

## **SOME RADIATIVE PROPERTIES OF THE CdS LAYERS ANNEALED IN PRESENCE OF CdCl<sub>2</sub>**

**Gaşin Petru<sup>1</sup>, Vatavu Sergiu<sup>1\*</sup>, Caraman Iuliana<sup>2</sup>**

<sup>1</sup>Universitatea de Stat din Moldova, 60 A. Mateevici st, Chişinău, MD2009, Republic of Moldova

<sup>2</sup>Universitatea Bacău, Calea Mărăşeşti 157, Bacău-600115, România

### **Abstract**

The analysis of the absorption and photoluminescence spectra of CdS layers at 78K has been performed for unannealed and annealed in CdCl<sub>2</sub> CdS/CdTe heterojunctions. The energy diagram of the recombination levels were established.

**Key words:** CdS, absorption, photoluminescence

### **INTRODUCTION**

The photovoltaic properties of the SnO<sub>2</sub>/CdS/CdTe/Metal solar cells are strongly influenced by the energy spectrum of the localized states in CdS layer. The thickness of CdS layer is considered to be 100÷10 nm for to minimalize the losses of the photogenerated charge carriers. This thickness has the same order of magnitude as the mean free path of the nonequilibrium charge carriers. The CdS layer has a nanocrystalline structure, which result in a essential changes of the recombination levels energy diagram. At the same time, the energetic diagram and the origin of the localized states depends on the annealing technology of CdS/CdTe heterojunction (HJ) in presence of CdCl<sub>2</sub> [2].

The perturbations of the energy diagram of the localized states are reflecting themselves in the electron-hole, as well as on the intensity of the green band in the photoluminescence (PL) spectrum of CdS [3]. The mean free diffusion length and lifetime of nonequilibrium charge carriers, two parameters affecting the solar cell's efficiency [4], depend on the energetic characteristics of the localized states and the type of the localized states in the energy gap of the component layers. Considering all details mentioned above, this paper presents the results of the analysis of the edge of fundamental band and PL of the CdS layers, having a variable thickness, as a part of SnO<sub>2</sub>/CdS/CdTe/Ni solar cells.

## EXPERIMENTAL

The CdS/CdTe HJ have been deposited by CSS technique on Glass/SnO<sub>2</sub> substrate. The SnO<sub>2</sub> resistivity was  $\sim 20 \text{ } \Omega/\text{cm}^2$  and the transmission coefficient in visible and near IR regions of spectrum was  $0.87 \div 0.95$ . The thickness of CdS layers was  $0.27\text{--}1.2 \text{ } \mu\text{m}$  and the thickness of CdTe layers –  $3\div 4 \text{ } \mu\text{m}$ . The activation of SnO<sub>2</sub>/CdS/CdTe cells – annealing in presence of CdCl<sub>2</sub> at  $\sim 450^\circ\text{C}$  for 30 min.

The optical transmission, reflection and PL spectra have been measured, using the spectrophotometric device based on MДP-2 monochromator. The spectral resolution of the device in the whole spectral range is  $\sim 0.5 \text{ meV}$ . The PL spectra have been excited by N<sub>2</sub> ( $\lambda=0,334 \text{ } \mu\text{m}$ ) at 78K.

