

Effect of heat treatment with CdCl_2 on the electrodeposited CdTe/CdS heterojunction

M. Rami, E. Benamar, M. Fahoume, F. Chraïbi, and A. Ennaoui

*Laboratoire de physique des matériaux, Département de Physique, Faculté des Sciences de Rabat,
B. P. 1014 Rabat-Maroc.*

CdS/CdTe heterojunction was subjected to chemical treatment commonly used in photovoltaic device fabrication to determine the resulting microscopic effect on the morphology and structure. CdS and CdTe thin films were electrodeposited successively onto indium tin oxide (ITO) from aqueous solution. Containing CdCl_2 and $\text{Na}_2\text{S}_2\text{O}_3$ for the deposition of thin film windows. The ITO/CdS resulting substrates was then used for the deposition of CdTe thin film absorber using aqueous solution of CdSO_4 and TeO_2 . Next CdCl_2 dip followed by 400°C heat treatment was used to modify the CdTe/CdS surface and interface. Scanning electron microscopy (SEM) and Atomic force microscopy (AFM) were used to evaluate the resulting surface morphology. X-ray diffraction analysis reveals that the heat treatment enhances the recrystallisation and shifts the CdTe peaks towards a smaller lattice parameter.

I. INTRODUCTION

Cadmium telluride, CdTe, is one of the few II-VI compounds used as absorber for solar cells. Its band gap energy is 1.45 eV, which corresponds closely to sunlight spectrum. CdTe has a direct transition type band structure, so the absorption coefficient is larger for light with wavelength below the absorption edge. Therefore, CdTe is an important candidate material for the fabrication of high efficiency solar cells.

On the other hand, cadmium sulphide (CdS), is known to act as a very suitable window layer for CuInSe_2 and CdTe based solar cells [1,2]. The band gap energy of CdS films exists near the photon energy of maximum solar radiation spectrum, however, the CdS films are prepared as thin as possible to avoid optical transmission losses and they show a high sheet resistance. Thus the deposition of CdS on transparent conducting oxide (TCO) films is necessary to compensate the sheet resistance of the CdS layer.

To date efficient TCO/CdS/CdTe thin films solar cells have been made by closed spaced sublimation (CSS)[3], electrodeposition [4,5,6,7], hot wall vacuum evaporation [8], and screen printing [9]. Efficiencies great than 10% have been achieved by several methods especially Chu et al [3] have reported an efficiency of 15.8% in CdTe cells by CSS process. Improvement from 10% efficiency regime have largely been accomplished through combined understanding of the materials properties and chemistry and related advancements in devices processing and interface engineering [10-11]. There are substantial differences in the characteristics of the CdS/CdTe cells presented by different groups [12], which are probably owing to the differences in the deposition technique of CdTe and CdS. Each technique has both advantages and disadvantages. Among the different techniques, electrodeposition is one of the most suitable low-cost methods. The material can be deposited on the desired area of the substrate and can easily be controlled, thus providing a film of reproducible quality.

Different laboratories have reported changes in the properties of the films after being subjected to chemical treatment in saturated solution of CdCl_2 in the methanol followed by thermal annealing between 400°C and 500°C for 30 min. Such treatments were found substantially increase the efficiency of CdTe/CdS cell. The exact mechanism for the improvement in efficiencies after treatment is still under investigation, but some of the observed effects are: inter-diffusion of S and Te in the junction, forming $\text{CdS}_x\text{Te}_{(1-x)}$ [13] decrease in the interface state density and grain growth [14] and the passivation of the grain boundaries [15].

In this present paper we report the preparation of CdS and CdTe by electrodeposition. Structural, optical, and morphological properties of CdTe/CdS/ITO are studied. The morphology analysis of the films is evaluated using atomic force microscopy and correlated with conventional scanning electron microscopy images. The influence of the annealing with CdCl_2 treatment on CdTe/CdS surface and interface are investigated.

II. EXPERIMENTAL DETAILS

The electrodeposition cell was Pyrex glass vessel with three electrode systems consisting of saturated potassium chloride calomel electrode (SCE) as reference, platinum sheet as counter electrode and an ITO/Glass as working electrode. The electrodeposition was carried out using a computer controlled potentiostat (EG&G PAR 273A). All potential reported here were applied with respect to SCE electrode.

