Faculty Profile

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Educational Qualification

Sr.	Name	Name of University	Subject	Class	Year	Page
No	of			Obtained		No.
	Degree					
1.	B. Sc.	Shivaji University,	Physics	Ist	1988	1
		Kolhapur				
2.	M. Sc.	Shivaji University,	Physics	Ist	1990	2
		Kolhapur				
3.	Ph.D.	Shivaji University,	Physics	-	2000	3
		Kolhapur				

Research And Training Portfolio A)Research

I. Publications:

1. International Research Paper Published in Scopus Indexed Journals

Sr. No.	Title of Research Paper	Name of Journal	Name of Publisher	Year	Impact Factor	DOI	Page No.
1.	Electrodeposition of CdS from non-aqueous bath	Materials Chemistry and Physics	Elsevier	1997	4.6	https://doi.or g/10.1016/S0 254- 0584(97)018 81-6	4
2.	Studies on the electrodeposition of CdS films	Materials Chemistry and Physics	Elsevier	1998	4.6	https://doi.or g/10.1016/S0 254- 0584(97)020 71-3	8

3.	Structural, optical and photoelectrochemical properties of electrodeposited CdSe thin films	Journal of Materials Science: Materials in Electronics	Springer	1998	2.8	https://doi.or g/10.1023/A: 10089664283 39	12
3.	Electrosynthesis of CdTe films from ethylene glycol bath	Materials Chemistry and Physics	Elsevier	2000	4.6	https://doi.or g/10.1016/S0 254- 0584(99)001 83-2	18
4.	Photoelectrochemical properties of CdX (X=S, Se, Te) films electrodeposited from aqueous and non-aqueous baths	Materials Chemistry and Physics	Elsevier	2001	4.6	<u>https://doi.or</u> g/10.1016/S0 254- 0584(00)002 80-7	23

II. State level / National level / International level conferences/ seminars

1) Research Seminar Attended (01)

Sr. No.		Title		Organize Institutes	International/ National/Regional	Date	Page No.
1.	Recent	Trends	in	Balwant College, Vita	National	29-07-2020	29
	Materials	Research			(Online Seminar)		

2) Research Conference Attended (01)

Sr.	Title	Organize Institutes	International/	Date	Page
No.			National/Regional		No.
1.	Advanced functional	Krishna Mahavidyalaya,	International	10-08-2020	30
	Nanomaterials and Their	Rethare Bk	(E-Conference)		
	Device Applications				

3) Research Webinar Attended (01)

Sr.	Title	Organize Institutes	International/	Date	Page
No.			National/Regional		No.
1.	Psychological Stress	Late ku. Durga K.	International	25-07-2020	31
	on Students due to CORONA	Banmeru Science			
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2.	New Education Policy	Karmaveer	Regional	28-08-2020	32
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Lade Sunil Jagannath who has been found duly qualified for the same. **In Testimony** whereof are set the Seal of the University and the Signatures of the Registrar and the Vice-Chancellor.



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Electrodeposition of CdS from non-aqueous bath

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Received 17 June 1996; revised 8 January 1997; accepted 8 January 1997

Abstract

CdS thin films have been prepared from non-aqueous solvent using electrodeposition technique. $Na_2S_2O_3$, CdSO₄ and EDTA (ethylenediaminetetra-acetic acid tetrasodium salt) were dissolved in ethylene glycol (EG) and structural and optical properties of CdS films have been studied. The X-ray diffraction showed that CdS films are polycrystalline in nature, with single hexagonal phase. Optical absorption showed that bandgap of CdS is 2.45 eV.

Keywords: Electrodeposition; CdS films; Structural properties; Optical properties; Room temperature

1. Introduction

Cadmium sulphide is a medium bandgap (2.42 eV) semiconductor material, having an absorption coefficient of 10^4 – 10^5 cm^{-1} , widely used in solar cells as well as optoelectronic and photoconductive devices [1]. Thin polycrystalline films of CdS are widely used in the fabrication of various devices including solar cells. The efficiency of solar cells is found to be improved with an increase in the conductivity of the CdS films.

A variety of deposition techniques have been reported in the literature for the preparation of CdS films, including anodic oxidation [2,3], cathodic reduction [4], and deposition from an aqueous solution containing a soluble metal salt and sulphur compounds. Recently, the cathodic electrodeposition of cadmium sulphide from a non-aqueous solution bath has been developed. CdS films have been prepared by electrodeposition using elemental sulphur [5–8] or triphenylstibine sulphide [9] as a sulphur source in dimethyl sulphoxide (DMSO), dimethyl formamide (DMF), diethylene glycol (DEG) or ethylene glycol (EG) as the solvent at bath temperatures between 100 and 140°C.

The aim of the present work is to study the structural and optical properties of CdS thin films electrodeposited from a non-aqueous solution bath consisting of sodium thiosulphate as a sulphur source in ethylene glycol solution.

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2. Experimental

It has been observed that $Na_2S_2O_3$ and EDTA are completely soluble in ethylene glycol, but CdSO₄ forms a white precipitate. When $Na_2S_2O_3$, CdSO₄ and EDTA are mixed together the resultant solution becomes completely transparent. Before inserting the substrates (stainless steel and titanium) in the electrolyte, which is kept at 90°C in an oil bath, the substrates were polished with smooth polish paper and cleaned with doubly distilled water. In order to remove the oily substrate surface, cleaned substrates were etched in 10% H_2SO_4 for 2 min then ultrasonically cleaned with doubly distilled water. Indium tin oxide (ITO) coated glass substrates were cleaned with boiled chromic acid for 30 min then cleaned with laboline solution and finally ultrasonically cleaned with double distilled water.

The CdS films have been prepared from 0.5 M Na₂S₂O₃, 0.05 M CdSO₄, 0.1 M EDTA in ethylene glycol solution on stainless steel, titanium and ITO coated glass substrates. Good quality CdS films have been deposited at current densities of 0.5 mA cm⁻² for ITO coated glass substrates, 1 mA cm⁻² for titanium and 1.5 mA cm⁻² for stainless steel substrates each of size 2×1 cm using a constant current source. Graphite of size 2.5×2.5 cm was used as the anode. The deposition bath temperature was 90°C, the pH 8 and the deposition time 90 min. Deposition potentials were estimated from polarization curves. Effects of bath temperature on deposition potentials was studied. The optical absorption studies were carried out with a UV–VIS–NIR spectrophotometer



Fig. 1. Polarization curves for (1) 0.5 M Na₂S₂O₃, (2) 0.05 M CdSO₄ and (3) 0.5 M (8 cm³) Na₂S₂O₃+0.05 M (2 cm³) CdSO₄+0.1 M (5 cm³) EDTA onto titanium substrates.

(Hitachi, model 330). The XRD patterns were obtained by using Philips diffractometer model PW-1710.

3. Results and discussion

3.1. Deposition potential

Deposition potential depends upon the temperature of the bath, the nature of the substrate, the pH of the solution bath,

the complexing agent concentration and the metallic ion concentration. The cathodic polarization curves obtained for 0.5 M Na₂S₂O₃, 0.05 M CdSO₄ and 0.5 M (8 cm³) Na₂S₂O₃ + 0.05 M (2 cm³) CdSO₄ + 0.1 M (5 cm³) EDTA for titanium substrates at 90°C are shown in Fig. 1. Estimated deposition potentials from polarization curves for different substrates at 90°C are as shown in Table 1. From Table 1 it is observed that the deposition potentials of Cd and S are different for different substrates. Also the deposition potential of CdS lies between those of Cd and S. Such results have been explained previously for other metals sulphide systems [10].

3.2. Effect of temperature

Temperature is a very important parameter for the preparation of CdS films in a non-aqueous medium by electrodeposition, because the quality of the deposit was found to be independent of sulphur and cadmium ion concentrations, but the deposit characteristics depend on the bath temperature [11].

The effect of bath temperature on deposition potential in the temperature range 60–110°C using stainless steel, titanium and ITO coated glass substrates as cathodes was studied. Estimated deposition potentials for different temperatures on different substrates are given in Table 2. The polarization curves for stainless steel substrates at different bath temperatures are shown in Fig. 2. From Table 2 it is observed that, as the deposition bath temperature increases, the deposition potential decreases. Generally a rise in temperature increases the grain size. The increase in grain size corresponds to a decrease in polarization potential at higher temperature [12].

Table 1

Estimated deposition potential from the polarization curves for different substrates at 90°C

Sr. no.	Bath composition	Deposition potenti	al (V/SCE) for the	e following substrates
		Stainless steel	Titanium	ITO coated glass
1	0.5 M Na ₂ S ₂ O ₃	- 1.13	-1.40	- 1.28
2	0.05 M CdSO ₄	-0.62	-0.50	-0.45
3	0.5 M (8 cm ³) $Na_2S_2O_3$ + 0.05 M (2 cm ³) CdSO ₄ + 0.1 M (5 cm ³) EDTA	-0.94	-1.13	-0.86

Table 2

Effect of bath temperature on deposition potential for bath composition 0.5 M (8 cm³) $Na_2S_2O_3 + 0.05$ M (2 cm³) CdSO₄ + 0.1 M (5 cm³) EDTA for different substrates

Temperature (°C)	Deposition potential ((V/SCE)		Observations
	Stainless steel	Titanium	ITO coated glass	
25 (RT)	- 1.23	- 1.49	-1.23	No deposition
60	- 1.14	-1.38	-1.17	Non-uniform less adherent
70	- 1.07	- 1.36	-1.14	Non-uniform less adherent
80	- 1.04	-1.22	- 1.00	Smooth very thin non-uniform
90	-0.98	-1.13	-0.88	Uniform yellow adherent
100	-0.92	-1.10	-0.70	Uniform, yellow some visible cracks
110	-0.84	- 1.06	-0.66	Very thin visible cracks



Fig. 2. Polarization curves for 0.5 M (8 cm^3) Na₂S₂O₃ + 0.05 M (2 cm^3) CdSO₄ + 0.1 M (5 cm^3) EDTA onto stainless steel substrates at different temperatures. (1) 25°C, (2) 60°C, (3) 70°C, (4) 80°C, (5) 90°C, (6) 100°C and (7) 110°C.

