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The photoluminescence of CdTe thin films in SnO_2-CdS/CdTe-Ni solar cells thermally treated in $CdCl_2$ solution

I. CARAMAN, G. I. RUSU[a*], L. LEONTIE[a]
Bacau University, 157 Calea Marasesti, 600115 Bacau, Romania
[a]*"Al.I. Cuza" University, 11 Carol I Bd., 700506 Iasi, Romania*

The photoluminescence (PL) spectra of CdS/CdTe heterojunctions from SnO_2-CdS/CdTe-Ni solar cell structures prepared by quasiclosed volume technique are analysed. The heterojunctions have been thermally treated for 15 min up to 7.5 h, at temperature ~690 K, in a $CdCl_2$ solution. The thermal treatment leads to formation of ionized centres, to whom excitons with energy 9-10 meV are bound, as well as of a layer of CdS_xTe_{1-x} solid solutions ($0 \le x \le 0.75$) at the heterojunction interface. By radiative annihilation of excitons from the heterojunction interface layer, a PL band peaked at 1.552 eV (at T=78 K) is formed. As a result of thermal treatment, the spectrum of recombination levels restructures and an impurity PL band with maximum at 1.44 eV forms. The long duration treatments result in the split of the impurity and exciton PL bands in two (sub)bands determined by the composition of heterojunction interface layer.

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1. Introduction

CdTe and CdS films prepared from vapor phase or by quasi-closed volume technique contain rather high density of structural defects, which form a broad spectrum of localised states with different ionization degrees [1, 2]. The thermal treatment in $CdCl_2$ solution leads to liquidation of some classes of short lifetime localised states [3], as well as to creation of long lifetime recombination levels [4, 5].

In the present paper the spectral distribution of photoluminescence (PL) for CdTe layer from SnO_2-CdS/CdTe-Ni solar cell structures is studied in dependence on the thermal treatment with $CdCl_2$, from which the composition of the heterojunction interface layer is determined.

2. Experimental

The CdS and CdTe films component of CdS/CdTe solar cells have been grown by quasi-closed volume technique. CdTe single crystals and CdS polycrystals were used as source materials. The evaporation temperature was 820-825 K and 900-910 K for CdTe and CdS, respectively. Mica plates have been used as substrates, maintained at 715 K for both compounds.

The excitation of photoluminescence (PL) was performed by means of a He-Ne laser (power: 30 mW, λ=632.8 nm). The PL spectra were recorded in temperature range 78-293 K by a spectrophotometric equipment based on a MDR-2 monochromator with diffraction grating (600 mm^{-1}), with an overall energy resolution of about 1 meV.

The PL spectra at 78 K for heterojunction interface have been recorded by exciting CdTe film, besides, for comparison purpose, the PL spectrum of free CdTe surface was registered.

The technology of sample preparation and the method of PL investigation were similar to those described in Refs. [6, 7].

The thermal treatment with $CdCl_2$ was performed at temperature 675-685 K, and its lenght varied between 15 min and 7.5 h.

3. Results and discussion

In polycrystalline CdTe and CdS thin films, the PL bands show broad contours which can be suitably described by a Gauss-type function [3]

$$I(h\nu) = \frac{1}{(2\pi)^{1/2}\sigma} \cdot \exp\left[-\frac{(h\nu - h\nu_0)^2}{2\sigma^2}\right], \qquad (1)$$

where I(hν) is the spectral radiance of PL radiation, $h\nu_0$ is the energy position of the band center, and σ is the standard deviation, expressed by

$$\sigma^2 = \frac{W^2}{8\ln 2}, \qquad (2)$$

with W the full (band) width at half maximum intensity (FWHM).

The photoluminescence of CdS/CdTe heterojunction, thermally treated for 15 min, is illustrated in Fig. 1. The PL spectrum from the free surface of the CdTe film (curve A) is composed (like in the case of untreated structures) of an exciton band peaked at 1.572 eV and an impurity band at 1.44 eV.

