



Optical and photosensitive properties of lamellar nanocomposites obtained by Cd intercalation of GaTe



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ABSTRACT

By Cd-vapor heat treatment, at temperatures from 623 to 833 K, of GaTe single crystals, GaTe–CdTe composite is formed. CdTe amount is increasing together with heat treatment temperature. Absorption, photoconductivity and photoluminescence spectra of the composite contain particularities characteristic to GaTe and CdTe components. The absorption and photoconductivity edges display two thresholds at 1.66 eV (GaTe) and 1.50 eV (CdTe). Short lifetime recombination states form at the surface of composite samples, leading to narrowing of the photoconductivity bands in the high energy region, up to 1.8 eV. Widening of the absorption and photoconductivity bands in the low energy region is determined by absorption processes taking place in both GaTe and CdTe components.

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1. Introduction

Gallium Telluride (GaTe) belongs to III–VI semiconductor group, the physical characteristics of which are determined by their specific layered structure. GaTe crystallizes in form of Te–Ga–Ga–Te stratified packings, displaying preponderantly covalent bonds between metal (Ga) atomic sheets inside an elementary package, and comparatively weak Van der Waals bonds between packings [1,2]. Due to its specific quasi-bidimensional structure, GaTe exhibits a marked anisotropy of mechanical properties (which facilitates intercalation of metal and molecular ions), as well as of electric, optical and photoelectric characteristics, strong excitonic luminescent emission and significant optical nonlinearity, which make it, together with its band gap of 1.68 eV at 300 K, promising as a future optoelectronic material [3–5].

Both chalcogen (Te) and metal (Ga) atomic planes of monoclinic (α) phase are perpendicular to the C_2 crystallographic axis (Fig. 1, a-inset) [6,7]. Long time preservation in normal ambient conditions (temperature, humidity, pressure) leads to formation of a yellow-gray native oxide layer on its surface. At the same time,

the surface electric conductivity is significantly increased, by 20–25%.

The fundamental absorption edge of GaTe, at temperatures from 1.6 to 300 K, is determined by direct optical transitions with formation of free excitons [8–11]. In photoluminescence (PL) spectrum of GaTe single crystals, at temperatures $T \leq 90$ K, the exciton emission band is prevailing. The energy position of the $n = 1$ exciton peak increases from 1.667 eV at $T = 300$ K, to 1.768 eV, at $T = 77$ K.

In this paper absorption and photoconductivity (PC) spectra (at room temperature) of single crystalline GaTe intercalated with Ga from vapor phase, as well as its PL spectra in temperature range of 78 K $< T < 170$ K have been studied.

2. Experimental details

GaTe single crystals were grown by the vertical Bridgman technique [12]. The synthesis of gallium telluride from its component elements (all of 5 N purity), taken in stoichiometric proportions, was performed in a three-zone vertical furnace. In this way polycrystals (comprised of pyramids) displaying two plan-parallel surfaces, optically perfect, oriented perpendicularly to the C_2 crystallographic axis were produced. By splitting bulk GaTe crystals perpendicularly to the C_2 axis, plan-parallel plates with thickness from sub millimeter up to micrometric range have been obtained.