The increase in temperature dissociates the complex [13] and hence the concentration of simple ions increases, leading to the discharge of ions at a lower potential. Also the rise in temperature of the bath enhances the rate of diffusion and increases the ionic mobilities and hence the conductivity of the bath [14]. Table 2 shows that the films deposited below 90°C are non-uniform in nature.

3.3. X-ray diffraction

Electrodeposition of CdS has been carried out from aqueous and non-aqueous solution baths. CdS films prepared from aqueous solution at room temperature (RT) show mixed, cubic and hexagonal phases [15]. CdS films prepared from a non-aqueous solution bath at 90–140°C are polycrystalline in nature with only the hexagonal phase which is necessary for better results in solar cells.

Structural properties of the CdS films were studied by Xray diffraction. Fig. 3(a) shows the XRD of CdS films deposited on stainless steel substrates from the bath 0.5 M $Na_2S_2O_3 + 0.05$ M CdSO₄ + 0.1 M EDTA in ethylene glycol solution. X-ray diffraction patterns in Fig. 3(a) shows that CdS films are polycrystalline in nature with orientations along the (002), (110) and (105) planes parallel to the substrates. These peaks correspond to the hexagonal phase. Some peaks of the stainless steel substrate are also observed which may be because of the very low film thickness. Fig. 3(b) shows the X-ray diffraction pattern of CdS deposited on ITO coated glass substrates. The X-ray diffraction pattern showed that



Fig. 3. X-ray diffraction pattern for CdS film deposited on (a) stainless steel substrate, (b) ITO coated glass substrate.

CdS films are polycrystalline with (002), (200) and (105) planes corresponding to CdS hexagonal phase. The hump may be due to the substrate as the film is very thin.

3.4. Optical absorption

Optical absorption studies of CdS films were carried out in the wavelength range 350–850 nm employing a UV–VIS– NIR spectrophotometer (Hitachi, model 330), for CdS films deposited on ITO coated glass substrate and stainless steel substrates. In order to estimate the bandgap energy E_g of the CdS, a plot of $(\alpha h\nu)^2$ versus $h\nu$ is plotted and is shown in Fig. 4. The direct bandgap of CdS is determined by extrapolating the straight line to the energy axis and it is found to



Fig. 4. Plot of $(\alpha h\nu)^2$ vs. $h\nu$ for determination of bandgaps of CdS film deposited on (a) ITO coated glass substrate, (b) stainless steel substrate at 90°C.

be 2.45 eV. The value is in good agreement with the reported value [7].

4. Conclusions

From the above study it is concluded that hexagonal CdS films can be electrodeposited onto various substrates from non-aqueous bath using ethylene glycol as a solvent at 90°C.

Acknowledgements

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References

[1] T.L. Chu, Shirley S. Chu, N. Schultz, C. Wang and C.Q. Wu, J. Electrochem. Soc., 139 (1992) 2443.

- [2] B. Miller and A. Heller, Nature, 262 (1976) 680.
- [3] J.F. Mc Cann and M. Skyllas Kazacos, J. Electroanal. Chem., 119 (1981) 409.
- [4] G. Hodes, J. Manassen and S. Neagu, Thin Solid Films, 90 (1982) 433.
- [5] A.S. Baranski and W.R. Fawcett, J. Electrochem. Soc., 127 (1980) 766.
- [6] A.S. Baranski, W.R. Fawcett, A.C. Mc Donald and R.M. De Nobriga, J. Electrochem. Soc., 128 (1981) 963.
- [7] E. Fatus, P. Herrasti, T. Garcia, F. Arjona and E.G. Camarero, Mater. Chem. Phys., 13 (1985) 497.
- [8] S. Sharma, T. Ashraf and R. Murti, Indian J. Pure Appl. Phys., 22 (1984) 122.
- [9] M. Cocivera and S. Preusser, 169th Electrochemical Society Meeting, Boston, MA, 1986, Abstract 336.
- [10] U.K. Mohite, K.M. Gadave and C.D. Lokhande, *Indian J. Eng. Mater. Sci.*, 2 (1995) 93.
- [11] C.D. Lokhande and S.H. Pawar, *Phys. Status Solidi* (a), 111 (1989)17.
- [12] A. Brenner, *Electrodeposition of Alloys*, Academic Press, New York, 1963, p. 139.
- [13] H. Marcus, Met. Finish., 9 (March 1952) 54.
- [14] S.B. Jundale and C.D. Lokhande, Mater. Chem. Phys., 38 (1994) 325.
- [15] S.C. Sahu and S.N. Sahu, Thin Solid Films, 235 (1993) 17.



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Materials Science Communication Studies on the electrodeposition of CdS films

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Abstract

Thin films of CdS have been electrodeposited from an acidic bath using CdSO₄, Na₂S₂O₃ and EDTA at pH 5 to 6 on to the stainless steel and fluorine-tin oxide (FTO) coated glass substrates. The structural, optical and photoelectrochemical properties of these films have been studied. An X-ray diffraction study revealed that CdS films deposited at 70°C are polycrystalline with a single hexagonal phase. The optical absorption studies showed that the bandgap of CdS is 2.42 eV. In order to increase the conductivity, the as-deposited films were annealed in a nitrogen atmosphere. CdS films deposited on to stainless steel substrates showed better I_{sc} and V_{oc} as compared to FTO coated glass substrates. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Electrodeposition; Thin films

1. Introduction

Polycrystalline thin films of CdS have received considerable attention during recent years because of their proven and potential applications in a variety of semiconducting devices such as solar cells, transistors, light activated valves, etc. [1]. The conversion efficiencies of the photoelectrochemical (PEC) cells with configuration CdS/NaOH–Na₂S–S/C have been reported [2,3]. The efficiency of these cells were found to improve with an increase in electrical conductivity of the CdS films [4,5].

Electrodeposition is an attractive method for the preparation of thin films, the main advantage being the easy control of growth rate through electrical quantities. This method has been successfully employed for the deposition of thin films of elementary, binary and ternary semiconductors [6].

The aim of the present paper is to electrodeposit CdS thin films in aqueous acidic solution on to stainless steel and fluorine–tin oxide (FTO) coated glass substrates, and to report on structural, optical and photoelectrochemical properties of the as-deposited and annealed films.

2. Experimental

2.1. Sample preparation

Thin films of CdS have been electrodeposited from the electrolyte containing 0.5 M Na₂S₂O₃ as a sulphur source, 0.05 M CdSO₄ as a cadmium source and 0.1 M EDTA as a complexing agent. Preparative parameters such as complexing agent, current density, bath composition, temperature and pH of the bath, etc., are optimized as reported elsewhere [7]. The stainless steel substrates were polished with soft polish paper, degreased in acetone and ultrasonically cleaned with double distilled water before use. The FTO coated glass substrates were cleaned in boiled chromic acid for 15 min, washed with laboline solution, rinsed in acetone and finally ultrasonically cleaned with double distilled water before use. A conventional three-electrode cell was used to obtain deposition potential. A saturated calomel electrode was used as the reference electrode and graphite as a counter electrode. The CdS films were cathodically deposited on to stainless steel and FTO coated glass substrates at 9 mA cm⁻² and 2.5 mA cm^{-2} respectively, using constant current source at different temperatures. The temperature was constant $(\pm 1^{\circ}C)$ during each electrodeposition, so the bath was first thermostatted at the required temperature.

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Sr. No.	Bath composition	Deposition potentials V/SCE for							
		Stainless steel substrate	FTO coated glass substrate						
1	0.5 M Na ₂ S ₂ O ₃	- 1.32	- 1.44						
2	0.05 M CdSO4	-0.80	-0.70						
3	0.5 M (8 cc) $\text{Na}_2\text{S}_2\text{O}_3 + 0.05 \text{ M}$ (2 cc) CdSO_4	- 1.08	- 1.38						
4	0.5 M (8 cc) $Na_2S_2O_3 + 0.05$ M (2 cc) $CdSO_4 + 0.1$ M (20 cc) EDTA	- 0.68	- 1.39						

Table 1 Estimated deposition potentials for different composition and substrates at room temperature (27°C)

The annealing treatments to the films are given in a tube furnace under a nitrogen atmosphere.

3. Results and discussion

2.2. Sample characterization

Deposition potentials were determined from polarization curves. The effects of temperature and pH on the deposition potential were studied. The optical absorption studies were carried out with a UV-VIS-NIR spectrophotometer (Hitachi model-330). X-ray diffraction patterns were obtained using a Philips X-ray diffractometer model PW-1710. Photoelectrochemical cells were fabricated using CdS deposited on to stainless steel and FTO coated glass substrates as photoanode, polysulphide as an electrolyte and graphite as a counter electrode. The cell performance was evaluated by measuring the open circuit voltage (V_{oe}) and the short circuit current (I_{sc}) under the illumination of 37 mW cm⁻².



Fig. 1. Polarization curves for (1) 0.5 M Na₂S₂O₃, (2) 0.05 M CdSO₄, (3) 0.5 M (8 cc) Na₂S₂O₃ + 0.05 M (2 cc) CdSO₄, (4) 0.5 M (8 cc) Na₂S₂O₃ + 0.05 M (2 cc) CdSO₄ + 0.1 M (20 cc) EDTA. When (a) stainless steel substrate ($- \cdot - 1$, 2, 3, 4) and (b) FTO coated glass substrate ($- \circ - 1$, 2, 3, 4) respectively were used.

3.1. Deposition potential

In order to determine deposition potentials, the cathodic polarization curves were obtained for 0.5 M Na₂S₂O₃, 0.05 M CdSO₄, 0.5 M Na₂S₂O₃+0.05 M CdSO₄ and for 0.5 M $Na_2S_2O_3 + 0.05 M CdSO_4 + 0.1 M EDTA$. Fig. 1 shows polarization curves for stainless steel substrate. By extrapolating the straight line portion to voltage axis, the values of deposition potential were determined, and are as shown in Table 1. As in actual deposition, due to polarization, the deposition potentials are always more negative than the standard reduction potential values. Also, inclusion of a complexing agent shifts the deposition potentials in the negative direction. However, hydrogen evolution starts at a much more negative potential, therefore thick and uniform deposits were obtained from the complexed bath. Similarly, the temperature of the bath was varied between 20-90°C and the cathodic polarization curves were obtained for reduction of CdS for 0.5 M (8 cc) $\text{Na}_2\text{S}_2\text{O}_3 + 0.05 \text{ M}$ (2 cc) $\text{CdSO}_4 + 0.1 \text{ M}$ (20) cc) EDTA bath. From the polarization curves the deposition potentials were established and are shown in Table 2. It is observed that as the bath temperature increases, deposition potential decreases. According to theory, the deposition of metals usually increases with increase in temperature, as polarization decreases. Increase in the temperature of the bath favours deposition of the materials due to the improved mass transport of complexed species towards the cathode [8,9].

