

Cost-Effective Fabrication Processes Of The Absorber CuInSe_2 (CIS) And The Buffer Cadmium Sulphide

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This paper reports a study of direct heated substrate chemical bath deposited Cadmium Sulphide buffer films. Impact of multi-depositions on both film thickness and its crystallinity features were studied. The absorption coefficient and index refraction of CdS were also determined. The absorber CuInSe_2 was grown by means of single-step electrodeposition. Structural analysis shows a quasi-amorphous films and morphological image shows a grained surface.

Keywords: Cadmium Sulphide, Copper Indium Di-Selenide, Electrodeposition, direct heated substrate chemical Bath deposition

I. INTRODUCTION:

Polycrystalline thin-film materials based on Cadmium Sulphide Copper Indium di-Selenide CdS-CuInSe_2 (CIS) are promising thin-film solar cells for various power and specialty applications. Impressive results have been obtained in the past few years for the thin-film of Copper Indium Gallium di-Selenide (CdS-CIGS) solar cells; scientists have achieved world-record, total-area efficiencies of 19.3% for a thin-film CIGS solar cell and 21.5% under concentration [1].

The fabrication of the absorber Copper Indium di-Selenide and the buffer layer Cadmium Sulphide thin films by means of one-step electrodeposition [2] and Directly Heated Substrates chemical Bath Deposition (DHSCBD), respectively [3] were performed. Morphological, structural as well as optical properties of the films were investigated by means of Scanning electronic microscope (JMS 6400), X-ray diffraction and spectrophotometer Cary 500 Scan model.

In the early days of CIGS research, the device was made with thick layer of CdS deposited by evaporation. A large improvement was made when evaporation was replaced by CBD (Chemical Bath Deposition). The main reason for the enhancement using thin CdS instead of ZnO for instance was its excellent conduction band alignment with the CIGS, since the band-gap of ZnO (3.3 eV) [4] is larger than that of CdS (2.4 eV) [3]. Attempts to completely remove the CdS and sputter deposit ZnO directly onto CIGS have failed.

II. THE BUFFER LAYER CdS:

DHSCBD was used to deposit homogenous and well adherent films of Cadmium Sulphide on

directly heated uncoated glass from an aqueous bath composed of thiourea 17×10^{-2} M as source of Sulphur, Cadmium Chloride as source of CdCl_2 1×10^{-2} M as source of Cadmium, ammonia NH_3 73×10^{-2} M to adjust pH to about 9 and Ammonium Chloride NH_4Cl 3.6×10^{-2} M as a complexing agent. After each deposition, which lasts 15 minutes the substrate was removed and the bath was renewed.

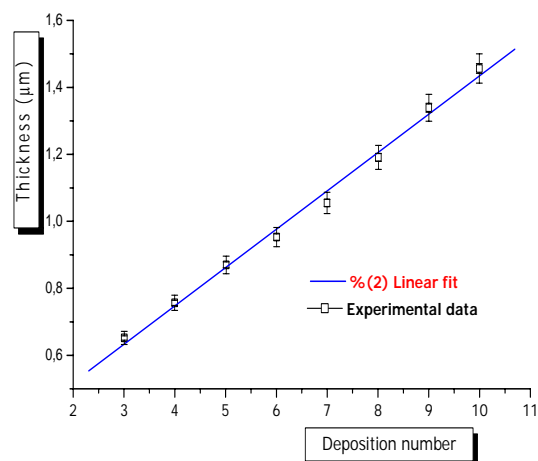


FIG. 1. Variation of the as-grown at 65°C films of CdS thickness versus deposition number.

The as grown films of CdS' thicknesses dependence on the deposition number were investigated. As expected and according to figure 1, the variation of the thickness as function of the deposition number shows a linear behaviour, which may enhance the films microstructure and possibly reduce their optical transmittance.