Details of deposition of CdS and CdTe were reported in our previous work [16,17]. Here we describe the deposition steps. The electrodeposition of CdS on ITO/Glass was carried out in aqueous solution prepared by dissolution of analytical grade reagents of cadmium chloride (0.2M) and $\text{Na}_2\text{S}_2\text{O}_3$ (0.01M) in tridistilled water. Hydrochloric acid was added to reach the desired pH (usually 2.2). The solution was kept at 85°C and magnetically stirred during the deposition at approximately

200 rpm. The cleaned ITO/Glass was kept at hot 90°C tridistilled water for about 15 min and then immediately transferred to CdS bath solution.

The solution was frequently filtered between depositions. Furthermore, when the bath precipitate began to change the colour from yellow to orange, a new solution was made up and used.

A clear CdS film of 70 nm thickness was deposited in about three hours at a potential $E = -640$ mV vs. SCE.

Just before the deposition of CdTe on CdS/ITO/Glass this latter first, was slightly mechanically cleaned with cotton tips, then also kept in an ultrasonic bath of water solution heated at a temperature $T = 90^\circ\text{C}$. We can note that the mechanical cleaning of the CdS layer eliminates the colloidal particles without destroying the nanostructure underneath because the adhesion of the CdS nanocrystallites to the ITO substrate is very strong.

Cadmium telluride films were cathodically deposited onto freshly prepared CdS films from a solution heated at $80\text{--}85^\circ\text{C}$, and containing 0.2M CdSO_4 and $0.5\text{--}1$ mM HTeO_2^+ . This latter is obtained by dissolving weighed amounts of TeO_2 (99.999 Aldreich) in H_2SO_4 (select pure 98%); periodic warming and immersion in ultrasonic bath aided the dissolution. The pH of the solution was adjusted to 2–2.2 by adding few drops of NaOH. The CdTe of around $2\mu\text{m}$ thickness was deposited in about two hours at a potential $E = -0.620\text{V}$ vs. SCE. Post deposition heat treatments were carried out by dipping the as deposited films in a CdCl_2 saturated methanol solution. The samples were then heat treated for 10 min at 400°C in a cube furnace in air.

X-ray diffractometer (Siemens D5000) with Ni-filtred CuK radiation was used for structural studies. Nanoscope III AFM from digital instrument, Santa Barbara, CA in contact mode was used for all atomic force microscopy measurement. We have also used the scanning electron microscopy (SEM: LEO 430 producer) for the morphological studies.

The optical transmittance and absorbance of the films were recorded in the wavelength range 200 nm to 1100 nm using a Perkin Elmer Lambda 2 UV-VIS spectrophotometer.

III. RESULTS AND DISCUSSION

CdTe layers have been prepared by electrodeposition on CdS/ITO as substrates. The films have brown colour and adhere strongly to the substrates. X-ray diffraction patterns of the electrodeposited CdTe on CdS is presented in figure 1. The as-deposited films are identified as polycrystalline CdTe with a cubic structure. They exhibit high preferential orientation along (111) direction with low intensity of (220) and (311) peaks. Elemental analysis of the electrodeposited CdTe on ITO substrate in the some conditions described above at $E = -620\text{mV}$ vs. SCE by EDAX reveals a ratio of Cd/Te close to 1. Figure 2 show the surface of the as-deposited CdTe on CdS imaged by SEM and AFM with approximately the some magnification. Both micrographs

show identical surface structure which is uniform, homogenate, and with grain size ranging from 160 to 280 nm. We can also observe that the grains appear to agglomerate.

The thermal and chemical processing steps that are critical in producing higher efficiency CdTe thin film devices have mixed correlation with changes in the film's physical properties. For this purpose, we have studied the structural, optical and morphological properties of CdTe/CdS thin films after CdCl_2 heat treatment. One can observe that the heat treatment with CdCl_2 at 400°C for