Table 2

Estimated deposition potentials at different temperatures on different substrates for bath composition 0.5 M (8 cc) $Na_2S_2O_3 + 0.05$ M (2 cc) CdSO₄ + 0.1 M (20 cc) EDTA

Sr. No.	Temperature	Deposition potentials V/SCE for									
	(°C)	Stainless steel	FTO coated glass								
1	20	- 1.05	- 1.53								
2	30	-0.67	- 1.35								
3	40	-0.63	- 1.30								
4	50	-0.60	- 1.28								
5	60	-0.57	-1.20								
6	70	-0.50	-1.17								
7	80	-0.48	- 1.08								
8	90	-0.45	-1.02								

Table 3

Estimated deposition potentials at different pH values on different substrates at room temperature (27°C) for the bath composition 0.5 M (8 cc) $Na_2S_2O_3 + 0.05$ M (2 cc) $CdSO_4 + 0.1$ M (20 cc) EDTA

Sr. No.	pH values	Deposition potentials V/SCE for				
		Stainless steel	FTO coated glass			
1	2	- 0.19	- 0.60			
2	3	-0.42	-1.25			
3	4	-0.61	- 1.30			
4	5	-0.66	- 1.36			
5	6	-0.78	-1.42			
6	7	- 0.98	- 1.44			
7	8	- 1.00	- 1.48			
8	9	- 1.01	- 1.50			
9	10	-1.14	-1.53			
10	I 1	- 1.23	- 1.55			

The cathodic polarization curves were obtained for the same bath with different pH values and deposition potentials were obtained for different substrates, as shown in Table 3. It is observed that as the pH value of the electrolyte changes from acidic to basic, the deposition potentials increase negatively which is attributed to the more stable complex formed with increasing pH. Similar types of observations are reported for Sm deposition at different pH values [10]. Good quality CdS films were obtained at pH 5.4 and temperature 70°C.

3.2. X-ray diffraction

X-ray diffraction patterns of the CdS film deposited on to a stainless steel substrate at 27°C (room temperature), 60°C, 70°C and 80°C are shown in Fig. 2. The XRD spectra of the CdS films deposited at room temperature show a mixed phase similar to those reported by other workers [11,12]. However, films deposited at 70°C are polycrystalline with a single hexagonal phase. The peaks at $2\theta = 26.7^\circ$ correspond to diffraction from (002) planes of CdS hexagonal phase. The intensity of the same peak has higher values as compared to CdS films deposited at room temperature, 60°C and 80°C. As-deposited (at 70°C) CdS films were annealed at 200°C in a nitrogen atmosphere for different times. X-ray diffraction pattern of these films are shown in Fig. 3. The XRD studies also show that the films that were annealed for 30 min has better crystallinity as compared to the films annealed for 15 and 45 min. Comparison of observed *d* values with standard ASTM data showed that the deposited material consists of polycrystalline CdS films with a single hexagonal phase.

3.3. Optical absorption

Optical absorption studies of CdS films deposited on FTO coated glass substrates are carried out in the wavelength range 350–850 nm, using a UV-VIS-NIR spectrophotometer. In order to estimate the bandgap energy E_g of the CdS film, the plots $(\alpha h\nu)^2$ versus $h\nu$ were plotted, as shown in Fig. 4(a). The bandgap for CdS is determined by extrapolating the straight line portion to the energy axis and it is found to be 2.42 eV. These results are in good agreement with the results reported previously [13]. Fig. 4(b) shows the graph of $(\alpha h\nu)^2$ versus $h\nu$ for CdS films deposited on fluorine–tin oxide coated glass when annealed in a nitrogen atmosphere at 350°C for 60 min. The bandgap of the annealed film is 2.46 eV. It is concluded that there is no significant change in the bandgap energy after annealing the film.

3.4. Photoelectrochemical characterization

Photoelectrochemical cells using CdS as a photoanode can be used as devices for the sustained conversion of low energy visible light to electricity [14].

In the present investigation the photoelectrochemical cell was formed using a CdS film that was electrodeposited on to



Fig. 2. X-ray diffraction patterns of CdS film electrodeposited on to a stainless steel substrates: (a) at 70°C, (b) at 60°C, (c) at 80°C, (d) at room temperature.



Fig. 3. X-ray diffraction patterns of CdS films electrodeposited on stainless steel substrate at 70°C and annealed in nitrogen atmosphere at 200°C for (1) 30 min, (2) 15 min, 3) 45 min.



Fig. 4. Plots of $(\alpha h\nu)^2$ vs. $h\nu$ for (a) as-deposited CdS films on FTO coated glass substrates and (b) annealed at 350°C in nitrogen atmosphere for 60 min.

stainless steel and FTO coated glass substrate as photoanodes, graphite as a counter electrode and 1 M NaOH + 1 M Na₂S + 1 M S as electrolyte. The illumination intensity was 37 mW cm⁻². CdS films deposited on to a stainless steel substrate and annealed in nitrogen atmosphere at 200°C for 30 min gives better results ($I_{sc} = 1.5 \text{ mA cm}^{-2}$ and $V_{oc} = 260 \text{ mV}$) compared to CdS films deposited on fluorine-tin oxide coated glass and annealed at 350°C for 1 h.

4. Conclusions

CdS films have been electrodeposited using an aqueous solution bath on to stainless steel and FTO coated glass substrates. The XRD pattern indicates that CdS films deposited at room temperatures show a mixed phase, however, films deposited at 70°C show a single hexagonal phase and its crystallinity enhances when annealed in a nitrogen atmosphere at 200°C for 30 min. The optical bandgap of CdS films was estimated to be 2.42 eV. The CdS films deposited on to a stainless steel substrate annealed in a nitrogen atmosphere shows better photovoltaic activity than the FTO coated glass substrates.

References

- [1] A.U. Warad, M.D. Uplane, S.H. Pawar, Mater. Chem. Phys. 13 (1985) 91.
- [2] C.D. Lokhande, M.D. Uplane, S.H. Pawar, Ind. J. Pure Appl. Phys. 21 (1983) 78.
- [3] S.S. Kale, U.S. Jadhav, C.D. Lokhande, Bull. Electrochem. 12 (9) (1996) 540.
- [4] L.P. Deshmukh, A.B. Palwe, Solar Energy Mater. 20 (1990) 341.
- [5] Hai-Ning Cui, Shi-Quan Xi, Thin Solid Films 288 (1996) 325.
- [6] C.D. Lokhande, S.H. Pawar, Phys. Status Solidi A 111 (1989) 17.
- [7] S.B. Jundale, C.D. Lokhande, Ind. J. Pure Appl. Phys. 31 (1993) 655.
- [8] A.S. Founda, M.M. Elsemongy, I.M. Kenawy, Ind. J. Technol. 20 (1982) 139.
- [9] A.S. Founda, A.K. Mohamed, Bull. Electrochem. 6 (7) (1990) 677.
- [10] S.B. Jundule, C.D. Lokhande, Mater. Chem. Phys. 27 (1991) 265.
- [11] H. Uda, S. Ikegami, H. Sonomura, Jpn. J. Appl. Phys. 29 (1990) 30.
- [12] D. Bhattacharya, M.J. Carter, Thin Solid Films 288 (1996) 176.
- [13] C.D. Lokhande, V.S. Yermune, S.H. Pawar, J. Electrochem. Soc. 138
- (2) (1991) 624.
 [14] A.B. Ellis, S.W. Kaiser, M.S. Wrighton, J. Am. Chem. Soc. 98 (1976) 27.

Structural, optical and photoelectrochemical properties of electrodeposited CdSe thin films

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Cadmium Selenide thin films have been electrodeposited from an acidic bath using $CdSO_4$ as a cadmium source and SeO_2 as a selenium source at pH = 3 on to stainless steel and fluorinetin oxide coated glass substrates. The CdSe films have been characterized by X-ray diffraction, scanning electron microscopy and optical absorption. X-ray diffraction spectra showed that CdSe is polycrystalline with single hexagonal phase. The intensity of the (002) peak increases remarkably by annealing in nitrogen atmosphere. A microstructural study revealed that the films were uniform and well covered the substrate. Optical absorption studies showed that the bandgap of the CdSe is 1.70 eV. It is observed that the conductivity of the CdSe films increases by annealing in nitrogen atmosphere. The photoelectrochemical activities of CdSe films deposited on stainless steel and fluorine-tin oxide coated glass have been studied by using CdSe/ 1M NaOH-1M Na₂S-1MS / C cell configuration and it is found that films deposited on stainless steel give better performance, photoelectrochemical (PEC) studies also reveal that the CdSe has n-type conductivity.

1. Introduction

Among the II-VI compounds, cadmium selenide is a promising semiconductor material for fabrication of heterojunction solar cells and photoelectrochemical solar cells [1]. Because of their suitable bandgap and high photosensitivity in the visible range of the solar spectrum, these materials can be advantageously used for low cost applications. Many workers [2,3] have studied the growth conditions of thin films for use in device fabrication. Samarth et al. [4] studied the crystalline structure of CdSe in the wurtzite form. Wynands and Cocivera [5] studied the carrier transport properties of electrochemically grown CdSe using resistivity and Hall effect measurements. Bawendi et al. [6] obtained X-ray diffraction patterns of CdSe nanocrystals and analysed them. Golan et al. [7] recently reported the epitaxial electrodeposition of wurtzite CdSe nanocrystals on a (111) gold substrate. A variety of deposition techniques have been reported in the literature and among these methods electrodeposition is an isothermal process mainly controlled by electrical parameters, which are easily adjusted to control film thickness, morphology, composition, etc. Also, it is easy and less expensive being used near to room temperature and with dilute reagents. In the literature, most of the CdSe films electrodeposited in aqueous acidic baths usually contain large concentrations of elemental selenium [8,9] which weakly crystallizes and micrographs showed a cauliflower-like appearance which remained unchanged after annealing.

