

Structural and Optical Properties of Electrodeposited CdS Thin Film

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ABSTRACT: Cadmium sulphide (CdS) thin films have been deposited on glass/conducting glass substrates using low-cost two electrode aqueous electrodeposition (ED) method. The structural and molecular structure of the resulting films has been characterized using X-ray diffraction (XRD) and Raman spectroscopy. The XRD results indicates that both as deposited and heat treated ED-CdS layers are polycrystalline and have a hexagonal crystal structure with preferential orientation along the (101) direction, while Raman measurement confirmed the two peaks at 303cm^{-1} and 608cm^{-1} corresponding to the first and second order longitudinal optical phonons (1LO) and (2LO) respectively. X-ray photoelectron spectroscopy (XPS) studies have been performed to detect the photoelectrons emitted from the sample surface and compare the results obtained on electrodeposited CdS with the vacuum cleaved CdS. The XPS spectra measurement identified two distinct Cd 3d peaks (i.e. $3d_{5/2}$ and $3d_{3/2}$) with their binding energies at ~ 405 and ~ 412 eV respectively. The S 2p peak has a binding energy of ~ 162 eV. The results indicate that the composition of CdS layers is 52.9:47.1. The bandgap of the heat treated films gives 2.42 eV using optical absorption measurements which are close to the bulk CdS. The results from the 3D-AFM measurement shows that the material tends to grow as columns (nanorods) leaving spaces in between in some areas.

Keywords: Electrodeposited, CdS, Thin Film, Window Material, and Two-Electrode System.

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INTRODUCTION

Cadmium sulphide (CdS) is among the binary compounds of group II-VI family and has a direct bandgap of 2.42 eV at room temperature. Its thin films are widely used in various materials such as light emitting diodes (LEDs), solar cells, electronic and optoelectronic devices (Izgorodi et al., 2009; Bicer et al., 2010; Peabहार et al., 2009). The thermal expansion coefficient of CdS at room temperature is $4.7 \times 10^{-6} \text{ K}^{-1}$ (Wald 1977) and has thermal conductivity of $0.25 \text{ W (cmK)}^{-1}$ (www.springer-material.com, 2011). Various methods have been

employed to deposit CdS thin films such as sputtering (Taneja et al., 2002), thermal evaporation (Patel et al., 2011), metal-organic chemical vapour deposition (MOCVD) (Berrigam et al., 1998), molecular beam epitaxy (MBE) (Boieriu et al., 2000), close space sublimation (Han et al., 2010), spray pyrolysis (Toušková et al., 1992), screen printing (Arita et al., 1991), chemical bath deposition (CBD) (Diso et al., 2009) and electrodeposition (ED) (Diso et al., 2010). CdS, being an n-type window material, can be combined with CuInGaSe_2 (CIGS) or CdTe to form a good heterojunction.

CIGS-based solar cells are currently best with a record efficiency of 20.3% and 15% for small scale laboratory and module respectively (Jackson et al., 2010), whereas CdTe-based solar cells have achieved a laboratory and module efficiency of 17.3% and 13.4% (<http://www.firstsolar.com>, 2011). As reported in the literature (Dharmadasa and Haigh 2006), the use of reference electrode in electrodeposition such as standard calomel or Ag/AgCl may be a problem because if such ions (especially Ag^+) leaks into the bath, it poisons the bath and therefore reduces the efficiencies of the solar cells. This result has been confirmed by Dennison 1994. For this reason, in this work, two electrode systems were used because of its simplicity and reduction of manufacturing cost.

