ANALYSIS OF OPTICAL PROPERTIES AND STRUCTURE OF GaTe - CdTe NANOCOMPOSITE

I. CARAMAN[a*], D. UNTILA[b], I. EVTODIEV[b], V. CANŢER[c], N. SPALATU[d],
D. RUSU[a], E. LUCHIAN[b], I. ROTARU[b]

[a]*Engineering Department, Vasile Alecsandri University of Bacau, Calea Marasesti 157, Bacau, 600115, Romania,*
[b]*The Laboratory of Scientific Research ''Photonics and Physical Metrology'', Faculty of Physics and Engineering, Moldova State University, A. Mateevici, 60, MD - 2009 Chisinau, Republic of Moldova*
[c]*Institute of the Electronic Engineering and Nanotechnologies, Academy of Sciences of Moldova, Academiei 3/3, MD – 2028, Chisinau, Republic of Moldova*
[d]*Tallinn University of Technology, Department of Materials Science, Ehitajate tee, 5, 19086 Tallinn, Estonia*

The CdTe-GaTe lamellar microcrystalline composite was obtained by thermal treatment in the temperature range from 623K to 833 K of mono-crystalline p-GaTe with the concentration of holes of $(1.5-3.0)*10^{14}$ cm^{-3}. The concentration of CdTe crystallites increases when the temperature of thermal treatment of GaTe lamellas increases. The CdTe layers forms on the outer surface of lamellas as well as inside the samples due to intercalation process of Cd atoms between layered packaging of Te-Ga-Ga-Te type. The edge of absorption band of GaTe-CdTe composite obtained at the temperature of 650K is determined by absorption process in CdTe crystallites. The width of direct bandgap at the temperature of 300K of GaTe crystals from composite is equal to 1.54 eV. The band with a maximum at (1.37-1.42) eV prevails in the photoluminescence (PL) spectrum at the temperature of 78K of CdTe-GaTe composite. This is characteristic to CdTe crystals with own structural defects. The activation energy of this band is equal to 0.14 eV.

1. Introduction

The GaTe compound belongs to the class of semiconductors with optical and electrical properties required for optoelectronic devices [1, 2, 3]. The GaTe crystallize in monoclinic lattice of $C_2^2(P2_1)$ space group [4]. The elemental cell consists of 12 molecules with 108 valence electrons [5,6].The single crystals of GaTe are composed of Te-Ga-Ga-Te type planar atomic packaging [7] with weak bonds between the packaging and ionic-covalent bonds inside [1, 2].

The atomic planes of Te and Ga in GaTe single crystals are oriented perpendicular to the C_2 crystallographic axis [3, 9]. The elemental cell is made up of two packs displaced from each other in the way to obtain a monoclinic crystal lattice with parameters a = 23.76 Å, b = 4.068 Å, c = 10.46 Å and β = 45.4° [10]. If the Ga atoms are arranged parallel to C_6 crystallographic axe inside the layered packaging, then the Ga-Ga bounds in GaTe will be in the plane of elemental layer [11]. Theoretical calculus of the structure of electronic bands based on states density in pure crystals of GaTe [12] as well as of states formed by impurity atoms of Ge and Sn [13] shows that GaTe is a semiconductor with direct bandgap. The absolute minimum of conduction band and the maximum of valence band are situated at the edge of Brillouin zone in Z point.

The values obtained for width of direct bandgap that was theoretically calculated in works

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* Corresponding author: iucaraman@yahoo.ca

[13, 14, 15] fluctuates in a large range from 0.939 eV to 1.34 eV. The measured width of bandgap (E_g) at the room temperature is 1.679 eV [16] and 1.676 eV for polarization $\vec{E} \perp b$ and 1.675 eV for $\vec{E} \parallel b$ [8]. These values corresponds to calculated one for monolayer of GaTe were E_g=1.66 eV [17]. The big differences between theoretical calculus and experiment for bands structure reported too for GaSe and InSe compounds [14].