In this study, polycrystalline CdSe thin films are electrodeposited on stainless steel and fluorine-tin oxide coated glass substrates from an aqueous acidic bath. The structural, optical and photoelectrochemical properties of the as-deposited and annealed CdSe films have been studied and the results are discussed at length.

2. Experimental

Cadmium selenide thin films were cathodically electrodeposited from analytical 0.05 M CdSO₄ and 0.01 M SeO₂ solutions onto stainless steel and fluorine-tin oxide coated glass substrates. The pH of the electrolyte was adjusted with concentrated H₂SO₄ using a LABINDIA µp controlled pH analyser. The electrodeposition potentials were estimated from polarization curves. All potentials were measured with respect to a saturated calomel electrode (SCE). The effects of composition, temperature, pH, etc. on deposition potentials were studied. Annealing of the films was carried out in a tube furnace under nitrogen atmosphere. The X-ray diffraction patterns were obtained using a Philips X-ray diffractometer model PW-1710. The optical absorption studies were carried out with a UV-VIS-NIR spectrophotometer (Hitachi model 330). Microstructural studies were carried out with scanning electron micrographs, obtained with a Cambridge Stereoscan 250 MK 3 assembly. Photoelectrochemical activities were studied using a polysulphide electrolyte and graphite as a counter electrode under $37 \,\mathrm{mW \, cm^{-2}}$ light illumination.

3. Results and discussion

Cathodic polarization curves were plotted for reduction of cadmium, selenium and cadmium selenide using





Figure 1 Polarization curves for a) $0.05\,M$ CdSO4, b) $0.01\,M$ SeO2, c) $0.05\,M$ CdSO4 + $0.01\,M$ SeO2 when stainless steel substrates were used.

Figure 2 Polarization curves for 0.05 M (5 cc) CdSO₄ + 0.01 M (5 cc) SeO₂ for different pH values (a=2, b=3, c=4, d=5, e=6) when stainless steel substrates were used.

stainless steel and fluorine-tin-oxide coated glass substrates. Fig. 1 shows polarization curves for 0.05 M CdSO₄, 0.01 M SeO₂ and 0.05 M CdSO₄ + 0.01 M SeO₂ when stainless steel substrates were used. Table I shows estimated deposition potentials for stainless steel and fluorine-tin-oxide coated glass substrates. It is observed that the deposition potential of CdSe lies between the reduction potential of cadmium and selenium [10].

The effect of electrolyte pH on the deposition potential of CdSe was studied within the pH range of 2 to 6 at room temperature. Fig. 2 shows polarization curves for different pH values for stainless steel substrates. Table II shows estimated deposition potentials for stainless steel and fluorine-tin oxide coated glass substrates. It is observed that as the pH changes from 2 to 6 the deposition potentials increase negatively. As the pH of the bath increases, the complex becomes strong, therefore a higher potential is required to gain the ions for the deposition. Similar results have been reported for other semiconducting materials [11].

The effect of bath temperature on the deposition potentials of CdSe at pH = 3 and volume ratio 1, was studied from room temperature to 90 °C. Table III shows estimated deposition potentials for stainless steel and fluorine-tin oxide coated glass substrates. It is observed that as the bath temperature increases the deposition potential decreases. The rise in bath temperature enhances the rate of diffusion and increases ionic mobilities and hence the conductivity of the bath. Also, the increase in temperature dissociates the complex and hence the concentration of simple ions increases which

TABLE I Estimated deposition potentials from polarization curves for different compositions and substrates

Bath composition	Deposition potenti	ials (V/SCE)
	Stainless Steel substrate	Fluorine tin oxide substrate
0.05 M CdSO ₄	-0.60	-0.62
0.01 м SeO ₂	-0.69	-0.72
$0.05 \text{ m} \text{ CdSO}_4 + 0.01 \text{ m} \text{ SeO}_2$	-0.58	-0.60

TABLEII Estimated deposition potential at different pH values for different substrates

pH value	Deposition potentials (V/SCE)				
	Stainless steel substrate	Fluorine-tin oxide substrate			
2	-0.56	-0.64			
3	-0.59	-0.60			
4	-0.60	-0.57			
5	-0.68	-0.54			
6	-0.74	-0.52			

 $TABLE \quad III \ Estimited \ deposition \ potentials \ at \ different temperatures for different substrates$

Temperature ($^{\circ}$ C)	Deposition potential (V/SCE)			
	Stainless	steel substrate Fluorine-tin oxide substrate		
30	-0.58	-0.60		
40	-0.56	-0.57		
50	-0.52	-0.58		
60	-0.48	-0.52		
70	-0.46	-0.50		
80	-0.44	-0.44		
90	-0.40	-0.40		

produces the discharge of ions at low potential. Similar results are reported for alloys and semiconducting compounds [12].

3.1. Photoelectrochemical study

During the last few years, photoelectrochemical (PEC) processes at semiconductor-electrolyte interfaces have found new interest because of their solar and non-solar applications [13]. In the present work, the films of different compositions were obtained on stainless steel substrates and their photoactivity was tested by noting



Figure 3 Plots of a) short-circuit current and b) open-circuit voltage versus cadmium to selenium volume ratio, respectively, when CdSe is deposited on stainless steel substrates.

the short-circuit currents and open-circuit voltages. From the polarity of the open-circuit voltage and short-circuit current, it is seen that electrodeposited CdSe is an n-type semiconducting material. Fig. 3 shows the variation of short-circuit currents and open-circuit voltage as a function of cadmium sulphate to selenium dioxide volume ratio. It is observed that as the Cd:Se volume ratio increases, short-circuit current and open-circuit voltage increase and attain maximum values at a 1:1 volume ratio, above which the open-circuit voltage and short-circuit current decrease [14]. The increase in photovoltage and photocurrent at a 1:1 volume ratio may be due to the better stoichiometry achieved at this volume ratio.

The CdSe films deposited on stainless steel and fluorine-tin oxide coated glass substrates were annealed, in a nitrogen atmosphere for different times and temperatures. Fig. 4 shows the variations of short-circuit current and open-circuit voltage as a function of annealing time. It is observed that for annealing time up to 30 min., short-circuit current increases and then decreases with further annealing time, however, a small variation of open-circuit voltage was observed. The increase in short-circuit current may be attributed to the improved crystallinity of CdSe films after annealing. Films electrodeposited on fluorine-tin oxide coated glass substrates were annealed at 350°C for 60 min in a nitrogen atmosphere show an increase in short-circuit current, however, these results are poor compared to results obtained for a stainless steel substrate.

3.2. X-ray diffraction

X-ray diffraction patterns of as deposited and annealed CdSe films on stainless steel and fluorine-tin oxide coated glass substrates were obtained. Fig. 5 shows X-ray diffraction patterns of as deposited and annealed CdSe film on stainless steel substrates. The peak of $2\theta = 25.40^{\circ}$ corresponds to diffraction from (002) planes of hexagonal CdSe phase, the stable structure of CdSe at room temperature is normally the hexagonal wurtzite [15]. Some peaks of stainless steel substrates were also observed due to the very small film thickness $(0.22 \,\mu m)$. The intensity of the (002) peak increased remarkably when as-deposited CdSe films were annealed in nitrogen atmosphere at 200 °C for 30 min. indicating an increase in the crystallite size. This result supports the observations obtained from photoelectrochemical studies. The CdSe films deposited on fluorine-tin oxide coated glass exhibit the weakest indication of diffraction from the (111) plane of CdSe cubic phase. As-deposited CdSe film annealed at 350 °C for 60 min shows the diffraction peak of a (002) plane, but the intensity of the same peak is low compared to film deposited on stainless steel substrates.

3.3. Optical absorption

Optical absorption studies of CdSe film deposited on fluorine-tin oxide coated glass substrates have been carried out in the wavelength range of 350 nm to 850 nm employing a UV-VIS-NIR spectrophotometer (Hitachi model – 330). As CdSe is a direct bandgap semi-



Figure 4 Variations of a) short-circuit current and b) open-circuit voltage as a function of annealing time for the CdSe electrodeposited on stainless steel substrates.

conducting material, the plot of $(\alpha hv)^2$ versus hv gives a straight line, extrapolation of the plot to the energy axis gives the bandgap. As-deposited films were annealed in a nitrogen atmosphere at 350 °C for various times. Fig. 6 shows the plots of $(\alpha hv)^2$ versus hv for deposited and annealed films. The estimated bandap values from the plots for as-deposited and annealed films are 1.83 eV and 1.70 eV, respectively. It is found that bandgap decreases after heat treatment, which may be attributed to the improved crystallinity of the films, as discussed previously.

3.4. Scanning electron microscopy

Scanning electron microscopy is a convenient and versatile method to study microstructure of the film and to determine the grain size. The micrographs of as deposited and annealed CdSe films on stainless steel substrates for different magnifications are as shown in Fig. 7. It is observed that the films have a homogenous, uniform surface without cracks or holes and well cover the substrate. The grain size of the film increased when annealed in nitrogen atmosphere at 200 °C for 30 min.

480

This results also supports the observations from X-ray diffraction and photoelectrochemical studies.

4. Conclusions

Electrodeposition of CdSe on stainless steel or fluorinetin oxide coated glass substrates is composition, temperature as well as pH dependent. The crystallinity of as-deposited films have been improved by appropriate annealing in a nitrogen atmosphere. An X-ray diffraction study revealed that the CdSe is a polycrystalline, single hexagonal phase with preferential orientation along (002) planes. An optical absorption study showed that CdSe is a direct bandgap material having a bandgap energy of 1.70 eV. The microstructural studies showed that annealing improves the crystallinity of the films. The photoactivities for as-deposited and annealed films were compared and it is found that annealed films on stainless steel substrates give better performance than asdeposited or annealed films deposited on FTO coated glass substrate. From PEC studies it is also seen that CdSe is an n-type material.





Figure 5 X-ray diffraction patterns of a) as deposited CdSe on stainless steel substrate and b) annealed in nitrogen atmosphere at 200 °C for 30 min.

Figure 6 Plots of $(\alpha hv)^2$ verses hv for a) as deposited CdSe on fluorinetin oxide coated glass substrate and b) annealed in nitrogen atmosphere at 350 °C for 60 min.





