The Role Of Cadmium Oxide Within The Thin Films Of The Buffer Cds Aimed At Solar Cells Based Upon CIGS Films Fabrication

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High quality Cadmium Sulphide thin films were grown on directly heated substrates of commercial glass by means of Modified Chemical Bath Deposition. Structural and optical properties of the obtained films were achieved. The impact of heat treatment in air at 450°C for one hour reveals the apparition of nano films of Cadmium Oxide on the surface of these buffer layers, which decreases dramatically the optical performance of the annealed films of CdS.

I. INTRODUCTION:

Cadmium Sulphide as buffer layers and Copper Indium-Gallium di-Selenide (CIS/CIGS) as absorbers makes part of the most promising materials for thin films solar cells applications.
The performance of polycrystalline thin films may be prepared by Vacuum evaporation [1,2] screen-printing [3,4],close-spaced sublimation [5], spray pyrolysis [5-9], pressure-printing [10-12], Molecular-beam Epitaxy (MBE) [13], Chemical Bath deposition (CBD) and Electrodeposition [14-28]. Thus, research in the optimization of the experimental parameters for thin films creation by CBD and Electrodeposition is a key factor in solar cell technology development.

Our current work deals with describing our recent results of long term experience with the fabrication of the buffer layer CdS [29].

Structural, morphological along with optical properties were investigated. Apparition of nano films of Cadmium Oxide on the buffer layer further to heat treatment was detected and its impact on optical features was studied. Serious decrease of optical performance was perceived.

II. MATERIALS FABRICATION:

Chemical Bath deposition:

Chemical bath deposition is a technique for controlling the homogeneous precipitation of water insoluble compounds and their solid solution. Thus, CBD of Cadmium Sulphide may be a highly reproducible and controllable technique which yields CdS layer with excellent optoelectronic and solar cell properties [30].

A complexing agent or ligand NH_3 was used and details of experimental set-up have been reported yet in our previous wok [29].

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CBD-CdS thin films were first introduced by **MAKRASHIN** and **TKACHEV** [31] and later by many other authors [32-38]. Formation of Cadmium Sulfide thin films is based upon two main mechanisms:

i. Heterogeneous mechanism: growth occurs ion-by-ion on the substrate surface, which is responsible for the formation of well crystallized adherent films of CdS to the glass substrates.
ii. Homogenous mechanism: growth of colloidal particles of CdS mainly on the bath solution and particularly upon the substrates leading to formation of poorly adherent films.

The Chemical deposition of CdS thin films consists of the deposition of Thiuorea in an alkaline solution of a Cadmium salt. The deposition process was based on the substrate preparation. The reaction process for the formation of CdS may be described by the following steps [32,33,39,40,41-43]:

Ammonium formation:

$$NH^{+}_{3}\,H_2O \rightleftarrows NH_4^{+} + OH^{-} \qquad K = 1.8\ 10^{-5}$$

Cadmium salt reaction with the amine to form the complex compound:

$$Cd^{2+} + 2OH^{-} \rightleftarrows Cd(OH)_2 \qquad K = 1.88\ 10^{-14}$$

Diffusion of the complex ion OH^- and Thiourea on the catalytic surface of CdS:

$$SC(NH_2)_2 + 3OH^{-} \longrightarrow 2NH_3 + CO^{2-}_{3} + HS^{-}$$

$$HS^{-} + OH^{-} \longrightarrow S^{2-} + H_2O$$

The Dissociation proceeds as follows [41]:

$$H_2S + H_2O \xrightarrow[K_1 = 10^{-7}]{} HS^- + H_3O^+$$

$$HS^- + H_2O \xrightarrow[K_2 = 10^{-14}]{} S^{2-} + H_3O^+$$

Thus the formation of CdS:
The global reaction for the process is given by:

$$Cd(NH)^{2+}_4 + S^{2-} \xrightarrow[K_3 = 7.1\ 10^{-28}]{} CdS + 4NH_3$$

$$CdS(NH_3)_4{}^{2+} + SC(NH_2)_2 + 4\ OH^- \longrightarrow CdS + 6\ NH_3 + CO_3{}^{2-} + H_2O$$

Micro-structural and optical investigations:

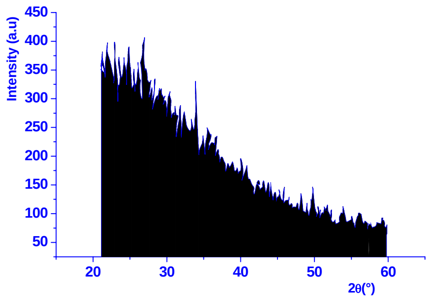

Figure 1:X-ray diffraction of the as-grown films of Cadmium sulphide on directly heated glass substrate at 65°C.

