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Optical properties of GaTe-ZnTe nanolamellae composite

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Abstract

A material composed of GaTe and ZnTe crystallites with average diameter of ~ 37 nm and 68 nm respectively was obtained by heat treatment at the temperature of 1000K and 1073K of GaTe plates in Zn vapour for 24 hours. The absorbance spectra of composite material obtained at 1073K and that calculated from diffuse reflection using the Kubelka-Munk formula contains the bands characteristic for light absorption in ZnTe and GaTe crystallites. The photoluminescence spectrum of composite material at the temperature of 80K is composed to the excitonic band in GaTe and impurity bands of ZnTe crystallites.
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1. Introduction

The $A^{III}B^{VI}$ semiconductors, with a typical representative of GaTe, belong to the class of lamellar materials. The single crystals of these compounds are formed from atomic planar package type B-A-A-B that has ionic-covalent bonds inside the package and weak polarization links between layers [1]. The structural anisotropy of these semiconductors determines the presence of strong anisotropy of mechanical, electrical and optical properties [2]. The valence bonds on the surface of the structural packages are closed and hence result in a low density of surface states ($\leq 10^{10}$ cm^2) [3].

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The undoped gallium monotelluride is a p-type semiconductor with direct electronic bands. The minimum of conduction band and the maximum of valence band for this material are situated in Z point of Brillouin zone [4-6]. The width of the bandgap at normal temperature (1.67 eV [7]) and the high values of the absorption coefficient ranks gallium mono telluride in the top 10 promising materials for photovoltaic and photoresistive applications [2,8-11].

Special attention is given to research of compound materials that consist of tellurium and Ga, In, Zn and Cd especially as micro- and nanomaterials. The goal is to use them as receptors of ionized radiation [6,12], thermoelectric devices [7,12-14] and as photocatalysts in energy conversion devices [15] with high stability to ionizing radiation.

The weak linkages between packages and the arrangement of elementary lamellae of Te-Ga-Ga-Te contribute to the formation of cracks that easily intercalate atoms and molecules [16-19]. Thus the nano-lamella structures with fundamentally new physical properties are created that are different than those for basic materials [20,21].

The crystalline structure and optical properties of the composite obtained from GaTe single crystalline plates by heat treatment at the temperature of 753K in zinc vapour are analyzed in this paper.

2. Experimental details

The GaTe single crystals were grown by vertical Bridgman-Stockbarger method [22]. The primary compound was synthesized from Ga (5N) and Te (5N) taken in stoichiometric quantities. The p-GaTe single crystalline plates with holes concentration of $(3.5\div4.0)\cdot10^{15}$ cm^{-3} (at room temperature) were used for the sample fabrication. The optically homogenous single crystalline plates with the thickness of ~ 1.0 μm to 2 ÷ 3 mm and surface area of 0.2 ÷ 0.4 cm^2 were obtained by splitting the material in the perpendicular direction of the C_2 crystallographic axis. The GaTe plates with about 2 mg/cm^3 of Zn were introduced into a quartz ampoule. After the evacuation of atmosphere up to $5\cdot10^{-7}$ Pa and sealing, the material was subjected to heat treatment at the temperature of 1000K and 1073K for 24 hours. The outer surface of the heat-treated plates was covered with a micro-dispersed layer of pale reddish colour.

The composition of the obtained material was investigated by XRD using a Shimadzu LabX 6000 diffractometer with CuKα radiation (λ = 0.154182 nm). The coefficients of transmittance *t* and the reflection *R* at the edge absorption band before the heat treatment of GaTe plate were measured with a spectrophotometric device with MDR-2 monochromator and a photomultiplier with a multi-alkaline photocathode (Na_2K-Sb-Cs) with spectral resolution of ~1 meV. The absorption coefficient α was calculated from the formula [23]:

$$\alpha = \frac{1}{d} ln \left\{ \frac{(1-R)^2}{2T} + \left[\left(\frac{(1-R)^2}{2T} \right)^2 + R^2 \right]^{1/2} \right\}, \quad (1)$$

where *d* is the plate thickness.

The absorbance of obtained composite was investigated by the diffuse reflectance method using Specord M-40 spectrophotometer equipped with integrating sphere. The BaF_2 powder with diffuse reflection coefficient of $R_d \approx 1.0$ was used as a prototype.