10000 X



20000 X



Figure 7 Scanning electron micrographs of CdSe film on stainless steel substrate (bath composition 0.05 M (5 cc CdSO₄ + 0.01 M (5 cc) SeO₂); a) as-deposited b) annealed in nitrogen atmosphere at 200 °C for 30 min.

References

- 1. C. D. LOKHANDE, R. V. DABHADE, P. S. PATIL and S. H. PAWAR, Bull. Electrochem 7 (1991) 319.
- 2. R. A. BOUDRAU and R. D. RAUH, *Solar Energy Mater*. 7 (1982) 835.
- 3. D. J. MILLER and D. HANEMANN, *ibid.* 4 (1981) 223.
- 4. N. SAMARTH, H. LUO and J. K. FURDYNA, *J. Electron. Mater.* 19 (1990) 543.
- 5. H. WYNANDS and M. COCIVERA, J. Electrochem. Soc. 139 (1992) 2052.
- 6. M. G. BAWENDI, A. R. KORTAN, M. L. STEIGER WALD and L. E. BRUS, *J. Chem. Phys.* **91** (1989) 7282.
- 7. Y. GOLAN, L. MARGULIS, G. HODES, I. RUBINSTEIN and J. L. HUTCHISON, *Surf. Sci.* **311** (1994) L 633.
- 8. R. K. PANDEY, S. R. KUMAR and A. J. N. ROOZ, *Thin Solid Films* **200** (1991) 1.

- 9. M. T. GUTIERREZ and J. ORTEGA, J. Electrochem. Soc. 136 (1989) 2316.
- 10. N. S. YESUGADE, C. D. LOKHANDE and C. H. BHOSALE, Thin Solid Films 263 (1995) 145.
- 11. S. B. JUNDALE and C. D. LOKHANDE, *Mater. Chem. Phys.* **37** (1994) 333.
- 12. U. K. MOHITE, K. M. GADAVE and C. D. LOKHANDE, *Indian J. Eng. Mater. Sci.* **2** (1995) 93.
- 13. S. B. JUNDALE and C. D. LOKHANDE, Indian J. Pure Appl. Phys. **31** (1993) 655.
- 14. R. C. BHARDWAJ, C. M. JADHAV and M. M. TAQUI KHAN, Solar Cells 13 (1984) 293.
- 15. Z. LOIZOS and N. SPYRELLIS, *Thin Solid Films* **204** (1991) 139.

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Electrosynthesis of CdTe films from ethylene glycol bath

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Abstract

Cadmium telluride thin films have been prepared by galvanostatic electrodeposition method using ethylene glycol bath onto different substrates at deposition temperature of 80°C. The films were characterized by X-ray diffraction, optical absorption, scanning electron microscopy and photoelectrochemical techniques. The effect of CdTe film annealing in nitrogen atmosphere on structural, optical and morphological was studied. X-ray diffraction study showed that films are polycrystalline with hexagonal phase. Optical absorption study revealed that CdTe is a direct band gap material with band gap of 1.52 eV. Scanning electron microscopy study revealed that the films are homogeneous without cracks or holes. No significant changes in crystal structure, optical bandgap and crystallinity were observed after annealing. From photoelectrochemical studies, it exhibited n-type conductivity. ©2000 Elsevier Science S.A. All rights reserved.

Keywords: Electrodeposition; Thin films; CdTe films

1. Introduction

The growth of high quality CdTe is important because of their potential applications in solar energy, X-ray detection, gamma ray detection etc. Thin films of CdTe are fabricated by a variety of methods, such as vacuum evaporation [1,2], metal-organic chemical vapour deposition [3], anodic and cathodic deposition [4,5] etc. Among these methods electrodeposition is an attractive method which has successfully been employed for the preparation of elemental, binary, intermetallic and ternary compounds. It is an isothermal process, mainly controlled by electrical parameters, which are easily adjusted to control film thickness, morphology, composition etc. [6].

Non-aqueous baths for semiconductor electrodeposition are interesting since they have attractive features and yet can be operated at lower temperatures. They do not suffer from hydrogen evolution. Gore et al. [7] have electrodeposited CdTe film on nickel plates at 160°C from CdCl₂, KI and TeCl₄ in ethylene glycol. The CdTe films were nearly stoichiometric and uniform with a cubic crystalline phase. Gheorghita et al. [8] electrodeposited CdTe films at 95–105°C using non-aqueous solution of 106 mM tri-*n*-butylphosphine telluride (BPT) and 6 mM lithium perchlorate as a supporting electrolyte. In order to improve crystallinity and adherence, the CdTe films were annealed under argon at 200°C for 60 min, followed by 400°C for 10 min in a Lindberg tube furnace. Pandey et al. in his earlier reports [9] have demonstrated the advantage of ethylene glycol based baths over aqueous acidic baths. It was shown that, one can deposit compact, coherent and stoichiometric layer of CdTe from non-aqueous bath [10].

In the present paper polycrystalline thin films of CdTe are electrodeposited at different temperatures on different substrates using non-aqueous (ethylene glycol) bath. The structural and optical properties of as-deposited, annealed and etched films are studied.

2. Experimental

Thin films of CdTe were electrodeposited from 0.05 M CdSO₄, 0.01 M Na₂TeO₃ and 0.1 N HClO₄ in ethylene glycol solution onto different substrates. It is observed that Na₂TeO₃ and HClO₄ are completely soluble in ethylene glycol but CdSO₄ forms a white precipitate. When Na₂TeO₃-HClO₄ and CdSO₄ are mixed together the resultant solution becomes completely transparent. Before inserting the substrates (stainless steel and titanium) in the electrolyte, the substrates were polished with smooth (zero grade) polish paper and cleaned with doubled distilled water. In order to remove the oily substances from the surface, cleaned substrates were etched in 10% H₂SO₄ for 2 min and ultrasonically cleaned with double distilled water. Fluorine doped tin oxide (FTO) coated glass substrates were boiled in chromic acid for 30 min and ultrasonically cleaned with

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double distilled water and dried with hot air. The deposition potentials for Cd, Te and CdTe were estimated from polarization curves. All potentials were measured with respect to saturated calomel electrode (SCE). The effects of bath composition and temperature on deposition potentials were studied. Annealing of the films was carried out in tube furnace in nitrogen atmosphere. Annealed films were etched in 3% HCl solution for 3 s and then rinsed with double distilled water. The X-ray diffraction patterns were obtained using Philips X-ray diffractometer model PW-1710. The optical absorption studies were carried out with a UV–VIS–NIR spectrophotometer (Hitachi-model 330). Scanning electron micrographs were obtained with Cambridge Stereoscan 250-MK-3 assembly.

Photoelectrochemical characterization was carried out by forming photoelectrochemical cell consisting of CdTe film as the cathode, graphite as the anode and 1 M polysulphide (NaOH-Na₂S-S) as the electrolyte.

3. Results and discussion

3.1. Deposition potentials

The cathodic deposition potentials depend upon bath temperature, nature of substrate, metal ion concentration, complexing agent and its concentration, etc. The cathodic polarization curves were obtained for 0.05 M CdSO₄, 0.01 M Na₂TeO₃, 0.01 M Na₂TeO₃ + 0.1 N HClO₄ and $0.05 \text{ M CdSO}_4 + 0.01 \text{ M Na}_2\text{TeO}_3 + 0.1 \text{ N HClO}_4 \text{ solutions}$ for stainless steel, FTO coated glass and titanium substrates. Fig. 1 shows polarization curves on stainless steel substrate at bath temperature 80°C for the reduction of Cd, Te and CdTe from their solutions. The estimated deposition potentials for Cd, Te and CdTe on various substrates and at different deposition temperatures are shown in Table 1. It is observed from the Table 1, that the deposition potentials of Cd, Te and CdTe are different for different substrates. The substrates are polycrystalline (as evidenced from XRD studies) and their orientations are varied from substrate to substrate. The deposited material gets deposited so as to attain the closest symmetry with the surface morphology of the substrate. The order of matching between the deposited

Fig. 1. Polarization curves for reduction of Cd from 0.05 M CdSO₄ (×), reduction of Te from 0.01 M Na₂TeO₃ (\bigcirc), reduction of Te from 0.01 M (10 cc) Na₂TeO₃ + 0.1 N (10 cc) HClO₄ (\odot) and reduction of CdTe from 0.05 M (10 cc) CdSO₄ + 0.01 M (10 cc) Na₂TeO₃ + 0.1 N (10 cc) HClO₄ (\bullet) for stainless steel substrates.

material and substrate gives different values of deposition potentials. In addition, the affinity of substrate material is different for different depositing material [11,12].

3.1.1. Effect of bath temperature on deposition potential

The temperature of the bath was varied between 60 and 100° C and cathodic polarization curves were obtained for a solution of 0.05 M CdSO₄, 0.01 M Na₂TeO₃ and 0.1N HClO₄ in ethylene glycol solution for different substrates. Fig. 2 shows the polarization curves for stainless steel substrate at different temperatures. The deposition potentials were estimated by drawing tangential line to the curve and taken intercept of it along voltage axis. The estimated deposition potentials from polarization curves are shown in Table 1. It is observed that as the bath temperature increases the deposition potential decreases. Generally, rise in bath temperature increases the grain size of deposited material and the increase in grain size results to a decrease in polarization.

Table 1

Estimated deposition potentials for different compositions, substrates and temperatures

Sr. No.	Bath composition	Temperature (°C)	Deposition potentials (V, vs. SCE) for		
			Stainless steel	Titanium	FTO coated glass
1	0.05 M CdSO ₄	80	-0.62	-0.48	-0.40
2	0.01 M Na ₂ TeO ₃	80	-0.76	-0.56	-0.40
3	$0.1 \text{ M Na}_2 \text{TeO}_3 + 0.1 \text{ M HClO}_4$	80	-0.50	-0.58	-0.62
4	$0.05 \text{ M} (10 \text{ cc}) \text{ CdSO}_4 + 0.01 \text{ M} (10 \text{ cc}) \text{ Na}_2 \text{TeO}_3 + 0.1 \text{ N} 10 \text{ cc} \text{ HClO}_4$	80	-0.48	-0.68	-0.54
5	$0.05 \text{ M} (10 \text{ cc})\text{CdSO}_4 + 0.01 \text{ M} (10 \text{ cc}) \text{ Na}_2\text{TeO}_3 + 0.1 \text{ N} 10 \text{ cc} \text{ HClO}_4$	60	-0.52	-0.75	-0.72
6	-do-	70	-0.51	-0.71	-0.69
7	-do-	90	-0.42	-0.60	-0.53
8	-do-	100	-0.38	-0.48	-0.48



Fig. 2. Polarization curves for reduction of CdTe from 0.05 M (10 cc) CdSO₄ + 0.01 M (10 cc) Na₂TeO₃ + 0.1 N (10 cc) HClO₄ at different deposition temperatures [60°C (×), 70°C (\bigcirc), 80°C (\bigoplus), 90°C (\bigoplus), 100°C (\bigcirc)]. The stainless steel substrate was used.

tion potential [13]. Additionally, the rise of bath temperature enhances the rate of diffusion and the ionic mobilities and hence the conductivity of deposition bath [14]. Similar results are reported for alloys and semiconducting compounds [15,16]. From other characterization (XRD) of films, it is concluded that good quality CdTe films are obtained at the bath temperature of 80°C.