The Te atoms planes from the neighbour packaging are displaced from each other and form cleave between them in which the atoms of different nature can set. The surface of the crystals is covered with a thin yellow-grey layer of own oxide after a long-term storage in the normal atmosphere. However, there is an increase of 20 ÷ 25% of the electrical conductivity on the surface. The edge of the absorption band in the temperature range of 1.6 ÷ 300 K is determined by direct optical transitions and formation of direct excitons [7, 8, 18, 19, 20]. The exciton emission band of GaTe single crystals at the temperatures smaller than 90 K prevails in the photoluminescence spectra.

The high electrical conductivity of CdTe micro-crystallites in thin layers are used for manufacturing solar cells that conversion efficiency of sun light at the surface of the Earth is about 20% [21]. The electrical characteristics of CdTe monocrystalline layers are determined by the diagram of energetic states in bandgap. The nature as well as the characteristics of states is determined from the analyses of photoluminescence (PL) bands [22, 23].

The crystalline structure, composition and some optical properties of composite obtained by intercalation of Cd atoms in GaTe crystal plates at the 633-833 K temperature are studied.

2. Materials and methods

The GaTe single crystals were grown by Bridgman-Stockbarger method [9]. The basic elements of Ga and Te of 5N purity were taken in stoichiometric quantities. The poly-crystallites were obtained with the shape of pyramids composed of two plane-parallel surfaces perpendicular oriented to the C_2 axis. The samples are optically transparent in the range of 0.62 to 22.1 μm. The p-type single crystals with the concentration of the gaps of $(1.5-30) \cdot 10^{14}$ cm^{-3} were obtained. The week polarization bonds between packaging allow obtaining plan-parallel plates with required sizes by perpendicular splitting on the C_2 crystallographic axis.

The GaTe plan-parallel plates with thicknesses of 0.3 - 1.5 mm were intercalated with Cd from vapour phase. The intercalation carried out in quartz vials with GaTe plates and 2 mg/cm^3 of Cd. After the atmosphere evacuation to $5 \cdot 10^{-5}$ Torr the vials were sealed. The treatment was provided at the temperature of 623 K and 653 K during 60 hours, at 723 K for 12 hours and at 833 K for 24 hours.

The surface of GaTe single crystal plates that was treated in Cd vapours at the temperature of 653 K and 623 K for 60 hours remains smooth (the magnification of 600). The surface of the plates treated at the temperature of 833 K for 24 hours is covered with granules with size from 0.5 μm to 10 μm.

The composition of the obtained material was analysed by XRD method using the DRON - 4 device ($\lambda_{CuK\alpha}$ = 0.154182 nm). The surface morphology of the samples was studied by AFM and SEM microscopies. The elemental composition of the surface layer of treated GaTe plates that were treated in Cd vapours was determined by EPMA method.

The photoluminescence of GaTe and GaTe:Cd was excited with He-Ne laser (λ = 6328 Å) with average power of 20 mW. The samples temperature was measured with Cu-Constantan K-type thermocouple. The photoluminescence spectra were measured with a monochromator system МДР - 2. The diffraction grating of monochromator was 600 mm^{-1} and the energy resolution of ~ 1 meV.

The diffuse reflection spectra of light from the microstructured surface of long-term treated GaTe lamellas in Cd vapours was recorded by spectrophotometer Specord M-40 with a photometric sphere for diffuse reflectance measurements. The pressed powder of BaSO$_4$ which coefficient of diffuse reflection is equal to 1 in the range of 700 − 1000 nm was used as a white standard material for diffuse reflectance measurements.

