

Evaluation of the Influence of Electro-deposition pH on the Physico-chemical Properties of Cadmium Sulphide for Photovoltaic Device Applications

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Abstract

An electrochemical set up was prepared to facilitate the deposition of cadmium sulfide (CdS) on fluorine doped tin oxide (FTO) substrate, as all other parameters were kept constant excluding the pH. The range of pH variation was (2.00 to 4.00)±0.02. Due to the condition of pH variation, three samples were produced, which were of pH values 2.00±0.02, 3.00±0.02 and 4.00±0.02. The precursors that formed the aqueous electrolyte solution were cadmium sulfate octahydrate (3CdSO₄·8H₂O) and sodium thiosulphate pentahydrate (Na₂S₂O₃·5H₂O) and they were expected to deposit Cadmium (Cd) and sulfide (S) respectively. The optical, structural, compositional and electrical of the already deposited CdS thin films were determined with the use of UV-Vis spectrophotometry, x-ray diffraction (XRD), Energy dispersive X-ray (EDX) and photochemical (PEC) cell measurements respectively. The optical absorbance measurement indicates the CdCl₂ treated samples showed different absorbance capacities, therefore, having various bandgaps. Interestingly, the bandgap of the sample of pH 2 is approximate to the standard value of bulk CdS, which is 2.42eV. The preferred peak of the electrodeposited thin film occurs at an angle of 28.86° along a corresponding hexagonal plane of CdS(101)H as shown by the XRD machine. Of all the deposited thin-films, the sample with a pH of 2 has the highest peak which shortens as the pH rises up to 4. The EDX analysis portrays a decrease in the ratio of Cd to S as the pH values rises to 4. The PEC measurement indicates that the conduction type all the samples of the electrodeposited CdS thin-films are n-type.

Keywords: Electrodeposition, CdS, pH, Optimisation, Two electrode

1 Introduction

Attention has been given to the study of the structural, optical, morphological and physical properties of binary compound such as CdS over the years because of its advantageous applications in optoelectronic and large area electronic devices. In photovoltaics, CdS often features as a window layer in the CdS/CdTe solar cells configuration in order to achieve the best efficiency. Quite a number of growth techniques of CdS have been reported in various literatures, but electrodeposition is preferred to them all because of its simplicity, low cost, scalability amongst all other attributes.(1; 2) The previous study on the electrodeposition of CdS helped to optimize deposited layers greatly as it has optimized some key parameters that determine the quality of the thin film layer.(3; 4)However, no literature seems to have explored the electrodeposition pH, a parameter, which can have an effect on the properties of the CdS thin films that can be deposited on the FTO. Therefore, the research work determines the possible effects of pH variation on the CdS thin film and evaluates the optimal pH for effective solar cells.

2 Experimental procedure

The aqueous electrolyte that was used for the electrodeposition process of the cadmium sulfide (CdS) layers was a solution of 18.5g of cadmium sulfate octahydrate ($3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$) and 2g of sodium thiosulphate pentahydrate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) in 400ml of de-ionized(DI) water. Both $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ and $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ served as precursors of cadmium(Cd) and sulfide(S) respectively. The experimental set up required that three similar baths of aqueous electrolyte were prepared and their conditions similarized, with an exception of the pH condition only. The need for the three baths is because a boundary of $(2.00-4.00) \pm 0.02$ of the pH condition implies that three samples can only be produced. The three samples possible within the stipulated boundary are of pH value 2.00 ± 0.02 , 3.00 ± 0.02 and 4.00 ± 0.02 . The three pH conditions for the three samples were achieved with use of either dilute Nitric acid (HNO_3) or ammonium hydrochloride (NH_4OH) to increase or reduce the pH as the case may be. Three 500ml polypropylene beakers contained the three separate baths of the aqueous electrolyte that were prepared.

