KINETICS OF PHOTOCONDUCTIVITY AND PHOTOLUMINESCENCE OF CdS/CdTe HETEROJUNCTIONS

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The photoluminescence and absoption spectral distribution close to the edge of fundamental band were studied in the CdS and CdTe films components of the CdS/CdTe heterojunctions. Recombination level energetic position was determined. The annealing of the CdS/CdTe heterojunctions in presence of $CdCl_2$ results in formation of new recombination levels, revealed by a luminescent band in the energy range of 1.6-1.7 eV and by the shift of the impurity band maximum to the red wavelength region by 50 meV.

1. Introduction

The presence in the semiconductor layers of the surface states leads to a slow decrease of the photosensitivity with the photon energy increase conditioned by the slow increase of the absorption coefficient for energies $\hbar\omega > E_g$. The concentration of the interface states, as well as recombination rate of the nonequilibrium charge carriers determines the optimal parameters of the semiconductor materials required for obtaining the maximum efficiency of the photovoltaic devices based on them.

CdTe is a semiconductor material, which has direct optical transitions, the edge of the absorption band is situated at ~ 1.45 eV. In the center of excitonic band, the absorption coefficient, in a narrow energy interval, close to the photoeffect energy threshold (~60 meV), increases by 4 orders of magnitude, reaching $\sim 10^5$. These parameters classify this material to be one of the perspective materials of the solar energetics.

The quantum efficiency of the photovoltaic cells based on CdS-CdTe heterojunctions varies in a large range and depends on the thickness of the CdS layer and kinetics characteristics of the recombination levels. The spectrum of the levels localized in the energy band of CdTe is a function of the annealing in presence of $CdCl_2$.

As a result of the analysis of absorption, luminescence and photosensitivity spectra, the energy of the recombination levels was determined. The dynamics of modification of the energy states as a result of thermal annealing in presence of $CdCl_2$ is being analyzed.

2. Experimental procedure

CdS−CdTe heterojunctions have been manufactured by consecutive deposition of CdS and CdTe thin films, using CSS, on glass (2x2 cm^2) covered with transparent conductive SnO_2 layer (conductivity 20-80 $\Omega^{-1}\cdot m^{-1}$, optical transmission ~85% in the 400-960 nm

spectral region). CdS thickness varied as 0.4-1.7 μm and CdTe − 4-6 μm. SnO_2 was used as an ohmic contact to CdS and Ni was used as CdTe back contact.As deposited CdS−CdTe were of low photosensitivity.At 100 mW/cm^2 the short-circuit current reaches 115-180 μA/cm^2, and the open circuit voltage is 0.30-0.34 V. For increase of the cell parameters, a heat treatment in presence of $CdCl_2$ is needed. SnO_2/CdS/CdTe structures were dipped into a $CdCl_2$:H_2O saturated solution and annealed in air 400°C for 30 min. After cleaning the CdTe surface from $CdCl_2$ residue, Ni deposition followed.After annealing, photovoltaic parameters are 18.6 mA/cm^2 and 0.65 V for the same illumination conditions. The *ff* equal to 0.4 was reported, showing a high series resistance. The refraction indexes and the thickness of CdS and CdTe have been determined from the transmission interference in the 400-2700 spectral region.

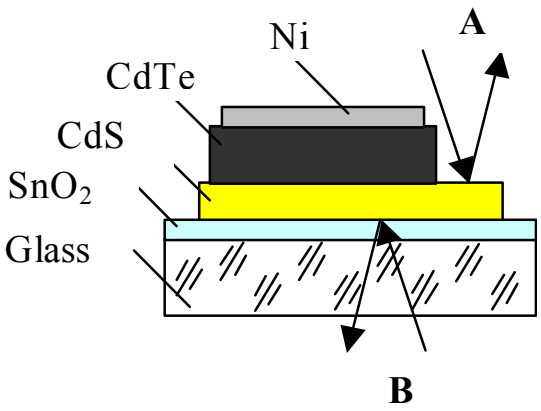


Figure 1. Photoluminescence excitation scheme for CdS

The absorption spectra have been measured by a photometric device with a МДР-2 monocromator, using the recording method developed by authors [1]. The energetic resolution, at the recording of the absorption and photoluminescence, was 0.5 meV.

