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# Light Emitters Based on CdTe Doped with Isovalent Impurities

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The problems of developing light-emitting structures based on *CdTe* with an extended range of operating temperatures and radiation-resistant parameters are studied. Optimal modes of diffusion of isovalent impurities *Mg* and *Ca* are established, the main optical parameters and characteristics of radiation sources are determined, and emitters are obtained, the high quantum efficiency $\eta \approx 10$ - 15% of which is determined by doping II-IV compounds with isovalent impurities. The design of devices has been developed and light emitters based on CdTe, whose radiation is determined by the interband recombination of free charge carriers and the dominant annihilation of bound excitons, have been fabricated by doping with isovalent impurities *Mg*, *Ca*.

**Keywords:** light emitters, cadmium telluride, isovalent impurity, high quantum intensity.

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## Introduction

Cadmium telluride is one of the widely used materials for functional electronic devices [1, 2]. This is due to a number of its physical and technical parameters that provide the appropriate properties and characteristics of various types of devices, especially in optoelectronics. Among them, photoelectronic detectors deserve special attention. The relatively wide band gap ($E_g$ – 1.50 eV) and direct band nature make it possible to obtain high efficiency devices in the high temperature region and are also optimal for converting solar energy into electrical energy [3, 4]. At the same time, the issue of obtaining efficient *CdTe*-based emitting light devices and the prospects for the use of *CdTe*-based thin films for photovoltaics due to their high efficiency and low cost remains topical [5]. It should be noted that this compound is one of the II-VI compounds in which the type of conductivity can be varied. However, the quantum efficiency of radiation from basic materials and devices based on it is significantly low. One of the reasons for this is the formation of intrinsic point defects (IPDs), which predetermine the formation of poorly controlled deep energy levels. They become the predominant channels of nonradiative recombination processes, significantly reducing the efficiency of radiation generation processes. Therefore, it is important to select the type of dopants and methods of doping with them [6]. There is also a growing need to expand the study of the properties of thin films (namely, structures and defects) to improve their efficiency for practical applications [7].

## I. Experiment

### 1.1. Test samples

Basic CdTe crystals were obtained by the basic Bridgman method. They have a characteristic electronic conductivity (*n*-type). Its value is $\sigma \approx 10^{-6}$ - $10^{-1}$ $\mathrm{Ohm}^{-1}\cdot\mathrm{cm}^{-1}$ at T = 300 K. As is known [8, 9], the *n*-type electrical conductivity of substrates is determined by donor states formed by intrinsic point defects (IPDs) crystal lattice, namely, vacancies in the sublattice of the metalloid $V_{Te}^{\bullet}$ with a depth of 0.03 eV and a metal atom in the $Cd_i$ interstices with 0.8 eV. The inversion of the conductivity type was obtained by doping the initial crystals with isovalent impurities (IVI) of *Mg* and *Ca*. For their introduction, classical diffusion methods and special treatment in an aqueous solution of $CaNO_3$ were used, respectively. To do this, the base material was cut with a string mechanical cutting plate into dimensions of 4×4×1 mm. Subsequently, the substrates were mechanically polished with ACM 20/14 and ACM 3/1 diamond pastes and polished on the corresponding fabric. The resulting substrates were boiled in dimethylformamide and thoroughly washed in running distilled and deionized water. The state of the resulting surface was monitored visually under an MBS-9 microscope at a magnification of at least $40^X$. Diffusion of *Mg* IVI was carried out according to the closed volume method at an annealing temperature $T_a \approx 850\ ^0$C. Samples of base *CdTe* and a sample of *Mg* diffusant were located on opposite edges of a quartz ampoule, which was evacuated to no worse than $10^{-4}$ Torr. Diffusion was carried out in an isothermal regime on a temperature plateau. Doping of IVI with *Ca* was carried out by special treatment by boiling at low temperatures ($\approx 110\ ^0$C) in an aqueous solution of $CaNO_3$ under the appropriate regime. The latter ensured doping with Ca impurity only in a thin near-surface layer.

### 1.2. Research methods

To determine the properties of the obtained samples, complex studies of optical properties were carried out, namely, optical transmission $T_\omega$, reflection $R_\omega$ and photoluminescence $N_\omega$. Recent studies were carried out according to an expanded methodology, which made it possible to determine the possibilities of the obtained samples for the creation of light-emitting devices on their basis [10]. Classical measurement techniques and using the λ-modulation method were used. Differential spectra $T'_\omega$, $R'_\omega$, $N'_\omega$ are obtained. Based on them, the main parameters, characteristics and properties of the studied samples were determined. A universal optical setup was used, in which an MDR-23 spectral device was used, a FEP-79 photodetector multiplier, a synchronous detection system, and optical radiation sources, namely, a special ELC/C halogen lamp and an LGN-21 nitrogen laser.

The spectral setup was calibrated according to the well-known technique for the radiation of a reference lamp, which made it possible to take into account the spectral quantum sensitivity of the setup $S_\omega$ in radiation studies. The applied research methods are consistent with the well-known ones [11].

