

THE LUMINESCENCE OF CdS and CdTe THIN FILMS, COMPONENTS OF PHOTOVOLTAIC CELLS

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The investigations of the photoluminescence spectra (78K) of CdS and CdTe thin films unannealed and annealed in presence of CdCl₂, components of SnO₂/CdS/CdTe/Ni heterojunctions are presented in this paper. The composition of CdS_xTe_{1-x} layer formed at the CdS/CdTe heterojunction interface has been estimated as x=0.06.

1. Introduction

As it was shown [1] CdS/CdTe heterojunction (HJ) based solar cells can have higher energetic characteristics than Si based solar cells [2]. The properties of CdS/CdTe heterojunctions depend on the thin film deposition technology [3], on the compounds used for manufacturing and thermal annealing regime [4]. The physical parameters, which influence the efficiency of the photovoltaic devices, are determined by the generation recombination mechanisms in the CdS and CdTe thin films and in the interface layer.

From the analysis of the photoluminescence (PL) spectra at 78K of CdS and CdTe films before and after thermal annealing in presence of CdCl₂, the spectrum of the recombination levels is determined. The composition of the interface layer is also presented in this paper.

2. Experimental

The CdS and CdTe layers, components of SnO₂/CdS/CdTe/Ni solar cells have been deposited by CSS and HWT. The CdTe:1% Sb single crystals and CdS powder (undoped) have been used as compounds for evaporation. The thicknesses of CdS layer was 0.5-1.4 µm, and the thicknesses of CdTe: 3-7 µm. As evaporated CdS/CdTe heterojunctions have been annealed in the presence of CdCl₂ at 690K for 15–60 min.

The photoluminescence spectra at 78K have been measured, by positioning the samples in the liquid nitrogen vapors. The PL excitation of CdTe films was carried out by He-Ne laser ($\lambda=0.6328$ µm). Its radiation allows the sounding of the energy spectra of the recombination levels in a CdTe layers, with the thicknesses less than de 0.1 µm. The surface density of the excitation flux was ~12 kW/cm². The PL of CdS films has been excited by N₂ laser ($\lambda=0.334$ µm) and with light, $\lambda=0.564$ µm, selected by a set of absorption filters from the spectrum of Hg lamp.

The luminescence spectrum has been decomposed by a monochromator with a diffraction grid (1200 and 600 mm⁻¹) and recorded by photomultiplier with a multialcaline photocathode sensitive in the 200-950 nm spectral range. The electrical signal has been analyzed in a selective regime with ~1 Hz band. The PL spectrophotometric device has been calibrated by using the Rhodamine 6J and GaAs single crystal etalon spectra.

3. Results and discussion

The PL spectra of the CdS layers – components of the CdS/CdTe HJ deposited by HWT and annealed for 30 min in the presence of CdCl₂ are shown in Figure 1. The spectrum consists of two

intensive bands – the band caused by radiative annihilation of the excitons, with maxima at 2.53 eV and yellow band, having a large maxima localized at ~2.1 eV. The presence of the green band with maxima at 2.4 eV is characteristic for crystalline CdS [5]. As one can see in Figure 1, the green band (C) with maximum at ~2.4 eV has a low intensity PL, in the spectrum registered from the SnO₂/CdS interface, and only a threshold can be seen from the “free” CdS surface (II) (Figure. 1).

The defects density at the SnO₂/CdS structure interface (I) is higher than the one at the free surface. This fact reflects itself in the intensity decrease of the excitonic line $\hbar\omega_{\max}=2.53$ eV and the increase of the impurity bands PL A ($\hbar\omega_A \approx 2.1$ eV) and C ($\hbar\omega_C \approx 2.4$ eV).

The edge of the light absorption in CdS films is formed by the first line of the excitonic series A ($\hbar\omega_A \approx 2.553$ eV). Assuming that these lines are related to the free excitons, than line B from the emission spectra, can be attributed to the radiative annihilation of the bounded excitons with participation of optical phonons, having the energy about $\sim 20 \div 23$ meV.