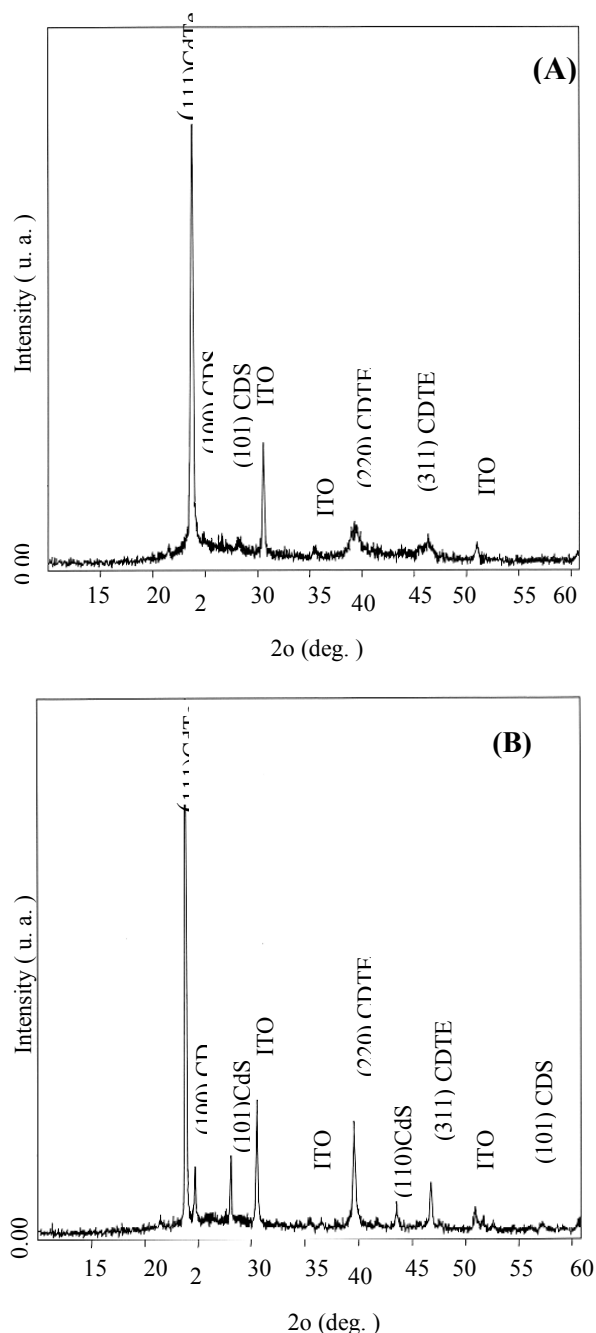


FIG. 1 : X-ray diffraction spectra of CdTe/CdS/ITO without annealing (A), and after annealing at 400°C for 10min in air with CdCl_2 treatment (B).

10min of CdTe/CdS changes the surface appearance to milky.

X-ray diffraction spectra of electrodeposited CdTe on CdS annealed at 400°C for 10min with CdCl₂ treatment are shown in figure 1-b. The annealed CdTe films exhibit a preferential orientation along (111) direction of the cubic structure. The (220), (311), and (400) peaks are more intense than those of the as-deposited CdTe films. However the intensity of the (111) peak is less than of about 9.7% than that of the as-deposited CdTe/CdS. This result indicates that the heat treatment produces near random orientation of the grains. The full width at half maximum of (111), (220) and (311) peaks of the films after annealed with CdCl₂ treatment are smaller than those of the as-deposited films. This result shows that the heat treatment enhances the recrystallisation of CdTe/CdS films. Furthermore, the (100), (002), and (101) peaks of the hexagonal CdS are enhanced. No significant shift in the peak position was observed compared to α -CdS given by ASTM tables. Peaks of the cubic phase sphalerite β -CdS were never been detected.

Table 1 summarises the change in the lattice parameter for CdTe films before and after annealing with CdCl₂. On can observe that the lattice parameter of the as-deposited films is slightly greater than that of CdTe powder. This increase in the lattice parameter can be explained by a compressive stress perpendicular to the growth plane. Heat treatment with CdCl₂ shifted all the diffraction peaks slightly towards a higher angle (i. e. smaller lattice parameter). This can be explained by the diffusion of the sulphur into CdTe to form CdTe_(1-x)S_x solid solution since sulphur which has a smaller atomic radius than Te substitute Te sits in the CdTe lattice, reducing then the interatomic bond length in the molecule.