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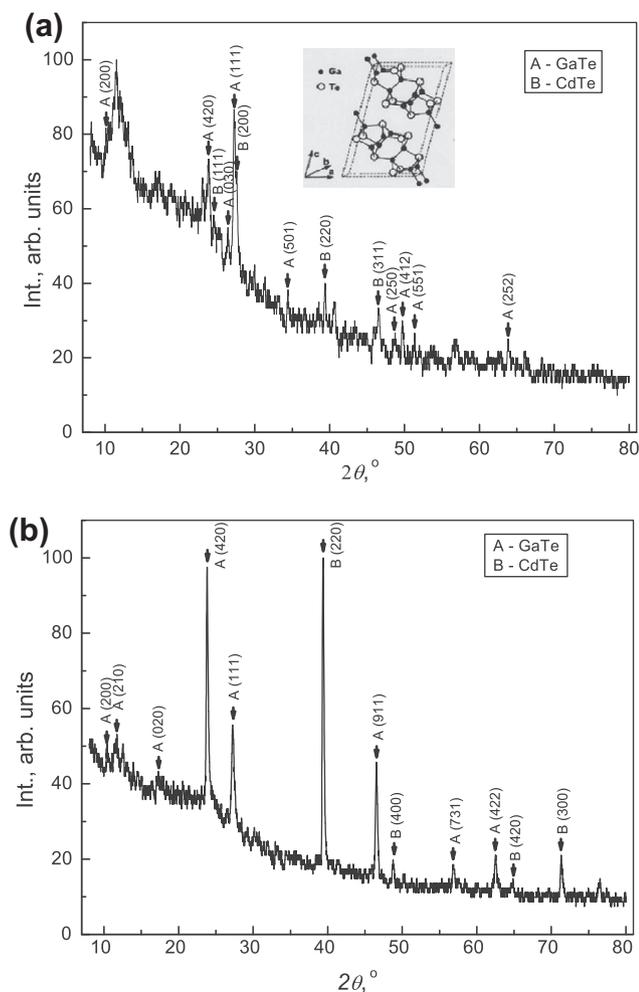


Fig. 1. XRD patterns of the composite obtained by Cd (2 mg/cm^3) heat treatment of GaTe single crystals at temperature of 653 K, for 60 h (a) and 833 K, for 24 h (b). A-GaTe; B-CdTe. Inset of (a): GaTe unit cell comprised of two elementary Te-Ga-Ga-Te packings.

As obtained plates exhibited p-type electric conductivity, with a hole concentration of $(1.5\text{--}30) \times 10^{14} \text{ cm}^{-3}$. Thin In films, used as electrodes in PC measurements, were deposited onto freshly split crystal surfaces by thermal evaporation under vacuum (10^{-5} Torr). In order to improve adhesion of In films on the surface of Cd-intercalated GaTe plates, these were submitted to a heat treatment in vacuum, at $\sim 520 \text{ K}$, for 15–20 min.

From primary GaTe plates rectangular samples, 0.3–1.5 mm thick, have been cut and were then put, together with 2 mg/cm^3 Cd (5 N) metal, in quartz ampoules with internal diameter of 10–12 mm. After pumping down to 5×10^{-5} Torr, ampoules were tight closed and submitted to a heat treatment at temperatures of 623 and 653 K for 60 h, and 833 K, for 24 h. Cd vapor pressure within the ampoules, at operating temperatures for intercalation (between 623 and 833 K), was in the range of 10^{-6} – 10^{-1} Torr.

Photoluminescence of samples obtained at 723 K was also studied, in order to reveal structural changes of Cd-treated GaTe crystals as a function of heat treatment temperature. The excess of Cd at the samples surface was evaporated and transported in the cold side of the ampoule.

Surface of single crystalline GaTe plates, heat-treated at temperatures of 623 and 653 K for 60 h, remains smooth (at $600\times$ magnification), while that of samples obtained by heat treatment at 833 K, for 24 h is granulated, displaying pyramidal inhomogeneities with dimensions (at the bottom) of 0.5–10 μm . Composition of intercalated single crystal GaTe samples has been studied by X-ray diffraction (XRD) analysis (a DRON-2.0 diffractometer, $\lambda_{\text{CuK}\alpha} = 1.54182 \text{ \AA}$).

Fig. 1 shows typical diffractograms for two GaTe samples intercalated by Cd-treatment at 653 K, for 60 h (a) and at 833 K, for 24 h (b). As can be observed from this figure, XRD patterns of examined samples display strong diffraction lines of both rhombohedral GaTe (base material) and CdTe. Samples prepared at 653 K show predominant GaTe diffraction lines, in particular the line for (420) planes, while for an increased temperature of heat treatment, from 653 to 833 K, the amount of CdTe appears also increased with respect to that of GaTe. Therefore,

we can admit that as a result of heat treatment of GaTe plates in Cd-vapor atmosphere, at temperatures $T \geq 653 \text{ K}$, a GaTe–CdTe composite is formed, with an increased CdTe amount together with heat treatment temperature.

