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Short paper

Optical and structural properties of CdS thin films prepared using electro-deposition technique

G.D.K. Mahanama[1]*, D.A. Madarasinghe[1], W.G.D. Dharmaratna[1] and D. Jayasundara[2]

[1]*Department of Physics, University of Ruhuna, Matara, Sri Lanka*
[2] *Sri Lanka Institute of Nanotechnology, Pitipana, Homagama, Sri Lanka*

Correspondence: * mahanama@phy.ruh.ac.lk; ORCID: 0000-0002-4761-4558

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Abstract. Cadmium Sulfide (CdS) thin films were electrodeposited successfully on to Indium Tin Oxide (ITO) coated glass substrates from an aqueous solution of pH 1.4 containing 0.3M $CdCl_2$ and 0.03M $Na_2S_2O_3$ or Thiourea with the aim of using in CdS/CdTe solar cells. Properties of CdS thin films prepared at different deposition voltages, deposition time periods, deposition temperatures and annealing temperatures were investigated using the current-voltage (I-V) plots. It was found that good quality CdS layers were formed under the deposition conditions of -1.13V for a period of 45 minutes in a solution of temperature at 46 ^oC. The performance of the CdS layers was improved significantly after annealing the samples at 400 ^oC for a period of 20 min. The properties of CdS thin films prepared by two and three electrode configurations and using two different electrolytes were compared using the current-voltage plots. It was found that there is a significant improvement of photocurrent of the samples prepared with two electrodes in Thiourea as the S source in comparison with the samples prepared with $Na_2S_2O_3$. The analysis of XRD spectra showed the hexagonal crystal structure of CdS films confirming the quality of the films prepared by this method. In addition, absorption spectra showed band gap value of 2.42 eV proving that the samples were of good quality. Atomic Force Microscopy (AFM) analysis showed that the roughness values of CdS samples were in the range of 10-15 nm. Film thicknesses of the samples were in the range of 175-225 nm according to the optical profilometric data.

Keywords. Cadmium sulfide, electrodeposition, electrolyte, two-electrode, photocurrent.

1 Introduction

Electrodeposition technique is a perspective competitor in thin film preparation because of several advantages such as the possibility for large-

scale production, minimum waste of components and easy monitoring of the deposition process (Dharmadasa and Haigh 2006). This technique is generally less expensive than the other methods. The composition of the electrolytes and deposition conditions play an important role in determining the quality of the deposited films. CdS/CdTe solar cells have emerged as a possible candidate for practical applications which can be produced at a low cost. Here we report the results of the CdS thin films prepared by varying the deposition voltage, period, temperature and annealing temperature. CdS layers were studied using X-ray diffraction, Scanning Electron Microscopy, Atomic Force Microscopy, Optical absorption spectroscopy and optical profilometry techniques.

2 Materials & Methods

Electrodeposition was performed in a conventional three-electrode cell. The three electrode cell contained a saturated potassium chloride calomel electrode (SCE) as the reference, a platinum sheet as the counter electrode and an ITO/Glass substrate as the working electrode. A Hokuto Denko HA-301 potentiostat was used to control the electro-deposition process and to monitor the photocurrent and voltage profiles. All plates were cleaned using an ultrasonic bath. The ITO coated glass substrates and counter electrode were polished and cleaned with acetone, methanol, dilute acetic acid and distilled water, respectively, before the deposition process. The bath consisted of $CdCl_2$ (0.3M) and $Na_2S_2O_3$ (0.03M) is used. The pH of the bath was maintained at a constant value of 1.4 (Dahiru 2011) throughout the study using hydrochloric acid. The solutions were prepared using analytical grade chemicals and de-ionized water. The area of the substrate to be deposited was kept fixed at 1.21 cm^2 for all studies. The temperature of the electrolyte was maintained at a constant value during the deposition period.

The photocurrent-voltage characteristics of CdS deposited samples, as deposited as well as annealed at different temperatures (200–500 °C) were studied. An incandescent lamp of 100 W was used as the source of light to illuminate the CdS layer for photocurrent-voltage measurements. The same procedure was repeated and the deposition process was carried out by changing the S source (Thiourea) (Aliyev and El-Rouby 2013) instead of $Na_2S_2O_3$) and two electrode configuration instead of three electrodes.