The luminescence spectra of CdS and CdTe layers have been excited by N_2 (λ=3341 Å) and He-Ne (λ=6328 Å) at room temperature and 77 K.

3. Experimental results and their interpretation

Fig. 2 shows the photosensitivity spectral dependence of the SnO_2/CdS/CdTe/Ni at 298 K. The violet and red edges of the W(ħω) are determined by the absorption edges of CdS films (Fig. 3) and CdTe (Fig. 4) [2]. As one can see from Fig. 2 and Fig. 3, for CdS layer thickness less than 1 μm, a part of the incident beam (ħω>2.3 eV) reaches the interface of the CdS-CdTe junction, but in this spectral range there is no nonequilibrium charge carrier generation. Such phenomena can be

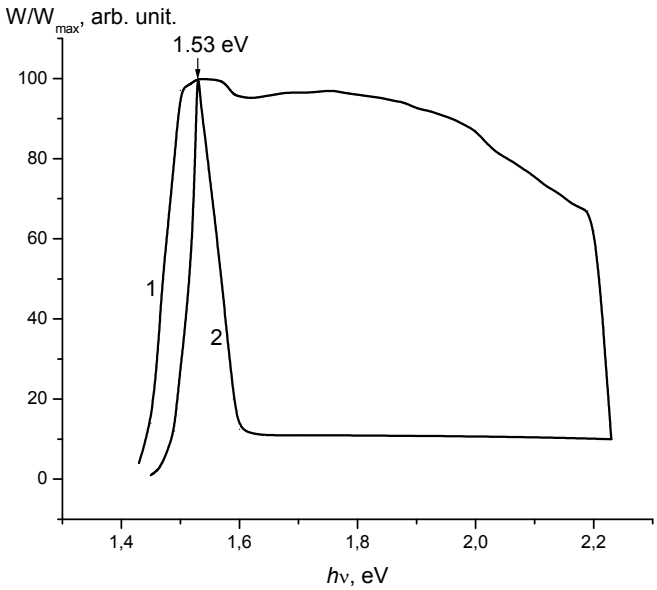


Figure 2. The spectral dependences of quantum efficiency for SnO_2/n-CdS/p-CdTe/Ni thin film solar cells at 300K (1) and at 78K (2)

explained if one supposes that nonequilibrium charge carriers generated in the interface layer (a region with a high concentration of the structural defects) recombine through the interface states. The analysis of the photoconductivity kinetics of CdS layer had shown that the lifetime of the generated electrons is less that 10^{-7} s. Taking into account than U_{oc} is about 0.5 V, the electrons, generated by the photons with energies from the fundamental absorption band region recombine in a layer having a thickness <2 μm.

