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Photoluminescence studies of the interface of CdS/CdTe heterojunctions

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The photoluminescence analysis of CdS/CdTe interface layer of CdS/CdTe heterojunction has been carried out in the 15-100 K temperature range. An attempt to correlate observed PL features with the CdS_xTe_{1-x} layer presence at the interface of the heterojunctions was made. It is assumed the 1.525 eV band has an excitonic origin and 1.37X PL band is a characteristic impurity band due to CdSTe layer. Comparative plots showing SnO_2/CdTe PL spectra are given as well.

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1 Introduction CdS/CdTe heterojunctions are one of the most promising candidates for solar energy conversion. It is well known that CdTe based solar cells show an efficiency of 16.5% [1]. Although the materials have been extensively studied, there is still a number of topics, which need attention, especially the ones focusing on efficiency limiting factors. Among them, one can name recombination levels (and their energetic position) formed in the components of the heterojunction, and especially at the interface. These localized states can be due to structural defects in the metal's sublattice (Cd), or in the chalcogen sublattice (S, Te). One of the possibilities is to study them by analyzing the photoluminescence (PL) spectra of the samples excited from the CdS/CdTe interface. Despite the fact that CdTe PL is extensively studied, one should mention a lack of data on the interface PL. A few attempts have been made by studying bevel etched samples [2], but the problem is still open for discussion. PL studies of CdS/CdTe interface can reveal radiative states due to different impurities and potentially explain their role and influence on the cells' performance. The role of impurities such as oxygen and chlorine, present in most high efficiency cells has been previously studied but the results are sometime contradictory. Impurities' influence at the interface by PL has still to be determined.

This paper describes research focused on correlating the PL characteristics of CdS/CdTe junctions to deposition methods of CdS, annealing in presence of cadmium chloride and oxygen presence in CdTe films.

2 Experimental details

Solar cell structures (i.e. CdS/CdTe heterojunctions with and without the back contact) were prepared on SnO_2 coated borosilicate glass by using previously described processes [3]. The transparent conductors were prepared in the form of a (SnO_2:F/SnO_2) bi-layer by using MOCVD. The chemical bath deposition (CBD) process was used for the preparation of CdS films at a temperature of 85 °C. The close-spaced sublimation (CSS) process was used for the preparation of CdS films at a temperature of 560 °C as well. Cadmium telluride films were deposited by using the close-spaced sublimation process (CSS). For this study, CdTe was deposited in inert (He), or O_2-containing ambient (He+O_2) at a substrate temperature in the range of 580-600 °C (unless specified in the text, one should consider that CdTe is deposited in He+O_2 ambient (!)). CdTe deposition was followed by typical $CdCl_2$ heat treatment [3].

The PL measurements were carried out using an Ar-Ion laser with maximum output power of 200 mW at 488 nm, the wavelength used for these measurements. The in-

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cident beam power, before the focusing lens was 50 mW. A grating-based monocromator (SPEX-500M) and a Ge detector (model EO-817L) were used for the signal spectral detection. The samples were cooled using a RMC Cryosystems (Model 22HC) closed-loop cryostat with a CTI-Cryogenics (Helix Technology Corporation) 8001 controller and 8300 Compressor. The lowest stable sample temperature was 15±0.5 K, using a LakeShore 805 Controller. The excitation intensity was varied by using neutral density filters. The measurement temperature range used was 15-100 K. Photoluminescence spectra were obtained by exciting the samples at the CdTe/CdS interface (i.e. the samples were excited through the glass substrate). The energetic resolution for the measurements was 0.5-3 meV.

3 Photoluminescence of CdS/CdTe interface

The low temperature PL spectra for the excitation from the interface have been briefly studied and compared together with the PL from free CdTe surface elsewhere [4]. The CdS films in the above mentioned paper have been deposited by CBD only. The key processing variations and their influence on the interface PL spectra will be discussed below, in the sections that follow.

The PL spectra are highly sensitive to the distribution of the impurities in the band gap. It is reasonable to expect that the recombination levels in the bandgap will be influenced by diffusion of S atoms from the CdS layer during deposition and annealing processes with a resulting formation of CdS_xTe_{1-x} solid solutions as previously shown in [5-7]. Due to the fact that a new compound is formed from a mixture of Cd, S and Te atoms one should expect the appearance of a characteristic excitonic peak and other features in the interface PL spectra.