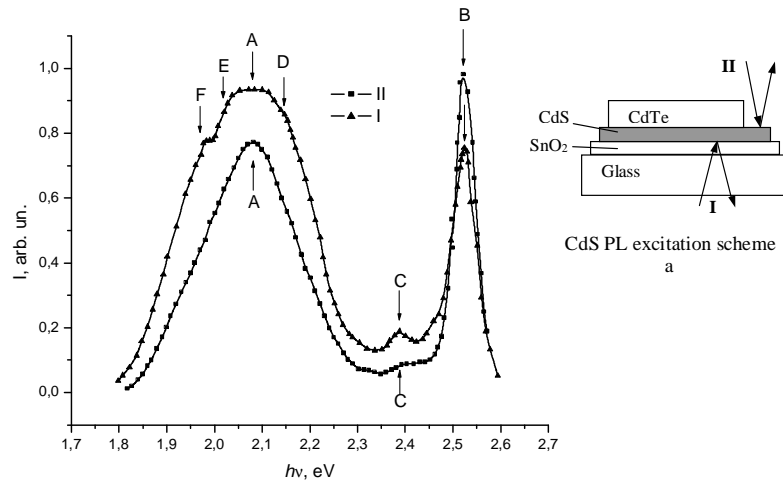


Fig. 1. The PL spectra (78K) for CdS HWT layer annealed in presence of CdCl₂- component of CdS/CdTe HJ.

The luminescence spectra of the undoped CdS single crystals at 78 K consist of three bands [6] – the excitonic band at ~2.583 eV, green band (2.384 eV) and yellow band localized in the 2.175 eV ÷ 1.907 eV photons energy region.

The PL spectra of CdS thin films, deposited by CSS, have an analogous shape to the one presented in Figure 1.

The bounded excitons radiation line contour is analyzed in [7] considering a simplified model. The tunneling relaxation in the bounded excitons system is assumed, along with the assumption that the probability of the tunneling “jump” does not depend on the distance between the exciton localization centers.

The intensity of the radiation of the excitonic line, excited with nonpolarized light (the majority of crystallites in CdS thin layers are oriented along *c* axis perpendicular to the surface) with $\hbar\omega > E_g$ and if the spin relaxation of the excitons is not considered (this parameter is about $10^{-11} \div 10^{-12}$ s in CdS and GaSe single crystals) [8] can be written:

$$I_{ex}(E) = G_0 \frac{\alpha_1 [1 + \alpha_1 (1 + \beta_1)]}{\left[\exp\left(-\frac{\varepsilon}{\varepsilon_0}\right) + \alpha_1 (1 + \beta_1) \right]^2} \quad (1)$$

where G_0 – the excitons generation rate, proportional to the intensity of the exciting beam; $\varepsilon_0 = \hbar\omega_{\max}$ – the energy of the maxima of the excitonic line. The nondimensional coefficients can be determined as follows:

$$\alpha_1 = \frac{\tau_{10}}{\tau_{ri}} \text{ and } \beta_1 = \frac{\tau_{ri}}{\tau_{nr}} \quad (2)$$

τ_{10}^{-1} is the probability of tunneling of the bounded excitons from the state localized at the edge of mobility with $\varepsilon=\varepsilon_0$ to all other states with energy less than the energy of the localized excitons; τ_{nr} – the average nonradiative recombination time of the bounded excitons; τ_{ri} – the average radiative recombination time of the bounded excitons.

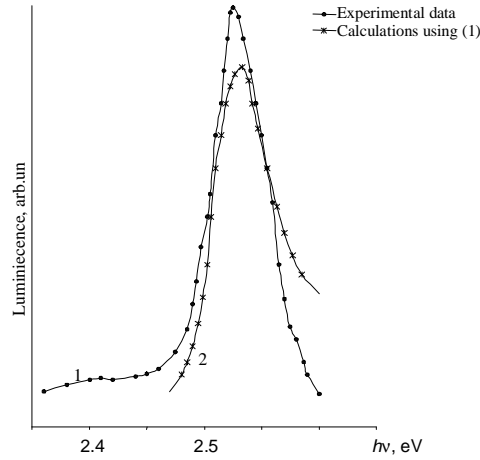


Fig. 2 The exciton PL spectra (78K) for CdS, experimental data 1 and fitted according to the considered model 2.