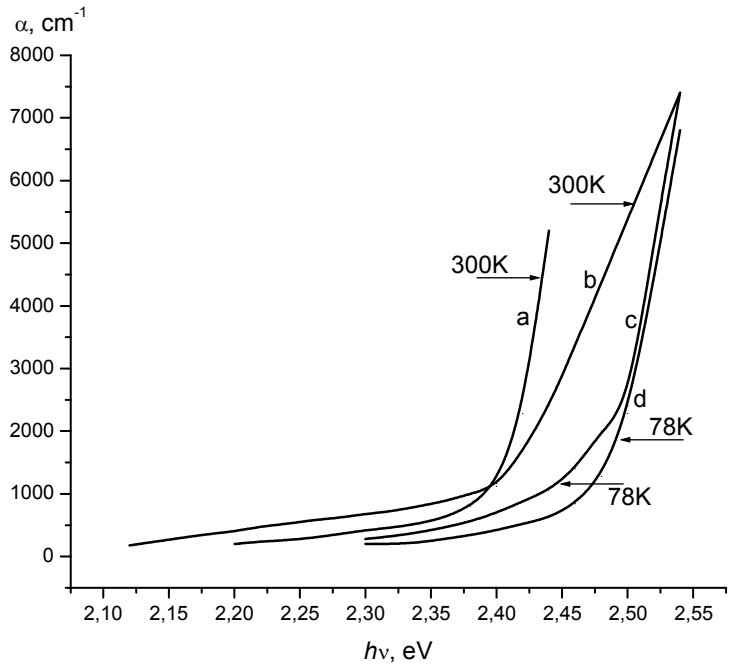


Figure 3. The absorption spectral dependences for the annealed n-CdS films at 78K (c) and at 300K (b) and for unannealed n-CdS films at 78K (d) and at 300K (a)

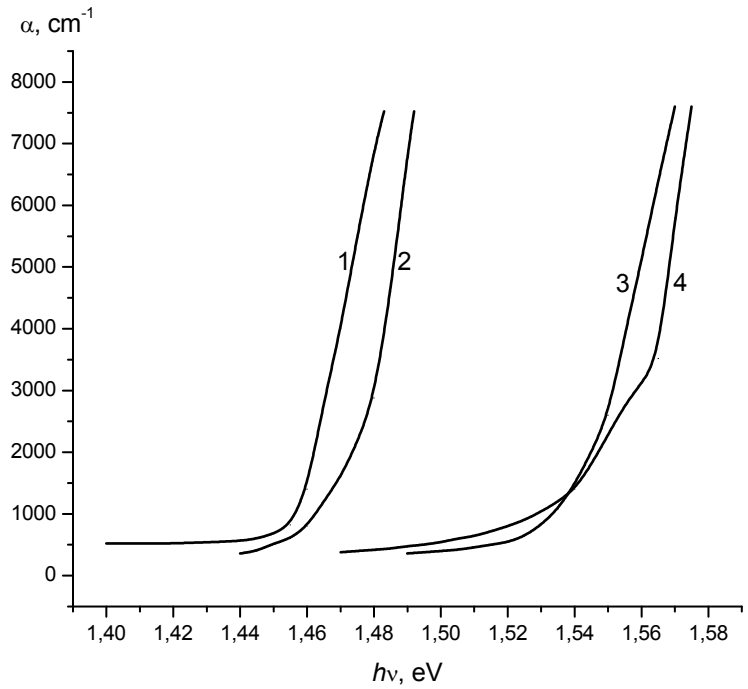


Figure 4. The absorption spectral dependences for the unannealed (1) and annealed (2) p-CdTe films at 300K and for unannealed (3) and annealed (4) films at 78K

