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EFFECT OF HEAT TREATMENT IN PRESENCE OF $CdCl_2$ ON THE PHYSICAL PROPERTIES OF pCdTe/nCdS HETEROJUNCTION SOLAR CELLS

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The article is a comprehensive study of the effect of heat treatment in presence of a cadmium chloride ($CdCl_2$) on the physical properties of pCdTe/nCdS solar cells. Heat treatment process plays a key role in enhancing the pCdTe/nCdS hetero-structure photosensitivity, thus improving the performance of solar cells based on them. This article outlines the changes in the structural characteristics and photoelectric properties of such solar cells before and after heat treatment process. The two most popular methods of the heat treatment process based on cadmium chloride are also discussed. One may consider the $CdCl_2$ heat treatment process as one of the very important stages of preparing CdTe/CdO/CdS solar cells, which improves the performance of these cells made in laboratories of the State University of Moldova.
Keywords: *Heterojunction, Solar cell, Chloride heat treatment process, Cadmium Chloride, Cadmium Telluride, Cadmium Sulfide.*

INFLUENȚA TRATĂRII TERMICE ÎN PREZENȚA CLORURII DE CADMIU ($CdCl_2$) ASUPRA PROPRIETĂȚILOR FIZICE ALE CELULELOR SOLARE CU HETERONCȚIUNEA pCdTe/nCdS

Prezentăm un studiu cuprinzător al efectului tratării termice în prezența clorurii de cadmiu ($CdCl_2$) asupra proprietăților fizice ale celulelor solare pCdTe/nCdS. Procesul de tratare termică joacă un rol-cheie în ameliorarea fotosensibilității heterostructurii pCdTe/nCdS, îmbunătățind în așa mod performanța celulelor solare bazate pe ele. În articol sunt conturate schimbările în caracteristicile structurale și proprietățile fotoelectrice ale acestor celule solare până la și după procesul de tratare termică. De asemenea, sunt abordate cele mai răspândite metode de tratare termică bazate pe clorura de cadmiu. Tratarea termică în $CdCl_2$ poate fi considerată o etapă foarte importantă în prepararea celulelor solare CdTe/CdO/CdS, care îmbunătățește performanța acestor celule fabricate în laboratoarele Universității de Stat din Moldova.
Cuvine-cheie: *heterojoncțiune, celulă solară, proces de tratare termică în clorură, clorură de cadmiu, sulfid de cadmiu.*

Introduction

Heterostructure pCdTe/nCdS is a promising choice for manufacturing low cost and high efficiency thin film solar cells. Recent studies had shown that the highest efficiency (η) of CdTe thin film solar cells is about 18.3%, and for a large area module the efficiency is of 15.3% [1], despite the fact that this value is still far from the theoretical one which is 28-30% [2]. CdTe/CdS solar cells efficiency enhancement is related to chloride heat treatment.

Chloride heat treatment process is carried out after the deposition of the absorbing layer CdTe in the CdTe/CdS solar cell in order to improve its performance. The heat treatment in the presence of $CdCl_2$ causes several changes in the physical parameters of CdTe and CdS films. Grain boundaries in CdTe thin films are considered to act as strong recombination centers [3]. Grain boundaries may also act as barriers to current transport. After the chloride heat treatment process, the CdTe and CdS films average grain dimensions usually increase [4]; the defects density in the films decreases; the grain boundaries are passivated. Consequently, the performance of solar cell is improving.

The heat treatment process in the presence of $CdCl_2$ is carried out by two experimental ways, either by a wet chemical process or by using a dry steam method. However, the second method is more convenient due to better control level. The wet $CdCl_2$ surface treatment is effective for small size cell fabrication but has several disadvantages for large area cell manufacturing, such as un-uniform delivery of the $CdCl_2$ and degradation due to the processing in a humid environment. Instead of the wet process, the employment of a $CdCl_2$ treatment in a process of physical vapor deposition and annealing would be desirable in terms of manufacturing technology [5].

$CdCl_2$ heat treatment process applied to CdS/CdTe heterojunction components plays a key role in improving the photosensitivity of heterostructures, thus improving the performance of solar cells based on it.

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Researchers [6] have studied the effect of "chloride" annealing of CdS/CdTe heterostructure on the output characteristics of ITO/CdS/CdTe/Cu/Au solar cells and the crystalline structure of CdTe layer. It has been proved that the transformation from the metastable hexagonal phase of cadmium telluride to a stable cubic modification is achieved by the chloride treatment. This improves significantly the photovoltaic properties of thin film CdS/CdTe heterostructures. Chloride annealing has been carried out after obtaining the final heterostructure. For this purpose, $CdCl_2$ film is deposited on the surface of CdTe layer by vacuum thermal evaporation. The resulting ITO/CdS/CdTe/$CdCl_2$ heterostructures are annealed in the air in a closed volume at a temperature of 430ºC for 25 min.