EXPERIMENTAL

Electrodeposited of CdS films

CdS thin films were cathodically electrodeposited onto glass/conducting glass substrates at $\sim 50^\circ\text{C}$ in an aqueous solution ($\text{pH} = 1.5 \pm 0.02$) containing 0.3M $\text{CdCl}_2 \cdot \text{H}_2\text{O}$ and 0.03M $\text{Na}_2\text{S}_2\text{O}_3$. The electrolytic bath was a 1000 ml water-jacketed glass beaker and a 500 ml plastic beaker which contained the 300 ml of electrolyte. Fluorine doped tin oxide (FTO) coated conducting glass substrates with the sheet resistance of $7 \Omega/\square$ were cleaned in organic solvents (methanol and acetone), dilute HNO_3 and finally rinsed in glacial acetic acid. In between different solvent, the glass/FTO substrate was rinsed with de-ionized water.

All chemicals used were analytical reagent grade of purity 5N (99.999%) from Fisher Scientific Ltd., and Sigma-Aldrich, UK. CdS films of about $0.6 \mu\text{m}$ thick were deposited in about 1hr while the solution is moderately stirred continuously. A two-

electrode system was used in this project in order to simplify the process and eliminate one impurity source; the reference electrode. A graphite anode and a glass/FTO cathode are used to pass an electric current through the electrolyte.

Measurement Techniques

X-ray diffraction measurement (XRD) was carried out using a Philips PW 3710 X-ray diffractometer using CuK_α radiation ($\lambda = 1.5418 \text{ \AA}$) in the range of $2\theta = 20\text{-}50^\circ$ for the structural analysis of the deposited film. The X-ray generator tension and current were 40 kV and 40 mA respectively. The values of lattice spacing (d), crystallite sizes (D) and full width at half maximum (FWHM) can be deduced using Bragg's formula and Scherer's equation (Cullity and Stock 2001) respectively.

$$2d \sin \theta = n\lambda \quad \dots\dots\dots (1)$$

$$D = \frac{k\lambda}{\beta \cos \theta} \quad \dots\dots\dots (2)$$

where, k is the Scherer constant taken to be 0.94, λ is the wavelength of radiation, β is the Full Width at Half Maximum (FWHM) $= \frac{1}{2}(\theta_2 - \theta_1)$ and θ is the diffraction angle.

The molecular structure of the deposited layer were studied using a Raman spectrometer (RENISHAW InVia Raman Microscope) with Ar^+ laser having wavelength 514 nm and 15 mW as the power source. XPS studies have been performed using an Escalab 250 spectrometer with a monochromatized Al anode x-ray source ($h\nu = 1486.6 \text{ eV}$) to detects the photoelectrons emitted from the sample surface. The binding energies obtained from the XPS analysis were standardized for specimen charging using C 1s as the reference at 284.5 eV. The samples were studied using a Cary 50 Scan UV-Visible spectrophotometer (Varian) for

investigating optical properties and for estimation of bandgap values. The bandgap energy E_g can be derived from Stern relationship (Sze and Kwok 2007) using:

$$\alpha = \frac{k(h\nu - E_g)^n}{h\nu} \dots\dots\dots (3)$$

Where, ν is the frequency, h is the Planck's constant and n take the value of either 1 or 4. The value of n is 1 and 4 for direct and indirect transition respectively.

RESULTS AND DISCUSSION

X-Ray Diffraction (XRD)

Figure 1 shows the XRD diffractogram obtained for glass/FTO substrate, as deposited and heat treated CdS. From the Figure, the results show that the films have highly oriented crystallites with the hexagonal structure (Wurtzite type) with preferential orientation along the c-axis {(101) direction} with diffraction peaks producing $d = 3.160 \text{ \AA}$ perpendicular to the substrate plane with low intensity of (102) and (103) peaks. Other peaks identified from the diffractogram are (100) and (110), as reported by most of the researchers in the field (Dharmadasa et al., 1996; Rami et al., 2000; Patil and Wani 2001; Salaoru et al., 2006). These peaks were assigned according to the Joint Committee on Powder Diffraction Standards, JCPDS (00-001-0780) data on hexagonal CdS.