The absorption spectra of samples have been determined from transmittance and reflectance measurements performed by means of a Specord M-40 spectrophotometer.

Photoluminescence excitation of both unintercalated and Cd-intercalated GaTe samples was performed by using a He–Ne laser radiation, with wavelength $\lambda = 6328 \text{ \AA}$ and power density of $\sim 800\text{--}1000 \text{ W/cm}^2$. Sample temperature was measured by a type T (Copper–Constantan) thermocouple. The PL and PC spectra were recorded by using a spectrophotometric installation based on a MDR-2 type monochromator with diffraction grating (1200 and 600 mm^{-1}). In PC measurements a DKCS-250 type Xe-arc lamp (130 W) was used as light source with quasi-continuous spectrum.

3. Results and discussions

In Fig. 2 absorption spectra of single crystalline unintercalated (curve 1) and Cd-intercalated GaTe plates at temperature of 623 K (curve 2) and 653 K (curve 3), for 60 h are presented. As can be observed from this figure, in a narrow energy range (20 meV), from 1.63 eV to 1.65 eV, the absorption coefficient of unintercalated sample displays an increase by over 20 times. Taking into account that the binding energy of electron–hole pair is of 25 meV at $T = 77 \text{ K}$ [13], it results that the fundamental absorption edge of GaTe crystals, in temperature range of 78–300 K, is formed by ($n = 1$) exciton–phonon interaction.

At photon energies $h\nu < 1.62 \text{ eV}$ (optical transparency region of GaTe), the absorption spectra of intercalated samples emphasize an absorption band with a threshold of $\sim 1.5 \text{ eV}$ (Fig. 2, curves 2 and 3). The mentioned particularity is seen to enhance together with increasing temperature of heat treatment, from 623 to 653 K (Fig. 2, curves 2 and 3). It is well known that the fundamental absorption edge of polycrystalline CdTe films at 300 K is located at 1.50–1.54 eV [14,15]. Presence of the absorption threshold by 1.5 eV allows us to admit that as a result of heat treatment, at 623–653 K, of GaTe single crystals in Cd vapors, outer Te atoms from the Te–Ga–Ga–Te packings (Fig. 1a) combine with Cd and form a GaTe–CdTe composite and free Ga. As can be seen in Fig. 2, increasing heat treatment temperature from 623 to 653 K leads to an increase in the absorption coefficient in the energy range of $1.46 \leq h\nu \leq 1.52 \text{ eV}$ (Fig. 2, curves 2 and 3), which indicates that similar CdTe layers do also form at the interface of stratified Te–Ga–Ga–Te packings.

Fig. 3 shows the spectral dependence of the photocurrent (divided by the number of incident photons and normalized to unity) for the primary GaTe plate (curve 1) and heat-treated one

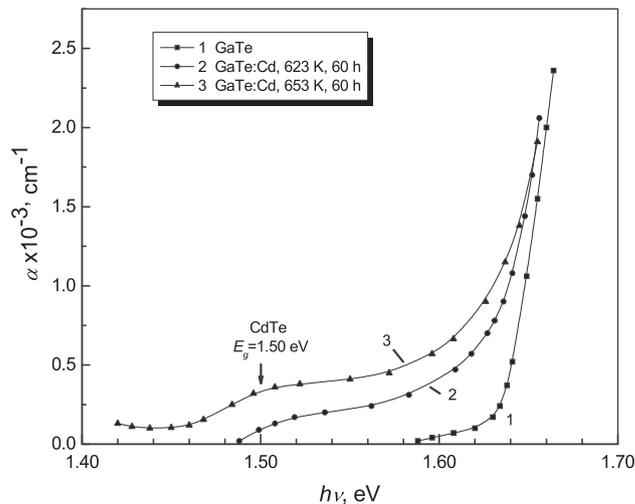


Fig. 2. Absorption spectra of untreated (curve 1), Cd-vapor treated GaTe single crystals at temperature of 623 K (curve 2) and 653 K (curve 3), for 60 h.

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