The profile of the exciton band is well described by means of a Gauss-type function (1). Since the energy of free excitons at 78 K is equal to 1.581 eV [8], it's natural to suppose that in presence of $CdCl_2$, ionized centres are created in the film, to whom excitons with binding energy of about 9-10 meV localise.

In a series of papers [2, 9-12], it was showed that the broad band with maximum at 1.44 eV is of impurity nature. It is due to the recombination of electrons from donor level with energy 0.015 eV (with respect to the conduction band edge) and holes localised onto the acceptor level with energy 1.30 eV (Cd vacancies) [2], therefore it is a donor-acceptor recombination band.

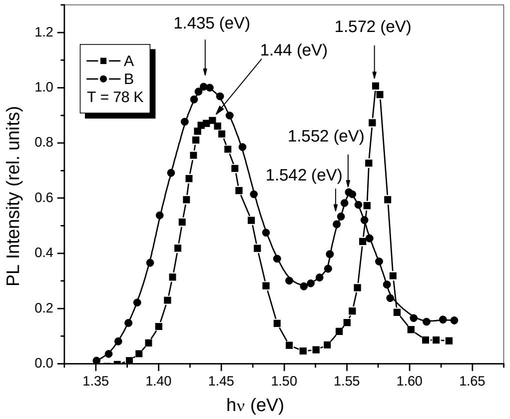

Fig. 1. PL spectrum, at 78 K, of CdTe film: A-free surface; B-heterojunction interface layer. Heat treatement for 15 min at 675 K.

The structure of the impurity band in the PL spectrum from the heterojunction interface layer (curve B) doesn't change practically as compared to that of free surface of CdTe layer, but its intensity is seen to increase by about 1.5 times and slowly displace towards lower energy range.

On the contrary, a completely different structure is demonstrated by the radiative band localised in the vicinity of the absorption edge, with maximum at $h\nu_1$=1.552 eV (curve B). First, the peak of the exciton band is shifted by ~20 meV towards lower energy domain with respect to the line of localised excitons ($h\nu_{ex}$=1.572 eV). Besides, it lays in a rather wide energy interval, between ~1.60 eV and 1.54 eV, and on its lower energy part a shoulder located at $h\nu_2$=1.542 eV is evidenced.

From the analyse of the intensity distribution in this band one can state that as a result of 15 min heat treatment, at CdS/CdTe heterojunction interface a layer containing a mixture of microcrystallites (since the diameter of the exciting beam was about 50-70 μm) belonging to CdS_xTe_{1-x} solid solutions range and CdTe single crystallites forms.

If one admit that the most probable energy of excitons from this layer (at heterojunction interface) is equal to 1.552 eV, then the band with maximum at 1.542 eV can be interpreted as a result of radiative annihilations of excitons localised by ionized centres created by structural defects in the interface layer, with a binding energy of 10 meV.

At longer heat treatments up to 30 min (Fig. 2), the intensity of exciton luminescence from free surface of CdTe film reduces by about 5 times, while that of the impurity band increases by ~3 times. A similar tendency is registered for the layer from heterojunction interface: the intensity of the exciton band ($h\nu_1$=1.552 eV) decreases by ~2 times, and that of the impurity band increases by ~1.5 times.

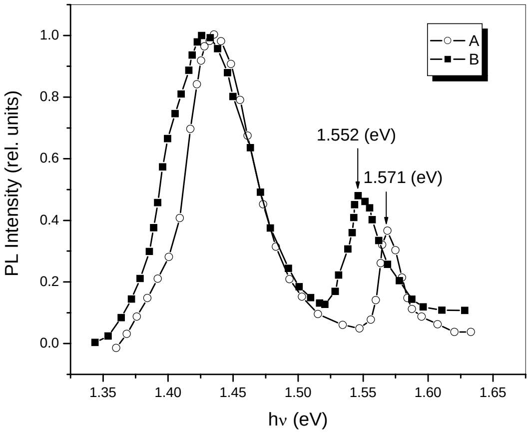

Fig. 2. Exciton luminescence of CdTe: A-from free surface; B-from heterojunction interface. Thermal treatement for 30 min at 678 K.