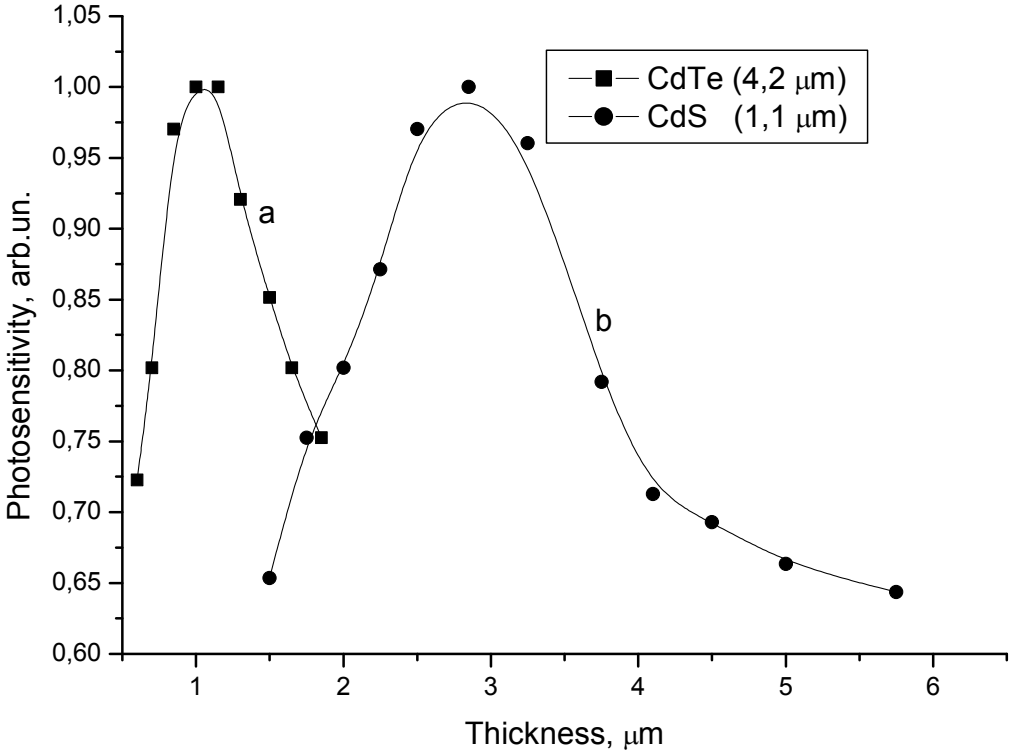


Figure 5. Photosensitivity vs. CdTe thickness (CdS 1.1 μm), and CdS thickness (CdTe 4.2 μm)

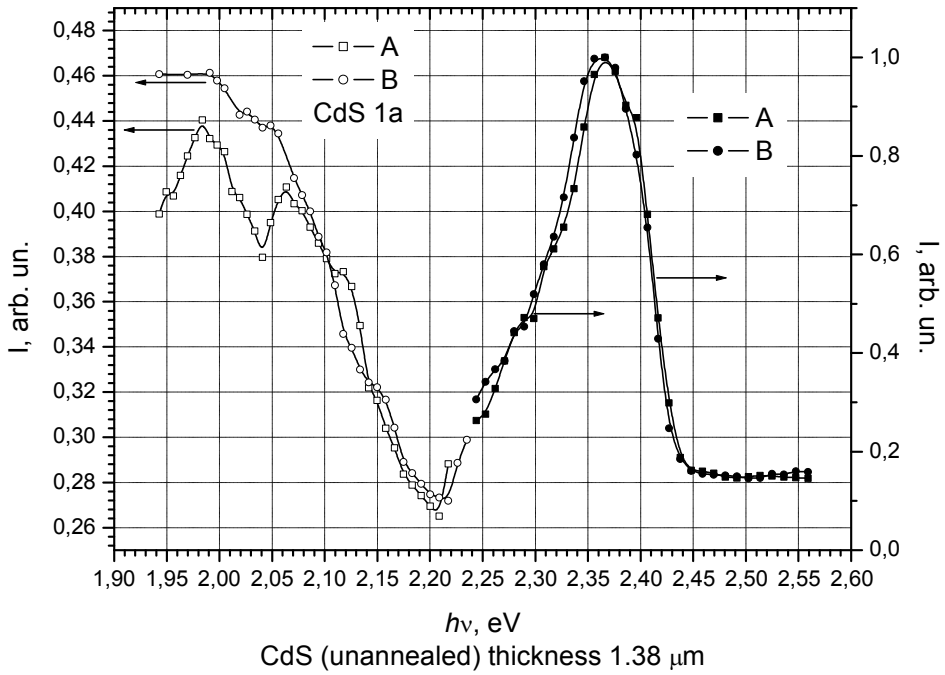


Figure 6a. Photoluminescence spectra of CdS films at 77K for SnO_2/CdS/CdTe/Ni structure unannealed ($\hbar\omega_{MAX}\approx 2{,}37$ eV) (A: $\hbar\omega_1=1.98$ eV, $\hbar\omega_2=2.07$ eV, $\hbar\omega_3=2.12$ eV)