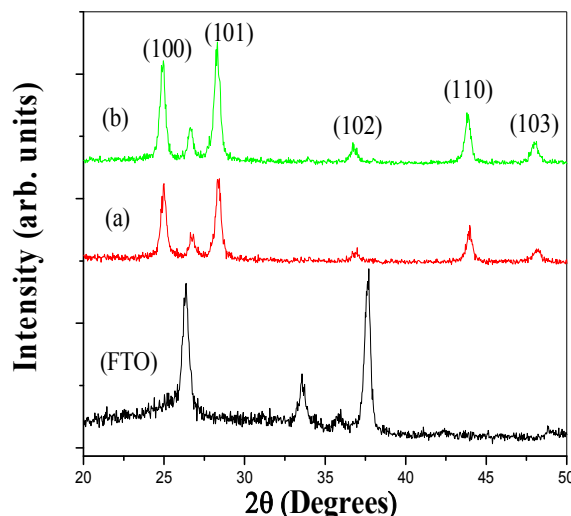


Figure 1: X-ray diffraction patterns of ED-CdS thin films grown on glass/FTO (a) as deposited and (b) heat treated.

After heat treatment in air at 400°C for 20 minutes, the intensity of all the peaks increases and sharpens which indicates the formation of large grains and the improvement of bulk crystalline properties. The heat treatment enhances the recrystallisation of CdS films reducing any stress within the films. The values of d , D and FWHM are presented in Table 1 using equation 1 and 2.

Table 1: Structural parameters of ED-CdS thin films grown on glass/FTO substrate.

	2θ (Degrees)		Lattice spacing d (Å)		Cryst allite size D (nm)	FW HM	h kl
	RP	OB	R P	O B			
A D	24. 99 3	24. 96 2	3. 56 0	3. 59 2	80.0	0.0 15	1 0 0
H T	24. 99 3	24. 96 2	3. 56 0	3. 57 2			
A D	28. 40 1	28. 36 7	3. 14 0	3. 16 0	51.5	0.0 30	1 0 1
H T	28. 40 1	28. 36 7	3. 14 0	3. 15 0			
A D	43. 69 4	43. 80 1	2. 07 0	2. 08 5	26.9	0.0 60	1 1 0
H T	43. 69 4	43. 80 1	2. 07 0	2. 07 8			

N/B: RP – reported values, OB – observed from the XRD, AD – as deposited and HT – heat treated. From the Table, it is observed that crystallite size for heat treated sample increases and the FWHM decreases; this is due to the coalescence of small crystals and the formation of large grains. A further decrease in the lattice spacing is observed for the heat treated sample. The observed lower value of d for heat treated sample is an evidence of stress release after the heat treatment. Similarly, the same trend is observed for FWHM.

RAMAN SPECTROSCOPY

The Raman spectra of bulk CdS and nano-particle CdS are shown in Figure 2 for

comparison (Singh and Chauhan 2009). Figure 3 shows the Raman spectra of ED-CdS layers grown on glass/FTO substrate. Two peaks were observed at 303 cm^{-1} and 608 cm^{-1} which correspond to the first and second order longitudinal optical phonons (1LO) and (2LO) respectively. It was reported by most of the researchers that the 1LO is between $300\text{--}305\text{ cm}^{-1}$ and the 2LO is in the range $600\text{--}606\text{ cm}^{-1}$ [(Chu et al., 2011; Shirai et al., 1996; Samantilleke et al., 2011). Froment et al., 1995, reported that for single crystal CdS bulk, the 1LO peak position and FWHM are typically 305 cm^{-1} and $9\text{--}10\text{ cm}^{-1}$ respectively. The FWHM of the 1LO calculated from this spectrum is 19 cm^{-1} , this increase may be due to the grain size effect (i.e. effect of finite size on vibrational properties in small crystallites (Chu and Dai 1992).

