

PHOTOELECTROCHEMICAL PROPERTIES OF PULSE ELECTRODEPOSITED CADMIUM SELENIDE FILMS

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CdSe films were deposited by the pulse plating technique in the presence of silicotungstic acid. The films deposited in the presence of silicotungstic acid exhibited hexagonal structure. The films exhibited a direct band gap of 1.67 eV. With addition of silicotungstic acid, the average grain size decreased from 17.1 nm to 11.7 nm, and the grain became more homogeneous. The surface roughness decreased from 2.83 nm to 1.97 nm after adding silicotungstic acid. The efficiency of the photoelectrochemical cells increases with addition of silico-tungstic acid.

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1. Introduction

Amongst the II – VI compounds, CdSe is a very important candidate for several optoelectronic applications like photodetectors, photovoltaic electrodes, image intensifiers etc. Several techniques have been employed for the deposition of CdSe films. In this work, CdSe films were pulse electrodeposited with and without the use of heteropolycyclic acid viz., silicotungstic acid. Earlier, heteropolycyclic acids have been employed for the deposition of CdSe and CdS films by the chemical bath deposition techniques. In general, the grain size has been found to decrease by the addition of polycyclic acid.

2. Experimental

CdSe films of area 2.5 cm² were deposited on titanium, tin oxide and stainless steel substrates at different duty cycles in the range 6.25 – 50 %, the substrates were first cleaned prior to deposition with dilute hydrochloric acid. All the etched electrodes were thoroughly washed in triple distilled water and finally degreased with acetone or trichloroethylene. AR grade cadmium sulphate and selenium di oxide were the precursors for the deposition bath, pH was adjusted to a value of 2 by the addition of dil.H₂SO₄. The pulse voltage/current, concentration and pH were optimized using the earlier report[1]. Under optimized condition, a concentration of 0.5 M CdSO₄, 0.1 M SeO₂ were taken. The deposition was carried out for a duration of one hour, at -870mV(SCE)[2], at room temperature. To this precursor different concentrations of silico-tungstic acid in the range of 0.001 to 0.01M was added during the deposition. The thickness of the films was estimated to be 1.6µm for as deposited films by gravimetric method. The films were heat treated in argon at different temperatures in the range of 450 - 550°C for a duration of 5 min.

The thickness of the films after heat treatment was around 1.5 μm . Reproducibility of the deposition process was checked by depositing about six sets of samples under each condition. The variation in results obtained with the different sets were within 2%.

3. Results and discussion

X-ray diffractograms of the films deposited at different duty cycles indicated the polycrystalline nature of the films (Fig.1). In all the figures, the prominent peaks corresponding to (100), (002), (101), (110), (103) and (112) reflections of CdSe were observed. The as deposited films exhibit hexagonal

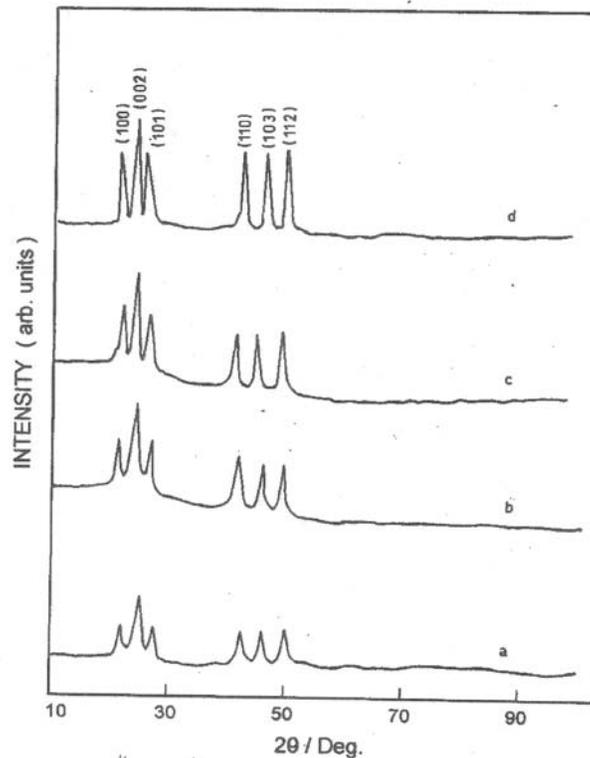


Fig.1 - X-ray diffraction pattern of pulse plated CdSe films at different duty cycles (a) 10 % (b) 15 % (c) 33% (d) 50%