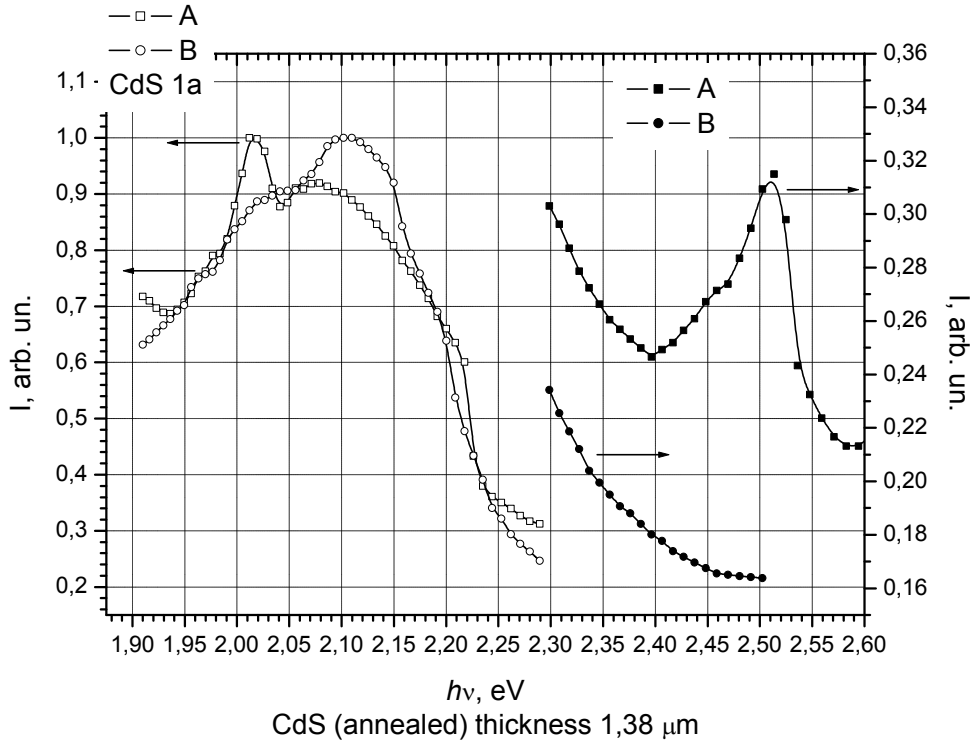


Figure 6b. Photoluminescence spectra of CdS films at 77K for SnO_2/CdS/CdTe/Ni structure annealed in presence of $CdCl_2$ ($\hbar\omega_i$=2.02 eV, $\hbar\omega_2$=2.10 eV, $\hbar\omega_{ex}$=2.52 eV)

The dependence of the normalized photosensitivity as a function of CdS layer thickness (curve a) for a CdTe layer thickness of 4.2 μm and CdTe thickness (curve b) for a CdS thickness of 1.1 μm one can see in Fig. 5. It is obvious (Fig. 5) that the optimal thickness for the film components of the heterojunction (HJ), for an effective photogeneration of charge carrier current through the junction is 1.0-1.2 μm and 2.5-3.2 μm for CdS and CdTe respectively.

Let us follow the influence of the heat treatment of CdS-CdTe HJ in presence of $CdCl_2$ on the diagram of the localized energetic states in the CdS band gap and CdTe by means of photoluminescence spectra. It is well known [3,4] that as a result of thermal annealing the photocurrent increases by 8-10 times.

The photoluminescence spectra of CdS layers recorded from the SnO_2 side (curve B) and "free" side (curve A) (the CdTe will be grown on this side) are given in Fig. 6. The CdS PL spectra for the unannealed HJ are shown in Fig. 6a and for the annealed structures in the presence of $CdCl_2$ in Fig. 6b. The thickness of CdS layer was ~1.0 μm. The PL spectra of unannealed films consist of two bands: green band with maximum at $\hbar\omega$=2.37 eV and yellow, localized in the $\hbar\omega$<2.2 eV region. As one can see, the energy of the green band is not affected by the structural defects at the SnO_2-CdS interface. The homogenization of the crystallites from A side, leads to a better revealing of the structure of the yellow band. There are maxima at $\hbar\omega_1$=1.98 eV and $\hbar\omega_2$=2.07 eV and a threshold at $\hbar\omega_3$=2.12 eV. The yellow band demostrates a complex structure of the recombination levels in the CdS band gap.