An example of the spectral distribution of the excitonic PL intensity with maximum at $\varepsilon_0=\hbar\omega_{\max}=2.53$ eV is shown in Fig. 2. As one can see, for energies $\varepsilon<\varepsilon_0$, the experimental plot correlates well with the dependence calculated according to (1), where $\alpha_1=0.02$ and $\beta_1=3.5$ were considered. The calculations according to (1) have considered exciton generation rate normalized to 1. The mechanism of PL radiation of the excitons localized on the ionized centers in CdS thin films is assumed to be according to the energetic relaxation of the bounded excitons with constant probability.

The PL spectra of CdTe deposited by HWT are presented in Figure 3. The thickness of CdS layer on which the CdTe layer was grown was ~ 1.3 μm and had a hexagonal structure and the thickness of CdTe was ~ 6.2 μm . As one can see from this figure, the excitonic PL can be observed only from the “free” side of CdTe layer(II). The maximum of the excitonic peak is localized at 1.580 eV and correlates well with the position of the free excitons in CdTe evidenced from the reflection and absorption spectrum [9]. A threshold at 1.558 eV is observed, which is caused by the radiative annihilation of the localized excitons (Their concentration is relatively low in these samples) with phonon emission or is the phonon replica of the resonant peak.

The absence of the excitonic line in CdTe layer at the interface of HJ is due to a high concentration of mechanical and structural defects caused by the lattice parameters discrepancy of the wurtzite type CdS films and zincblende type CdTe films.

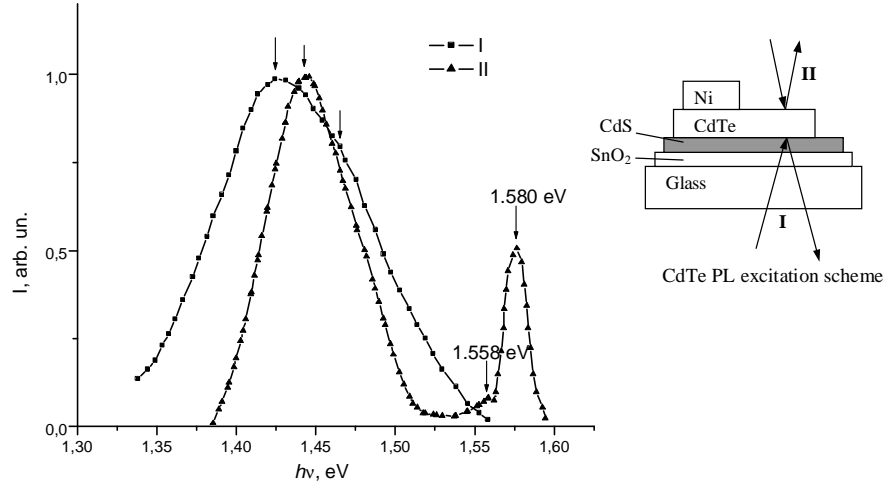


Fig. 3. The PL spectra (78K) for CdTe HWT (6.20 μm) thin film, annealed in the presence of CdCl_2 for 30 min, component of CdS/CdTe HJ.

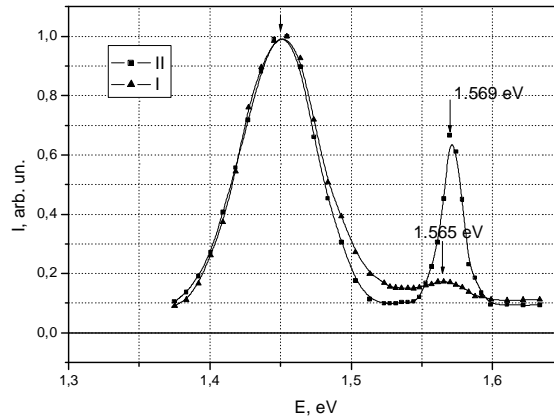


Fig. 4. The PL spectra (78K) for unannealed CdTe CSS (3.86 μm) thin film, component of CdS/CdTe HJ.