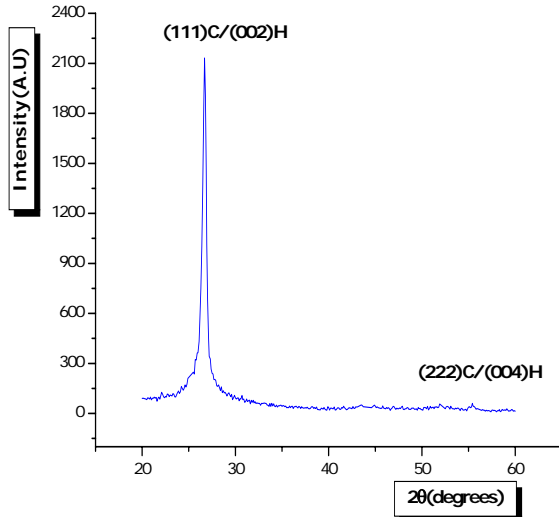


FIG. 2. X-Ray diffraction of the as grown films of CdS (Thickness 0.76 μm).

X-ray diffraction studies illustrate a polycrystalline structure of the as grown films with a preferred orientation in (111) C or/and (002) H.

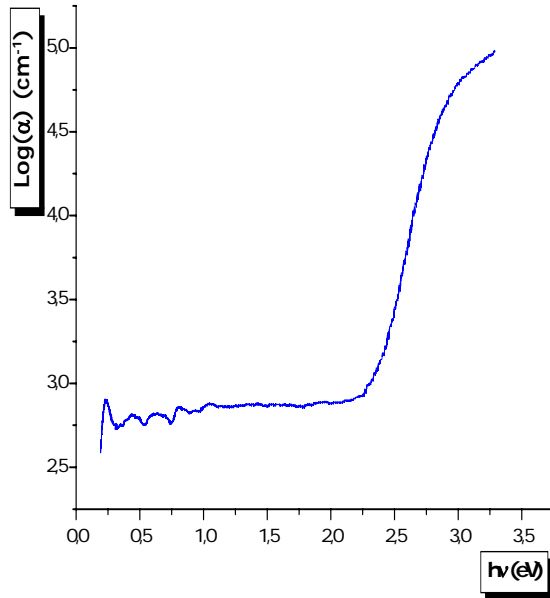


FIG. 3. Variation of the absorption coefficient logarithm ($\log \alpha$) versus wavelength.

In the other hand, the plot of $\log (\alpha)$ versus energy; where α is the absorption coefficient of CdS thin films; has shown a direct band gap semiconductor character of our films.

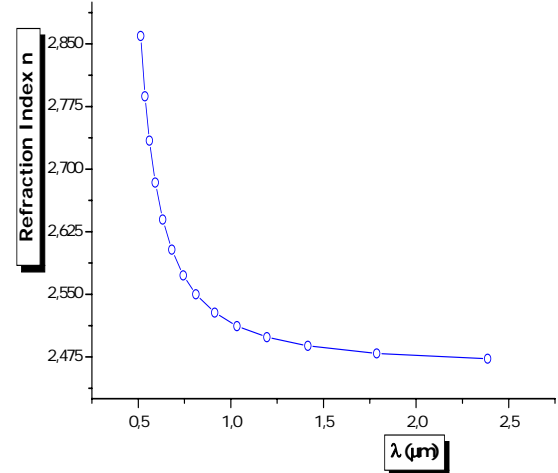


FIG. 4. Index refraction fit to Sellmeier theoretical model of the as-grown at 65°C CdS thin films.

The figure 4 shows the experimental variation of the refraction index of the as-deposited films of Cadmium Sulphide at 65°C as function of wavelength values as well as its fit to Sellmeier formula [5]:

$$n^2(\lambda) = n_\infty^2 + b^2 (\lambda^2 - \lambda_0^2)^{-1}$$

Where n_∞ is the refraction index extrapolated in the infinite, b and λ_0 are constants characterizing our films of CdS.

According to the experimental data, the parameters characterizing our semi-conductor were then inferred:

$$\begin{aligned} n_\infty &= 2.42. \\ b &= 0.3881 \mu\text{m} \\ \lambda_0 &= 0.4873 \mu\text{m} \end{aligned}$$

III. THE ABSORBER CuInSe₂:

Good quality of the absorber Copper Indium di-Selenide thin films were obtained by means of one-step electrodeposition, which is one of the very promising technique [6-8], because this way is being called to reduce highly the costly techniques used to produce the world record Copper Indium di-Selenide produced at NREL [1, 9-11].