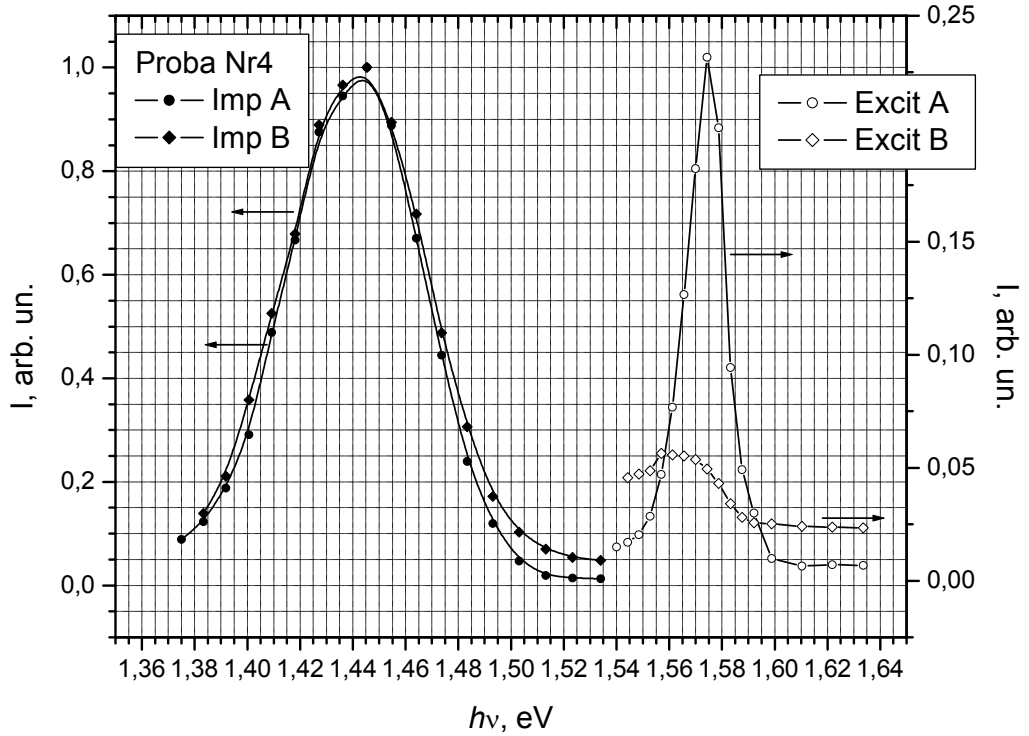


Figure 7a. Photoluminescence spectra of CdTe films at 77K for SnO_2/CdS/CdTe/Ni structure unannealed($\hbar\omega_{ex}$=1.575 eV, $\hbar\omega_{imp}$=1.45 eV)

