

Effect of Bath and Annealing Temperature on Optical and Electrical Properties of CdS thin Films

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ABSTRACT

CdS thin films were fabricated using Chemical Bath Deposition (CBD) to be applied as the window layer of inorganic CdS/CdTe solar cells. CdS was grown using cadmium sulfate, thiourea, ammonia and ammonium hydroxide on fluorine doped tin oxide (FTO) glasses. Bath temperature of the films was varied from 40 ºC to 80 ºC to study their optical and electrical properties. It was revealed that the optical band gaps and fractional thicknesses increase when moving away from the bath temperature range of 50 ºC – 60 ºC, potentially due to different CdS deposition mechanisms at higher and lower bath temperatures. The effect of temperature for one hour annealing in air was also investigated between 100 °C to 500 °C. The optical band gap, film thickness and optical transmittance were discussed as a function of annealing and bathtemperature. The best transmission as well as the film quality was obtained when deposited at a bath of 80 ºCand air-annealed at 200 ºC.

Key words: *CdS, thin films, Inorganic solar cells, Chemical Bath Deposition, CBD, Transmittance, XRD, SEM*

1.0 INTRODUCTION

Fossil fuels have been formed from the fossilized remains of the pre-historical plants and animals. They provide around 66% of the world's electrical power and 95% of the world's total energy demand. With the end of the fossil fuel era arriving faster than mankind thought, the civilization is now forced to invent alternative energy sources to meet their energy demand. Alongside that, with ever increasing concerns about environmental protection, extracting energy from renewable green sources has become akey priority in our search of newer and renewable next generation power sources.

Out of all the abundant renewable energy resources, such as wind power, geothermal energy and biomass; solar energy is believed to be a reliable and potentially viable alternative reusable green-energy source. Among various different solar cell technologies, thin film solar cells stand out due to its promising efficiencies in the range of 16-18% so far, with limited experimentation in comparison to other solar cell technologies as well as their stability[1].

One of the promising material systems for solar cell mass production is the p-CdTe/n-CdS/TCO/glass structure. As CdTe has a near optimal band gap (1.45 eV) for solar absorption, it has been recognized as a good solar cell absorber layer[2]. The n-CdS (2.42 eV) forms one side of the electrical junction and acts as the window layer. The calculated theoretical efficiency for CdS/CdTe solar cell has been estimated at around 29% but in practicality the conversion efficiency of 16% was achieved with the application of a post deposition $CdCl_2$ treatment of the CdTe layers which is leading to efficiencies as high as 15.8% [3].

CdS plays a key role as the window layer in CdS/CdTe heterojunctions. The physical properties of CdS are heavily dependent on the fabrication methodology. Consequently, numerous ways are present to synthesize by various researchers. Fabricationapproaches such as chemical bath deposition (CBD)[4-6], thermal evaporation[5], close-spaced sublimation (CSS)[7], chemical pyrolysis deposition (CPD)[7], and metal organic chemical-vapor deposition (MOCVD)[8,9] are some of the commonly used mechanisms. Among all of these methods, CBD stands out as it is a simple and low cost method to prepare high quality thin film materials[4-6]. This article discusses about potential ways by which the performance of the window layer can be optimized by further investigating its dependency on bath temperature and annealing temperature. Furthermore, probable mechanisms of CdS deposition with respect to the bath temperature are also discussed.

2.0 EXPERIMENTAL

The experimental setup consists of a water beaker, whose temperature was controlled automatically with a magnetic hot plate. Magnetic stirring was utilized to promote heterogeneous growth of CdS on the substrates. The glass substrates were positioned inside the beaker at 45^o angle using a custom designed Teflon sample holder.

The films were deposited on 3.5×1.5 cm^2 FTO glasses. Prior to the deposition, substrates were cleaned with detergent to wash away any dust or other macroscopic impurities on the surface. Then the cleaning was continued with diluted HCl, deionized water followed by ultra sound sonication and organic solvents. The organic solvents used for the cleaning process were acetone, methanol and iso-propanol. Substrates were cleaned by dipping them in the above solvents at 80 ºC for 5 min in each, followed by carefully drying with nitrogen gas.

All the films were deposited in a reaction vessel containing aqueous solutions of 0.1 M cadmium sulfate ($CdSO_4$, 99% purity), 0.2 M thiourea ($CS[NH_2]_2$, 99% purity) as cadmium and sulfur sources and 25% w/w ammonia solution (NH_3) volume of 1.1ml.

A pale yellow transparent CdS film which highly adheres to the FTO glass substrate was obtained by maintaining above conditions for one hour. Consequently, the film was rinsed with deionized water followed by sonication to remove loosely adhered CdS particles before drying with nitrogen gas. In order to conduct the optical and structural analysis CdS was removed from one side of the substrate by chemical etching using diluted HCl. Then the film was rinsed with deionized water and dried with nitrogen gas.