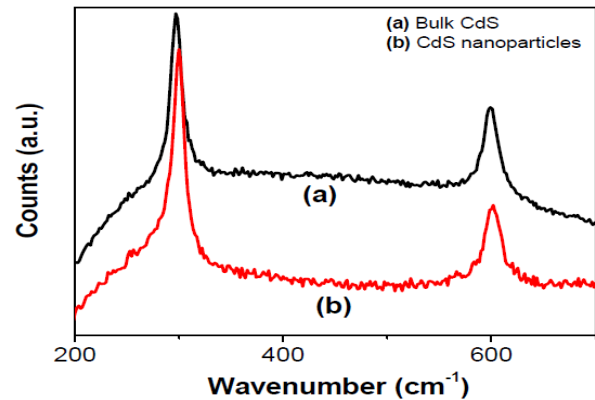


Figure 2: Raman spectra of CdS Bulk and nanoparticles (Singh and Chauhan 2009).

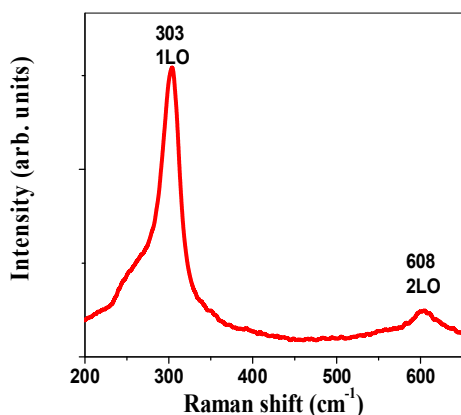


Figure 3: Raman spectra of ED-CdS grown on glass/FTO substrate (courtesy: Inst. of Mater. Research, Univ. of Leeds).

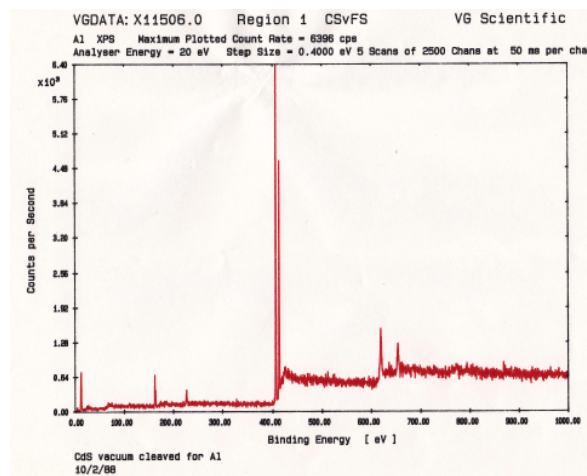


Figure 4: XPS spectrum of CdS cleaved in vacuum (courtesy: Prof. I. M. Dharmadasa).

X-RAY PHOTOELECTRON SPECTROSCOPY (XPS)

The XPS spectrum of vacuum cleaved CdS is shown in Figure 4 together with spectrum obtained for an ED-CdS layer in Figure 5 for comparison. The two XPS spectra reveals that electrodeposited CdS has a similar spectrum to that of a clean cleaved CdS except for the additional presence of C and O peaks which may be due to surface contamination. From Figure 5, two distinct Cd 3d peaks (i.e. $3d_{5/2}$ and $3d_{3/2}$) are observed and presented more clearly in Figure 6. The binding energies associated with Cd ($3d_{5/2}$ and $3d_{3/2}$) appeared at ~ 405.6 and ~ 412.3 eV respectively. Similarly, Figure 7 shows the S 2p peak and has a binding energy of ~ 162.5 eV. The atomic ratio for Cd:S given from the XPS spectra is 52.9:47.1. All these peaks and binding energies are very close to those found by other researchers and summarised in Table 2 (Dharmadasa et al., 1989; Mazón-Montijo et al., 2010; Vemuri et al., 2010; Karimi et al., 2009).