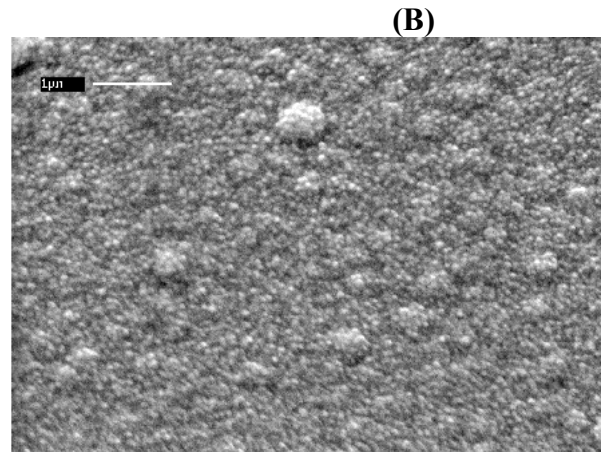
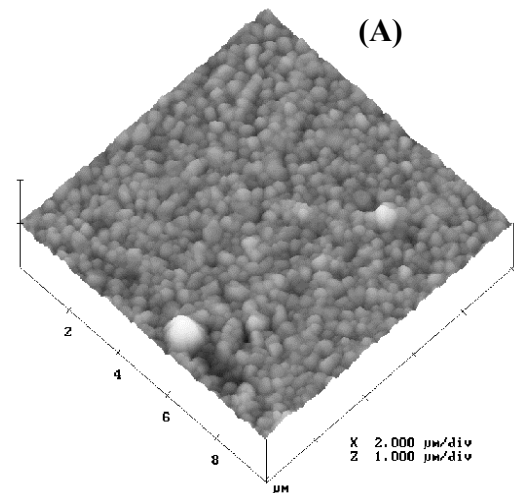
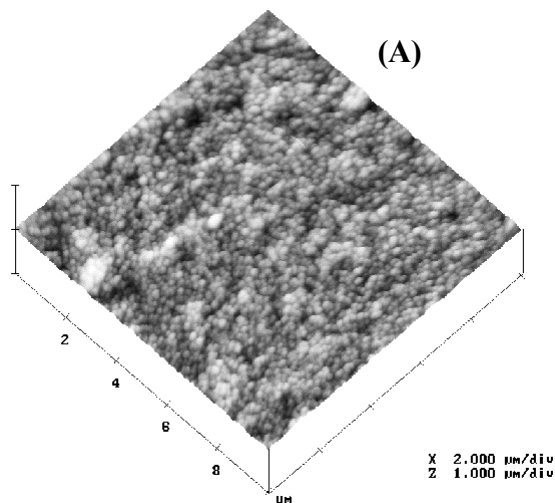


FIG. 2 : Surface topography of the as-deposited CdTe/CdS imaged by AFM (A) and SEM (B).

	a (Å)	d (AFM) (nm)	d (SEM) (nm)	<r> (nm)	I(111) (cps)
Powder (CdTe)	6.481				
As deposited	6.495	180-280nm	160- 240nm	13	867
After treatment	6.430	400-560nm	380- 480nm	24	783

Table1: Lattice parameter (a) , grains size measured from AFM(d(AFM) and SEM(d(SEM))), mean roughness <r>, and (111) peak intensity of the CdTe/CdS/ITO/ Glass before and after heat treatment with CdCl₂ at 400°C for 10min in air.

An illustration of the change in microstructure due the annealing with CdCl₂ treatment is shown in figure 3. It is clear from the AFM and SEM images that the CdCl₂ heat treatment completely recrystallizes grains with increasing their size (Table 1).



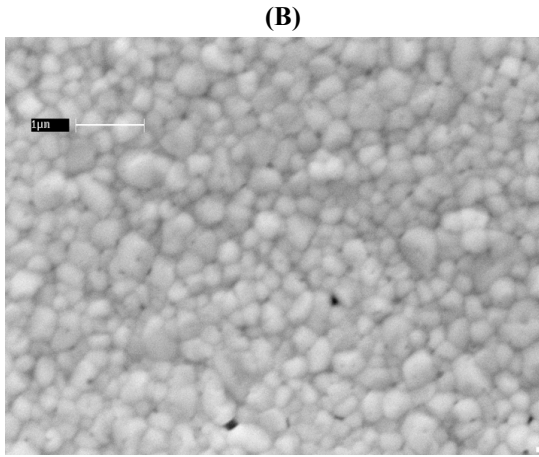


FIG. 3 : Surface topography of CdTe/CdS heat treated at 400° C for 10min with CdCl_2 observed by AFM (A) and SEM (B).

An important parameter shown in table 1 is the mean roughness. The mean roughness of the as deposited films is about 13 nm. After heat treatment with CdCl_2 the roughness increases and becomes approximately twice times greater than the as deposited CdTe films. This can be explained by the procedure of the heat treatment with CdCl_2 of the films. An appropriate chemical etching is suitable to minimise the roughness of the surface of the film. Table 1 shows also a comparison of the grains size of the CdTe films measured by AFM and SEM before and after annealed. The grains size value measured by both techniques have the same order of magnitude. This comparison confirms the reliability of the AFM to produce the SEM image under the same magnification conditions.