In order to investigate the bath temperature dependence, temperature was varied from 40 – 80 ºC in steps of 10 ºC before annealing at 200 ºC for one hour. Effect of annealing was studied using the samples fabricated at 80 ºC bath.The deposited samples were annealed at 100 ºC, 200 ºC, 300 ºC, 400 ºC and 500 ºC for 1 hour in air.

The structural propertieswere characterized by X-ray diffraction (XRD) by Cu Kα radiation using Siemens X-Ray Diffractometer D5000 and the fractional thicknesses of the deposited films on FTO were approximated by using X-ray fluorescence (XRF) spectroscopy (Helmut Fischerscope* X-ray). In order to study the surface morphology of the deposited films, Scanning Electron Microscopy (SEM) images were taken for the films prepared using 40 ºC and 80 ºC baths.

3.0 RESULTS AND DISCUSSION

Pale yellow depositions on the immersed parts of the glass plates were clearly visible in all the depositions. The XRD peak analysis revealed that the thin film was in fact CdS. (Fig. 1).

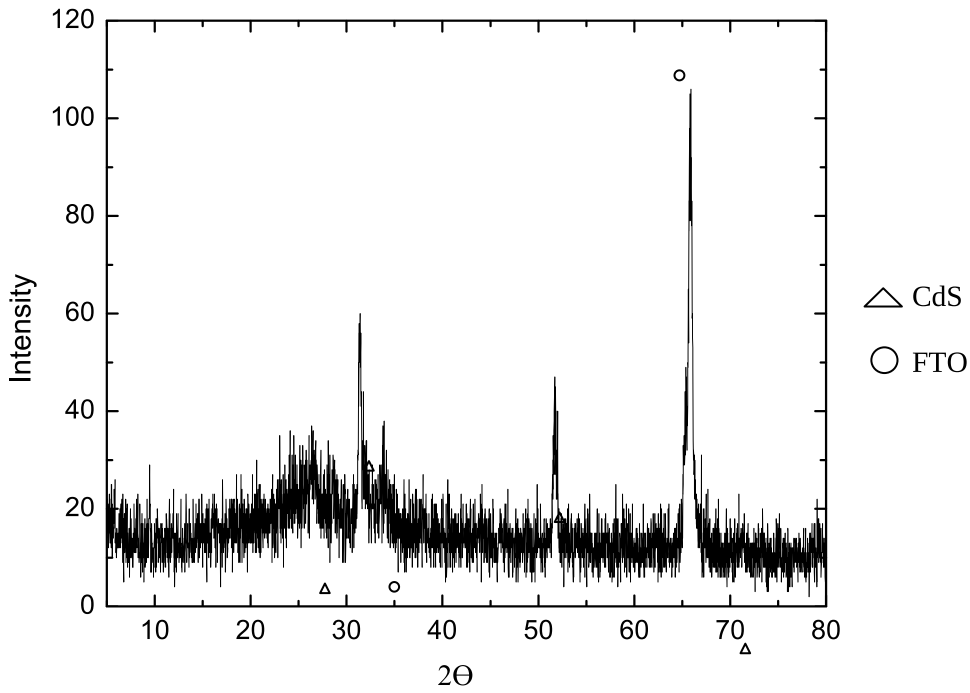


Fig. 1: XRD pattern of the CdS thin film deposited on FTO at 80 ˚C

Optical band gaps of the fabricated samples were calculated using UV-Visible spectrometry(UV-1800 Shimadzu) before and after annealing the sample at 200 ºC.The results obtained are given in the Fig. 2.

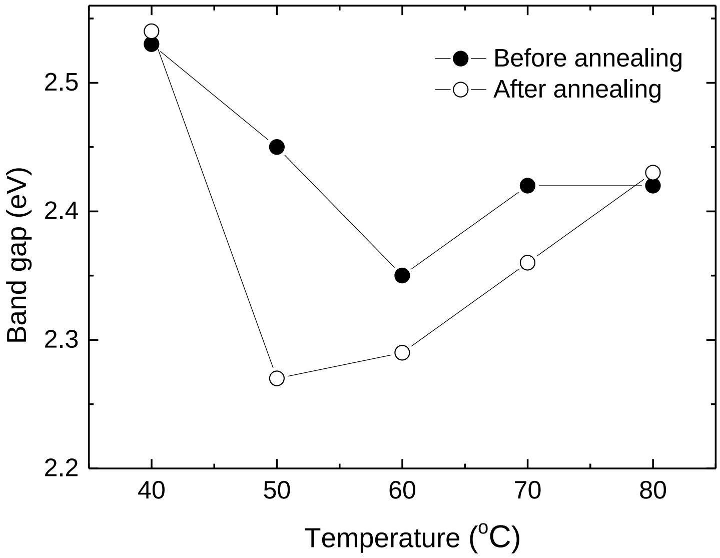


Fig. 2: Variation of fractional thickness and band gap (before and after annealing)of CdS thin film deposited onFTO substrateswith respect to bath temperatures

As shown in Fig. 2, band gap after annealing was found to reach a minimum around 50 ºC for CdS on FTO substrates. For almost all the cases band gap after annealing was lower in comparison to before annealing value at a given temperature.