The PL spectra at 78K for the CdTe deposited by CSS (CdTe–3.86 μm , CdS–1.14 μm), component of CdS/CdTe HJ unannealed are presented in Figure 4. The spectrum recorded from the “free” CdTe surface CdTe (II) and from the excitation of the interface layer (I) consist of two bands – impurity band at 1.450 eV and excitonic band at 1.569 eV (II) and 1.565 eV at the interface of HJ (I). One can notice that the intensity of the excitonic band at the interface of HJ is ~ 3.5 weaker, indicating the presence of a high defects concentration, which create ionized centres (the excitons are bounded on them) and screen the electron-hole bonds.

The PL spectra (78K) of CdTe film (~ 4 μm) annealed for 15 min is presented in Figure 5. The excitonic band recorded from the exterior CdTe surface and the one from the CdS/CdTe HJ interface (I) has a symmetric shape and can be described by a Gauss contour, which can be written as:

$$y = y_0 + \frac{A}{W \sqrt{\frac{\pi}{2}}} \exp \left[-\frac{2(x-x_0)^2}{W^2} \right] \quad (3)$$

where: A –total area under the curve from the baseline, y_0 –baseline offset, W – 2 “sigma”, approximately 0.849 the width of the peak at half height, x_0 –center of the peak (corresponding to the

maximum of the excitonic line). The parameters from (3) satisfying the experimental data are given in Table 1.

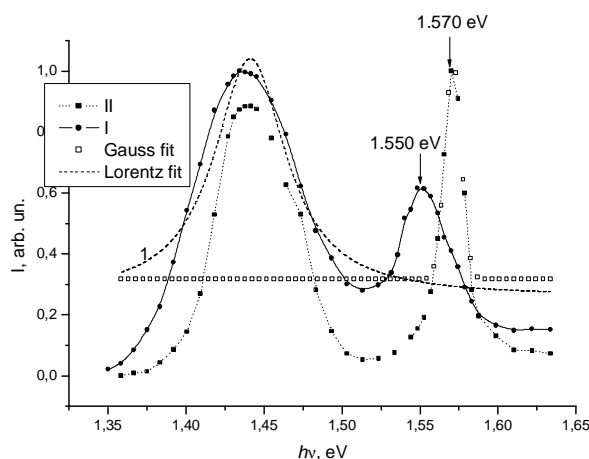


Fig. 5. The PL spectra (78K) of CdTe CSS ($\sim 4 \mu\text{m}$) thin film, annealed in the presence of CdCl_2 for 15 min, component of CdS/CdTe HJ.

Table 1. The parameters from (3) satisfying the experimental data– Gaussian fit.

y_0	0.31689	± 0.05446
x_0	1.57118	± 0.00215
W	0.01027	± 0.00444
A	0.00923	± 0.00367

The maximum of the excitonic peak is positioned at 1.570 eV and it is shifted by $\sim 11 \text{ meV}$ to lower energies region relative to the energy of free excitons. The Lorentzian approximation has been performed for impurity band. As one can see from the experimental curve $I_{\text{PL}}=f(\hbar\omega)$ and the Lorentzian fit, the last one has on the entire PL band contour. The algebraic expression of the band by a Gaussian points at a one type of recombination levels of radiative recombination [10].

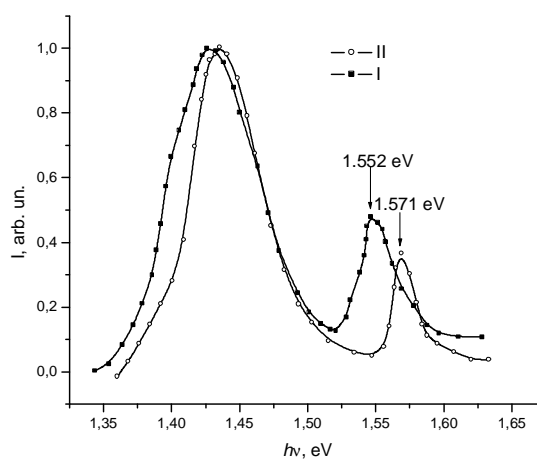


Fig. 6. The PL spectra (78K) of CdTe CSS ($\sim 4 \mu\text{m}$) thin film, annealed in the presence of CdCl_2 for 30 min, component of CdS/CdTe HJ.