3. Results and discussion

The relatively weak bonds between the atomic planes of chalcogen (Te atoms) from the surface of Te-Ga-Ga-Te layered packaging and the Ga atoms within the packaging stimulates the formation of Ga_2O_3 and TeO_2 oxides on the outer surface of GaTe single crystal plates thermally treated in normal atmosphere [25].The ZnSe-InSe and ZnSe-GaSe heterojuctions that are photosensitive in visible-infrared range of spectrum were obtained by thermal treatment of InSe and GaSe plates in Zn vapours [26].
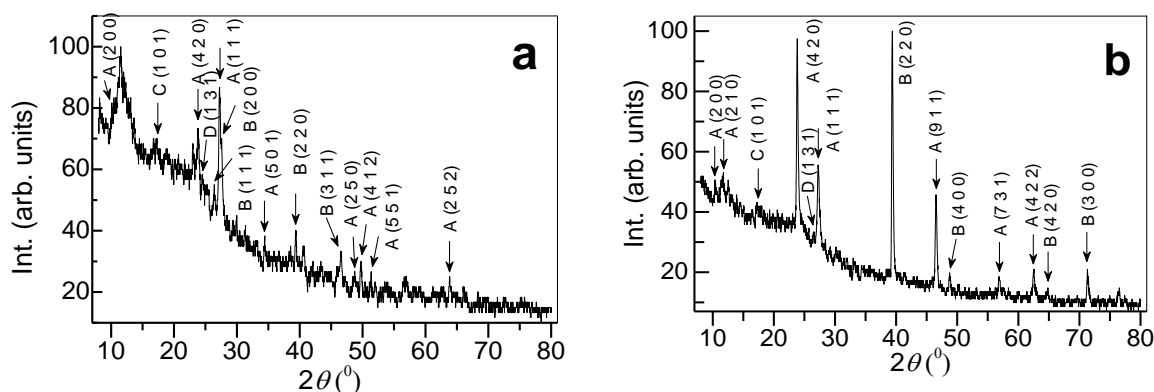

Fig. 1. The XRD diffraction of the composite obtained by the treatment of GaTe single crystals in Cd vapours (2mg/cm³) at the temperature of: (a) – 653 K for 60h; (b) – 833 K for 24h and the diffraction lines from atomic planes of crystals: A - GaTe; B - CdTe; C - Ga₂Te₃; D - Ga₇Te₁₀.

In the Fig. 1 is presented the typical XRD diffractogram of two samples of GaTe treated in Cd vapours at the temperature of 653 K for 60 hours (a) and for 24 h at the temperature of 833 K (b). As it can be seen from Fig.1., the Miller index (h k l) of CdTe crystals are presented as well as the series of intense lines that are distributed in the range of angles of 2Θ. The addition lines from XRD diagram were identified using PCPDFWIN and ICSD cards. These lines are assigned to diffraction from (h k l) planes of CdTe, Ga_2Te_3 and Ga_7Te_{10} crystallites. The intensity of diffraction lines from the (h k l) planes of CdTe crystals increases when the temperature of thermal treatment increases from 653K to 833K. Also the intensity of diffraction lines from the crystallographic planes (2 2 0), (4 0 0) and (4 2 0) of CdTe crystals is amplified for composite obtained at the temperature of 833K. The XRD diagram of the sample obtained at the temperature of 653K shows the diffraction lines of GaTe and CdTe crystallites and two lines at $2\Theta\approx17°$ and $2\Theta\approx 23°$. These lines are the diffraction of plane ensembles with Miller index (1 0 1) of Ga_2Te_3 and (1 3 1) of Ga_7Te_{10} crystallites. The presence of diffraction lines of Ga_2Te_3 and Ga_7Te_{10} together with the lines of CdTe and GaTe crystals shows that the forming process of CdTe-GaTe composite take place with phase transformations in Ga-Te compounds. The chain of phase transformations can be written as:

$$6GaTe + 3Cd \frac{653K}{833K} Ga_7Te_{10} + 4Ga + 3CdTe \qquad (1)$$
$$Ga_2Te_3 + 3Cd \rightarrow 3CdTe + 2Ga \qquad (2)$$
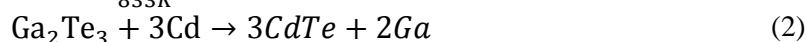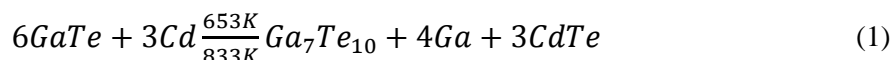
The thermal treatment of GaTe monocrystalline plates in Cd vapours at the temperatures higher than 653K leads to intercalation of Cd atoms between the layered packaging of primary crystals of GaTe, formation of GaTe-CdTe microcrystalline composite and Ga as clusters.