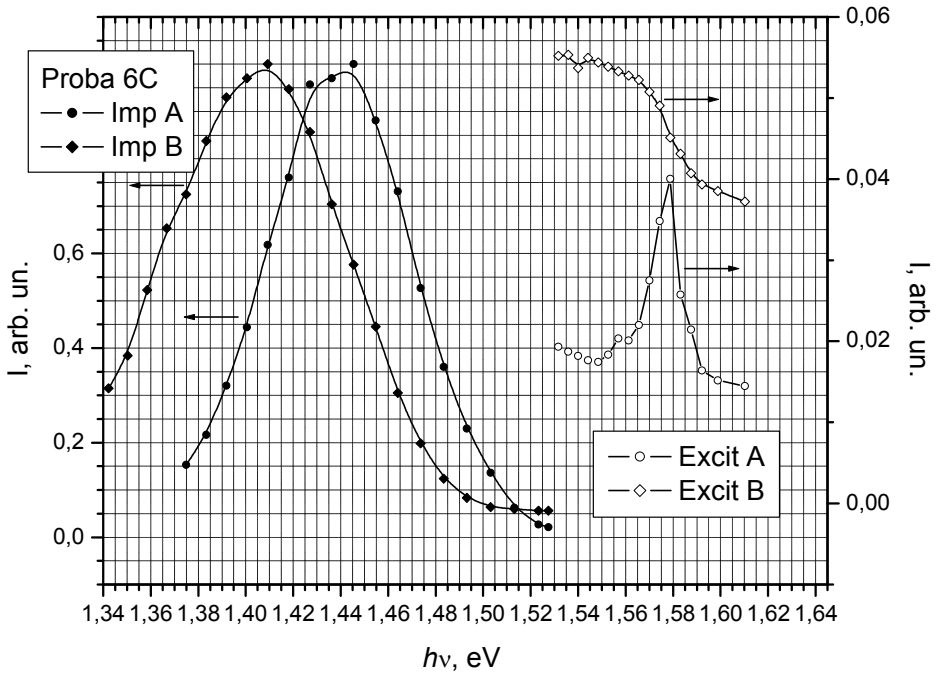


Figure 7b. Photoluminescence spectra of CdTe films at 77K for SnO_2/CdS/CdTe/Ni structure (30% fotocurrent decrease) annealed in presence of $CdCl_2$

The thermal annealing in the presence of $CdCl_2$ results in an essential modification of the diagram of the recombination levels in CdS layer. The green band in the region of CdS-SnO_2 junction is suppressed, but the yellow band's intensity increases, having a broadened maximum at ~2.10 eV and a narrow one at 2.02 eV. Probably, as a result of heat treatment, a diffusion of Sn atoms occurs and at the same time Cd, Cl and O atoms diffuse as well in CdS layer. This process results in a new energetic diagram for the interface layer SnO_2-CdS.

There is a entirely different behavior of PL spectra recorded from CdTe side. The annealing results in disappearance of the defects in the metal's sublattice and excitonic luminescence lights up with maximum at $\hbar\omega_{ex}$=2.52 eV. There is a threshold at low energy side of the excitonic line situated at 60 meV from it. As a result of thermal annealing, a broad band of the recombination levels, positioned at 0.5 eV from the valence band top is formed in the CdS bandgap. These levels determine the CdS radiative spectra.

The analysis of the luminescent spectra of CdTe as a part of HJ is presented in this paper for two HJ, one having the maximum photocurrent and one having 30% less photocurrent.

Fig. 7 gives the PL spectra for CdTe layer at 77 K. The luminescence of the unannealed films consists of excitonic line $\hbar\omega_{ex}$=1.575 eV and an impurity band (with no structure) $\hbar\omega_{imp}$=1.45 eV.

The structural defects in the CdS-CdTe heterojunction strongly suppress the excitonic line (Fig. 7a curve B), and do not influence the structure of the impurity band. Taking into account that the intensity of the impurity band increases by 5 times we can conclude that the structural defects cause the increase of the concentration of the recombination levels, responsible for the formation of the impurity band.