CdS growing mechanism is two fold; ion by ion and cluster by cluster. Ion by ion method is less thermally activated with low activation energy where as cluster by cluster is believed to occur at elevated temperatures. For the CdS system, deposition kinetics was reported to change at a bath temperature of about 60 ºC[10]. The variation of the band gaps (after annealing) of the CBD CdS are also in agreement with some previous work[10].

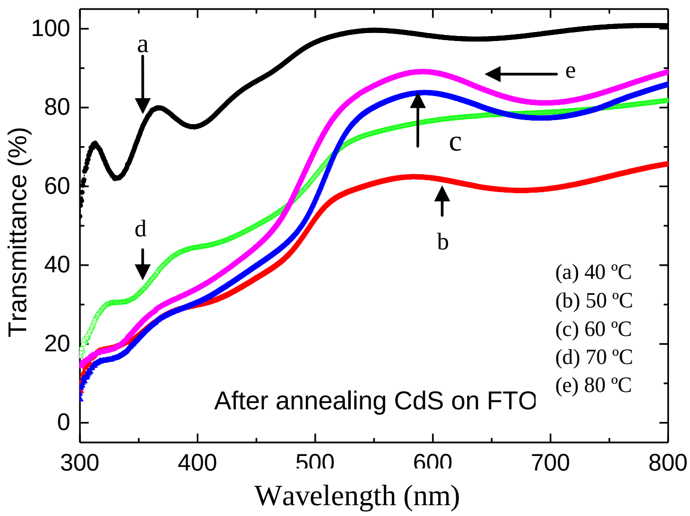
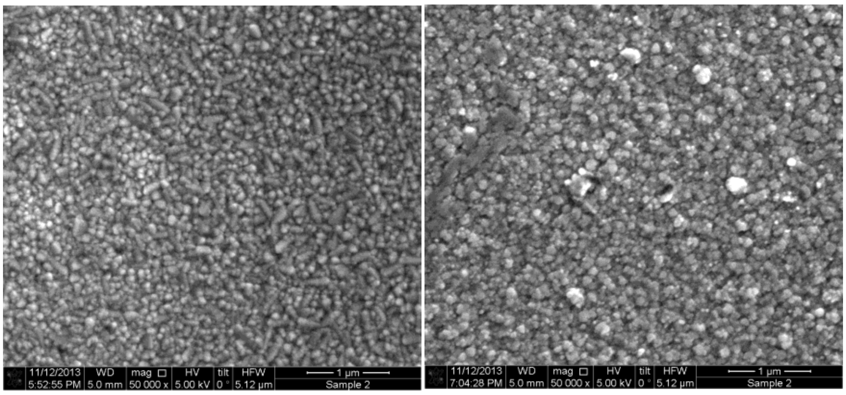


Fig. 3: Variation of transmittance of CdS thin film deposited on FTO at different bath temperatures

This explains that the variation of the band gap of the fabricated films in our work can be related to the deposition orientation. Nonetheless, films fabricated at elevated temperatures exemplified higher quality and uniformity in comparison to ones deposited at lower temperatures.When the transmittance measurements were studied for the films fabricated on FTO, at 80 ºC produced the highest transmittance out of the films deposited at elevated temperatures as seen in Fig. 3. Greater values for the film deposited at 40 ºC can potentially be due to lower film thicknesses.

From the SEM images, it was apparent that two different mechanisms are possibly involved in the deposition of CdS as discussed above. The sample fabricated at low temperatures had smaller cluster sizes with respect to that fabricated at higher temperatures. This suggests the existence of ion by ion and cluster by cluster mechanisms at different bath temperature values (Fig. 4).



(a) (b)

Fig. 4: SEM of CdS on FTO at bath temperatures: (a) 40 ºC and (b) 80 ºC

In order to examine the variation of electrical properties of deposited films at different bath temperatures, a photo electrochemical (PEC) experiment was performed in a glass cell for all the deposited films. A Tungsten filament lamp of 100 W was used to illuminate an area of 5 mm^2 of the working electrode (CdS). The electrolyte and the counter electrode were 0.01 M $Na_2S_2O_3$ and a Pt plate with a diameter of 5 mm respectively. The PEC results confirmed that all the CdS films were n-type. Furthermore PEC values were found to be stable with time for the films deposited at higher bath temperatures.