The PL spectra of primary GaTe plates was excited with radiation of He-Ne laser (λ = 632.8 nm, W=5 mW). The PL of composite material obtained as a result of GaTe single crystalline plates heat treated in zinc vapour was excited by N_2 laser radiation (λ = 337.4 nm).

3. Experimental results and discussion

As is shown in Fig. 1 and the Table, the diffraction lines characteristic for GaTe crystallites in the material are presented together with a series of intense diffraction lines from the lattice structure with Miller indices (h k l) of the ZnTe crystallites. The high intensity of the XRD lines indicates a high concentration of the ZnTe crystallites in the composite material. The XRD line with the highest intensity corresponds to X-ray diffraction from the (1 0 0) and (1 0 1) planes.

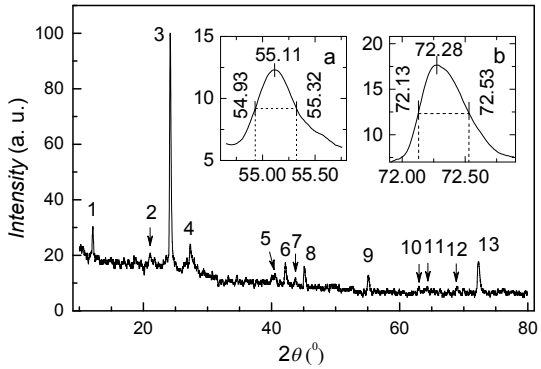


Fig. 1. XRD diffractogram of the GaTe compound intercalated with Zn at the temperature of 1000K for 24 hours. Inset: The contour of diffraction line from: (a) - (4 2 1) planes assembly of GaTe compound; (b) - (1 0 5) planes assembly of ZnTe compound.

Table. The composition of the material obtained by heat treatment of GaTe plates in Zn vapour at 1000K for 24 hours.

Nr.	Experimental Values		ICDD-JCPDS cards				
	2θ (°)	I (a. u.)	Compound	PDF	2θ (°)	I	h k l
1	12,11	30,4	Ga_7Te_{10}	85-0007	12,205	8,8	0 1 2
2	21,09	20,80	GaTe	44-1127	21,04	10	4 0 0
3	24,18	100,00	ZnTe	80-0022	24,028	99,9	1 0 0
4	27,31	24,00	ZnTe	80-0022	27,246	93,2	1 0 1
5	40,53	13,6	GaTe	44-1127	40,32	10	-10 0 2
6	42,16	17,6	ZnTe	80-0022	42,266	71,6	1 1 0
7	43,74	12,00	Ga_7Te_{10}	85-0007	43,752	20,9	6 0 0
8	45,09	16,00	Ga_7Te_{10}	85-0007	45,250	17,0	1 4 6
9	55,11	12,80	GaTe	44-1127	55,01	50,0	4 2 1
10	62,95	8,80	GaTe	44-1127	62,87	10,0	4 2 2
11	64,37	8,80	ZnTe	80-0022	64,232	20,1	2 0 3
12	68,98	8,80	ZnTe	80-0022	68,339	8,8	2 1 1
13	72,28	17,60	ZnTe	80-0022	72,182	12,7	1 0 5

The lines with 2θ angle of 12.11°, 43.74° and 45.09° correspond to X-ray diffraction from the planes (0 1 2), (6 0 0) and (1 4 6) of the Ga_7Te_{10} crystallites. They indicate the fact that at the temperature of 853K the phase transformation of GaTe compound occurs. As a result of these transformations free Te atoms appear and interact with Zn forming the ZnTe crystallites.

The average size D of the GaTe and ZnTe crystallites were calculated using Debye-Scherrer formula [24]:

$$D = \frac{0{,}9\lambda}{\beta \cos\theta}, \tag{2}$$

where λ is the wavelength of the CuK_α radiation, β is the diffraction line FWHM (in radians) and θ is the angle of Bragg diffraction.

In Fig. 1(Inset) are shown the contours of XRD lines with the 2θ angle of 55.11° and 72.28°. The β parameter was determined from Fig. 1 and is equal to $6.80 \cdot 10^{-3}$ rad and $6.98 \cdot 10^{-3}$ rad respectively. Thus the average diameters of the GaTe and ZnTe crystallites are equal to ~ 37 nm and 68 nm respectively.