The SEM image of the GaTe lamella surface treated in Cd vapours at the temperature of 623 K for 60 hours is shown in Fig. 2. As it can be seen from Fig.2, two types of phases that size varies from submicron to tens of micro-meters form on the surface of the GaTe plates. The elemental composition of these two types of clusters determined by EPMA is shown in Table 1.
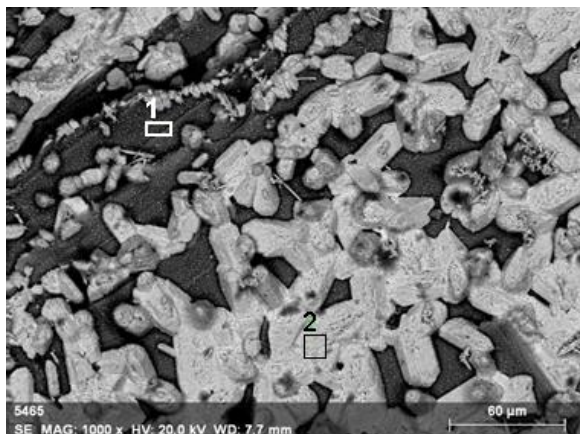
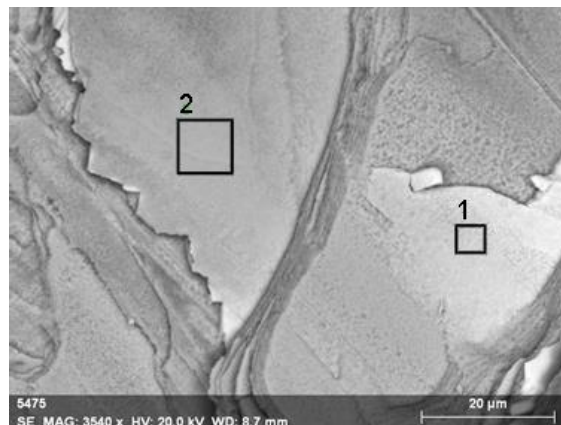*Fig. 2. The SEM image of GaTe sample surface treated at the temperature of 623 K for 60 hours in Cd vapours.*

Fig. 3. The SEM image of GaTe sample interface treated at the temperature of 623 K for 60 hours in Cd vapours.

Table 1. The distribution of chemical elements in clusters formed on the surface of the GaTe by treatment in Cd vapours at the temperature of 623 K for 60 hours

Spectrum	Element	Series	Atom. C, % m	Error, %
1	Gallium	K-series	89,27	2,0
	Tellurium	L-series	5,55	0,3
	Cadmium	L-series	5,18	0,2
		Total:	100,00	
2	Gallium	K-series	3,41	0,1
	Tellurium	L-series	92,51	2,8
	Cadmium	L-series	4,08	0,2
		Total:	100,00	

As shown in Table 1, the Ga with a small quantity of CdTe (∼5.18%) and the excess of GaTe (∼0.38%) is concentrated in region 1 while the Te (∼85%) with small quantities of CdTe (∼4.08%) and GaTe (∼3.4%) is concentrated in the region 2. Therefore at the temperature of 653K on the other surface of GaTe plates take place decomposition of GaTe crystals with separation in clusters of Ga and Te. Also the small quantity of CdTe compound forms at this temperature.

Table 2. The distribution of chemical elements in planar layers in different regions within the GaTe samples treated at the temperature of 623 K in Cd vapours.

Spectrum	Elementul	Seria	Atom. C, % m	Error, %
1	Gallium	K-series	33,06	0,6
	Tellurium	L-series	66,45	2,1
	Cadmium	L-series	0,49	0,1
		Total:	100,00	
2	Gallium	K-series	44,67	0,8
	Tellurium	L-series	54,63	1,9
	Cadmium	L-series	0,70	0,1
		Total:	100,00	

The dark regions are Ga enriched with small amounts of Cd, while white areas represent clusters of Te with small amounts of CdTe and GaTe. However, they differ in the mechanisms of development of these two types of cluster.

In the Fig. 3 is reproduced the SEM image of the interface between Te-Ga-Ga-Te packages of GaTe plate treated in Cd vapours at the temperature of 623K for 60 hours. The planar layer is observed from Fig.3. The concentration of atoms is shown in Table 2.