structure with preferential orientation in the (111) direction. As the duty cycle decreases, the intensity of the peaks decrease, the width of the (111) peak is observed to increase with decrease of duty cycle for an increase of OFF time from 1s to 15s. As the OFF time increases, the intensity of peaks are observed to decrease gradually and for OFF times greater than 15s only peaks corresponding to Cd were observed along with the Ti peaks. Hence films were prepared with OFF times $\leq 15\text{s}$. The thickness of the films are also found to decrease with increase of OFF time, this is understandable, since the number of pulses decrease for the same total deposition duration, viz., one hour. The XRD patterns of the CdSe films deposited with different concentrations of silicotungstic acid and at a duty cycle of 6 % is shown in Fig.2. In this case the as deposited films exhibited peaks corresponding to the hexagonal phase. The absorption co-efficient(α) at various wavelengths has been calculated using the equation[3],

$$\alpha = 2.303A/t \quad (1)$$

where A is the absorbance value at a particular wavelength and t is the thickness of the film. The band gap of the films were determined by plotting a graph between $(\alpha h\nu)^2$ vs $h\nu$. Extrapolation of the linear region to the $h\nu$ axis gives the band gap of the material. Fig.3 indicates a direct band gap of 1.70 eV for the films heat treated at 550°C irrespective of duty cycle. An absorption coefficient of 10^4 cm^{-1} was obtained [4].

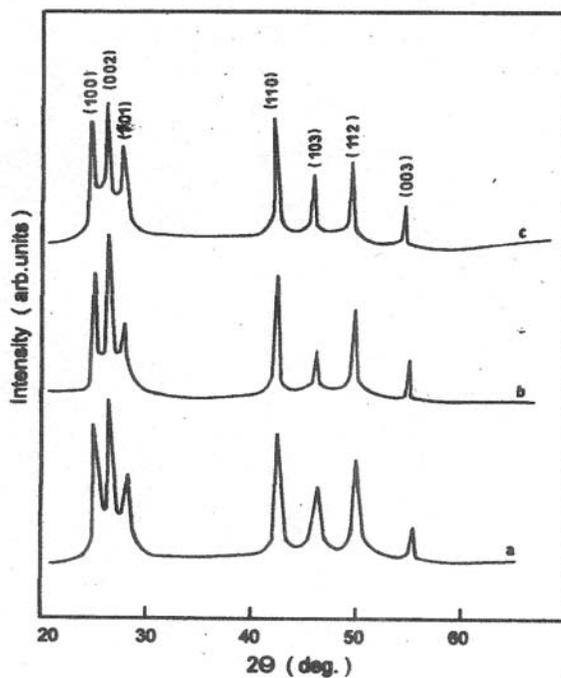


Fig.2 - X-ray diffraction pattern of CdSe films deposited at 6 % duty cycle and with different concentrations of silicotungstic acid (a) 0.01M (b) 0.05M (c) 0.001M.

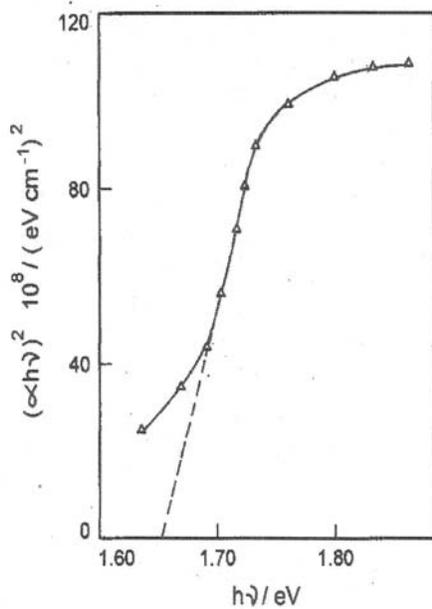


Fig.3 - $(\alpha h\nu)^2$ vs $h\nu$ plot of CdSe films heat treated at 550 C.