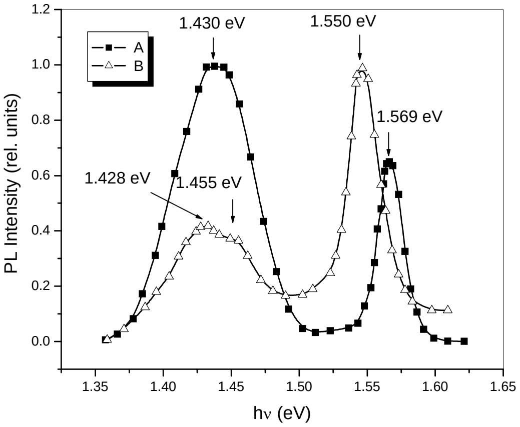

Fig. 3. PL spectrum from CdTe film surface, thermally treated for 1 h at 678 K. A-free surface; B-heterojunction interface layer.

The large width of the exciton PL band (curve B-heterojunction interface layer) suggests presence of an assembly of radiative recombination mechanisms taking place in this region. As was stated above, by heat treatment a compound of CdS/CdTe type forms in the interface layer, containing screening factors (e.g. excitons) for the electron-hole bonds; besides, there are also CdTe single crystallites in which localised excitons with binding energy of about 10 meV form. The last statement is based on the rapid thermal quenching of the outer band ($h\nu_l$=1.552 eV). This band lays between radiative band of free excitons ($h\nu$=1.582 eV) up to 1.53 eV. Similar broad bands are also registered for a series of other $A^{II}B^{VI}$ and $A^{III}B^{VI}$ solid solutions, especially in multilayer structures (superlattices etc.) [13, 14].

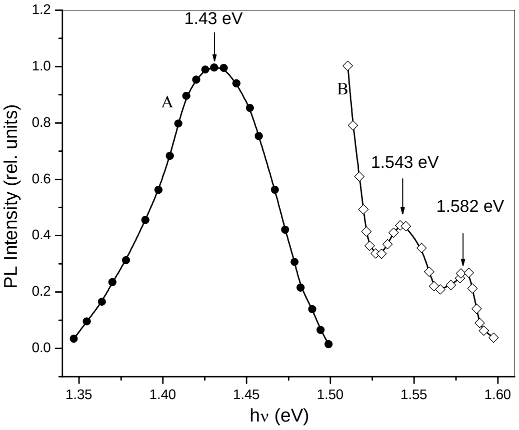

Fig. 5. PL spectrum of CdS/CdTe heterojunctions, thermally treated for 7.5 h at 678 K.A-impurity band; B-exciton band.

In Fig. 3 the spectral dependences of photoluminescence from free surface of CdTe film (curve A) and CdS/CdTe heterojunction interface (curve B) after 1 h heat treatment in $CdCl_2$ are shown. As can be easily ascertained, this procedure leads to a poor displacement (ΔE=2 meV) of the radiative annihilation peak of excitons localised in the CdTe surface layer towards lower energy range. A similar shift is also registered for the exciton band of CdTe interface layer from CdS/CdTe heterojunction. The increase of the heat treatment duration up to 1 h leads to an increment of the density of states contributting in the formation of the impurity band with maximum at 1.44 eV.

As can be seen in Fig. 3, the impurity PL band from heterojunction interface is also modified by this band (at 1.44 eV). The illustrated spectrum contains two subbands peaked at 1.428 eV and 1.455 eV. If one takes into account that as a result of heat treatment, the S atoms from CdS layer preponderantly diffuse (as compared to Cd atoms) into CdTe layer [9, 15-19], thus forming CdS_xTe_{1-x} solid solutions [12], then the band at 1.428 eV can be ascribed to recombination of electrons from donor level with energy 15 meV and holes from acceptor level with energy (1.28-1.30) eV, created by Cd vacancies [2]. At increasing heat treatment duration, the density of localised states responsible of impurity luminescence (the band peaked at about 1.43 eV) diminishes. Consequently, a heat treatment for 1 h points up a defect dominated CdTe surface for heterojunction interface layer. The defects show up in the intermediary compound CdS_xTe_{1-x} (solid solution), which forms at CdS/CdTe interface. The Gaussian shape of the exciton band and weak impurity band indicate a high homogenity degree of this interface layer.

