INVESTIGATION OF THE CdTe EPITAXIAL LAYERS EDGE RADIATION SPECTRUM STRUCTURE

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Recently the interest toward alternative energy sources had sharply increase. Solar energy conversion into electrical one is among the most perspective kinds of non- traditional kinds of energy supply. Cadmium telluride is one of the most perspective materials of II-VI wide band gap semiconductors suitable for solution of this problem. Cadmium telluride has a band gap of 1,45 eV corresponding to solar radiation maximum, posses high values of charge carriers mobility and is a semiconductor in which direct optical transitions are realized. It is the only II-VI compound which can be relatively easy obtained both as of n-type as well as p-type conductivity. However, its wide practical utilization in photo converters is limited, on the first hand, by the difficulties of fabrication of high quality films, and also by the defects compensation and self compensation processes. One of the important directions in the photo converters work parameters enhancement is the development of the efficient technology of single crystal and polycrystalline CdTe layers growth with the given physical properties.

The purpose of the given work were studies of the structure and radiation properties of $CdTe/Al_2O_3$ layers.

CdTe layers of 10-50 um thickness, grown by quasi-closed volume method and HWT in the conditions close to thermal equilibrium [1,2] were studied, n- CdTe crystals with the resistivity of 10^2 -10^6 Ohm-cm were used as evaporation sources. The sapphire (01-AI2O3) plates of thickness~3OO-5OO um oriented by (0001) plane were used as substrates.

The surface structure was studied by metal-microscope of (MMP-2P) type. The epitaxial layers crystallographic studies by accelerated electrons diffraction at reflection were carried out by using an (3IM10A) unit. The electron diffraction patterns were recorded on the diffraction length (sample-photographic plate distance) of 600 mm.

Photoluminescence (PL) was excited by a nitrogen laser of JITH-21 type with the wavelength of A,=337,l nm (3.68eV), 10 ns pulse, duration repetition pulses frequency of 100 Hz, the excitation maximum level lo=3 10^{23}phot/(cm^2 s).

Low temperature cathodoluminiscence (CL) of the layers was excited by accelerated electrons beam of the energy of 20-50 keV. The electrons beam diameter was of 0,05-1 mm; excitation pulse duration at its FWHM was of 20-50ns; electron current density varied in the limits 0,01-1 A/cm^2; pulses repetition frequency 100 Hz.

The electron diffraction patterns taken from $CdTe/Al_2O_3$ layer along to [112] direction consisted of a right form grill of point like reflexes accompanied by tails characteristic for crystals faceted [3], Electron diffraction patterns along [110] direction contained bars symmetrical toward the central beam degenerating into Kikouchi lines, which witness about single crystal structure and high structural quality of the layers. The layers had single phase cubic structure and oriented by (111) CdTe II (0001) $A1_2O_3$ plane.

The luminescent analysis is the most efficient method of impurity-defects structure studies of semiconductors. It was used for the studies of the reproducibility of initial material in CdTe layers by collation of their radiation properties. Besides, the influence of the epitaxy temperature on CdTe layers PL spectral dependence was studied. It was established that substrates temperature variation practically does not influence the structure of the luminescence spectrum of the layers, leads to the redistribution of edge and impurity band for the layers grown at low condensation temperatures (the super saturation coefficient a »1). In such layers this band intensity increases by few times comparable to the intensity in the luminescence spectra of the parent crystals. The layers synthesized at the thermal equilibrium (a«l) were characterized by the best reproducibility not only of the radiation properties structure of the parent material but also of the edge and impurity radiation intensities ratio.

PL spectra recorded at 77 K for parent single crystals (curves 1-3) and $CdTe/Al_2O3$ single crystal layers, fabricated in quasi-closed volume at the optimal temperature regimes (curve l'-3'), are given in fig.l. The undoped n-CdTe (p=10^5 -10^7 Ohm-cm) (curve 1), cadmium enriched n-CdTe: Cd (p=10^3 Ohm -cm, curve

2) and indium doped n-CdTe: In ($p=10^2$ Ohm -cm, curve 3) were used as sublimate. One can see that layers PL spectra structure is entirely determined by the radiation properties of the parent materials.