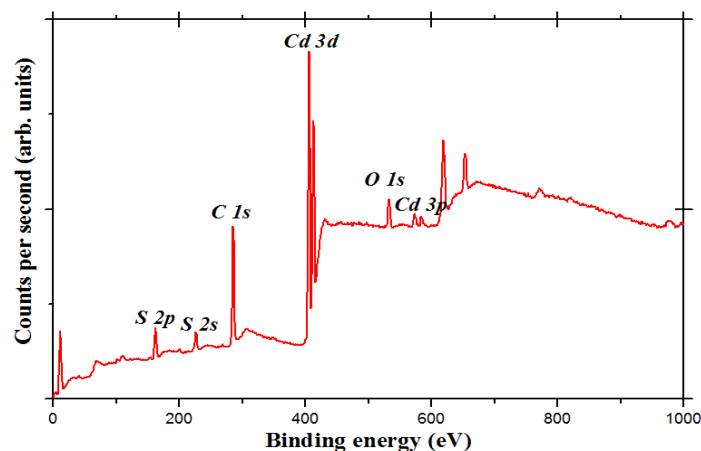


Figure 5: Typical XPS survey spectrum of the ED-CdS pattern grown on glass/FTO substrate (courtesy: Inst. of Mater Research, Univ. of Leeds).

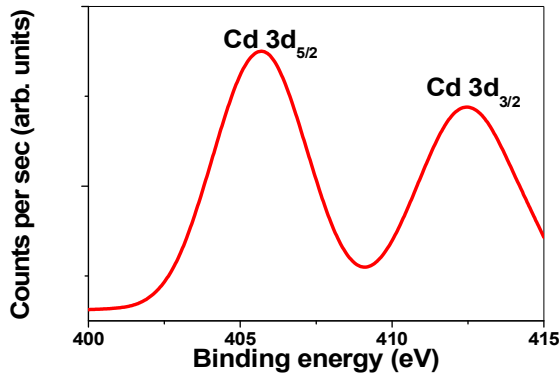


Figure 6: XPS spectrum of ED-CdS grown on glass/FTO substrate close-up survey for Cd 3d core (courtesy: Inst. of Mater Research, Univ. of Leeds).

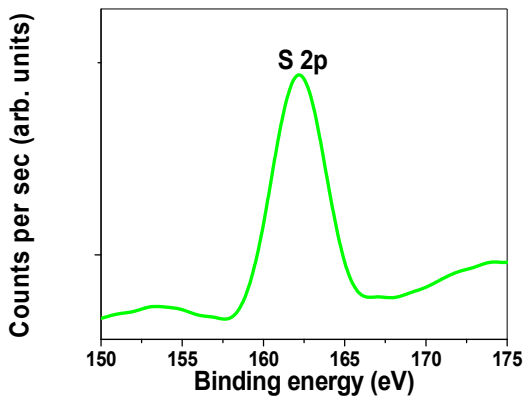


Figure 7: XPS spectrum of ED-CdS grown on glass/FTO substrate close-up survey for S 2p core (courtesy: Inst. of Mater Research, Univ. of Leeds).

Table 2: Summary of CdS XPS results

Method	Binding energy (eV)			Ref.
	Cd 3d _{5/2}	Cd 3d _{3/2}	S 2p	
CBD	405.5	412	161.70	34
ammonia-free chemical process	405.1	411.8	161.6	32
	405.3	412	161.8	
ED	405.2	412	162	31
RF magnetron sputtering	405	412	161	33
ED	405.6	412.3	162.5	this work

OPTICAL BAND GAP MEASUREMENTS

The graphs of optical absorption for (a) as deposited and (b) heat treated ED-CdS are shown in Figure 8. The values of E_g were determined by plotting the square of absorption (A^2) against photon energy ($h\nu$). From the graphs, it is observed that as deposited sample produced a bandgap of 2.20 eV. After heat treatment at 400°C in air for 20 minutes, the bandgap increased to 2.42 eV which agrees with the theoretical value of CdS thin films (Diso et al., 2010; Dharmadasa et al., 1996; Rami et al., 2000; Patil and Wani 2001; Salouru et al., 2006). Therefore, heat treatment is a vital step, samples are heated rapidly and cooled down slowly allowing optimum grain growth during recrystallisation, and therefore improve the overall efficiency of the solar cells.