Figure 4 shows the transmission wavelength for electrodeposited CdTe/CdS/ITO before and after CdCl_2 treatment with annealing at 400°C for 10min in air. A shift in the optical absorption edge at low energy after the 400°C in air heat treatment is apparent between the two curves of the transmission. Using absorption data, the band gap energy, E_g , was estimated by plotting the $(\alpha h\nu)^2$ vs. $h\nu$ (figure 5). The linear nature of the plot indicates that the CdTe is a direct band gap material. The intercept on the energy axis gives the values of the direct band gap; E_g as 1.45eV for the as-deposited films and 1.40 eV for the heat treated CdTe/CdS films.

The shift in the band edge and the lattice parameter is due to the formation of $\text{CdS}_x\text{Te}_{1-x}$. As consequence, is that the heat treatment decrease slightly the band gap to 1.40 eV.

All the above results, the shifts in the lattice parameter, optical absorption, band gap and the change in the grain size are consistent with the formation of $\text{CdS}_x\text{Te}_{(1-x)}$ which causes by the heat treatment with CdCl_2 .

The sulphur content, x , of the $\text{CdTe}_{(1-x)}\text{S}_x$ films was determined quantitatively from the lattice parameter by assuming a Vegard's relation $x = 1.508 (6.481 - a)$ where a is the lattice parameter of the sample. The sulphur content is about $x=0.076$

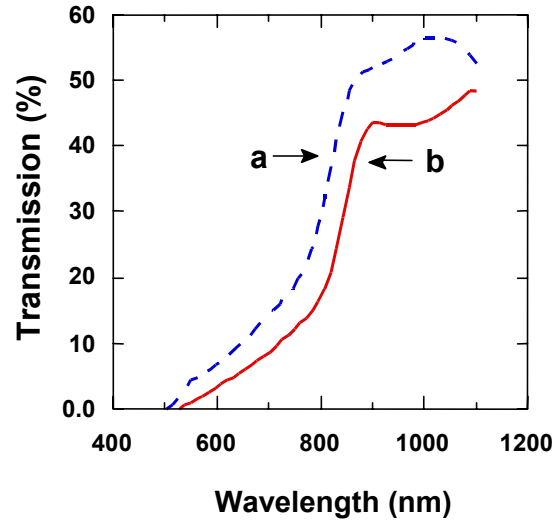


FIG. 4 : Transmission spectra of CdTe/CdS thin films: as-deposited (a) and after annealed with CdCl_2 treatment (b).

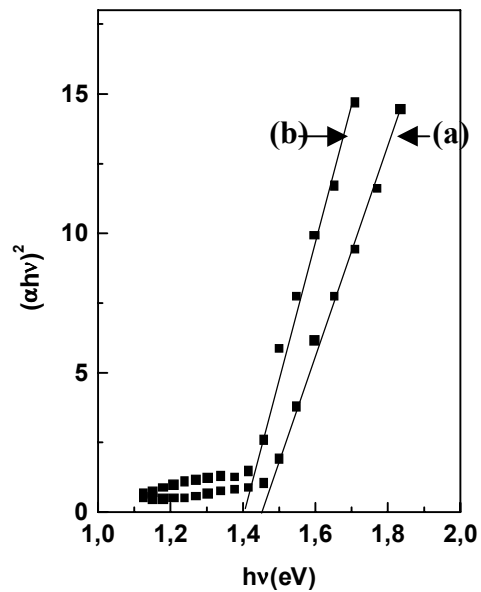


FIG. 5 : $(\alpha h\nu)^2$ versus $h\nu$ plot for CdTe/CdS films: as-deposited (a) and after annealed with CdCl_2 treatment (b).

IV. CONCLUSION

The electrodeposition technique is an ideal and simple tool for the elaboration of CdS, and CdTe thin films for use in solar cells applications. The CdTe/CdS structure consists of the cubic phase CdTe films oriented along (111) direction on the hexagonal phase CdS films. Morphological and structural studies show that the electrodeposition of CdTe on CdS has a good quality. A morphology study of CdTe before and after CdCl_2 heat treatment that needed to produce high efficiency device shows that the as grown films have a very compact structure with grains size ranged from 160 to 280nm.

After the annealing with CdCl_2 treatment the grains become bigger and have an average grain of about 430nm. XRD measurement reveals that the heat treatment with CdCl_2 shifts the CdTe peaks towards a smaller lattice parameter. Furthermore the optical measurement shows that this treatment shifts the optical absorption edge at low energy and decreases slightly the band gap to 1.4eV. As consequence is that the heat treatment with CdCl_2 improves the quality of the CdTe thin films and the heterojunction CdTe/CdS.

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