3.1 CdS/CdTe interface PL (CdS thin film deposited by CSS) The low temperature PL spectra obtained by exciting the CdS/CdTe side of an unannealed sample consists of two bands with peak intensities localized at 1.373 eV and 1.525 eV as shown in Fig. 1a. One can follow the modification of the PL spectra with temperature increase. The 1.373 eV band peak intensity decreases much faster than the same parameter for 1.525 eV band. The spectrum has more or less simple structure allowing its fitting by two Gaussian shaped bands. The 1.373 eV band is shifting to lower energies as the temperature increases. It is localized at 1.311 eV at 84 K. The thermal shift cannot be explained considering the bandgap temperature variation only. The presence of another (close energetically position) recombination level might be possible (this band is formed as a result of CB to acceptor transitions – Fig. 1c). Its temperature dependence can be described by a well known formula (1).

$$I = \frac{I_0}{1 + A \cdot exp\left(\frac{\Delta E}{kT}\right)} \tag{1}$$

The experimental data show the presence of a quite shallow 8 meV level. It is quite problematic to conclude at this time on its nature: is it a donor or an acceptor one? This question is open for discussion and one should take into account the CdSTe compound formation.

The fitting of the spectra by elementary Gaussians allowed a more detailed analysis of the 1.525 eV band. It has been observed that it shifts to lower energies (down to 1.495 eV) along with temperature increase; its halfwidth is almost constant with temperature increase. The investigation of its behaviour with the excitation power P (Fig. 1 c) point at a linear dependence of P^n type (n = 1.21). Assuming that this band might have an excitonic origin, and due to high concentration of defects, it is mostly probably a bound exciton. Its ionization energy E_i can be determined from Eq. (2) [8].

$$I = \frac{I_0}{1 + A \cdot T^{3/2} \cdot exp\left(\frac{E_i}{kT}\right)} \tag{2}$$

The analysis of the experimental data gives E_i =15 meV.

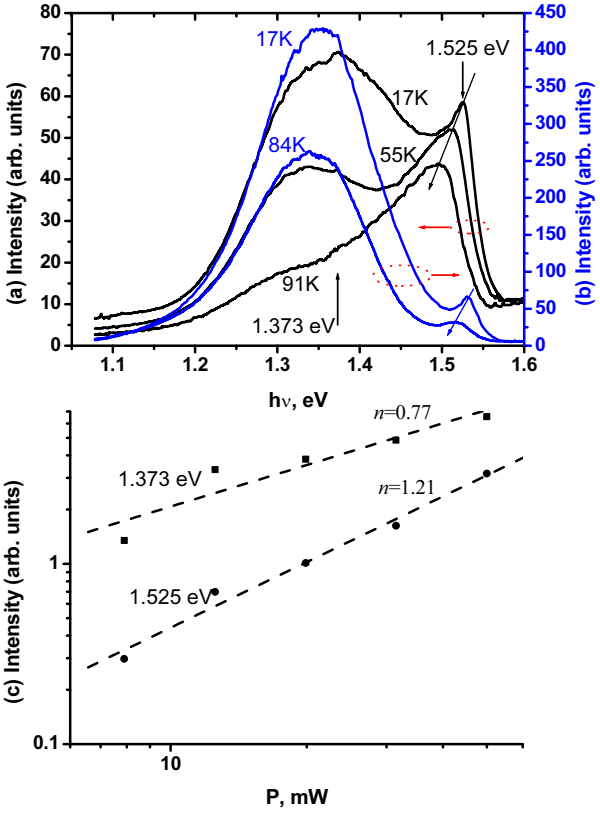


Figure 1 The PL spectra of CdS/CdTe interface layer (different temperatures), component of the SnO_2/CdS/CdTe heterojunction, CdTe deposited in He+O_2 ambient, (a – as-deposited, b – annealed in presence of $CdCl_2$, c – excitation intensity dependencies of the 1.373 eV and 1.525 eV band for unannealed samples at 17 K).

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Thermal annealing results in a restructured diagram of radiative levels in the band gap as one can see in Fig. 1b. The radiative transition in the 1.530 eV is less intensive (a 5 meV shift of the 1.525 eV previously observed band) relative to 1.351 eV band.

The 1.351 eV band position at different excitation intensity increase has a weak saturation tendency. The temperature quenching of this band can be described by equation (1), having the thermal activation energy of 15 meV. The conclusion might be the one considering a D-A transition responsible for radiative emission. The donor activation energy should be in a range of 1 meV.