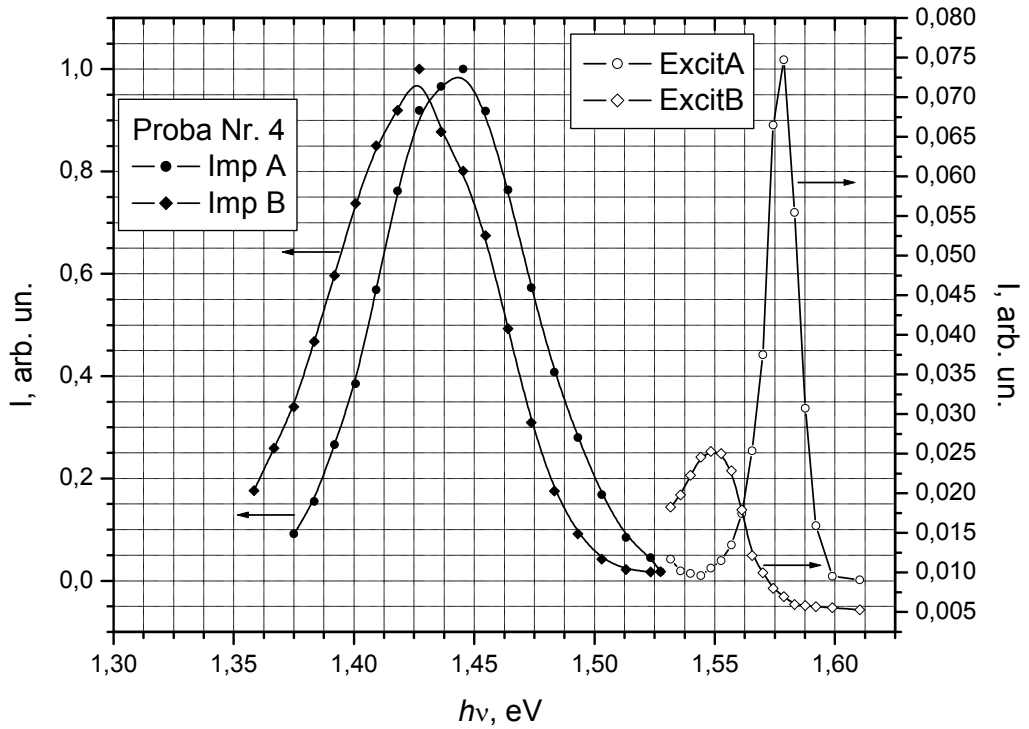


Figure 7c. Photoluminescence spectra of CdTe films at 77K for SnO_2/CdS/CdTe/Ni structure annealed in presence of $CdCl_2$ ($\hbar\omega_{ex}$=1.572 eV, $\hbar\omega_{imp}$=1.445 eV)

The annealing modifies the structure of the PL spectra (Fig. 7b). The excitonic line is suppresed at the "free" surface. At the interface of the junction a layer appears, being characterized by low energy levels (a complete suppresing of the excitonic line and formation of a band in the 1.54-1.57 region). The maximum of the impurity band recorded from the interface of CdS-CdTe structure is shifted to lower energy region by ~30 meV, relative to thsame band recorded from the "free" surface.

Fig. 7c represents the radiative spectrum of CdTe film annealed in $CdCl_2$, part of the HJ, having a high value of photocurrent. The PL spectra from "free" surface consist of excitonic line with a maximum at 1.572 eV and an impurity band with a maximum at 1.445 ev. The structure of the PL spectrum in the interface layer is modified. One can see that the excitonic line is suppressed, and a new band appeared. The latter is shifted by 25 meV from the excitonic line to the low energy region. The impurity band is modified as well. The maximum at 1.445 eV decreases and it appears as a step, but the band at $\hbar\omega$=1.425 eV increases. One can conclude, that CdTe layers with a high photogeneration, have low energy radiative levels and the energy state diagram is completed by levels with a high lifetime, this fact being demonstrated by the studies of the kinetics of photoconductivity of CdTe.

4. Conclusions

- SnO_2/CdS/CdTe/Ni solar cells are photosensitive in the 1.45-2.25 eV energy range. The generation of the nonequilibrium charge carrier occurs in CdTe layers in the junction region.
- As a result of annealing of CdS-CdTe HJ in the presence of $CdCl_2$ along with modification of the energy states diagram in CdTe bandgap, localized levels are formed. The latter screen the e-h (exc.) bonds in CdS films. The CdTe PL spectra are modified as well.
- The structural defects of CdTe layer from the interface of the junction result in suppress of the excitonic luminescence and the amplification of the 1.42 eV band. As a result of heat treatment new recombination levels were formed in CdTe, near the junction. They revealed themselves by the shift to lower energies by ~20 meV of the impurity bands ($\hbar\omega$=1.425 eV). A new band was formed (1.55 eV) along with suppressing of excitonic line.

References

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