The annealing effect on CdS films were studied at different temperatures using the above selected conditions. Deposited films were annealed at 100 ºC to 500 ºC for one hour at each temperature. As the annealing temperature increases, the optical transmittance decreases and the absorption edge shifts towards lower energy region and becomes much sharper as shown in Fig. 5.

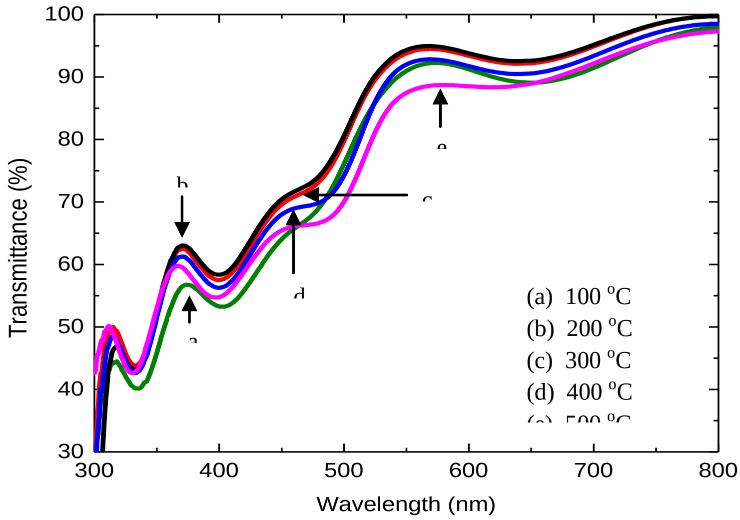


Fig. 5: Variation of transmittance of CdS thin films annealed at different temperatures

It is a known fact that the thermal annealing improves crystallinity of materials grown at a low temperature. This is mainly because atoms can move to a stable position owing to thermal energy[11]. Band gap calculations for the films deposited at 80 ºC bath showed a slight decrement with increasing annealing temperature as indicated in Fig. 6. A red shift of band gap can be expected to be observed with increasing annealing temperature due to grain size increments and compositional changes associated with the thin film[11].It is generally accepted that cubic phase of CdS is metastable. In literature, themetastable cubic phase has been observed to change to more stable hexagonal phase at even higher annealing temperatures above ~500 ºC[12]. Even though our results do not provide evidence for that, it remains a work for the future.

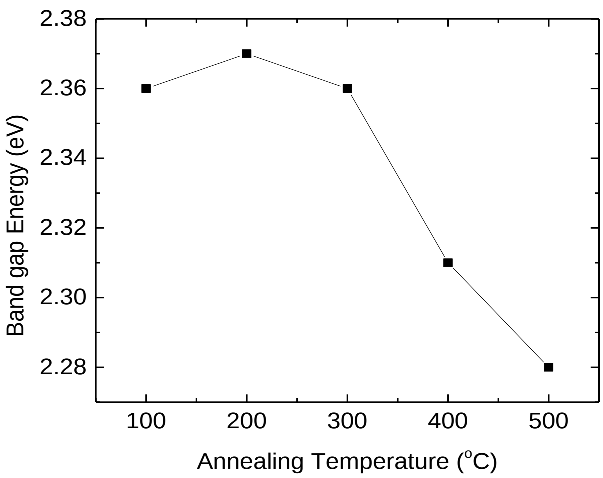


Fig. 6:Variation of energy band gap of CdS thin film at different annealing temperatures on FTO substrate at bath temperature of 80 °C

4.0 CONCLUSION

CdS thin films were fabricated successfullyusing CBD method on FTO glasses. Bath temperature dependence on the CdS film deposition was examined. Films fabricated at solution temperatures from 40 ºC to 80 ºC were studied for their optical and electrical properties. The results revealed elevated optical band gaps and fractional thicknesses when moving away from the bath temperature range of 50 ºC – 60 ºC. This result is potentially due to different CdS deposition mechanisms at lower and higher bath temperatures. SEM images supported the argument that the ion by ion mechanism could be taking place at the lower temperatures whereas the cluster mechanism at elevated temperatures. Films fabricated at higher bath temperatures were found to exhibit highquality and uniformity in comparison to others. Electrical characterization confirmed the type of the semiconductor film and also revealed that higher bath temperatures yield more stable films. With the increasing annealing temperature the transmittance edge was shifted toward the higher wave length. The best transmission (about 90%) was obtained for the air-annealed films at temperature of 200 ºC deposited at 80 ºC bath.

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