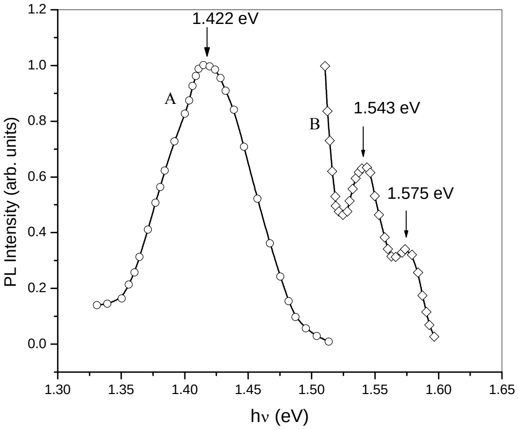

Fig. 4. PL spectrum of CdS/CdTe heterojunctions, thermally treated for 3 h at 678 K. A-impurity band; B-exciton band.

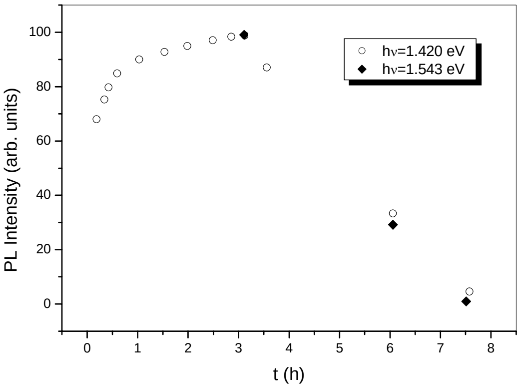

Fig. 6. Maximal intensity of PL bands in function of thermal treatment duration. A-impurity band; B-exciton band.

A longer heat treatment of CdS/CdTe heterojunctions in $CdCl_2$, of 3 h and/or more, leads to the split of the exciton band from CdS_xTe_{1-x} interface layer in two bands localised at about 1.543 eV and 1.575 eV, respectively (Figs. 4 and 5). As can be seen in these figures, the structure of PL spectrum doesn't practically change at increased heat treatment lenght from 3 h up to 7.5 h.

Fig. 6 presents the dependence of the peak intensity (normalised to unity) for the impurity band located by 1.42 eV and the exciton band peaked at 1.542 eV, on the treatment lenght. As can be ascertain from this plot, a heat treatment of 15-60 min results in an enhancement of the impurity PL band from CdTe interface layer, while for durations in the range (3-7.5) h, the intensity of this band is seen to reduce up to ~30 times. A much more rapid attenuation is observed for the exciton band located at 1.543 eV, thus an increasing duration of heat treatment from 6 h to 7.5 h leads to reduction of respective band intensity by ~20 times.

As can be found in Figs. 1-5, the exciton band lays towards higher energy range up to (1.60-1.61) eV. This feature can be explained if one admit that as a result of 1 h heat treatment in $CdCl_2$, at heterojunction interface CdS_xTe_{1-x} solid solutions, with continual composition range, are formed.

Further heat treatment up to 3.5 h leads to apparition in this region of an additional layer with determined composition, in which the exciton energy is equal to 1.54 eV.

As a result of heat treatment, in the first stage (15-60 min) defects present in the metal sublattice are liquidated, which results in an enhanced exciton (especially, free exciton) luminescence. At the same time, the energy diagram of localised states changes, so the intensity of the impurity band slowly increases.

A heat treatment with a lenght of over 3 h leads to an increase in the free charge carrier density and, consequently, to the extinction of the exciton and impurity bands (Fig. 6). The formation of impurity levels and the increase of the free charge carrier concentration, which take place as a consequence of the heat treatment, lead to a much stronger screening of electron-hole bonds as compared to that of the impurity luminescence [9]. This is produced since the exceeding electrons weakly influence the recombination mechanisms through localised deep levels.