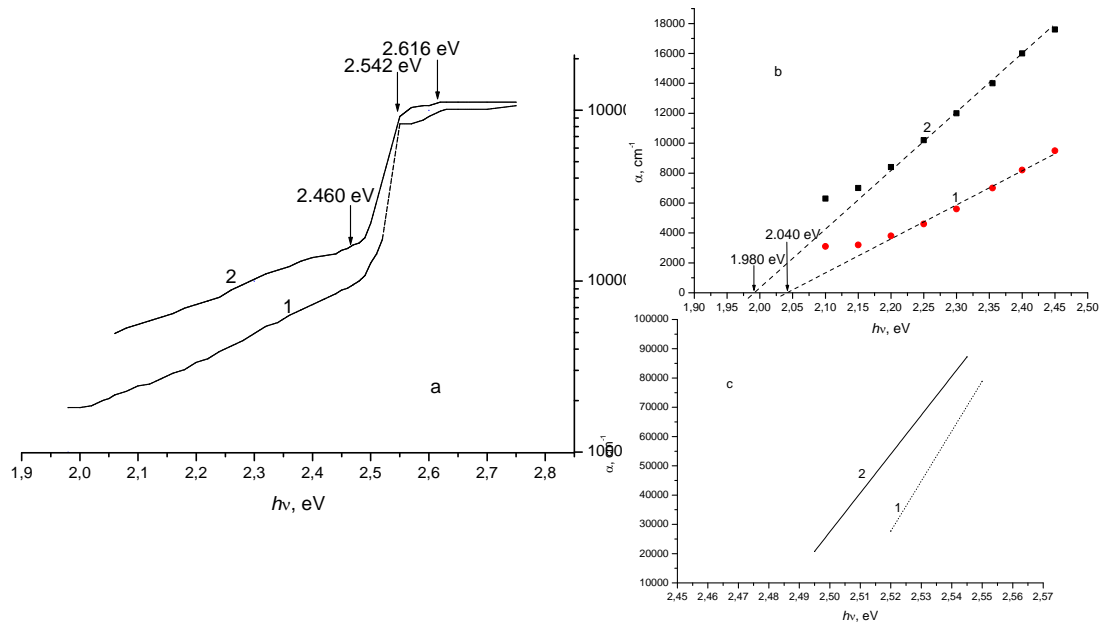
The absorption coefficient  $\alpha$  has been determined using the optical transmission and reflection data for samples with thicknesses satisfying the inequality:  $0.5 \leq \alpha d \leq 2.5$  (1).

## RESULTS AND DISCUSSION

The absorption spectra of CdS layers unannealed and annealed in presence of CdCl<sub>2</sub> are shown in Figure 1 curves 1 and 2 respectively. The  $\alpha=f(\hbar\omega)$  plot can be divided in three parts: the photons energy range  $\hbar\omega < 2.5 \text{ eV}$  – the absorption coefficient slowly decreases with photon energy decrease, the photons energy between 2.5 and 2.55 eV – the absorption coefficient increases from  $\sim 10^4 \text{ cm}^{-1}$  up to  $\sim 10^5 \text{ cm}^{-1}$  and the third energy region  $2.55 \text{ eV} \leq \hbar\omega \leq 2.9 \text{ eV}$  – the absorption coefficient is approx.  $\sim 10^5 \text{ cm}^{-1}$  and does not depend on the photon energy.

The annealing of the HJ in CdCl<sub>2</sub> results in the increase of the absorption coefficient, especially in the impurity absorption region ( $\hbar\omega < 2.5 \text{ eV}$ ). This process is determined by the increase of the concentration of the levels localized in the CdS band gap. The Cd atoms diffused in this layer are the most probable cause of the localized levels formation in the CdS band gap. At the same time, the localized levels, with the activation energy of the same order of magnitude as the binding energy of excitons are formed. As one can see from inset a, Figure 1, the  $\alpha=f(\hbar\omega)$  slope in the low energy region of the excitonic absorption – decreases.

Let us analyse the spectral dependence of the absorption coefficient of CdS layers in the mentioned above regions.



**Figure 1** The absorption spectra of CdS layers unannealed (1) and annealed (2) in presence of CdCl<sub>2</sub>.

The absorption coefficient value is less than  $10^4 \text{ cm}^{-1}$  for the unannealed CdS layers (curve 1) and for the annealed ones in the  $\hbar\omega < 2.5 \text{ eV}$  energy range. For CdS compound such values of  $\alpha$ , is characteristic for impurity absorption [5]. The  $\alpha=f(\hbar\omega)$  plot is presented in the inset b, Figure 1 (the ordinate scale is linear) from which by extrapolation of the linear segment to  $\alpha=0$ . The energy interval between the impurity level and the conduction band, for unannealed and annealed CdS layers, has been estimated as 2.04 eV and 1.98 eV.

As one can see from the plot (Figure 1, a, c), the absorption coefficient increases by an order of magnitude. The absorption coefficient exponentially increases with photon energy increase.