3 Results and Discussion

Current-voltage characteristics of CdS layers prepared at various deposition voltages [(-) 900 mV – (-)1300 mV] and as deposited and annealed samples

were studied. The best deposition voltage was found to be -1100 mV from the above measurements. This was verified by a Voltammogram (Aliyev and El-Rouby 2013), which provided the exact deposition voltage (-1130 mV) for a stable CdS thin layer. The deposited CdS samples were annealed at different temperatures for 20 min and it was found that the best performance was shown by the layers annealed at 400 °C.

The current-voltage curves of CdS thin films deposited at different time periods (15 min to 60 min) were also studied. It was found that the layer thickness was low for a shorter deposition time period (15 min) due to insufficient time. As the deposition time was increased to 45 minutes the deposited films were smooth and adhered well on to the substrate. However, when the deposition time period was increased to 60 minutes and above the film dissolved into the bath due to the longer immersion time in the acidic medium (Figen Kadirgan *et al.* 1997). By varying the temperature of the electrolyte solution in the range 30 °C to 50 °C, it was found that good quality CdS layers were produced at 46 °C. At lower temperatures (≤30 °C) the deposition process took a longer time. At higher temperatures (>50 °C) the deposition was rapid but the CdS layer easily flaked off from the glass substrate showing a rapid decrease of current.

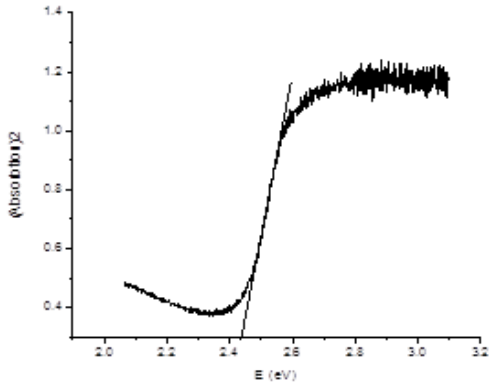

Fig. 1. Absorption spectra of a good quality CdS sample

Absorption spectra of prepared CdS samples were measured in three different laboratories and all measurements showed that the band gap value was 2.42 eV confirming the quality of the samples. This is the exact value of the band gap expected from a good quality CdS material according to the literature (Sze 1981). Absorption spectra of a good quality CdS sample prepared is shown in Figure 1.

XRD measurements were taken in the range of $2\theta = (20° - 80°)$ using Cu K_α radiation ($\lambda = 1.5418$ Å). The XRD spectrum obtained for a heat treated CdS

layer deposited on glass/ITO substrate using electrodeposition method is shown in Figure 2. According to the standard X-ray diffraction patterns, the three broad peaks observed in the spectra at around 26.52°, 43.93°, 51.90° reveal a cubic lattice structure of CdS (Zinc blend). These peaks could be related to the (222), (220), and (322) planes of the cubic phase, respectively (Reddy et al. 2003). The positions of several peaks were used to determine the CdS phases and there are more hexagonal phases compared to the cubic phases. It is difficult to separate cubic peaks from hexagonal peaks because they are overlapping in the same regions. The results show that the films have highly oriented crystallites with the hexagonal structure (Wurtzite type) with preferential orientation (Aliyev and El-Rouby 2013).

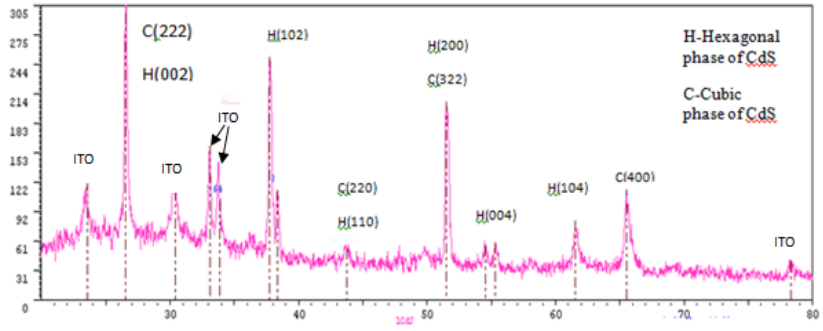

Fig. 2. XRD spectrum of a CdS layer produced

Crystallite sizes related to XRD peaks shown in figure 2 were calculated using the Scherer formula and given in the Table 1. Average grain size is ~ 69.1 nm which is correlated with SEM image given below.