It is known that in the hot wall reactor the chemical compound vapors are in thermal equilibrium and CdS substrate temperature is greater than in the quasiclosed volume technique. Thus, a structural homogenization over all CdTe layer thickness is expected in the first case.

Fig. 7 presents typical PL spectral curves of CdTe layer from CdS/CdTe heterojunctions prepared in a hot wall reactor and thermally treated for 30 min at temperature ~700 K, in $CdCl_2$. By comparing curves A (for the free CdTe layer surface) and B (for CdS/CdTe heterojunction interface), one observe that both exciton (***a*** and ***a***') and impurity (***b*** and ***b'***) bands appear as symmetrical curves that can be described by a Gauss-type distribution function.

At the same time, at CdS/CdTe frontier probably a new layer with intermediary composition is formed. The energy position of the exciton peak corresponding to this layer, equal to 1.545 eV, is in good accordance with the energy of the exciton peak from CdS/CdTe heterojunction interface prepared by quasiclosed volume technique and thermally treated for about 3 h or more.

By analysing the exciton PL of CdTe layer from CdS/CdTe heterojunction interface as a function of heat treatment duration (in presence of $CdCl_2$), one can conclude that as a result of this procedure, by diffusion of the volatile component from CdS (sulfur) and $CdCl_2$ (cadmium), at heterojunction interface CdS_xTe_{1-x} solid solutions are formed. Similar solid solutions also form at the interface of heterojunctions prepared by hot wall technique. If a Gaussian shape of the exciton radiative annihilation band is considered as a criterium for layer structural perfection, then it results (Fig. 3) that the average duration of the heat treatment in standard regime (for temperature and $CdCl_2$ vapor concentration), leading to formation of CdS_xTe_{1-x} layer with minimum defect density, is ~60 min.

By appealing to the linear dependence of exciton energy on x value from [21?], one can conclude that by 1 h heat treatment of CdS/CdTe heterojunctions in $CdCl_2$ solution, at temperature 680 K, at the CdS (hexagonal structure)/CdTe (zinc-blende structure) boundary an intermediary layer forms, with average composition x=0.06.

Besides, a heat treatment with a lenght (3-7) h leads to formation, within heterojunction region, of the compound with x=0.085. A similar composition is registered for the interface layer from heterojunctions prepared in the hot wall reactor and thermally treated in $CdCl_2$ for ~30 min.

4. Conclusions

The thermal treatment of CdS/CdTe heterojunctions in $CdCl_2$ solution leads to formation of ionized centres, to whom excitons with energy 9-10 meV are bound.

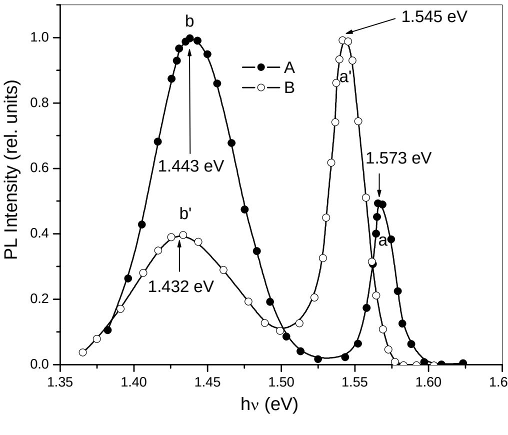

Fig. 7. Typical spectral dependence of PL for CdTe layer from CdS/CdTe heterojunctions prepared in a hot wall reactor.

At the interface of CdS/CdTe heterojunction heat-treated for 15-60 min, a layer of CdS_xTe_{1-x} solid solutions is formed, in which the peak of the exciton radiative annihilation band is localised at 1.552 eV. The solid solutions form a continuous row with composition in the range $0 \leq x \leq 0.75$.

The composition of the intermediary layer depends on the heat treatment duration.

The heat treatment of SnO_2-CdS/CdTe heterojunctions, with a duration between 15 min and about 3 h leads to amplification of the peak intensity of donor-acceptor band. Longer duration treatments result in the split of the exciton PL band and formation of localised states leading to the quenching of both impurity and exciton photoluminescence.

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*Coresponding author: girusu@uaic.ro