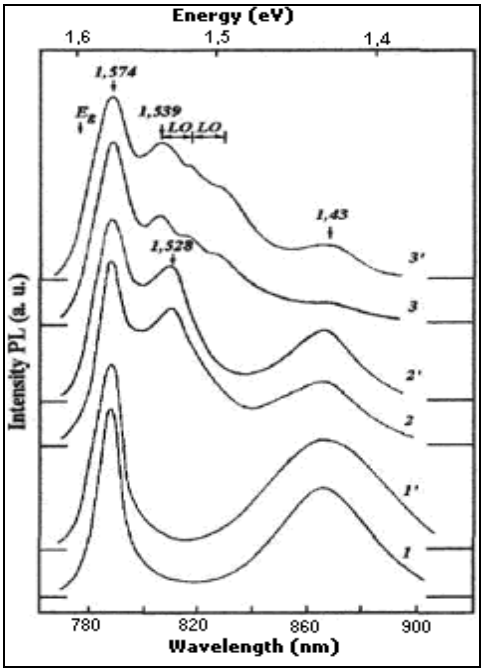

Fig.l. PL spectra at 77K of parent crystals: CdTe:In (1); CdTe: Cd (2); CdTe (3) and CdTe layers (l',2\3')

In all PL spectra of CdTe layers the edge band 1,574 eV is predominant. The same band is rather pronounced in the spectra of CdTe: In layers. For to establish its nature, the PL spectra analysis for these layers at different excitation levels and temperatures, was carried out.

The radiative recombination of the parent crystal (curve 1) and for the layers (curves 2-6) at 77 K at different excitation levels are given in fig. 2. The spectra consist of two bands: the fundamental at 1,574 eV and a large nonstructured one with the maximum at 1,43 eV. The electron transitions responsible for the maximum 1,574 eV are related to high exitons or nonequilibrium charge carrier densities in semiconductor at high exitation levels. Based on such analysis it is supposed that non-elastic exciton-exciton interaction of

$$(E_k^{1S}, E_{k'}^{1S}) \rightarrow (\hbar\omega, E_{k''}^{1S}) \quad \textbf{(1)}$$

type are playing the r role in the band forma [5].

Tho 1S-excitons wit **k'** wave vectors

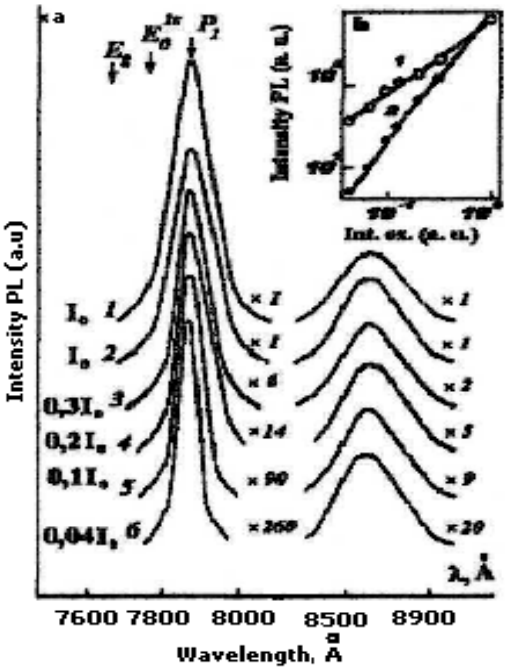

Fig. 2. PL spectral distribution at 77K of the parent CdTe crystal (1) and CdTe/Al_2O3 layer at different excitation level (2-6). On the insertion the spectral dependence of the bands: 1,43 eV - curve 1; 1,574 eV - curve 2

are interacting in such process, as a result of which one IS exi gains k" pulse and the second radiatively recombines with energy

$$\hbar\omega = \text{Eg} - \text{Els} - 2\text{koT}, \quad (2)$$

where Eg=l,597 eV-is CdTe band gap at 77 K; Ei_S=10 meV-exciton banding energy in IS state; ko-Boltsman constant, T lattice temperature. As a confirmation of such mechanism radiative recombination, the following band properties could be: -spectral placement of its peak (1,574 eV) with a rather good accuracy coincides with the calculated according to formula (2) value of 1,573 eV; the band possesses a light asymmetry with a more sharp long wavelength slope. Of all P-type bands such form is characteristic for P-band of luminescence [6]; -squared dependence of the radiation intensity on the excitation level (fig. 2. curve 2 on die insertion).

The PL spectra temperature dependence of CdTe:In layer are given in fig.3. The exiton band maximum position shifts to long wavelength region with temperature increase with a coefficient«2,9-10'[4] eV/K (curve 1 in the insertion). Its value is in agreement with the temperature shift rate of P-band:

$$d/dt\,(\hbar\omega_{max}) = dEg/dT\text{-}2K, \quad (3)$$

which is $d(fto_{max})/dT$=2,410^ eV/K. The FWHM of the fundamental band increased with temperature increase with the coefficient of «1,3 -10'[4] eV/K (curve 2). The observed peculiarities witnesses in the favor of exciton-«xciton recombination, responsible for short wavelength radiation.