As the annealing time increase up to 30 min (Figure 6), the intensity of excitonic PL from the exterior surface of CdTe decreases ~ 3 times and the intensity of the impurity band increases. The same tendency has been observed for the layer at the interface of HJ. In this case, the intensity of the excitonic PL $\hbar\omega=1.552$ eV decreases relative to 15 min annealed sample.

The PL spectra from the exterior surface of CdTe side (II) and from the CdS/CdTe interface (I) HJ after 1 h annealing in presence of CdCl₂ are given in Figure 7. As a result of this technological procedure the maximum of radiative annihilation of the localized excitons in CdTe (II) layer shifts to lower energy region ($\Delta E=3$ meV). A small shift to lower energies, is observed for the excitonic band (I) at the interface of HJ. The annealing time increase up to 1 h in presence of CdCl₂ results in the increase of the concentration of impurity states which form the impurity band at 1.44 eV.

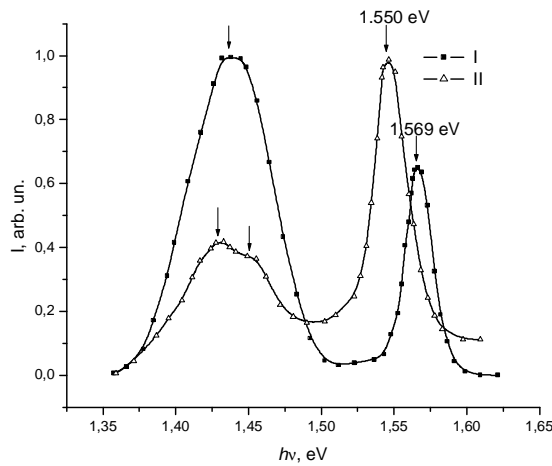


Fig. 7. The PL spectra (78K) of CdTe CSS (~ 4 μm) thin film, annealed in the presence of CdCl₂ for 60 min, component of CdS/CdTe HJ.

The excitonic PL band at the CdS/CdTe HJ interface annealed 1 h, has a symmetric shape characteristic for the localized excitons, described by classic energy distribution of the excitons (Gauss). The annealing time increase decreases the concentration of the localized states, responsible for the impurity band formation (~ 1.43 eV). The complex structure of the impurity band at 1.425-1.465 eV reveals itself. So, as a result of 1 h annealing the structural defects are revealed at the interface of the junction. These defects appear at the same time as the formation of an intermediary compound between CdS and CdTe (CdS_xTe_{1-x} solid solutions). The Gauss shape of the excitonic band and the low intensity of the impurity band indicates the high homogeneity of the layer at the CdS/CdTe interface.

As it was shown CdS and CdTe form continuous series of solid solutions CdS_xTe_{1-x} [11, 12]. Considering, that for x values from 0 to 0.2 the optical band gap of CdS_xTe_{1-x} decreases linearly and analyzing the position of the excitonic band (from the presented spectra), one can estimate the average composition of the interface layer. An intermediary layer between hexagonal CdS and zincblende CdTe, for CSS CdS/CdTe HJ 1 h annealed, is formed, with an average composition $x=0.06$.

4. Conclusions

The PL spectra of the CdTe layers obtained by HWT consists of a band determined by radiative annihilation of free excitons ($\hbar\omega=1.580$ eV) and a large D-A recombination band at $\hbar\omega=1.541$ eV. Due to lattice parameter mismatch of CdS and CdTe, localized states are formed at the interface of the junction, which screen the excitonic bonds. In the interface layer the recombination takes place through donor and acceptor states.

The PL Spectra of CSS CdTe layers, components of CdS/CdTe HJ, consists of an impurity band at 1.450 eV (the same bands are present in HWT CdTe) and a band determined by excitons localized on ionized states with a ~ 10 meV binding energy. The impurity band is amplified and the exciton band intensity decreases at the interface of CdS–CdTe heterojunctions.

The Gaussian fits well the contour of the excitonic and impurity PL bands of CdTe thin films.

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