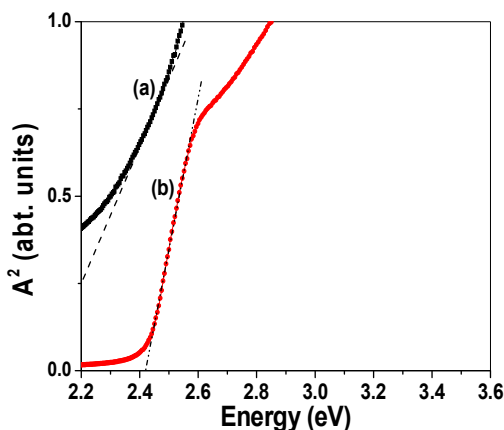


Figure 8: Optical absorption curves for (a) as deposited and (b) heat treated ED-CdS grown on glass/FTO substrates.

3D-AFM Measurement

The 3D-AFM picture of ED-CdS is shown in Figure 9. From the Figure, CdS fabricated have highly ordered and densely packed nano-rod arrays oriented perpendicular to the glass/FTO substrates and grow upwards after nucleation on the FTO surface. The 3D-AFM reveals the existence of tightly packed nano-rods. The presence of nano-rods provides advantages because of band bending due to enhanced surfaces and hence creating an additional internal electric field perpendicular to their axis. It also minimises recombination of electrons and holes in which the electrons flow along the axis of the nano-rod and holes could flow in the opposite direction along the vicinity of the surface layer of the nano-rod.

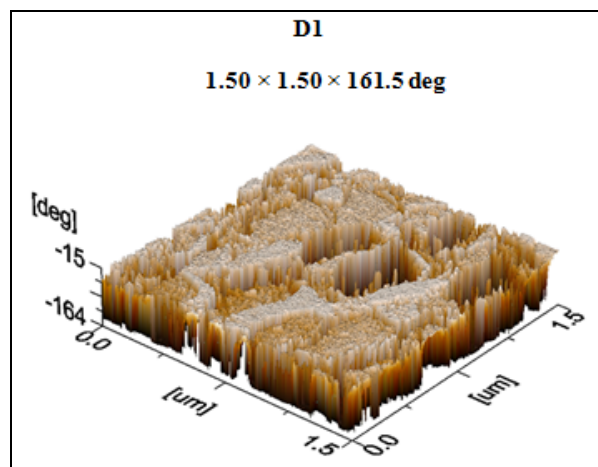


Figure 9: 3D-AFM image of ED-CdS grown at 1500 mV on glass/FTO substrate (courtesy: Inst. of Org. Catalysis & Electrochem., Kazakhstan).

CONCLUSION

CdS have been deposited on glass/FTO substrates using a low-cost aqueous electrodeposition method. The XRD results indicates that both as deposited and heat treated ED-CdS layers are polycrystalline and have a hexagonal crystal structure with preferential orientation along the (101) direction. From the literature (McGregor 1999), it is known that hexagonal structure performs better in terms of light absorption. Two peaks observed at 303 cm^{-1} and 608 cm^{-1} corresponding to the first and second order longitudinal optical phonons (1LO) and (2LO). The XPS spectra measurement identified two distinct Cd 3d peaks (i.e. $3d_{5/2}$ and $3d_{3/2}$) with their binding energies at ~ 405 and ~ 412 eV respectively. The S 2p peak has a binding energy of ~ 162 eV. Optical absorption measurements gives a bandgap of ~ 2.42 eV for heat treated sample which is similar to the CdS bulk material. 3D-AFM measurements shows that

the ED-CdS layers have highly ordered and densely packed nano-rod arrays oriented perpendicular to the glass/FTO substrates.

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