The data from Table 2 shows that the Van der Waals interface between packaging are enriched with Te. This result confirms that the monocrystalline GaTe plates after thermal treatment at the temperature of 623 K dissociate and the Te accumulates mainly on the surface. Also at the temperature of 623K a small quantity of Cd atoms (0.49 – 0.70% at.) intercalate in a depth of GaTe monocrystalline plates.

The pressure of Cd vapours increases more than 3 times when the treatment temperature increases from 623 K to 720 K. However, the probability of formation of chemical compound of CdTe from Cd atoms from vapour and Te from the surface of elemental packaging increased. In Fig. 4 is the SEM image of the surface of the GaTe plate treated at the temperature of 720 K for 12 hours in Cd vapours. The surface of GaTe plate is covered with two types of formations (region 1 and 2) as it can be seen from Fig.4, the values are presented in Tabele 3.
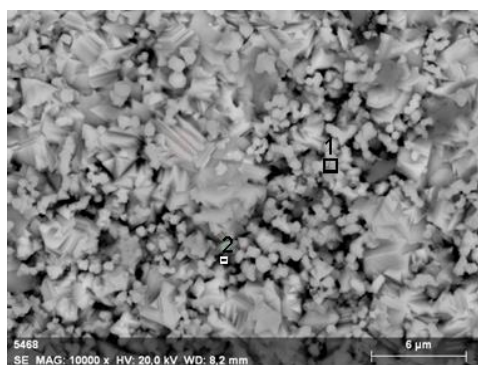

Fig. 4. The SEM image of the surface of the GaTe plate treated at the temperature of 720 K for 12 hours in the vapours of a Cd.
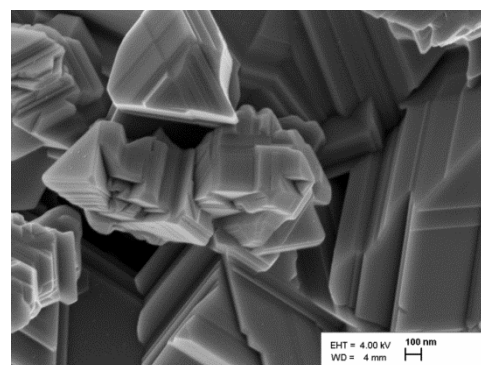
Fig. 5. The orientation of CdTe crystallite on the surface of GaTe plate.

Table 3. The elemental composition of white (zone 1) and dark (zone 2) areas

Spectrum	Element	Series	Atom. C, % m
1	Gallium	K-series	2.98
	Tellurium	L-series	41.95
	Cadmium	L-series	55.07
		Total:	100.00
2	Gallium	K-series	1.61
	Tellurium	L-series	49.30
	Cadmium	L-series	49.09
		Total:	100.00

It is easy to see that the newly formed layer cover the surface of GaTe plate with areas which sizes are from tenth μm^2 (dark areas) to several tens of μm^2 (white areas). The area 1 from Table 3 contains an excess of Cd and probably 2.5 – 3.0% of GaTe while in 2nd area the new compound of CdTe is concentrated.

The surface of GaTe plate is covered with CdTe crystallites which sizes are micrometric (Fig.5.) by thermal treatment at the temperature of 720K for 12 hours in Cd vapours. The CdTe crystallites grown as the plates oriented parallel to initial GaTe plate.

Therefore it can be concluded that thermal treatment at the temperature of 720K of GaTe monocrystal plates in Cd vapour leads to coverage of GaTe with a polycrystalline layer of CdTe. The CdTe crystallites are oriented in a way that grown on (1 1 1) direction perpendicularly to C_2 axe. The presence of microcrystals on outer surface and at the interface of packaging lead to intense light dissipation.

The edge of the absorption band of the sample obtained by treatment at 720 K for 12 hours was analysed from the measurements of light diffuse reflection using the Kubelka - Munk function [11]:

$$F\left(R_\infty\right) = \frac{(1-R_\infty)^2}{2R_\infty} = \frac{\alpha}{S} \tag{3}$$

where R_∞ is the diffuse reflectance, α is the absorption coefficient and S is the dissipation factor.