Table 1: Crystallite sizes of XRD peaks shown in Figure 2

2θ (Degrees)	FWHM	hkl	Crystallite size (nm)
26.52	0.030	002	55.8
37.84	0.015	102	122.6
43.93	0.050	220	40.2
51.90	0.045	200	58.8
61.65	0.040	104	67.3
65.52	0.050	400	69.9

SEM image of an annealed electrodeposited CdS layer taken by the Philips XL30 scanning electron microscope is shown in Figure 3. The material

clusters are in the nanoscale range with an average size of 175-200 nm. These grains seem to be packed together each other with small gaps in between. Small gaps or pin holes seen in SEM between the grains indicate the growth of CdS as islands.

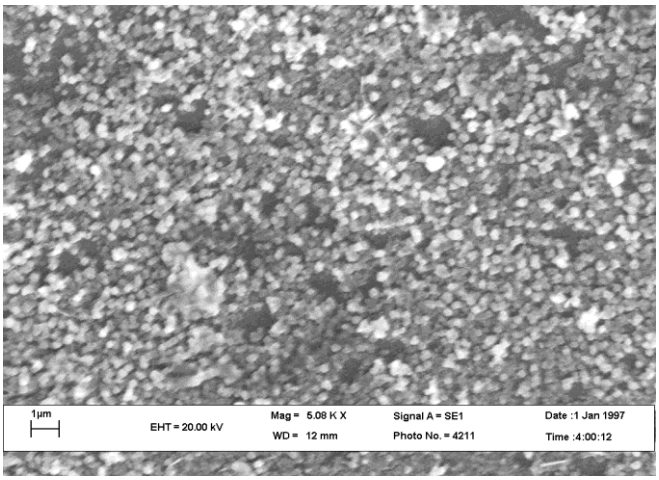

Fig. 3. SEM image of heat treated ED-CdS layer on glass/ITO substrate

Atomic Force Microscopy (AFM) measurements were performed on heat treated CdS samples produced. The result shown in Figure 4 indicates that the film roughness values are in the range of 10-15 nm.

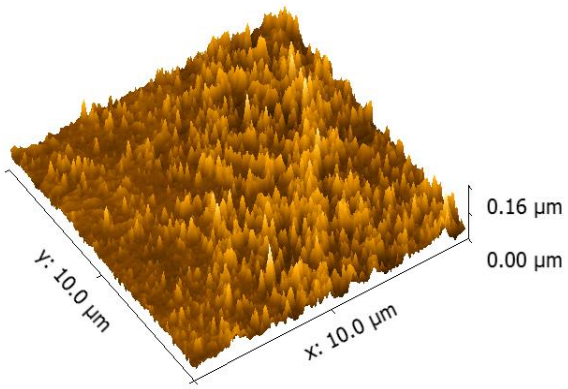

Fig. 4. AFM image of a CdS sample

CdS layers fabricated are densely packed in some regions and indicate perpendicular orientation to the glass/ITO substrates and grow upwards after nucleation on the ITO surface. The AFM image reveals the existence of tightly packed nano-rods with length equal to 175-200 nm the CdS layer.

These observations are consistent with the SEM results. 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 minimizes 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 (Dahiru 2011). Thickness of the CdS samples was measured using optical profilometer and the values are in the range of 175-225 nm. These values are very well matched with thickness values determined from AFM measurements.

4 Conclusion

CdS layers were successfully electrodeposited on ITO glass substrate by using an aqueous solution containing 0.3M $CdCl_2$ and 0.03M $Na_2S_2O_3$ or Thiourea as the electrolyte. The analysis of photocurrent-voltage characteristics indicated that good quality CdS layers were formed when the deposition was conducted for a period of 45 minutes under the deposition voltage of -1.13V in the solution of pH value 1.4 at the temperature of 46 ^oC. A more stable CdS layer with better photo response was obtained by annealing the deposited layer at the temperature of 400 ^oC for 20 minutes. CdS thin films prepared with Thiourea as the S source have produced better currents than the films prepared with $Na_2S_2O_3$ as the S source. In addition, CdS samples prepared with two-electrode configuration have shown an improvement of the photocurrent in compared with three-electrode configuration. This might be due to the poisoning of the electrolyte with the leakage of unwanted ions into the bath from the calomel electrode in the three electrode configuration. Band gap of 2.42 eV calculated from absorption spectra of CdS samples confirms the good quality of the sample prepared. This result was confirmed by measurements performed at three different laboratories. XRD spectra of electrodeposited CdS samples have shown hexagonal phase crystal structure confirming the good quality of CdS layers in compared with the cubic phase crystals reported with chemical bath deposition (CBD) method. Atomic force microscopy data shows that the roughness values of the CdS samples are in the range of 10-15 nm. Film thickness was in the range of 175-225 nm.

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