconducting film deposited, was illuminated with a beam light from a 1000 watt halogen lamp. Cha in the potential was then recorded. Inten of illumination was varied using a Dimmerstat (Automatic Electric Private Limited, Mumbai) to study the dependence of photopotential on relative light intensity.

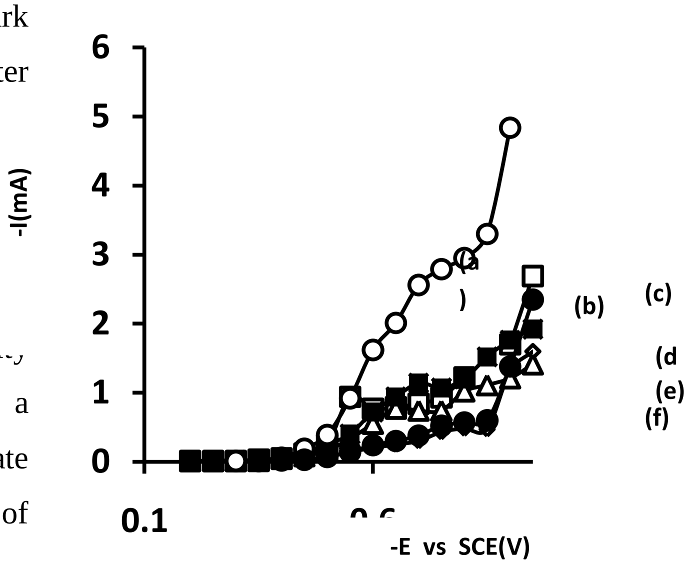

Fig. 1. Current voltage behaviour in solution containing 0.05M CdS)$_4$, 0.01M SeO_2 and $TlNO_3$ (a) 5 x 10^{-4}M, (b) 5 x 10^{-5}M , (c) 1 x 10^{-3}M ,(d) 1 x 10^{-5}M , (e) 1 x 10^{-4}M, and (f) 5 x 10^{-3}M.

RESULTS AND DISCUSSION

In order to identify the potential domain within which the deposition may take place, current voltage behaviour of different electroplating solutions containing 0.05M $CdSO_4$, 0.01M SeO_2 and variable concentration of $TlNO_3$ is examined. The results are presented in Fig. 1. These results show that the relevant electrochemical activity is expected within -0.5 V to -0.85 V versus saturated calomel electrode. These results also show increase in the overall current on increasing the concentration of $TlNO_3$ in the solution. However on electrolysis of only 10^{-3} M $TlNO_3$ solution without addition of $CdSO_4$ or SeO_2, the current was only 0.02 mA even on application of potential up to -0.90V versus saturated calomel electrode.

In our earlier studies for the deposition of cadmium selenide thin films, the electroplating solution consist of 0.05 M $CdSO_4$ along with 0.01M SeO_2 were found to be suitable [13]. Thus thallium doped cadmium selenide films were prepared using electroplating solution containing 0.05 M $CdSO_4$, 0.01 M SeO_2 and 10^{-3} M $TlNO_3$ by applying different deposition potential within - 0.50 V to – 0.85 V range. These films were tested for their optical properties in 1.0 M cadmium acetate solution containing 0.01 M KI and 50 mM I_2 solution. It was found that a deposition potential of -0.70 V is the most suitable for obtaining the electrodeposited thin films of thallium doped cadmium selenide of better photo response [14]. Further photo activity data shows that the electrodeposited films become anodic upon illumination indicating their p-type semiconducting nature.

Photo electroactivity data obtained using titanium supported electro deposited (CdTl)Se films of variable composition is depicted in Table 1. Increased inclusion of cadmium in the electrodeposited films leads to enhanced photo response. Thallium doped cadmium selenide deposited films are likely to be susceptible to corrosion. With a view to ascertain ability of these films to withstand photocorrosion, the thin films were subjected to uninterrupted illumination in I_3^-/I_2 redox solution. The result shows that the electrodeposited films are resistant towards photocorrosion in substantial measure.

With a view to study the influence of thallium inclusion on band gap, photo action spectra in 300 nm to 1000 nm range were employed. Photoaction spectral studies reveal that the threshold wave length $\lambda\tau$, changes perceptibly with composition of thin film. Band gap values obtained from Ep^2 versus $\lambda\tau$ curves and calculated in accordance to the equation

$$Eg = \frac{hc}{\lambda\tau\ e}$$

where Eg is band gap; c, the velocity of light; e, the electronic charge; and h, the Plank constant.