The type of optical transitions and the bandgap of the composite obtained on the outer surface of GaTe plate were determined using the equation:

$$[h\nu \times F\left(R_\infty\right)] = B\left(h\nu - E_g\right)^n \tag{4}$$

where B is a constant that does not depend on energy, E_g is the width of band gap, n is the factor that determines the type of optical transitions (n = 2 for indirect optical transitions and n = 1/2 for direct optical transitions).

In the Fig. 6 it is shown the dependence $\left(F\left(R_\infty\right) \times h\nu\right)^2$ of energy hν. From the extrapolation of the linear segment of the function $\left(F\left(R_\infty\right) \times h\nu\right)^2 = f(h\nu)$ to zero was determined the width of the direct bandgap of the GaTe - CdTe composite (1.546 eV). This value is 0.12 meV smaller than the width of bandgap in GaTe [28].
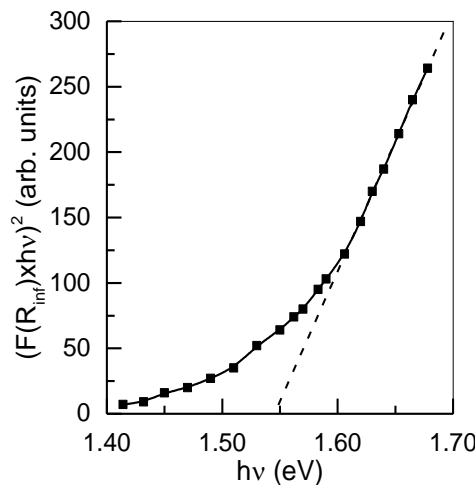

Fig. 6. The bandgap width of the GaTe composite plates treated at the temperature of 630 K for 24 hours in the Cd vapours

The width of direct bandgap for CdTe layers depends on the temperature of growing [29] and varies in large range of energies from 1.56 eV for CdTe layer grown at the temperature of 250°C to 1.49 eV for the grown temperature of 20°C [30]. Therefore it can conclude that thermal treatment at the temperature of 650K of GaTe plates in Cd vapour for 24 hours leads to the CdTe polycrystalline layer formation at the interface between packaging of Te-Ga-Ga-Te as well as the outer surface of GaTe. The edge of absorption band of this layer is determined by direct optical transition with the width of bandgap at the temperature of 300 K equal to 1.546 eV. This value correlates well with the width of the bandgap energy of the edge of optical absorption band of direct transitions in thin layers obtained by condensation of CdTe vapours on quartz substrate [27].

It is characteristic for photoluminescence emission spectra (PL) at 80 K that CdTe compound obtained by different methods (epitaxial layer, spray - pyrolysis, quasi-closed volume)

has the donor-acceptor band in the region from 1.4 eV to 1.45 eV, a small intensity band at 1.23 eV [31, 32, 33] and the emission of free excitons band at 1.57-1.58 eV [34].

The Fig. 7 presents the PL of GaTe single crystal plate (a) and of CdTe-GaTe composite obtained by treatment of GaTe monocrystals in Cd vapours at the temperature of 833 K (b) for 24 hours and for 60 hours at the temperatures of 623 K (c) and 53 K (d).