Atomic force micrograph of the CdSe films deposited at different duty cycles. With decrease of the duty cycle, the average grain size decreased from 52.6 nm to 41.7 nm, and the grain became more homogeneous. Meanwhile, the surface of the films became smoother. The root-mean-square roughness decreased from 4.70 nm to 3.70 with decrease of duty cycle. Atomic force micrographs of CdSe films deposited with silicotungstic acid indicated decrease of crystallite size and surface roughness. Table.1 shows the results.

Table.1. Variation of Crystallite size and surface roughness with concentration of silicotungstic acid for the CdSe films deposited at 50 % duty cycle

Concn of acid(mM)	Crystallite size(nm)	Surface roughness(nm)
0.01	11.0	2.384
0.05	15.5	2.356
0.075	16.4	2.096
0.10	17.1	1.965

The XPS spectra of the CdSe films annealed at different temperatures is shown in Fig.4. The binding energies of the Cd($3d_{5/2}$ and $3d_{3/2}$) and Se($3d_{5/2}$ and $3d_{3/2}$) level are observed. After annealing the area under the selenium binding energy curves decrease indicating a small amount of loss of selenium upon evaporation from the sample due to heat treatment. The peak energy levels associated with Cd($3d_{5/2}$ and $3d_{3/2}$) appeared at 405 and 411.7 eV respectively, which are in good agreement with the literature[5,6]. These findings are characteristic of the Cd in CdSe and are in good agreement with the literature. The binding energies of the Se($3d_{5/2}$ and $3d_{3/2}$) levels were observed at 53.9 and 59.2 eV respectively.

Photo-electrochemical measurements were made on the films deposited with different concentrations of silicotungstic acid. It is observed that the output parameters are higher than the results obtained with the films deposited without the acid. Table 2 shows the results of photovoltaic parameters.

Table 2. PEC Characteristics of CdSe films pulse plated at a duty cycle of 10 % and with different concentrations of silicotungstic acid and post heat treated at 550°C(Intensity – 60 mW cm⁻²).

Concn of Silico tungstic Acid(mM)	V _{oc} (V)	J _{sc} (mA cm ⁻²)	ff	η (%)
0.01	0.33	5.50	0.40	1.17
0.025	0.40	6.00	0.47	1.88
0.05	0.52	7.00	0.48	2.91
0.075	0.58	8.00	0.64	4.84
0.10	0.60	9.00	0.59	5.33

4. Conclusion

Thin films nanocrystalline CdSe photoelectrodes with reasonable efficiencies can be easily deposited by the pulse plating technique in the presence of silicotungstic acid. Films with nanocrystallites in the range of 11 – 20 nm can easily be obtained.

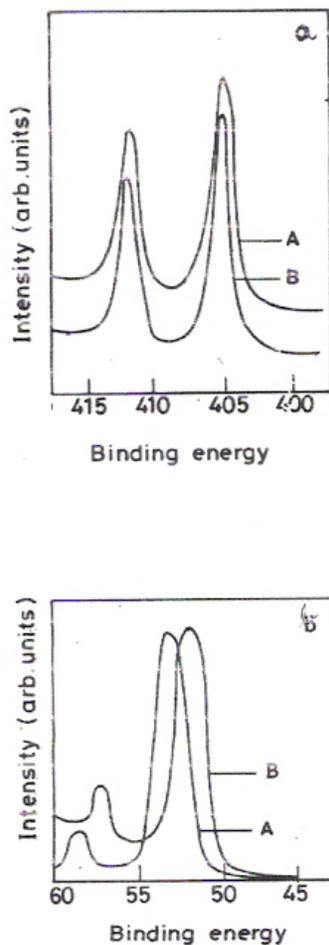


Fig.4. XPS binding energies of (a) Cd, (b) Se of CdSe films deposited at a duty cycle of 10 % (A) as deposited (B) post heat treated at 525°C.

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