The 1,43 eV band in CdTe is ascribed to donor- acceptor pair (DAP) recombination [6]. Its intensity linearly increased with the excitation level increase (Fig.3., curve 1 on the insertion), and maximum is

shifted to shorter wavelengths. It is well known, that energy position of DAP line depends on the distance between donor and acceptor according to relation:

$$E(r)=E_B K E_A+E_D)+e^2/\varepsilon r \qquad (4)$$

The band maximum shift to shorter wavelengths with temperature increase is related to the decrease of charge carriers average radiation time of life, and as a result the radiation transitions through close located centers occur. According to relation (4) 'this leads to the increase of Coulomb's term e^2/er into radiation quantum energy.

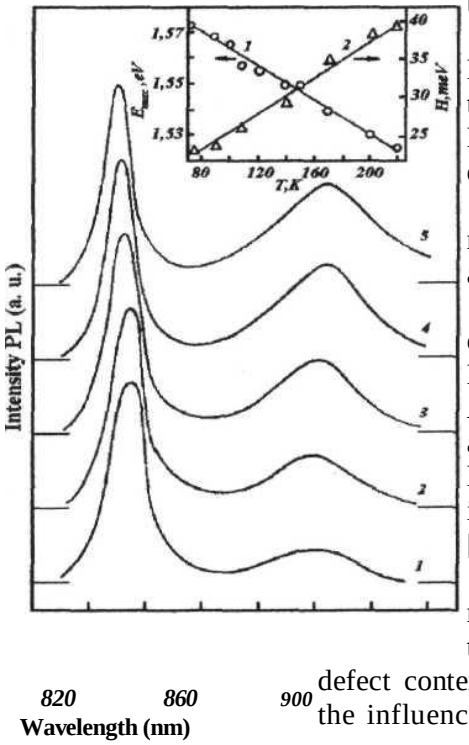

Fig.3. CdTe: In layers PL spectra at different temperatures : 1-120K; 2-110K; 3-100K; 4-90K; 5-70K. On the insertion: temperature dependence of the excitation

By knowing the shallow donor ionization energy E_D, one can determine, with accuracy up to Coulomb's term, the corresponding acceptor optical ionization energy E_A In our case the In impurity atoms are acting like donors with E_D=0,011eV [8]. One can consider, that 1,43 eV band in CdTe: hi layers appears as a result of radiative 1 transitions from shallow donor 0,011 eV to acceptor with E_A=0,15 eV.

The temperature quenching of 1,43 eV band occurs by following an exponential law. By using the Mott' s formula [9], the activation energy of this process AE«0,14 eV was determined corresponding to the acceptor depth calculated by formula (4). In CdTe:In layer the uncontrolled impurities, or a complex including native defect and impurity could be acceptors [10.11].

From the given analysis of radiative transitions, responsible for 1,574 eV and 1,43 eV lines, it follows that their intensities ratio reflect the level of impurity defect content in the studied layers. At the steady excitation level the influence of one of the indicated bands intensity is related to the decrease of the second band intensity.

One should observe that PL spectra structure of CdTe.In layers depends on the method of their fabrication. In the luminescence spectra of CdTe:In layers (p=10^4 Ohm-cm), obtained by evaporation of the indium doped sublimate, the 1,43 eV band was prevailing. When in the spectra of the layers having the same p value, but In doped during their growth from stoichiometric CdTe, the 1,574 eV line is predominant. The obtained results indicate, that in the first case the radiative transitions are related, mainly, to the impurity-defects structure, stipulated by the compensating centers formation. As higher the doping level of the parent material was, as stronger the compensation effects were also expressed in the fact, that the layers resistivity was, at least by 1-2 orders of magnitude higher than the resistivity of the doped sublimate.