During the "chloride" treatment, the efficiency of solar cells increases by 5-6 % due to the interfacial interaction of $CdCl_2$ with CdTe layer [7]. The solar cells' efficiency increasing is mainly due to the minority carriers life time increase. This probably is related to the elimination of the deep levels in the band gap and passivation of the grain boundary surface of the cadmium telluride layer [8].

The effect of $CdCl_2$ on the structural properties of CdS thin films deposited by two methods: chemical bath deposition (CBD) and close-space sublimation (CSS) have been investigated [9]. CdS/(CSS) films have a hexagonal structure and good crystallinity; $CdCl_2$ treatment does not cause significant changes but decreases the density of planar defects. Before the heat treatment process, CdS/(CBD) films have a cubic structure and its degree of crystallinity is less than that of CdS/(CSS) films. But after the annealing in $CdCl_2$, these films are recrystallized to hexagonal phase. As a result, a good degree of crystallinity and a low density of planar defects are achieved. The uniform coverage and the presence of the oxygen are considered key issues in the creation of the CBD films which are well-suited for photovoltaic applications. Fig. 1 shows CdTe films before and after $CdCl_2$ heat treatment process which is carried out at 400°C for 15 - 20 minutes, thereby minimizing the defects and achieving high efficiency devices [10].

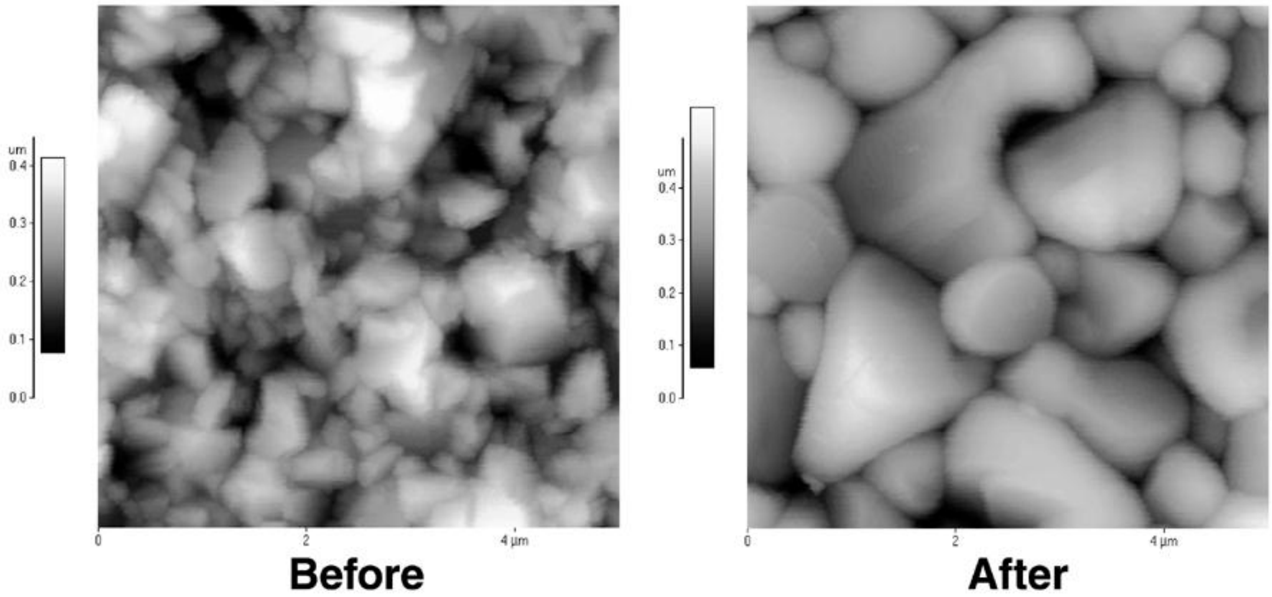


Fig.1. AFM image of CdTe films before and after the dry method of heat treatment in $CdCl_2$.

Many studies have recently explained the mechanisms responsible for enhancement of the solar cell characteristics due to $CdCl_2$ heat treatment [11]. Furthermore, the analysis of "The current density - voltage - temperature (J-V-T)" dependence has indicated that the $CdCl_2$ treatment leads to change the predominant mechanism of charge carriers flow from the interface recombination/tunneling to depletion region recombination [11], which decreases the surface states density.

The results of the light JV measurement of ITO/CdS/CdTe/Cu/Au solar cells prepared by using cadmium chloride layer of varying thicknesses are shown in Fig.2.