The preparation of the thin films of the ternary semi-conductor CIS was achieved by means of one-step electrodeposition. The bath consists of a single solution of $\text{CuSO}_4 = 3 \times 10^{-3}$ M, $\text{In}_2(\text{SO}_4)_3 = 3 \times 10^{-3}$ M, $\text{SeO}_2 = 5 \times 10^{-3}$ M and acid citric = 0.1 M as complexing agent.

The growth of the films of CIS was performed at room temperature in cell containing the classical three-electrode system; Saturated Calomel Electrode (SCE) as reference, Platinum electrode as counter electrode and Molybdenum as work electrode. The

pH of the bath was adjusted to about 2.1 by adding few drops of H_2SO_4 .

Scanning potentiostat-galvanostat PGP 201 model monitored by measure interface into a personal computer is used and the substrate of Molybdenum were promptly prepared; washed in bi-distilled water rinsed in acetone and acetone solution, cleaned again abundantly in bi-distilled water and dried with Nitrogen gas before deposition procedure. The obtained films of CIS were then washed in $[NH_3:H_2O]$ (1:5) solution, so rinsed in bi-distilled water and finally dried with hear drier. The deposition lasts about 55 minutes and the potential adopted was -500 mV.

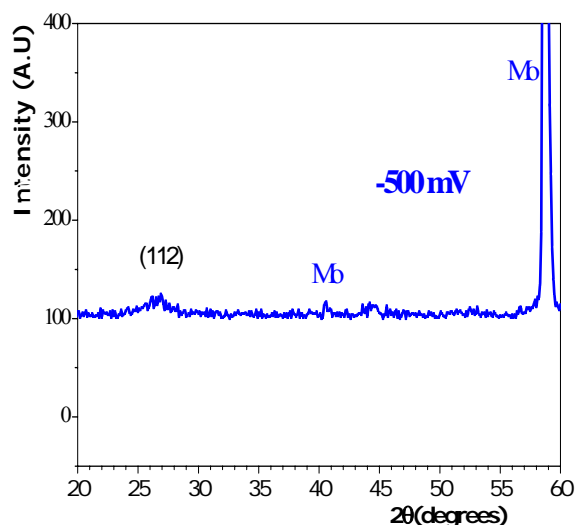


FIG. 5: XRD patterns of the as- grown $CuInSe_2$ on Molybdenum substrate at 500 mV vs. SCE.

XRD patterns of the as-grown films of CIS at -500 mV shown on figure 5 reveal a quasi-amorphous structure of the deposited films. However, we can notice the presence of the small peak oriented in (112) direction. In the other hand, morphological studies show a bloc of small grain with an almost compact structure (figure 6).

During the growth process, we have often encountered the problem of weak adherence of CIS films to the molybdenum substrates. So, in order to overcome this defiance and also to enhance the mechanical properties of our films along with improving their crystallinity features, adequate heat treatment was used [2].

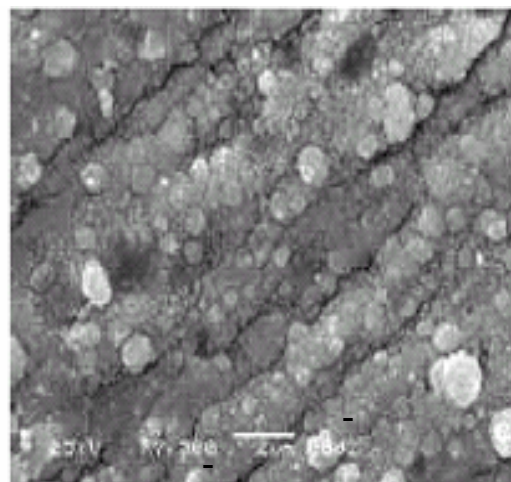


FIG. 6: SEM micrograph of the as-grown films of CIS at -500 mV vs. SCE.

IV. CONCLUSION:

Two types of thin films were prepared. The former: the buffer Cadmium Sulphide was grown using DHSCBD. Linear behaviour of thickness versus deposition number was noticed. Thick film of $0.76 \mu m$ shows polycrystalline aspect with a proffered orientation in (111) C/ (002) H direction. Absorption coefficient and refraction index were determined. The latter; weak adherent and quasi-amorphous thin films with grained surface of the ternary Copper Indium Di-Selenide were prepared by means of one-step electrodeposition.

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