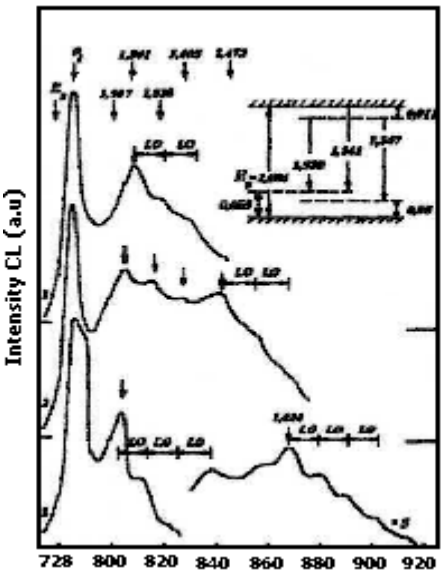

Fig.4. The undoped CdTe layer Cl spectra (1) and CdTe: In layer with the concentration of electrically active In n=2-10^{15}cm^{-3} (2) and n=5-10^{16} cm^{-3} (3). On the insertion: diagram of the electron transitions responsible for the edge radiation in CdTe layers.

In CdTe/Al_2O3 layers the width of the intermediate layer, formed in CdTe, at its interface with saphire substrate, was estimated. For this purpose the layer by layer etching of CdTe film with a subsequent study of PL spectra was carried out. Its was established, that the spectra structure and luminescence bands structure practically did not change with thickness up to 3-4 um.

The excited states diversity in II-IV wide band gap compounds the most complete is realized in the radiative

transitions at low lattice temperatures. Therefore we studied the low temperature CL of CdTe:In layers. The impurity-defects content dependence on CdTe layers doping level was studied by the collation analysis of their CL with the spectra of undoped CdTe layer.

The CL spectra at 4,2 K of the undoped layer (curve 1) and of CdTe :In layers of different concentration of electric active impurity: $n=5\text{-}10^{15}$ cm^{-3} (curve 2) and $n=2\text{-}10^{16}$ cm^{-3} (curve 3) are given in fig.4. One can see, that the main band in the spectra of all studied samples at low temperatures, is the band at 1,582 eV. As at 77 K, it corresponds to exciton-exciton interaction and is related to the excitation of one of two interacting excitons in n=2 state of continuous spectrum, and radiative recombination of the second. The P_2 line position in the radiation spectrum corresponds to the energy value, calculated according to formula (2) for n=2. With the In content increase in CdTe layers, this line FWHM increase and its intensity decrease, was observed. The named band enlargement could be related by the superposition of its long wavelength edge with the 1,578 eV (curve 3).

The nonphonon lines at 1,578-1,547 eV in the doped layers are related to, so called, I-FV series of the edge radiation of CdTe [7,12] (transitions diagram on the insertion, fig.4.). According to this model, the 1,528 eV line, situated at the LO phonon energy distance from 1,547 eV band, is stipulated by the radiative transition of the electrons from shallow donors (E_D=0,011 eV) onto acceptor (E_A=0,067 eV). Besides, the edge radiation of the undoped CdTe layer is characterized by the presence of 1,541 eV line. It is related to radiative transition of free electron to acceptor with E_A=0,05 eV.

In the long wavelength region of spectrum of lightly doped CdTe:In layers (curve 2,flg.4) the radiation consisting of 1,495 eV and 1,472 eV, concealing 1,43 eV band, was observed. The given lines are also related to DAP recombination [13]. The enlargening of the long wavelength edge radiation and smoothening the phonon structure of 1,472 eV line was observed, depending on the excitation level increase, which could be related to the luminescence multiplasmon process in the conditions of high excitation levels [14]. In the CL spectra of CdTe:In layers with high concentration of active In at the temperatures of 4,2 K the 1,43 eV line LO-phonon structure was clearly resolved (curve 3).

It is known [7] that the intensity distribution of the lines responsible for the optical transitions, where at least one component is discrete, is determined by Poison's formula:

$$I_0=IoN^a/n! \quad (n=0,1,2,3\ldots..) \quad (5)$$

Where: I_n-is intensity of the line, appearing at the simultaneous emission of photon and n LO-phonons. N-parameter determines the average number of the emitted phonons at electron transition. For the lines of 1,578 eV, 1,541 eV, 1,547 eV and 1,43 eV the value of N parameter is 0,21; 0,21; 0,32; and 1,45 eV correspondingly. According to the used model, the electron transitions occur from shallow donors, possessing comparable the same ionization energy, to different acceptors. Hence the observed distinctions of N parameter reflect the different depths of the acceptors, which are the final state of the radiative transitions in CdTe:In layers.

By using empiric formula for CdTe [7]

$$N=76(eV^2)E_A^2 \quad (6)$$

the values of acceptor centers ionization, participating in the radiative transition, were determined. Their values are indicated on the diagram of the optical transitions (fig.4. insertion).

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