The electrodeposited CdS thin-films were grown on $7\Omega/\text{sq}$ sheet resistant fluorine doped tin oxide (FTO) substrate coated on highly transparent glass. The experiment adopted a 2-electrode electrodeposition configuration in which the glass/FTO substrate served as the cathode while a high purity graphite rod served as the anode. The glass/FTO substrate had an area of $2.5 \times 2 \text{ cm}^2$. Prior to the growth of the CdS thin-films, the glass/FTO was washed in an ultrasonic bath containing soap solution and rinsed in running DI water before being decreased using methanol and acetone. After washing and rinsing the glass/FTO, it was attached to a graphite rod with the use of polytetrafluoroethylene (PTFE) tape by winding them until they are firm. Every chemical and material utilized was purchased from Sigma Aldrich Ltd, UK.

The equipment used to power the two electrode configuration was an ACM GillAC potentiostat. After the deposition have been completed, the glass/FTO/CdS layers were rinsed in DI water, dried in a steam of nitrogen gas, and cut into two equal halves in which one is left as-deposited while the other is half will be treated with cadmium chloride (CdCl_2). Cadmium chloride treatment is well known for improving the overall properties of CdS.(5)

The deposited CdS samples were finally characterized for their optical properties, structural properties, compositional property and electrical properties using Cary50 Scan UV-visible spectrophotometer, Philips PW 3710X'pert X-ray diffraction (XRD) machine and photoelectrochemical (PEC) cell measurement.

3 Result and Discussion

3.1 Optical Bandgap Determination

Optical absorption measurements were carried out on the samples grown within the range of $\text{pH}(2.00-4.00) \pm 0.02$. The three samples were treated with CdCl_2 under the same conditions and a set time limit. The optical absorption technique helps to estimate the band gap of each CdS layer and its conformity with the energy band gap of the bulk CdS.

Figure 1 displays the graphical representation of the optical absorbance spectra for the CdS layers grown at different pH values. The square of absorbance (A^2) was plotted against the energy of photons ($h\nu$), whereby h connotes the planks constant and ν connotes the incidence of photon frequency. The extrapolation of the straight line section of the graph to the energy of photon axis (at $A^2 = 0$) gave an estimate of the band gap energy.

From the observations made on the graph, it is observable that the band gap is within the range of $(2.41 - 2.49)\text{eV}$. It is quite obvious from the graph that the sample with a pH of 2 is closer to the standard value of bulk CdS which is 2.42eV .(6) The CdCl_2 treatment must have improved the layers by pin holes removal, recrystallization of the lattice structure an improvement in material composition.(7) The variation in band gap for the three different samples can be attributed to the individual properties of the elements that make up the binary configuration. The elements could be surplus or deficient at certain conditions determined

by the pH values. We can establish that the pH within the boundary of approximately $(2.00 - 2.25) \pm 0.02$ supports more growth of sulfide elements while a pH within the range of approximately $(2.25 - 4.00) \pm 0.02$ supports more growth of cadmium elements.