Table 1. Variation of photoactivity of deposited films with concentration of thallium nitrate in the electroplating solution. Electroplating solution: 0.05M $CdSO_4$, 0.01M SeO_2 and variable concentration of $TlNO_3$

$[TlNO_3]$ (M)	**E_D (mV)**	**E_L (mV)**	**E_P (mV)**
1×10^{-5}M	-548 -602 -551	-341 -387 -329	207 215 222
5×10^{-5}M	-647 -620 -544	-415 -378 -316	235 242 228
1×10^{-4}M	-668 -686 -648	-390 -403 -398	278 283 250
5×10^{-4}M	-621 -646 -718	-317 -336 -421	304 310 297
1×10^{-3}M	-697 -661 -530	-414 -385 -340	283 276 262
5×10^{-3}M	43 -563 -533	370 -216 -202	326 347 331
1×10^{-2}M	-514 -630 -490	-380 -401 -325	134 169 165

Table 2. Variation of Band gap values of (CdTl)Se thin films with variation in the concentration of $TlNO_3$ in the electroplating solution: Electroplating solution: 0.05M $CdSO_4$, 0.01M SeO_2 and variable concentration of $TlNO_3$

$[TlNO_3]$ (M)	**λ_T (nm)**	**Band gap (eV)**
0	708	1.76
1×10^{-5}M	722	1.73
5×10^{-5}M	734	1.70
1×10^{-4}M	776	1.61
5×10^{-4}M	835	1.50
1×10^{-3}M	898	1.39
5×10^{-3}M	1006	1.24
1×10^{-2}M	1058	1.18

Cadmium selenide has a band gap of 1.7 eV whereas in the case of thallium selenide it is 0.75 eV. A lowering of band gap is expected with progressive inclusion of thallium in the electrodeposited thin films. The result presented in Table 2, shows the variation in the band gap with increase in the concentration of thallium in the thin films.

Thin films may be visualized as solid solution of cadmium selenide and thallium selenide. The covalent radii of Cd and Tl are comparable and accordingly the adduct (CdTl)Se is expected to be a solid solution. The band gap of thin film is not proportional to concentration of Tl ion in the electroplating solution perhaps because of Tl content in the thin films being somewhat different from that of Tl ion in the electroplating solution. This is likely as found in some similar cases.

In order to investigate electrochemical corrosion behaviour of the thin films variation of current with potential was studied to obtain Tafel plots. A representative plot is shown in Fig. 2.

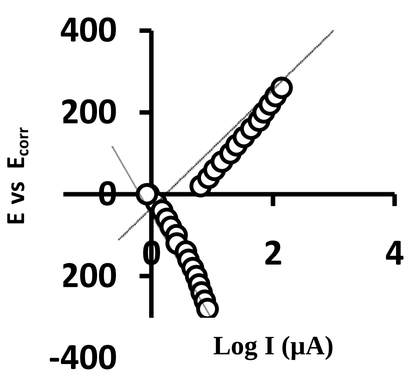

Fig.2. A typical Tafel plot

Electroplating solution: 0.05M $CdSO_4$, 0.01M SeO_2 and 10^{-3} M $TlNO_3$

Table 3. Variation of corrosion rate with concentration of $TlNO_3$: Electroplating solution: 0.05M $CdSO_4$, 0.01M SeO_2 and variable concentration of $TlNO_3$.

$[TlNO_3]$ (M)	E_{corr} (i = 0) (mV)	i_{corr} (μ_A cm^{-2})	Corrosion rate (10^{-9} g/s)
0	-12.99	8.20	8.12
1×10^{-5}	13.01	6.81	6.75
5×10^{-5}	-83.84	5.61	5.55
1×10^{-4}	-49.24	3.06	3.03
5×10^{-4}	-36.93	2.87	2.84
1×10^{-3}	-50.88	1.97	1.95
5×10^{-3}	81.65	1.37	1.36
1×10^{-2}	-48.66	13.04	12.92

The anodic and cathodic Tafel plots are described by

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

Where η is overvoltage of the them film electrode with respect to its value at equilibrium, the so called corrosion polential E_{corr}, i, the current at applied polential; and i_{corr}, the corrosion current. E_{corr} and i_{corr} were obtained using paralac data analysis technique. Cathodic and anodic Tafels β_c and β_A are obtained from the slopes of Tafel plots .The corrosion rate is generally expressed is g/s and is measured using equation.

$$\mathcal{R}_{corr} = \frac{icorr \times (E.W)}{F}$$

Where EW is the equivalent weight of the deposited film and F, the Faraday constant.

The corrosion parameters were also measured for (CdTl)Se thin films prepared using electroplating solution containing different concentration of $TlNO_3$ .The results are presented in Table 3. These results show that the corrosion rate decreases sharply with increase in the concentration of $TlNO_3$ in the electroplating solution. This shows formation of more and more uniform and stable thin films. However when concentration of $TlNO_3$ exceeds 5 x 10^{-3}M in the electroplating solution the deposited thin films exhibit very high corrosion rate due to formation of amorphous films.

CONCLUSION

The above studies illustrate the possibility of the preparation of (CdTl)Se thin films of variable composition by electrochemical codeposition technique. The inclusion of thallium improves the quality of thin films in terms of their photoresponse and corrosion characteristics. This also causes lowering of the band gap of the deposited semiconducting material.

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