The nature of the 1.525 and 1.530 eV bands it is complicated to interpret, but the analogous of this band is found if PL from CdTe side is excited. Although the band has similar energetic position, it is believed that this peak is mostly probable is a trace of the excitonic line (free or bound) which belongs and characterizes CdSTe intermediate layer. Mostly probable, S, being an isovalent defect in CdTe might have the role of a trap, binding excitons. 1.525 eV peak halfwidth is 10-20 meV. Sample's interface has not been subjected to the analysis by modulation techniques like described in [5, 6], allowing the determination of the composition of the solid solution x in CdS_xTe_{1-x} compound. Nevertheless, if one admits that the band gap of this compound can be described by Ref. [9]:

$$E_g(x) = 1.54 - 0.90x + 1.84x^2 \qquad (3)$$

in addition, considering the position of the excitonic line to be 1.525 eV (bound exciton) and its ionization energy determined above, the composition x can be estimated. It is assumed that the exciton Rydberg is similar to CdTe the composition x is equal to 0.054. Depending on value of x the exciton's binding energy can vary up to 27 meV [9]. It is more appropriate to consider low sulphur diffusion level (at least as an estimation, due to short annealing time), thus a value of exciton's binding energy in the range of 10-15 meV [9] is taken into account.

The possibility of existence of an excitonic peak is determined by the high quality of the CdS and CdTe films deposited by CSS at high temperatures.

3.2 CdS/CdTe interface PL (CdS thin film deposited by CBD) Most of the results and plots of data related to interface PL are published in [4]. A comparative analysis will be given in concluding remarks.

3.3 CdS/CdTe interface PL (CdS thin film deposited by CBD; CdTe is deposited in He ambient only) The PL spectra in this case will mostly exclude the effect of oxygen presence in films. The spectra itself is given in Fig. 2a. It represents a very broad band covering the 1.000-1.550 energetic interval at 17 K. It has a complex structure determined by a huge defects concentration in film. It can only be assumed that the spectrum consists of a quite large number of Gaussians, each of them being determined by and impurity transitions.

Thermal annealing in the presence of chlorides of the whole sample results in an essential modification of the spectrum (Fig. 2b). The spectra consist of practically a single Gaussian shaped band with peak intensity at 1.371 eV. The behaviour of this band at different excitations shows a saturation tendency at high excitation rate, suggesting a D-A transition to be the one causing the radiative recombination (Fig. 2c).

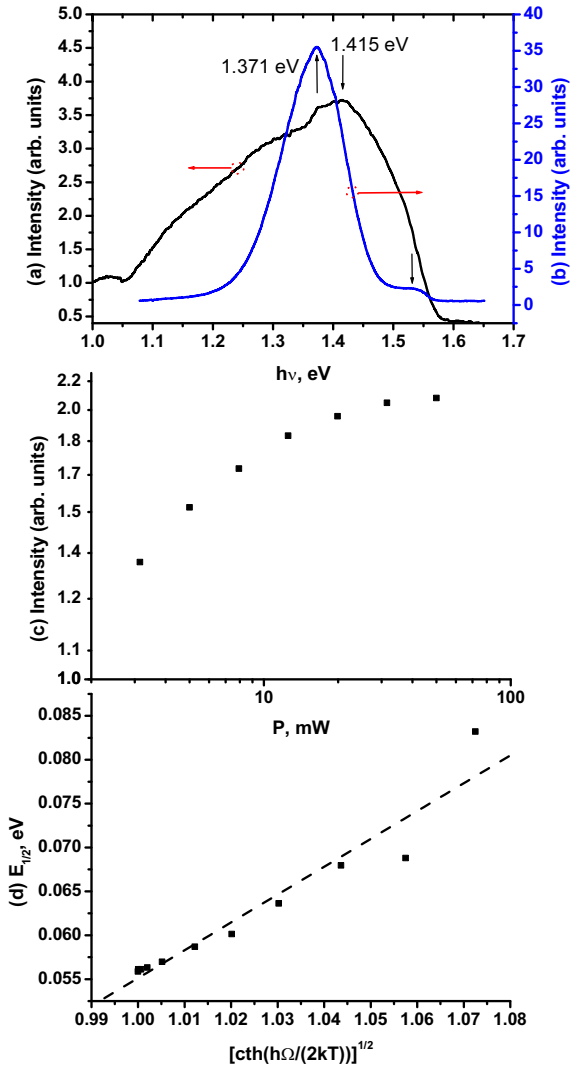


Figure 2 The PL spectra of CdS/CdTe interface layer (17 K), component of the SnO_2/CdS/CdTe heterojunction, CdTe deposited in He ambient, (a – as-deposited, b – annealed in presence of $CdCl_2$, c – excitation intensity dependencies of the 1.371 eV band for annealed samples at 77 K, d – halfwidth temperature dependence of 1.371 eV band; fit by use of Eq. (4)).

Another proof of the D-A nature of this band comes if one is analyzing the temperature dependence of the halfwidth of this band $E_{1/2}$. Analytically it can be described by the Ref. [10]:

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$$E_{1/2} = E_0\left[cth\left(\frac{h\Omega}{2kT}\right)\right]^{1/2} \quad (4)$$

where $h\Omega$ is the LO phonons energy. The phonons energy of 21 meV has been considered during the fitting process due to unavailable data for phonons energy in CdS_xTe_{1-x}. The $E_{1/2}$ temperature dependence in appropriate coordinates can be fitted by a straight line (Fig. 2d). The most probable assignment of the defects to a donor or an acceptor needs additional experiments.