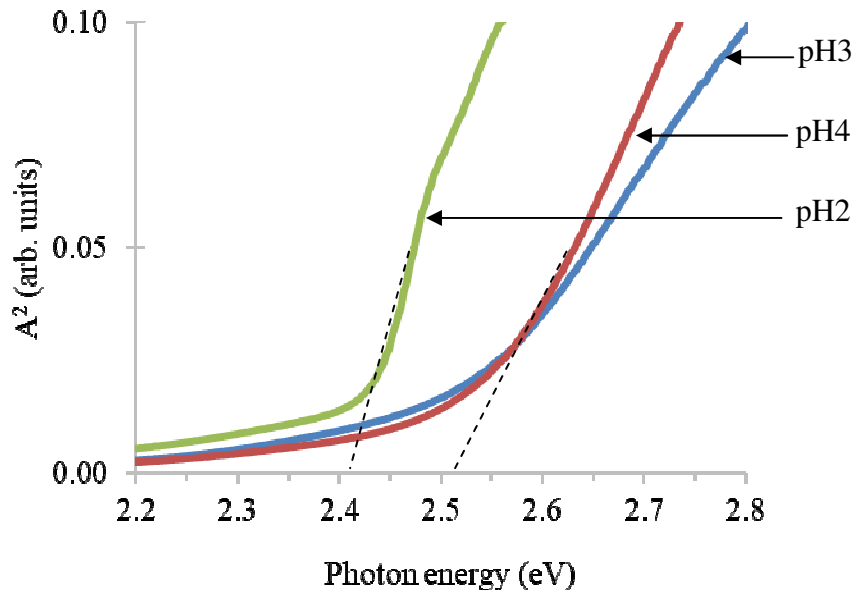


Figure 1: Optical absorption spectra for electrodeposited CdS thin films treated with CdCl_2 between pH values of 2-4.

3.2 X-ray diffraction (XRD) Measurements

This section presents the results obtained from the X-ray diffraction studies. The X-ray diffraction study was performed on the three samples of deposited CdS thin films. As it has been stated earlier, the difference between the three samples is the pH at which their layers were grown, which is within the range of $(2.00 - 4.00) \pm 0.2$. All other possible variables that affect the quality of deposition were optimized as we intend to investigate the effect of pH variations on the physiochemical properties on the CdS layers for solar cell optimization. X-ray diffraction study can inform on the phase of the crystal and unit cell dimensions. The samples were treated with dilute cadmium chloride (CdCl_2). The treatment is well known to improve the properties of the deposited layers from previous research works.

By examining the graph, it was discovered that all the CdS thin films of different pH values are polycrystalline with a preferred peak orientation along the CdS (101)H plane which coincides at an angle of 28.86° . We can also observe that there is a peak present at angle 26.68° and 24.9° with a corresponding plane of CdS(002)H and CdS(100)H respectively. The two planes CdS(002)H and CdS(100)H will be neglected due to the fact that they occur at the same angle as that of underlying FTO peaks, and can be presumed to belong to the FTO layer. In analyzing the layers more focus was given to the preferred peak orientation of plane CdS(101)H at an angle of 28.86° . Figure 2 shows that the peak orientation at 28.86° fades away as we approach the sample of pH value 4. This implies that there is deterioration in its crystal structure as we increase the growth pH value for deposition. At an angle of approximately 34° , we can observe that there is a peak that occurs only on the two samples of pH value 3 and 4. This peak although not indicated on the FTO line emanates from the FTO layer. Previous research works on thin film layers attest to this assumption.(8) The XRD machine could have made some errors in measurement. Previous literatures has it that CdS can grow in two different crystalline structures, namely the hexagonal (wurtzite structure) and the cubic (zinc blend structure) with the hexagonal being the more metastable phase.(9)The XRD machine shows the presence of the hexagonal CdS phases only. Of course the CdCl_2 treatment has eradicated any presence of the cubic CdS phases. Elemental Cd and S could also be present in the non-

treated layers. But the diffusion of excess sulphur and the formation of CdS from the reaction of elemental Cd and S as a result of the treatment caused them to disappear.(10)

The crystalline size D can be calculated by using the Sherrer's formula given by equation 1. From the equation λ is the wavelength of the X-rays used (1.542Å), β is the full width at half maximum (FWHM) of the diffraction peak in radian and θ is the Bragg angle.

$$D = \frac{0.94\lambda}{\beta \cos\theta} \tag{Equation 1}$$

3.3 Compositional study

The EDX (energy dispersive X-ray) machine was used to determine the atomic composition of Cd and S for the CdCl₂ treated samples grown with various pH values. The number of samples grown within the range of (2.00-4.00)±0.02 were three with pH values of 2.00±0.02, 3.00±0.02, and 4.00±0.02. The three samples were used to analyze the effect of pH on the compositional qualities of the electrodeposited CdS thin-films. Figure3 gives us an overview of the atomic ratio of Cd to S in the electrodeposited CdS thin films grown at different pH values as observed by the EDX. Another element,(Sn) Tin was also discovered in the layers. The presence of Sn can be attributed to the underlying glass/FTO layer used as a substrate.