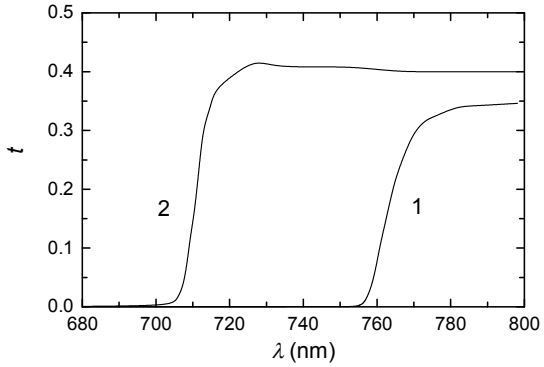


Fig. 2. Transmission spectrum of GaTe plates at the temperature of 293K (curve 1) and 80K (curve 2).

As is shown in Fig. 2 the GaTe single crystals used for the composite are optically transparent at wavelengths longer than the optical threshold. The GaTe compound is a semiconductor with high refractive index which causes high values of reflectance coefficient R in the near IR region.

The index of reflection varies from 3.35 to 3.22 in the spectral range from 800 nm to 1000 nm. These values correspond to a total reflection coefficient from 0.45 to 0.43. Therefore the transmission coefficient cannot exceed the values of 0.55 and 0.58 in this spectral range. The difference between experimental data (Fig. 2) and the calculated results is probably determined by the exfoliation process in elementary packages that generate multiple reflection [26] and light absorption of free charge carriers. After the heat treatment of GaTe plates in Zn vapour the samples are not optically transparent for visible and near IR regions and simultaneously the incident light is strongly scattered.

These two properties satisfy the application of Kubelka-Munk theory to determine the absorbance of the sample from measurements of diffuse light reflectance. The absorbance is determined from formula [27]:

$$F_{R_\infty}(h\nu) = \frac{\alpha}{S} = \frac{(1-R_\infty)^2}{2R_\infty}, \tag{3}$$

where F_{R_∞} is the Kubelka-Munk function; α - absorption coefficient; S - light scattering factor which can be considered constant in a narrow wavelength range, but depends on the grain size of the sample; R_∞ - diffuse reflectance coefficient.

In Fig. 3 is presented the spectral dependence of Kubelka-Munk function from energy for GaTe-ZnTe composite obtained by heat treatment in Zn vapour for ~ 24 hours of GaTe plate with the thickness of 270 μm (1073K (curve 1)) and of 220 μm (1000K (curve 2)).

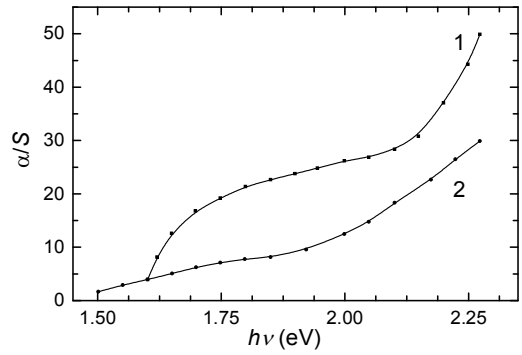


Fig. 3. Spectral dependence of Kubelka-Munk attenuation function form energy of ZnTe-GaTe composite obtained at temperature of 1073K (curve 1) and 1000K (curve 2).

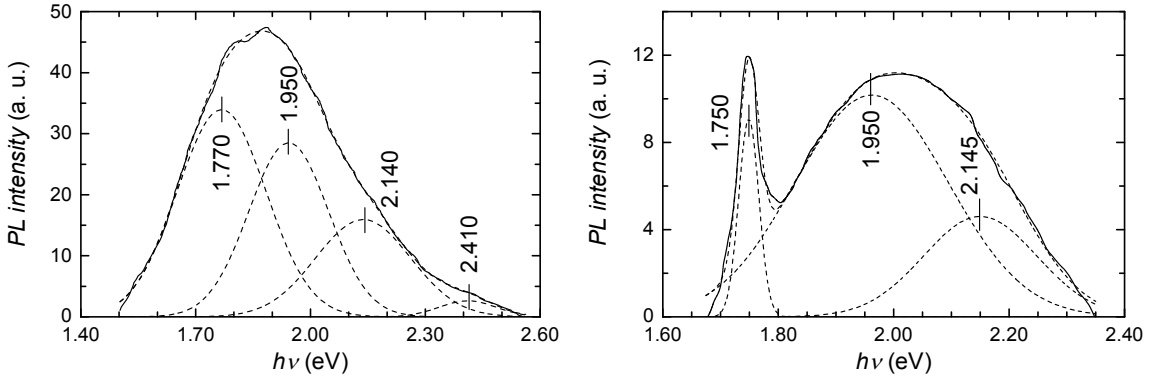


Fig. 4. PL spectrum at the temperature of 80K of the GaTe-ZnTe composite obtained at 1000K (a) and 1073K (b).