3.2. Variation of CdTe film thickness with deposition time

Thin films of CdTe were prepared from 0.05 MCdSO₄ + 0.01 M Na₂TeO₃ + 0.1N HCIO₄ in ethylene glycol solution for different time durations at deposition temperature of 80°C. Fig. 3 shows variation of CdTe film thickness deposited on stainless steel substrate with deposition time. It is observed that initially as deposition time increases, CdTe film thickness increases, attains maximum thickness and then decreases with further increase in deposition time. The maximum thickness ($0.54 \times 10^{-4} \text{ cm}$) is attained in the first 30 min and with further deposition



Fig. 3. Variation of film thickness with deposition time $(0.05 \text{ M} \text{ CdSO}_4 + 0.01 \text{ M} \text{ Na}_2\text{TeO}_3 + 0.1 \text{ N} \text{ HClO}_4$ in ethylene glycol at current density 2.5 mA cm⁻² on stainless steel substrate).

time, the film thickness decreased to 0.45×10^{-4} cm for the 60 min. This is attributed to the increase in the rate of dissolution than the rate of deposition after attaining the maximum thickness [17].

3.3. X-ray diffraction

X-ray diffraction patterns of CdTe film electrodeposited from $0.05 \text{ M} \text{ CdSO}_4 + 0.01 \text{ M} \text{ Na}_2\text{TeO}_3 + 0.1 \text{N} \text{ HClO}_4$ at 80°C for different substrates were obtained. Fig. 4 shows the X-ray diffraction pattern of CdTe film deposited on FTO coated glass substrates. CdTe film deposited on FTO coated glass was polycrystalline with (110), (202), (210), (105)planes hexagonal phase of CdTe. As-deposited film was annealed at 350°C for different time durations in a nitrogen atmosphere. No significant increase in peak intensity was observed after CdTe film annealed for 60 min. CdTe film deposited on stainless steel substrate was also polycrystalline with (002), (102), (110), (112), (213), (107) planes corresponds to hexagonal phase. As-deposited CdTe films on stainless steel substrate were annealed at 200°C in nitrogen atmosphere for different time durations. No significant increase in peak intensities were observed when film was annealed for 30 min. However, additional Te peaks were also observed.

3.4. Optical absorption

CdTe film were deposited on FTO coated glass substrate from 0.05 M CdSO₄ + 0.01 M Na₂TeO₃ 0.1N HClO₄ in ethylene glycol solution at 80°C using current density of 0.5 mA cm^{-2} . Optical absorption study was carried out in the wavelength range of 550–850 nm. As CdTe is a direct



Fig. 4. X-ray diffraction patterns of (a) as-deposited and (b) annealed CdTe film was deposited on FTO coated glass substrate.



Fig. 5. Plots of $(\alpha h \nu)^2$ vs. $h\nu$ for as-deposited (\bullet), annealed (\bigcirc) and etched (\odot) CdTe film was deposited on FTO coated glass substrate.

bandgap material, the plot of $(\alpha h\nu)^2$ versus $h\nu$ gives a straight line and extrapolation of straight line part of the plot to the energy axis gives value of band gap. Fig. 5 shows the plots of $(\alpha h\nu)^2$ versus $h\nu$ for as-deposited, annealed and etched films. The estimated bandgap value for as-deposited, annealed and eatched CdTe films are 1.52, 1.50 and 1.47 eV respectively. No significant change in band gap of CdTe was observed after heat treatment.

3.5. Scanning electron microscopy

CdTe film deposited on stainless steel substrate was used to study the surface morphology. Fig. 6 shows micrographs of as-deposited, annealed and etched films at $25,000 \times$ magnifications. It is observed from the micrographs that the films are homogeneous, uniform surface without cracks or holes. Change in morphology of CdTe film was observed when CdTe film was annealed at 350° C. Loosely bounded CdTe particles are removed and fine grained smooth surface is clearly observed after etching the films in 3% HCl.

3.6. Photoelectrochemical characterizations

Photoelectrochemical characterizations of CdTe based photoelectrochemical cell was canied out using tungsten filament lamp at 37 mW cm⁻² illumination intensity. The CdTe films were found to be photoactive with $I_{sc} = 4.2$ mA cm⁻² and $V_{oc} = 270$ mV. By considering the changes in the polarity of illuminated CdTe electrode, it was concluded that the CdTe film show n-type conductivity.

4. Conclusions

Electrodeposition of CdTe thin films on different substrates is possible using non-aqueous ethylene glycol bath. X-ray diffraction study revealed that electrodeposited CdTe films are polycrystalline with hexagonal crystal structure. No significant change in bandgap and crystallinity of CdTe



Fig. 6. Scanning electron micrographs of CdTe films at $25,000 \times$ magnification for as-deposited (a), annealed (b) and etched (c) films deposited on FTO coated glass substrates.

film was observed after annealing the film at 350° C. Optical absorption study showed that the CdTe is a direct bandgap material with bandgap 1.52 eV. Surface morphology of CdTe revealed that the surface is compact, uniform and crack free.

References

- [1] K.C. Sarmah, H.L. Das, Thin Solid Films 198 (1991) 29.
- [2] R.D. Gould, S. Gravano, B.B. Ismail, Thin Solid Films 198 (1991) 93.
- [3] A. Rohatgi, S.A. Ringel, P.V. Meyers, C.H. Liu, V. Rananathan, Solar Cells 27 (1989) 219.
- [4] M.P. Panicker, M. Knaster, S.A. Kroger, J. Electrochem. Soc. 125 (1978) 566.
- [5] D. Ham, K.K. Mishra, A. Weiss Rajeshwar, Chem. Mater. 1 (1989) 619.
- [6] C.D. Lokhande, S.H. Pawar, Phys. Stat. Sol. (A) 111 (1989) 17.
- [7] R.B. Gore, R.K. Pandey, S.K. Kulkarni, Solar Energy Mater. 18 (1989) 159.
- [8] L. Gheorghita, M. Cocivera, A.J. Nelson, A.B. Swartzlander, J. Electrochem. Soc. 141 (1994) 529.

- [9] R.K. Pandey, G. Razzini, L.P. Bicelli, Solar Energy Mater. Solar Cells 26 (1992) 285.
- [10] R.B. Gore, R.K. Pandey, S.K. Kulkarni, J. Appl. Phys. 65 (1989) 2693.
- [11] R. Weil, Plating and surface finishing, Dec. (1987) 70.
- [12] Y. Fukumoto, M. Fujita, T. Hayashi, in: Proc. Int. Conf. on Electrodeposition Electroforming, Indian Institute of Science, Bangalore, 20–22 February, 1986, p. 491.
- [13] A. Brenner, Electrodeposition of Alloys, Academic Press, New York, 1963, p. 139.
- [14] S.B. Jundale, C.D. Lokhande, Mater. Chem. Phys. 38 (1994) 325.
- [15] U.K. Mohite, K.M. Gadave, C.D. Lokhande, Indian J. Eng. Mater. Sci. 2 (1995) 93.
- [16] S.J. Lade, C.D. Lokhande, Mater. Chem. Phys. 49 (1997) 160.
- [17] S.B. Jundale, C.D. Lokhande, Mater. Chem. Phys. 27 (1991) 265.



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Photoelectrochemical properties of CdX (X=S, Se, Te) films electrodeposited from aqueous and non-aqueous baths

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Abstract

Polycrystalline CdX (X=S, Se, Te) films are electrodeposited from aqueous and non-aqueous (ethylene glycol) baths onto different substrates at different temperatures. In order to increase the conductivity of the films, as-deposited films are annealed in a nitrogen atmosphere. Photoelectrochemical studies are carried out using 1 M NaOH–1 M Na₂S–1 M S electrolyte under light intensity of 37 mW/cm². From photoelectrochemical characterisations it is concluded that the deposited CdS, CdSe and CdTe are n-type semiconductors. Interestingly the CdX films deposited from aqueous and non-aqueous baths showed comparable photoelectrochemical properties. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Polycrystalline films; Photoelectrochemical properties; Semiconductors

1. Introduction

In recent years, electrodeposited thin film semiconductors are popular in the field of solar cells, optoelectronic devices, solar selective coating, etc. Particularly cadmium chalcogenides have received considerable attention during recent years because of their proven and potential applications in a variety of semiconducting devices. Cadmium chalcogenides (CdS, CdSe and CdTe) in the forms of single crystals, sintered pellets and polycrystalline materials have been employed in photoelectrochemical (PEC) cells. The stable PEC cells are obtained with S^{2-}/S_2^{2-} redox couple [1–3]. Reasonable efficiencies (\sim 8–9%) have been obtained with polycrystalline films by many workers using polysulphide electrolyte. In polycrystalline thin films, surface states mar the efficiency and have been successfully removed by the chemical [4,5] and photoelectrochemical etching [6]. Tenne reported the effect of photoelectrochemical etching on the performance of CdS based PEC cells [7]. However, changes in surface crystallinity and formation of thin layers of sulphur has been found when CdSe is dipped in S^{2-}/S_2^{2-} electrode [8–11]. This would give rise to dislocation or grain boundaries near the surface, which may act as recombination centres for the minority carriers and decrease the efficiency. Surface etch, preferably photoelectrochemical etch improves the efficiency of the PEC cell based on the single crystalline or thin films CdTe electrodes [12]. Photoetching removes some of the recombination centres resulting in an increase in efficiency [13–15]. Lokhande reported that the efficiency and stability of PEC cells are strongly dependent on the preparation condition of the electrodes, electrolytes and on experimental conditions during test [16].