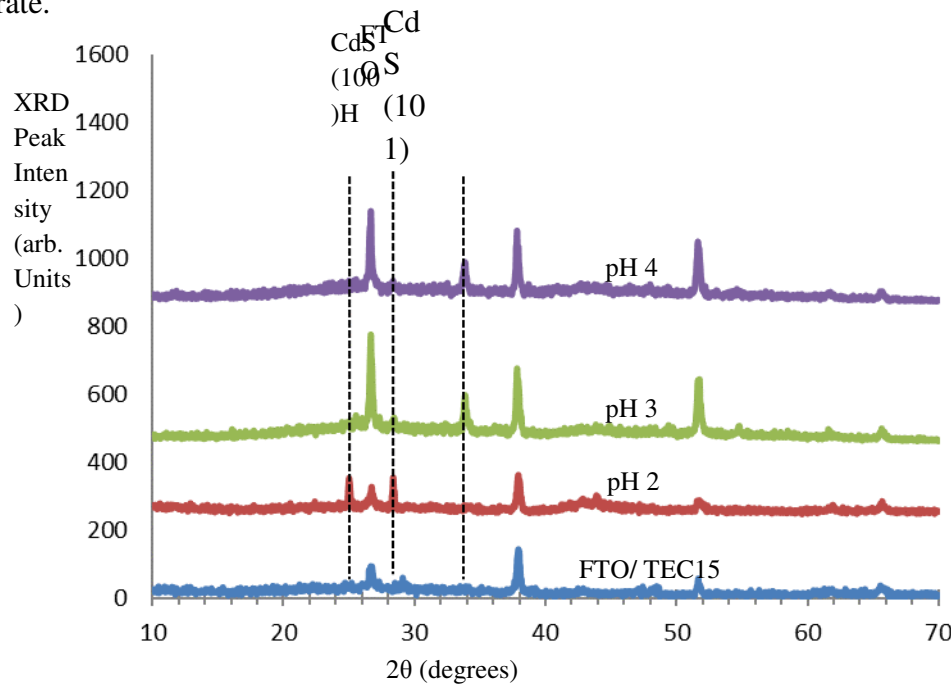


Figure 2: typical XRD patterns of CdS layers grown between pH values of 2 and 4 for CdCl₂ treated CdS layers