A shoulder in the 1.52 eV region indicated the presence of additional radiative transition but their analysis is difficult. One can connect this band to the one seen in Fig. 1.

4 Concluding remarks

Several general features should be underlined as a result of the analysis of the whole data. One should notice that photoluminescence spectra have a common feature – all spectra do not reveal any phonon replica, but this does not mean that there is not any.

In addition, there were not excitonic spectra characteristic to CdTe observed (free exciton in CdTe is localized at 1.591 eV at 17 K) – caused by He and O_2 in concentrations enough to screen exciton formation.

About the nature of the 1.37X eV band: This band is not a commonly observed one in CdTe. 1.36 eV band has been reported for the interface PL [11], being assigned to Cl_{Te}–V_{Cd}. To exclude wrong assignments, the SnO_2/CdTe interface PL has been studied (Fig. 3) for samples obtained with different technological variations. One can observe that there is no trace at all indicating a possibility of existence of 1.371 eV band. So, the nature of the latter can be definitely assigned to the presence of S atoms in CdTe. It can be mentioned that this band might have the same role in CdSTe solid solutions as the 1.45 eV band has in CdTe.

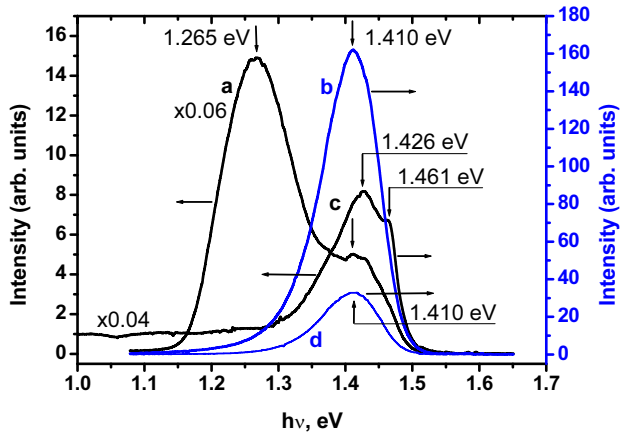


Figure 3 The PL spectra of SnO_2/CdTe interface layer (17 K), component of the SnO_2/CdTe heterojunction, CdTe deposited in He+O_2 ambient (a, b) and in oxygen free ambient (c, d), (a, c – as-deposited, b, d – annealed in presence of $CdCl_2$).

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References

[1] X. Wu et al., in: Proceedings 17th European Photovoltaic Solar Energy Conference, Munich, Germany, 2001, Vol. 1 (WIP-Renewable Energies and Florence, Italy: ETA, 2002), pp. 995-1000.
[2] D. P. Halliday, J. M. Eggleston, and K. Durose, Thin Solid Films **322**, 314 (1998).
[3] C. S. Ferekides, D. Marinskiy, V. Viswanathan, B. Tetali, V. Palekis, P. Selvaraj, and D. L. Morel, Thin Solid Films **361/362**, 520 (2000).
[4] S. Vatavu, H. Zhao, V. Padma, R. Rudaraju, D.L. Morel, P. Gaşin, Iu. Caraman, and C.S. Ferekides, Thin Solid Films **515**, 6107 (2007).
[5] S. Vatavu, in: Proceedings Thin-Film Compound Semiconductor Photovoltaics, MRS Spring Meeting, San Francisco, USA, 2007, edited by William Shafarman, Timothy Gessert, Shigeru Niki, and Susanne Siebentritt, Mater. Res. Soc. Symp. Proc. (Warrendale, PA) **865**, F5.22 (2005).
[6] S. A. Vatavu, Ph.D. Thesis, Moldova State University, Chisinau, Moldova, 2006.
[7] K. D. Rogers, J. D. Painter, D. W. Lane, and M. Healy, J. Electron. Mater. **28**, 112 (1999).
[8] J. I. Pankove, Optical Processes in Semiconductors (Prentice-Hall Inc., New Jersey, 1971 (in Russian: Mir, Moscow, 1973), p. 133.
[9] K. Wei and F. H. Pollak, J. Appl. Phys. **85**, 7418 (1999).
[10] D. Kyury, Luminescence of Crystals (Izd. lit. inostr, yaz., Moscow, 1961), p. 199 (in Russian).
[11] M. A. Hernandez-Fenollosa, D. P. Halliday, K. Durose, M. D. Campo, and J. Beier, Thin Solid Films **431/432**, 176 (2003).

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