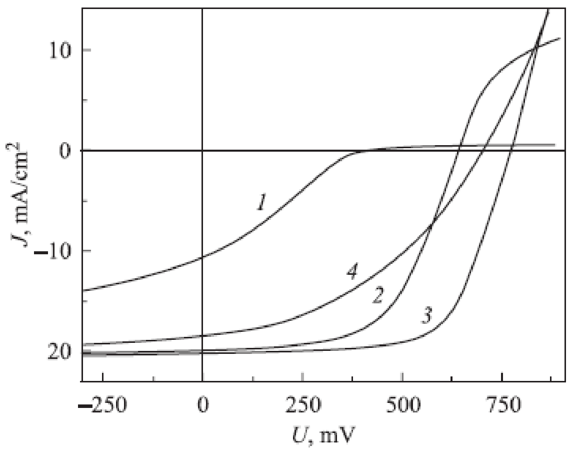


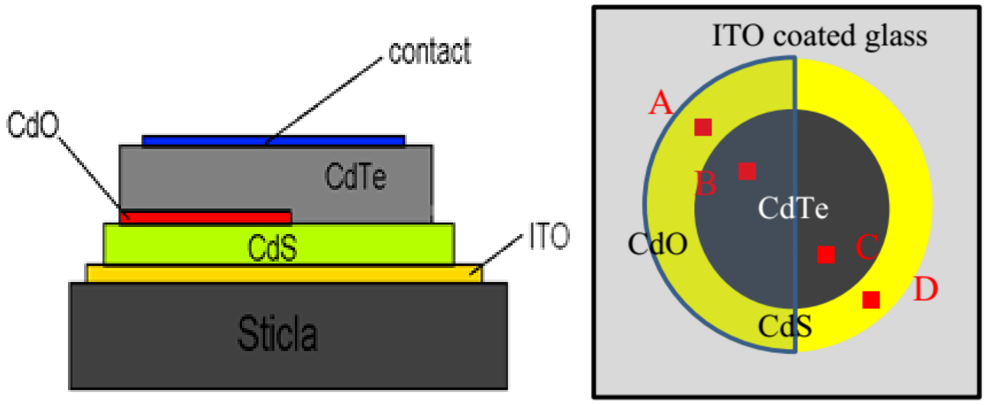
Fig.2. Effect of $CdCl_2$ layer thickness on the light IV for ITO/CdS/ CdTe/Cu/Au. (1) without $CdCl_2$ layer.

Figure 2 has clearly shown that the increasing of the $CdCl_2$ layer thickness up to a certain value leads to the optimization of photovoltaic properties of CdS/CdTe solar cells. And excessive thickness of cadmium chloride layer decreases the efficiency of photovoltaic processes in the cadmium telluride layer.

Chloride heat treatment process is very essential in CdS-CdTe heterojunctions because it enhances their photosensitivity. By using quasi-closed space sublimation method, CdS-CdTe heterostructures are produced by successive deposition of CdS and CdTe layers onto glass substrates (2 x 2 cm^2), which are covered by transparent

(~80%) and conducting (~10^{-3} Ωm) SnO_2layer. The thickness of layers is 0.3- 0.6 µm and 8 - 14 µm for CdS and CdTe respectively.

Before CdTe layer's deposition, a thin CdO layer (5–50 nm) is deposited onto a part of the CdS layer as it is shown in (Fig.3).



(a) (b)

Fig.3. (a) Cross section of CdS - CdTe heterostructure with a CdO buffer layer, (b) view from above of the heterostructure :A(CdS/CdO), B(CdS/CdO/CdTe), C(CdS/CdTe) and D(CdS).

CdO layer is deposited by magnetron sputtering; CdO layer's thickness is controlled by the time of sputtering and determined by the calibration curve of the dependence of CdO layer thickness on sputtering duration. $CdCl_2$ heat treatment process has been applied to the resulting SnO_2/CdS/CdO/CdTe/Ni heterostructures in order to enhance their photosensitivity. For this purpose, the structures have been exposed to a methanol–$CdCl_2$ solution for 3–5 h. Then, a heat treatment at 380ºC has been carried out for 30 min.

The measurements have indicated that chloride heat treatment enhances the crystal structure of the layers, reduces the density of defects in the transition region of the heterojunction and forms CdS_xTe_{1-x} solution at the interface. As a result, the minority charge carriers life time is increasing, thereby improving the performance of the solar cell.

Conclusion

In this article, the effects of $CdCl_2$ heat treatment of CdTe films on the structural and photoelectric properties of CdTe and CdS-CdTe thin films solar cells have been investigated. It was shown that $CdCl_2$ treatment followed by annealing during cell preparation enhances the recrystallization and diffusion processes at the CdS-CdTe heterojunction interface. Significant improvements in CdS/CdTe solar cell efficiency are commonly observed as a result of a $CdCl_2$ heat treatment.

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