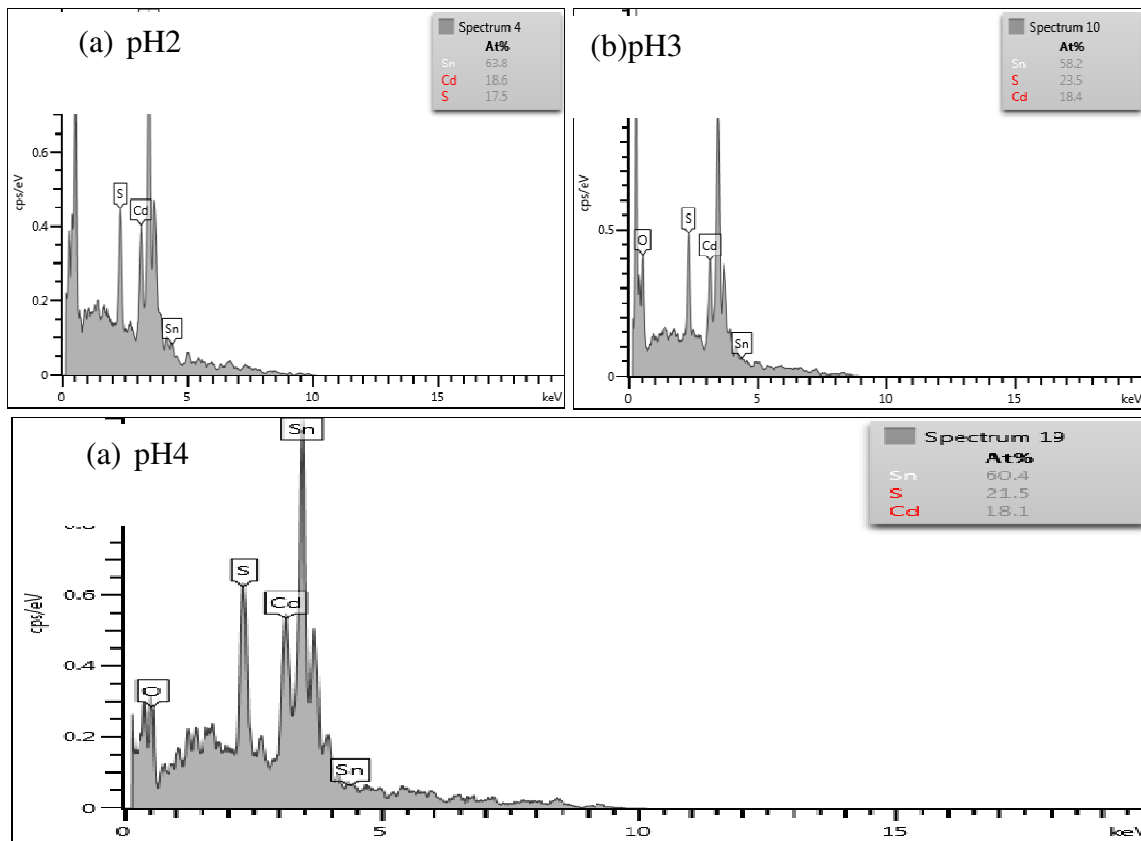


Figure 3: EDX results of the CdCl₂ treated CdS thin films grown at (a)pH2, (b) pH2, and (a) pH4. Figure 3 clearly informs us on the chemical and elemental composition of the three samples of CdS layers. They are identified by the energy signatures they emit as a result of the high electron beam that will impinge on the layers. (11) From Figure 3(a) we can tell that the atomic composition for Cd is 18.6% while that of S is 17.5% for a pH of 2. Figure 3(b) reveals that the atomic composition of Cd and S is 18.1% and 21.5% respectively for a pH value of 3. Lastly Figure 3(c) shows that Cd has a composition of 18.4% and S has a composition of 25.3%. The data generated from the EDX machine can be extracted and tabulated with the inclusion of a column that presents the calculated cadmium to sulfide atomic ratio for each samples. From this table a graph given by Figure 4 is plotted of atomic ratio against pH value.

Table 1: Summary of the EDX spectra of electrodeposited CdS thin films after CCT

pH	Cd	S	Sn	Cd
2	18.6	17.5	63.8	1.063
3	18.1	21.5	60.4	0.842
4	18.4	23.5	58.2	0.783

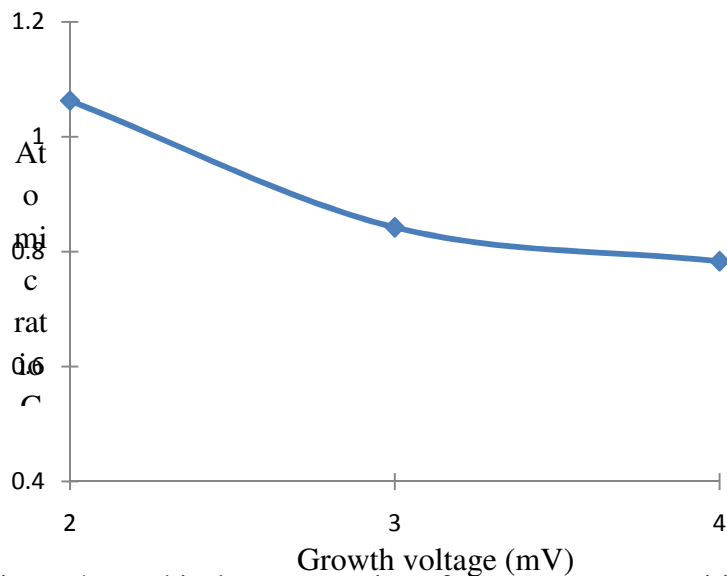


Figure 4: graphical representation of percentage composition ratio of Cd to S atoms at different deposition pH values