As can be observed from Fig. 3 (curve 2), the heat treatment at 1000K leads to a weak granulation of GaTe plate. The slow growth of $F_{R\infty}(h\nu)$ function with energy may be caused by the dispersion of absorption coefficient in GaTe plate. It is known [23] that the absorption coefficient of GaTe single crystals in the spectral range of 1.7 eV ÷1.93 eV increases ~ 2 times. More pronounced are the details of light absorption in the GaTe-ZnTe composite crystals obtained at the temperature of 1073K (Fig. 3, curve 1). Two slopes are highlighted clearly in Fig. 3, one in the region of 1.60 ÷ 1.75 eV determined by absorbance in GaTe crystallites and another in 2.15 ÷ 2.25 eV region caused by the light absorption in the ZnTe crystallites from the composite.

The PL spectrum recorded at the temperature of 80K for GaTe-ZnTe composite obtained at 1000K (Fig. 4,a) presents a broad band in the energy range of 1.5 ÷ 2.55 eV with the maximum at ~ 1.90 eV. This PL band well decomposes in four Gauss curves with the maximums at 1.770 eV, 1.950 eV, 2.140 eV and 2.410 eV.

The PL spectrum at T = 80K of GaTe single crystal (Fig. 5) used for GaTe-ZnTe composite contains the direct exciton emission band with the maximum at 1770 eV and a low intensity impurity band in the range of 1.62 ÷ 1.72 eV.

We can conclude by comparing Fig. 4,a with Fig. 5 that the band with maximum at 1.770 eV is caused by annihilation of localized exciton radiation in GaTe crystallites and the bands with maximum at 1.950 eV and 2.140 eV are PL bands of impurities in ZnTe crystallites of the composite. In the PL spectrum at 80K of the GaTe-ZnTe composite obtained at 1073K (Fig. 4,b) is clearly highlighted a band with maximum at 1.750 eV and the band with a large contour localized in the spectrum range of 1.8 ÷ 2.35 eV. The band localized at 1.750 eV can be interpreted as excitons radiative annihilation with the ionization of acceptor levels located at ~20 meV from the valence band in GaTe. The PL bands with maxima at 1.950 eV and 2.145 eV can be considered as impurities in ZnTe crystallites.

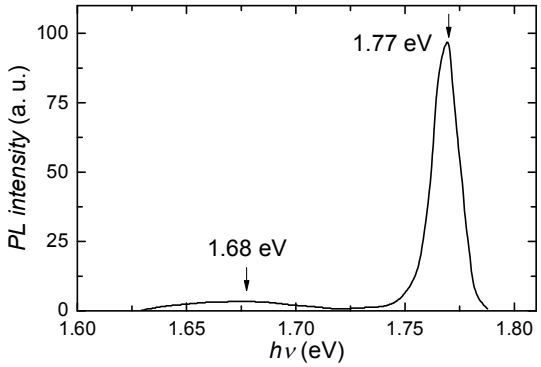


Fig. 5. PL spectrum the temperature of 80K of GaTe single crystal.

4. Conclusions

Material composed of GaTe and ZnTe crystallites was obtained by heat treatment at the temperatures of 1000K and 1073K of GaTe single crystalline plates in Zn vapour. The average diameters of the GaTe and ZnTe crystallites from composite are equal to ~ 37 nm and 68 nm, respectively.

The absorption spectra at room temperature of composite obtained at the temperature of 1073K contains two slopes of pronounced increase of light in GaTe and ZnTe crystallites. They are localized in the spectral range of 1.65 ÷ 1.75 eV and 2.15 ÷ 2.25 eV, respectively.

The PL spectra of GaTe-ZnTe composite obtained by heat treatment at the temperature of 1000K and 1073K of GaTe single crystalline plates in Zn vapor contains the exciton emission band in GaTe crystallites and two impurity bands in ZnTe crystallites.

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