In the present paper, cadmium chalcogenide films have been prepared from aqueous and non-aqueous medium using galvanostatic electrodeposition method. In order to increase the conductivity, as-deposited films were annealed in nitrogen atmosphere and to remove loosely bounded particles, annealed films were etched in 3% HCl solution for 3 s. Photoelectrochemical properties such as conductivity type of photoanode, current–voltage characteristics, photovoltaic characteristics and spectral response, etc. are studied and results are compared. It is observed that, films electrodeposited from aqueous and non-aqueous baths are polycrystalline with n-type semiconducting property and show comparable photoelectrochemical properties.

2. Experimental

Thin films of CdS, CdSe and CdTe have been electrodeposited on different substrates at different temperatures using aqueous and non-aqueous solution baths. The preparative parameters for getting good quality films are shown in Table 1 [22,23,27,28,32]. As-deposited films were annealed in a tube furnace in nitrogen atmosphere. Annealed films were etched in 3% HCl solution for 3 s and then rinsed

^{*} Corresponding author.

Table 1										
Estimated value	ues of	preparative	and	post-preparative	parameters	to	obtain	cadmium	chalcogenide	films

S. no.	Bath composition	Substrate Bath			Current	Deposition	Annealed in N2 atn	Annealed in N2 atmosphere	
			Temperature (°C)	pН	density	time (min)	Temperature (°C)	Time	
1	$0.05 \text{ M} (2 \text{ cm}^3) \text{ CdSO}_4 + 0.5 \text{ M}$ $(8 \text{ cm}^3) \text{ Na}_2 \text{S}_2 \text{O}_3 + 0.1 \text{ M}$ $(20 \text{ cm}^3) \text{ EDTA} (disodium salt)$	Stainless steel	70	5.4	9.0	60	200	30	
2	0.05 M (2 cm ³) CdSO ₄ +0.5 M (8 cm ³) Na ₂ S ₂ O ₃ +0.1 M (5 cm ³) EDTA (tetrasodium salt) in EG	Stainless steel	90	8.0	1.5	90	200	30	
3	0.05 M (5 cm ³) CdSO ₄ +0.01 M (5 cm ³) SeO ₂	Stainless steel	27	3.0	6.0	20	200	30	
4	0.05 M (5 cm ³) CdSO ₄ +0.01 M (5 cm ³) SeO ₂ +0.1 M (20 cm ³) EDTA (tetrasodium salt) in EG	FTO coated glass	90	8.5	0.1	30	350	60	
5	0.05 M (10 cm ³) CdSO ₄ +0.01 M (10 cm ³) Na ₂ TeO ₃ +0.1 N (10 cm ³) HClO ₄	Stainless steel	30	2.0	3.0	30	200	30	
6	0.05 M (10 cm ³) CdSO ₄ +0.01 M (10 cm ³) Na ₂ TeO ₃ +0.1 N (10 cm ³) HClO ₄ in EG	FTO coated glass	80	3.0	0.5	30	350	60	

with double distilled water. Etched films were used in PEC studies.

Photoelectrochemical (PEC) cell was fabricated using cadmium chalcogenide (CdS, CdSe and CdTe) thin films as a photoanode of area $1 \times 1 \text{ cm}^2$ and graphite of area $2.5 \times 2.5 \text{ cm}^2$ as a counter electrode. The distance between the photoanode and counter electrode was 0.3 cm. The redox used was aqueous 1 M NaOH-1 M Na₂S-1 M S. A 500 W tungsten filament lamp was used as light source. To prevent heating of the cell, water filter was interposed between the lamp and the cell. To avoid absorption of light in the electrolyte, the front face of the cell was made flat. The current-voltage characteristics in dark and under light and photovoltaic output characteristics of the PEC cell were studied under light intensity of 37 mW/cm² using two electrode configuration. The spectral response of the PEC cell was studied using a monochromator specol (Carl Zeiss Zena, Germany).

3. Results and discussion

3.1. Photoelectrochemical studies of CdS films electrodeposited from aqueous and non-aqueous bath

3.1.1. Conductivity type of CdS films

Photoelectrochemical cell with configuration 1 M NaOH–1 M Na₂S–1 M S was formed. It is observed that, even in dark, PEC cell gives some voltage and current. The polarity of this voltage is negative towards the CdS electrode. The origin of this voltage is attributed to the difference between two half cell potentials in the PEC cell and can be written as

$$E = E_{\text{graphite}} - E_{\text{CdS}}$$

where E_{graphite} and E_{CdS} are the half cell potentials when dipped in the electrolyte.

When the above junction is illuminated with a light intensity of 37 mW/cm^2 , the short circuit current I_{sc} increases with negative polarity towards CdS electrode showing that the CdS films electrodeposited from aqueous and non-aqueous baths are of n-type semiconductors [17].

3.1.2. Current-voltage characteristics

The current–voltage characteristics of etched CdS films, were studied in the voltage range of ± 0.8 V, in the dark and under light illumination. It is observed that in the dark the forward current increases rapidly with applied bias. The increase in forward current can be attributed to the small contact height and increase in tunnelling mechanism [18]. The *I–V* characteristics in the dark and under light illumination showed the rectifying nature of the cell.

Fig. 1 shows the *I*–*V* characteristic in the dark and under light illumination in the forward bias for CdS electrodeposited films from aqueous and non-aqueous baths. Using famous diode equation, junction ideality factor is calculated as

$$I = I_0 e^{eV/nKT}$$

where I is the forward current in dark, I_0 the reverse saturation current, V the applied forward bias voltage and n is the junction ideality factor.

Inset in Fig. 1 shows the plot of $\log I$ versus V for CdS films in dark and under light illumination. The estimated values of junction ideality factor are as shown in Table 2. It is seen that the values of junction ideality factors are greater than the ideality value. It is also observed that the values of the junction ideality factors are slightly increased under illumination which may be due to increased charge recombination centres [19,20].



Fig. 1. Current–voltage characteristics of CdS film electrodeposited from aqueous and non-aqueous bath ((\bullet) CdS (aqueous) in dark, (\Box) CdS (aqueous) in light, (\blacktriangle) CdS (non-aqueous) in dark, (\bigcirc) CdS (non-aqueous) in light). Inset shows log *I* vs. *V* for the above cells.

3.1.3. Photovoltaic power output characteristics

Photoelectrochemical cell was fabricated using CdS films as the photoanode and graphite as a counter electrode. The photovoltaic output characteristics were studied under light intensity of 37 mW/cm². Fig. 2 shows photovoltaic power output curves for CdS film deposited from aqueous and non-aqueous baths. The photovoltaic efficiency (η %) is calculated using the following equation:

$$\eta = \frac{I_{\max} V_{\max} A}{P_{hv}} \times 100$$

where $P_{h\nu}$ is the power density of the incident radiation, *A* the light collecting area, I_{max} and V_{max} are, respectively, the current and voltage obtained at the maximum power point on the photovoltaic power output curve.

The fill factor (FF) is calculated using the following equation:

$$FF = \frac{I_{\max} V_{\max}}{I_{sc} V_{oc}}$$

Table 2

Estimated values of junction ideality factor in dark and under light illumination of $37\,\mathrm{mW/cm^2}$

S. no.	Thin films	Junction ideality factor in			
		Dark	Under light		
1	CdS (aqueous)	1.67	2.12		
2	CdS (non-aqueous)	2.48	2.8		
3	CdSe (aqueous)	2.55	2.89		
4	CdSe (non-aqueous)	2.89	3.93		
5	CdTe (aqueous)	2.89	3.77		
6	CdTe (non-aqueous)	3.2	3.62		



Fig. 2. Photovoltaic power output plots for (\bullet) CdS (aqueous) and (\blacktriangle) CdS (non-aqueous) films. Illumination intensity was 37 mW/cm².

where I_{sc} is the short circuit current and V_{oc} is the open circuit voltage.

Series resistance R_s and the shunt resistance R_{sh} were evaluated from slopes of the power output curve using the relation [21]

$$\begin{bmatrix} \frac{\mathrm{d}I}{\mathrm{d}V} \end{bmatrix}_{I=0} \approx \frac{1}{R_{\mathrm{s}}}$$
$$\begin{bmatrix} \frac{\mathrm{d}I}{\mathrm{d}V} \end{bmatrix}_{V=0} \approx \frac{1}{R_{\mathrm{sh}}}$$

The parameters estimated from power output plots are shown in Table 3. It is seen that the efficiencies obtained from the CdS films deposited from aqueous and non-aqueous baths are comparable, although it has been reported earlier that the CdS films deposited from aqueous bath have better crystallinity and surface coverage as compared to CdS films from non-aqueous baths [22,23].

3.1.4. Spectral response studies

Spectral response study of the PEC cells was carried out by measuring I_{sc} as a function of wavelength λ . Before the measurement, PEC cell was kept in dark for some time and the response was measured using progression from longer wavelength to shorter wavelengths. Fig. 3 shows the variation of I_{sc} with λ for the PEC cells formed with CdS films from aqueous and non-aqueous baths. The decrease in photocurrent on longer wavelength side is attributed to the non-optimised thickness and the transition between the defect level [24]. Decrease of photocurrent on short wavelength side might be due to the absorption of light in the electrolyte and high surface recombination of the photogenerated carriers by surface states [25,26]. It is also observed that the spectral response maxima I_{sc} for CdS film deposited from aqueous medium has higher values, this result supports the result

Estimated important parameters nom photovolate power output curves of eaching indes based i De cons								
S. no.	Thin films	$\overline{I_{\rm sc} \ ({\rm mA/cm}^2)}$	$V_{\rm oc}~({\rm mV})$	FF (%)	η (%)	$\overline{R_{\rm s}(\Omega)}$	$R_{\rm sh} (\Omega)$	
1	CdS (aqueous)	1.28	265	41.41	0.38	37	416	
2	CdS (non-aqueous)	0.73	500	32.87	0.32	384	1666	
3	CdSe (aqueous)	10.5	355	38	3.83	17	125	
4	CdSe (non-aqueous)	7	550	37.09	3.86	41	250	
5	CdTe (aqueous)	7.1	280	41.9	2.25	18	250	
6	CdTe (non-aqueous)	4.2	270	33.73	1.03	40	142	

Table 3 Estimated important parameters from photovoltaic power output curves of cadmium chalcogenides based PEC cells^a

^a Illumination intensity was 37 mW/cm².