The PL emission band of composite obtained by thermal treatment at the temperature of 623 K for 60 hours of GaTe monocrystals in Cd vapours (Fig.7c) can be decomposed in three Gauss-type curves with the maximums at the energies of 1.430 eV, 1.372 eV and 1.299 eV. The PL impurity band with maximum at 1.430 eV is well studied in [35, 36] and it is considered as PL impurity band. The interpretation of this band is in accordance with the nature of the sample because this band can be found in PL stectra of CdTe samples obtained by different methods.
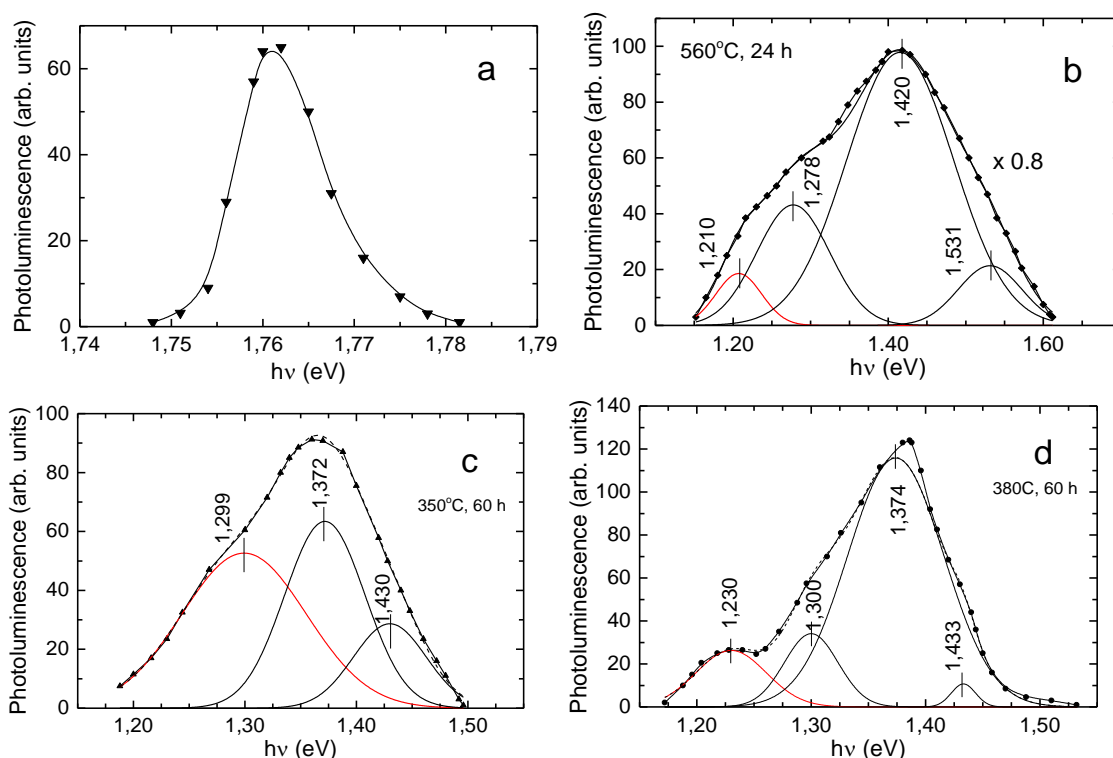

Fig. 7. The PL of GaTe single crystal plate (a) and of CdTe-GaTe composite obtained by treatment of GaTe monocrystals in Cd vapours at the temperature of 833 K (b) for 24 hours and for 60 hours at the temperatures of 623 K (c) and 653 K (d).

Thus the 1.43 eV in [37] is associated to donor-acceptor emission or di-phonon replica (2LO) of A-type centre emission band [38]. The relative intensity of this band decreases for composite obtained at the temperature of 653 K (Fig.7d) and disappear in PL spectrum for sample obtained at the temperature of 833 K (Fig.7b). It can be assumed that the 1.43 eV band is related to defect concentration in CdTe crystals from composite. The PL band with a maximum at 1.372 eV is presented in PL spectra of CdTe-GaTe composite obtained at the temperature of 623 K and 653 K (Fig.7c and Fig. 7d). This band was related in PL spectra of CdTe crystals doped with Ga at low temperatures [39]. The Ga forms acceptor levels with the energy of 20 meV in bandgap for p-type crystallites and 40 meV for n-type crystallites. It can be concluded that PL bands at low energies (1.230 eV and 1.300 eV) have a donor-acceptor nature with the participation of donor levels of Ga impurities from CdTe crystallites in composite. The Ga atoms in the free state as the dopant is obtained as the result of reaction between Cd and Te vapours from GaTe crystals. The donor-acceptor bands from smaller energies are shifted with ~22meV to lower energies as it can be seen from Fig.7b and Fig.7d. This kind of shift can be explained by the increase of Ga atoms concentration in CdTe crystals. The presence of oxygen in CdTe thin layers leads to formation of

PL band at small energies (1.23 eV at T=20K) [40, 41]. The oxydes like Ga forms in CdTe donor levels and acceptor levels through that the PL bands with the maximums at 1.42 eV, 1.278 eV and the band with the maximum at 1.210 eV are forming.