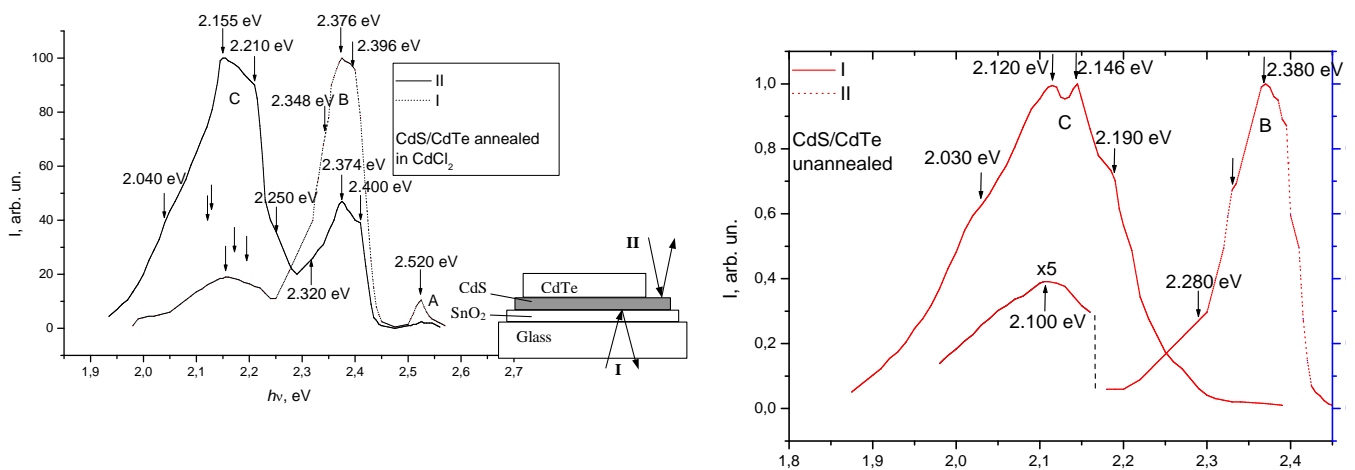
As it was shown in [6], the exponential dependence of the absorption coefficient on the energy fits also the wings of the bands formed by the free excitons interacting with optical phonons. The characteristic plot for these functions can be written as follows:

$$\Delta \ln(\alpha/\alpha_0)/\hbar\omega_0 = \sigma/kT \quad (2)$$

where:  $\sigma$  characterizes the measure of exciton-phonon interaction and it is a characteristic parameter for a given compound. As one can see from curves 1 and 2 Figure 1  $\sigma$  increases as a result of thermal annealing of CdS in the presence of CdCl<sub>2</sub>. Considering that the thermal annealing do not influence the excitons energies, one can conclude that structural changes occur in CdS layer after annealing that stimulate the excitons and optical phonon interaction.

Two thresholds one can see in  $\alpha=f(\hbar\omega)$  plot for  $\hbar\omega > 2.5$  eV localized at 2.542 eV and 2.616 eV, which have been identified as the first lines in the a and c excitonic lines.

The characteristic PL spectra of CdS layers grown on SnO<sub>2</sub> substrate are given in Fig. 2. The PL spectral dependence from the exterior layer surface Figure 2 (curve II) as well as from the SnO<sub>2</sub>/CdS interface (curve I) consists of three bands localized in the 1.95 – 2.55 eV energy range. One can notice from Figure 2, that only A band with intensity maximum at 2.520 eV has a symmetrical shape characteristic for exciton radiative annihilation. The first line of the A exciton series evidenced from the absorption maximum of the absorption is localized at 2.542 eV. The energy interval between these two energy states is ~22 meV. The A band can be explained as the radiative recombination of the bounded excitons, localized on a certain ionized centre with a optic



**Figure 2** The photoluminescence spectra for CdS/CdTe heterojunctions in presence of CdCl<sub>2</sub>. Inset – the PL excitation scheme.

phonon emission. The binding energy of the exciton is estimated to be 6-8 meV.

Due to the difference in lattice parameter of SnO<sub>2</sub> and CdS compounds, the structural defects are formed at the interface of the junction, which screen the electron-hole bonds and as a result the excitonic PL band is ~5 times weaker.