Fig. 3. Spectral response curves for (\bullet) CdS (aqueous) and (\blacktriangle) CdS (non-aqueous) films. Illumination intensity was 37 mW/cm².

obtained from photovoltaic power output characteristics and X-ray diffraction studies. Using the spectral response maxima, the bandgap of CdS was calculated to be 2.38 eV.

3.2. Photoelectrochemical studies of CdSe films electrodeposited from aqueous and non-aqueous bath

3.2.1. Conductivity type of CdSe films

Photoelectrochemical cell with configuration CdSe/1 M NaOH–1 M Na₂S–1 M S was formed. In dark, PEC cell gives some voltage and current and the polarity of this voltage is negative towards the CdSe electrode. When the above junction is illuminated, short circuit current I_{sc} was increased with negative polarity towards CdSe electrode showing that the CdSe is a n-type semiconductor.

3.2.2. Current-voltage characteristics

The I-V characteristics of CdSe films electrodeposited from aqueous and non-aqueous bath were studied. Fig. 4 shows the I-V characteristics for forward bias of the PEC cell in dark and under light illumination. In the dark it is observed that I-V characteristics showed the rectifying behaviour. The rectifying behaviour remains same under illumination. Inset in Fig. 4 shows $\log I$ versus V plots in dark and under light illumination. The estimated values of junction ideality factor are shown in Table 2. It is observed that the value of the junction ideality factor deviate from ideal values in dark and under light illumination, similar to the results obtained with CdS film electrode.

3.2.3. Photovoltaic output characteristics

Photovoltaic output characteristics were studied for CdSe films electrodeposited from aqueous and non-aqueous bath under light intensity of 37 mW/cm². Fig. 5 shows power output characteristics for CdSe films. The parameters estimated from the power output characteristics are as shown in Table 3. It is observed that the films deposited from both baths showed nearly same efficiency (3.8%). It is also observed that the film deposited from non-aqueous bath have greater I_{sc} value than the film deposited from non-aqueous bath. This result is supported by the results obtained from X-ray diffraction and scanning electron microscopic studies [27,28].



Fig. 4. Current–voltage characteristics of CdSe films ((\bigcirc) CdSe (aqueous) in dark, (\square) CdSe (aqueous) in light, (\blacktriangle) CdSe (non-aqueous) in dark, (\bigcirc) CdSe (non-aqueous) in light). Inset shows log *I* vs. *V* for the above cells.



Fig. 5. Photovoltaic power output plots for (\bullet) CdSe (aqueous) and (\blacktriangle) CdSe (non-aqueous) films.

3.2.4. Spectral response studies

Spectral response studies were carried out by measuring I_{sc} as a function of wavelength λ . Fig. 6 shows the spectral response curves. It is observed that I_{sc} values are greater for CdSe film deposited from aqueous bath than for non-aqueous bath. This result supports the result obtained from X-ray diffraction and power output characteristic studies. From peak in spectral response studies, the estimated bandgap values are 1.78 eV for both CdSe films.

3.3. Photoelectrochemical studies of CdTe films electrodeposited from aqueous and non-aqueous bath

3.3.1. Conductivity type of CdTe films

Photoelectrochemical cell with configuration CdTe/1 M NaOH-1 M Na2S-1 M S was formed. Using similar logic,



Fig. 6. Spectral response curves for (\bullet) CdSe (aqueous) and (\blacktriangle) CdSe (non-aqueous) films.



Fig. 7. Current–voltage characteristics of PEC cells formed with CdTe films ((\bullet) CdTe (aqueous) in dark, (\Box) CdTe (aqueous) in light, (\blacktriangle) CdTe (non-aqueous) in dark, (\bigcirc) CdTe (non-aqueous) in light). Inset shows log *I* vs. *V* for the above cells.

the PEC studies showed that the CdTe films are n-type semiconductors. In case of CdTe, electrodeposition method has resulted in both the types (n or p) of semiconductor formation depending upon the bath composition and preparative conditions. However, in our case, both the baths resulted in n-type semiconductor formation. Generally chalcogenide ion deficiency shows n-type behaviour in cadmium chalcogenides. In the present case, films are tellurium rich, due to which CdTe shows n-type. Similar results of CdTe films electrodeposited as n-type have been reported by others [29–32].

3.3.2. Current-voltage characteristics

Forward bias current–voltage characteristics of the CdTe films electrodeposited from aqueous and non-aqueous baths are as shown in Fig. 7. It is observed that in dark and under illumination current increases exponentially in forward bias direction showing the characteristics of diode.

Inset in Fig. 7 shows log *I* versus *V*. The estimated values of junction ideality factors are as shown in Table 2 and deviate from ideal values.

3.3.3. Photovoltaic power output characteristics

Photovoltaic output characteristics were studied using CdTe films as photoanode and graphite as a counter electrode, under light intensity of 37 mW/cm². Fig. 8 shows the power output characteristics for CdTe films. The photovoltaic parameters are estimated as shown in Table 3. It is observed that CdTe film deposited from aqueous medium shows greater efficiency than the film deposited from non-aqueous medium. This result is supported by the fact



Fig. 8. Photovoltaic power output plots for PEC cells formed with (\bullet) CdTe (aqueous) and (\blacktriangle) CdTe (non-aqueous) films.

that films deposited from aqueous medium have improved crystallinity and compactness compared to non-aqueous bath.

3.3.4. Spectral response studies

The variation of short circuit current with wavelength for CdTe film was studied. Fig. 9 shows spectral response curves for CdTe PEC cells formed with aqueous and non-aqueous bath. The estimated value of bandgap of CdTe films do not deviate.



Fig. 9. Spectral response curves for PEC cells formed with (\bullet) CdTe (aqueous) and (\blacktriangle) CdTe (non-aqueous) films.

4. Conclusions

Electrodeposition of CdS, CdSe and CdTe films from aqueous and non-aqueous bath are carried out. Annealing and etching increase the efficiency of the thin film electrode in the polysulphide electrolyte. PEC study revealed that CdS, CdSe and CdTe are n-type semiconductors. The PEC results reported with aqueous and non-aqueous baths are inferior in comparison with the higher values of η reported in the literature. However, in our case both the baths resulted into really equal magnitudes of η values except for CdTe films. In case of CdTe, the film from aqueous bath showed nearly double the value of η than the film obtained from non-aqueous bath.

References

- [1] A.B. Ellis, S.W. Kaiser, M.S. Wringhton, J. Am. Chem. Soc. 98 (1976) 1635.
- [2] H. Minoura, H. Okala, M. Tsuiki, Nippon Kagaku Kaishu Kaishi (Japan) 10 (1977) 1443.
- [3] G. Hodes, J. Manassen, D. Cahen, Solar Energy Mater. 4 (1981) 373.
- [4] A. Heller, K.C. Chang, B. Miller, J. Electrochem. Soc. 124 (1977) 697.
- [5] A. Heller, K.C. Chang, B. Miller, J. Am. Chem. Soc. 100 (1978) 684.
- [6] R. Tenne, G. Hodes, Appl. Phys. Lett. 37 (1980) 428.
- [7] R. Tenne, Appl. Phys. 25 (1981) 13.
- [8] H. Gerischer, J. Gobrecht, J. Ber. Bunsenges, Phys. Chem. 82 (1978) 520.
- [9] A. Heller, B. Miller, Electrochem. Acta 25 (1980) 29.
- [10] D. Cahen, B. Vainas, J.M. Vandenberg, J. Electrochem. Soc. 128 (1981) 1484.
- [11] R. Noufi, P.A. Kohl, J.W. Rogers, J.M. White, A.J. Bard, J. Electrochem. Soc. 126 (1979) 1949.
- [12] G. Hodes, Nature 285 (1980) 29.
- [13] N. Muller, R. Tenne, Appl. Phys. Lett. 39 (1981) 283.
- [14] P. Lamasso, Solid State Commun. 43 (1982) 627.
- [15] V.D. Das, L. Damodare, J. Appl. Phys. 81 (1997) 1522.
- [16] C.D. Lokhande, Solar Cells 22 (1987) 133.
- [17] S.S. Kale, U.S. Jadhav, C.D. Lokhande, Bull. Electrochem. 12 (9) (1996) 540.
- [18] K. Rajeshwar, R. Thompson, P. Sing, R.C. Kainthla, K.L. Chopra, J. Electrochem. Soc. 128 (1981) 1744.
- [19] A. Chemseddine, R. Morineau, J. Lirage, Solid State Ionics 9 (1983) 357.
- [20] M. Green, Thin Solid Films 50 (1978) 145.
- [21] T.J. Coutes, Solar Energy Mater. 50 (1978) 99.
- [22] S.J. Lade, C.D. Lokhande, Mater. Chem. Phys. 49 (1997) 160.
- [23] S.J. Lade, M.D. Uplane, C.D. Lokhande, Mater. Chem. Phys. 53 (1998) 239.
- [24] A. Heller, K.C. Chang, B. Miller, J. Electrochem. Soc. 124 (1997) 607.
- [25] J. Reichman, M.A. Russak, in: A.J. Nozik (Ed.), Photoeffects at Semiconductor–Electrolyte Interface, Vol. 146, ACDSSYM, 1981, p. 359.
- [26] S.N. Frank, A.J. Bard, J. Am. Chem. Soc. 97 (1975) 7472.
- [27] S.J. Lade, M.D. Uplane, M.M. Uplane, C.D. Lokhande, J. Mater. Sci. Mater. Electron. 9 (1998) 477.
- [28] S.J. Lade, M.D. Uplane, C.D. Lokhande, Thin Solid Films, submitted for publication.
- [29] M.P. Panickar, M. Knaster, F.A. Kroger, J. Electrochem. Soc. 125 (1978) 566.
- [30] J. Touskova, D. Kindl, J. Tousek, Solar Energy Mater. 18 (1989) 377.
- [31] A. Darkowshi, M. Cocivera, J. Electrochem. Soc. 132 (1985) 2768.
- [32] S.J. Lade, M.D. Uplane, C.D. Lokhande, Mater. Chem. Phys. 63 (2000) 99.



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