The PL spectrum of GaTe monocrystal at the temperature of 78K presents a narrow band with a maximum at 1.762 eV and the width of the band at ½ of intensity of ~24meV. The maximum of absorption of non-ionized excitons at the temperature of 77K is situated at 1.768 eV [7]. The maximum of this band at the temperature of 90K is shifted to lower energies with ~ 4meV [18]. Therefore the emission band with a maximum at 1.762 eV (Fig.7) can be considered as the radiate annihilation of localized excitons with bound energy of 6 meV. The PL spectrum of CdTe-GaTe composite at the temperature of 623K (Fig.7c) presents a band in the energy range from 1.19 eV to 1.38 eV.

The intensity of PL spectra is strongly influenced by the temperature and completely quenching at the temperature T≥200K. The thermal quenching of PL donor-acceptor band is described by the function:

$$L(T) \ = \ L(0) \left[1 + a \exp\left(-\frac{E_i}{kT}\right)\right] \tag{5}$$

where L(T) and L(0) are the PL intensity at temperature of T and T = 0K, E_i is the activation energy of PL, α is a parameter that determines the rate of temperature and k is the Boltzmann constant.
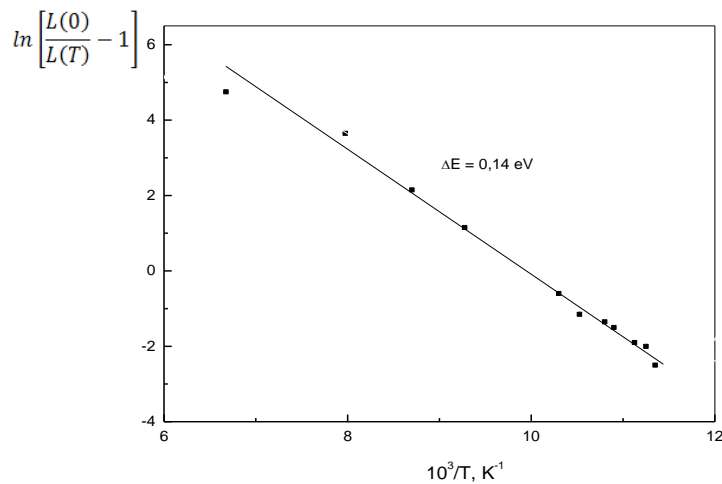

Fig. 8. The intensity of PL peak function of the inverse temperature for CdTe - GaTe composite obtained at the temperature of 833 K for 24 hours

As it can be seen from Fig. 8, the activation energy E_i for 1.42eV band in the temperature range from 90K to 130K for CdTe-GaTe composite obtained at the temperature of 833K (Fig.7b) are equal to 0.162 eV. This value was calculated from the line segment of the intensity dependence of the inverse temperature. The thermal activation energy of PL band with a maximum at 1.4 eV is equal to 95 meV for CdTe composite doped with In [43]. Also In forms the level with smaller energy. The CdTe crystallites from composite are doped with Ga together with the formation of Cd -Te bound from outer layer of atomic packaging of Te-Ga-Ga-Te. When the In dopant is replaced by Ga, as it can be concluded from above, keeps the energy of PL emission band, but the thermal activation energy increases from 95 meV to 162 meV.

5. Conclusions

The new material from CdTe and GaTe material is forming by thermal treatment at the temperatures from 623K to 833K for 24 to 60 hours of mono-crystalline plates of GaTe in Cd

vapours. This material has optical and PL properties characteristic for CdTe crystals in CdTe-GaTe stratified layers. The micro-crystallites of CdTe lay on natural surface of GaTe from composite as layer oriented parallel to (0 0 1) surface.

The direct optical transitions take place in the polycrystalline layers of CdTe composite. The width of the bandgap at the temperature of 300 K is 1.546 eV.

The PL spectra of CdTe - GaTe composite are determined by the CdTe component and impurity states in the band gap of this compound. The dominant PL band with a maximum in the range of 1.38eV - 1.42 eV is related to the presence of defects (Te gap) in CdTe compound. The thermal activation energy of the band with a maximum at 1.42 eV PL determined from the temperature dependence of the PL intensity is equal to 140 meV.

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