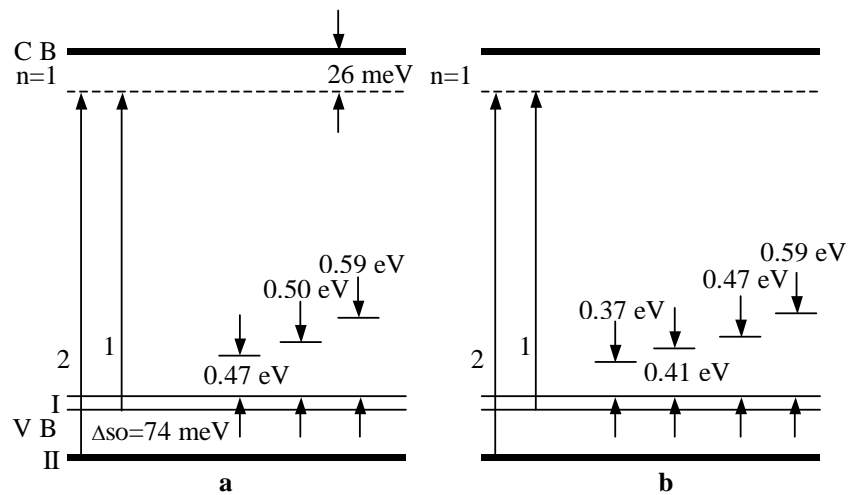
The presence of the defective layer at the SnO<sub>2</sub>/CdS interface result in the decrease of the intensity of green band (B), but the orange band (C) is strongly amplified. As it comes from the analysis of curves I and II, the structural defects in CdS are responsible for the band in 1.95 – 2.25 eV energy region.

The B and C bands (Figure 2) are the result of two or three elementary band superposition. One can estimate the probable energies of the component bands without any decomposition of the complex bands into elementary ones. This can be done by using the maxima and threshold energies on the band contour. The green band (B) can be considered as a superposition of three

elementary bands, having maxima at 2.400 eV, 2.374 eV and 2.320 eV, and the orange band – four band having energies: 2.250 eV, 2.210 eV, 2.155 eV and 2.04 eV.

The PL spectrum of unannealed CdS layer consists of green band (B), with the maximum at 2.380 eV and orange (C), with the maximum at 2.120÷2.140 eV. At the same time of the green band a threshold at ~2.28 eV reveals itself, which probably is a result of two band superposition: an intensive band at 2.38 eV and another, having a much less intensity with maximum at 2.26÷2.27 eV. The orange band can be formed by at least three elementary bands, two of them with the same intensity at 2.150 eV and 2.120 eV and a much weaker one at ~2.03 eV.

As it came from the analysis CdS layers deposited on Glass/SnO<sub>2</sub> substrates unannealed and annealed in presence of CdCl<sub>2</sub>, the radiative recombination energy levels are formed along with layer structural homogenization. The schematic diagram of the localized states in CdS, layers component of SnO<sub>2</sub>/CdS HJ before (a) and after (b) annealing are presented in Fig. 3.



**Figure 3** The schematic diagram of the localized states in CdS, layers component of SnO<sub>2</sub>/CdS HJ before (a) and after (b)

### CONCLUSIONS

1. The fundamental absorption band edge for annealed samples in CdCl<sub>2</sub> is determined by the active impurity absorption in the photons energy range of  $\hbar\omega < 2.5$  eV and by optical transitions with the formation of excitons. The analysis of the absorption spectra (78K) the energies of the first lines of the A and C exciton series were determined 2.542 eV and 2.616 eV respectively.
2. The structural defects and uncontrolled impurities from optically active energy states are localized at 0.58 eV from the valence band top. As a result of thermal annealing, new states are formed, the average energy of which is of 0.64 eV from the valence band top.
3. From the radiation spectra of the CdS layers, component of the SnO<sub>2</sub>/CdS (HJ) the energy diagram of the recombination levels were established, which participate to the impurity

luminescence both in unannealed and annealed layers. One should mention that the level with the energy of 0.59 eV is active as at the light absorption as well as its emission.

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