The graph plotted shows a decrease in the atomic composition of cadmium in favour of sulfur with a reduction in pH value. As we approach a pH of 4, it is obvious that the sulfur increases in composition. This graphical illustration implies that a higher pH favours the growth of sulfur. It is also observable that sample grown at a pH of 2 is the closest to stoichiometric deposition. The result obtained in this section agrees with both the PEC measurement result and the XRD result.

3.4 Photoelectrochemical (PEC) Study

The PEC results depicted in Table 2 and Figure 5 distinctively shows that the layers grown for the three different samples of varying pH are all n-type in electrical conduction. The negative signal indicates they are n-type. (12) This property is based on the fact that CdS layers are made up of cadmium interstitials and sulfide vacancies in their crystal lattice. The C interstitials and S vacancies act like an intrinsic donor defect in the CdS layer. (13; 14) This observations made are only true for the layers treated with CdCl₂. Table 2 gives the tabulated result of the PEC signal for the different samples when it was as-deposited and treated with cadmium chloride.

Table 2: Summary of the EDX spectra of electrodeposited CdS thin films after CCT

pH	PEC signal (mV)	
	As-deposited(AD)	cadmium chloride treated(CCT)
2	-48	-112
3	-62	-150
4	-66	-178

The graph of Figure 5 plotted from table 2 illustrates that the PEC signal increases towards the negative direction as the pH value increases. It signifies that there is more potential for conductivity in the layers as the pH value increases. The magnitudes of the PEC signal in the CdCl₂ treated layers were higher than in the as-deposited layers. This might be as a result of the improvement of the depletion layer at the CdS/electrolyte junction due to the enhancement of the electronic quality of the CdS layer.

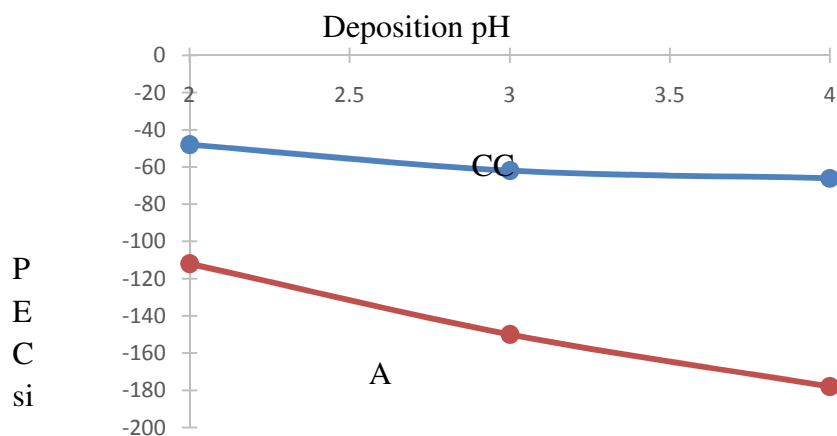


Figure 5: PEC signal against deposition pH of the CdS thin films

4 Conclusion

The various characterization techniques employed to evaluate the effect of pH on the physicochemical properties of the two electrode electrodeposited CdS thin film were in concordance with each other. The bandgap of the thin films were within the range of (2.41-2.49)eV. The thin film of pH 2 with a bandgap of 2.41 was the closest to the standard value of bulk CdS. The XRD studies shows that the CdS thin films are all crystalline. The closest CdS film to stoichiometry was the CdS thin film of pH 2. The PEC measurements indicate that all the CdS thin films are n-type.

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