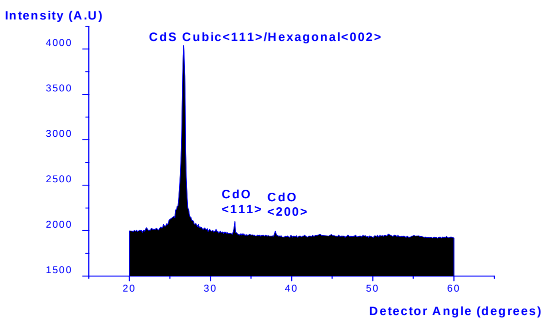

Figure 2:X-ray diffraction of the heat treated films of Cadmium sulphide on air at 450°C for one hour

Figure 1 shows X-ray diffraction patterns of as-grown films of CdS; we can notice the amorphous aspect of these films. However, heat treatment at 450°C for one hour leads to remarkable enhancement of the crystalline structure of the annealed films. Polycristalline structure of CdS thin films were obtained (Figure 2), with a preferential orientation towards <111>C/<002>H direction, which is likely due to the rearrangement of ions/atoms of Cd and S inside the CdS lattice and to the diffusion of these elements into the bulk of the films, which might provoke an increase of the lattice parameter and the apparition of the oxide Cadmium nano layers on the top of CdS.

The annealing of the CdS thin films leads to the improvement of crystalline qualities of these films.

In the other hand, we have investigated the impact of the apparition of Cadmium Oxide on the CdS films, Figure 3 shows clearly a drastic reduction of transmittance level, which will probably decrease band gap value of the annealed CdS films in air at 450°C for one hour.

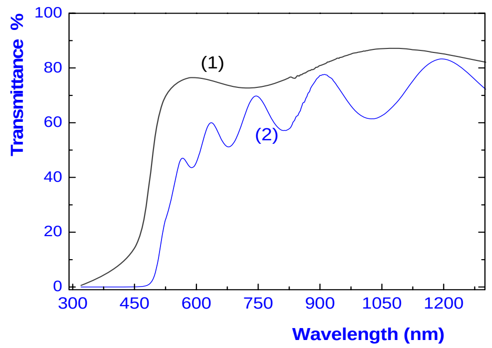

Figure 3: Transmittance versus wavelength for the (1): as-grown films, (2): annealed samples for an hour at 450°C in Air, respectively.

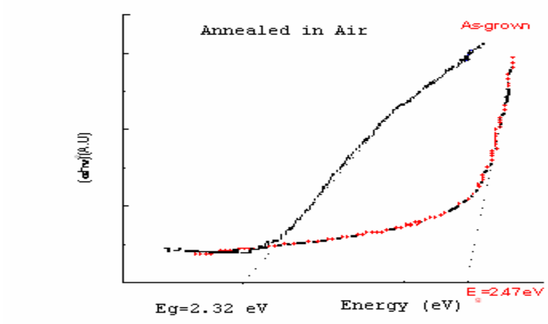

Figure 4: Optical transmission measurements were used to determine the band-gap of the films

III. CONCLUSION:

Well crystallized films of the buffer CdS were fabricated using low cost, simple and up-scaling technique viz. Modified Chemical Bath Deposition on directly heated substrate of commercial glass.
We have also noticed the apparition of CdO after heat treatment and discuss its deleterious impact, mainly on the optical properties.

At last, we have reported that heat treatment of CdS thin films in Air at 450°C provoke the reduction of the band-gap from 2.47 to 2.32 eV. As result of decrease of strain within the films of CdS or/and to the absorption and desorption of gases during heat treatment.

Through these investigations we can suggest CdS as a buffer layer in the solar cells based on CIS thin film absorber to accommodate lattice parameter mismatch between CIS and the window layer ZnO as well as band bending of conductions and valences bands of these thin films.

Acknowledgment:

This work was partially supported by the CNRST/CNRS cooperation program (Chimie 06/07).

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