## II. Discussion of research results

Obtaining and studying the possibility of creating light emitters based on *CdTe* crystals revealed the decisive role of IVI and the method isovalent substitution (IVS) in the formation of highly efficient radiation [12]. Its localization in the marginal region is also important. It has been found that when *CdTe* is doped with IVI *Mg*, high-intensity radiation is formed exactly in accordance with the energy value $E_g$ of the band gap. It should be noted that doping with classical impurities using known technological processes (diffusion and ion implantation) does not provide materials for devices with luminescence in the edge region [13]. A typical luminescence spectrum of *CdTe:Mg* covers the near infrared spectral region starting from λ = 0.885 μm (Fig. 1).

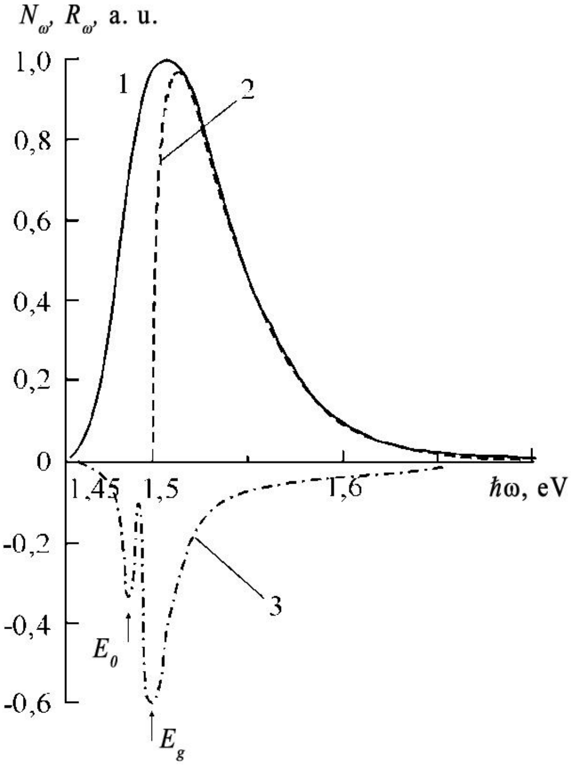

**Fig. 1.** Spectra of photoluminescence (1) and optical reflection (3) of *CdTe:Mg* layers at 300 K. Curve 2 was calculated using formula (1).

The emission spectrum of the *CdTe:Mg* layers is a wide asymmetric band. It covers both the photon energy range $\hbar\omega > E_g$ ($E_g$ = 1.5 eV) and $\hbar\omega \leq E_g$. Consider the characteristic features.

In the region $\hbar\omega > E_g$ the spectral distribution of radiation from the experimental curve is in good agreement with the well-known analytical expression for interband transitions of free charge carriers [13, 14]:

$$N_\omega \sim (\hbar\omega)^2 \sqrt{\hbar\omega - E_g}\, exp\left(-\frac{\hbar\omega - E_g}{kT}\right), \qquad (1)$$

where *k* is constant Boltzmann, *T* is temperature.

The properties characteristic of interband recombination are also observed, namely: a) the maximum of the emission spectrum $\hbar\omega_m$ is located at photon energies slightly higher than $E_g$; b) the position $\hbar\omega_m$ does not depend on the intensity (excitation level *L*) of photoexcitation; c) the temperature dependence of $\hbar\omega_m$ is similar to $E_g(T)$. The above features indicate precisely the interband radiative recombination of free electrons and holes in the region $\hbar\omega > E_g$ of photon energies. The above indicates the formation of radiation with photon energy $\hbar\omega > E_g$ as a result of interband recombination of free charge carriers.

Radiation in the range $\hbar\omega \leq E_g$ unambiguously reveals its nature in studies of modulation spectroscopy [14]. The differential radiation spectrum $N'_\omega$ is a complex curve in shape. Its character essentially depends on the excitation level *L*, Fig. 2. Characteristic properties are observed. First, the point $E$ of the section of the curve with the abscissa axis (characterizes the maximum $\hbar\omega_m$ of the ordinary $N_\omega$ curve) shifts with an increase in the excitation level $L$ to the region of lower photon energies. Second, at large $L$, a number of equidistant kinks $N'_\omega$ are observed on the low energy "wing" of the curve, the energy distance between which is 21 meV, which agrees with the energy of the *LO* phonon in *CdTe* [6, 12]. Thirdly, the intensity $I$ of this low-energy band of radiation with the level of excitation varies according to the law $I \sim L^{1,5}$.

The established features of radiation at $\hbar\omega \leq E_g$ are characteristic of the annihilation of excitons during their inelastic scattering by free charge carriers [14]. Since, as a result of doping, the hole conductivity of the *CdTe:Mg* surface layers is obtained, it would be logical to admit that they are holes. It is the increase in their concentration that adequately explains the shift of point $E$ towards lower energies with increasing $L$ since the probability of exciton scattering increases. Most likely, the excitons are bound to the isovalent *Mg* impurity.

Levels involving *Mg* appear on the differential reflection curves $R'_\omega$, curve 3 in Fig. 1. At the energy $\hbar\omega = 1{,}48$ eV, a peak is observed, which is formed by optical transitions involving *Mg* levels. The depth of occurrence of *Mg* centers is determined by the difference $E_g - \hbar\omega = 20$ meV. Accordingly, the excitons are most likely bound to the isovalent *Mg* impurity. Its short-range potential leads to a sharp increase in the efficiency of exciton radiation, as well as its temperature stability. As a consequence, intense radiation is observed at $T = 300$K. Note that the quantum efficiency of *CdTe:Mg* radiation in

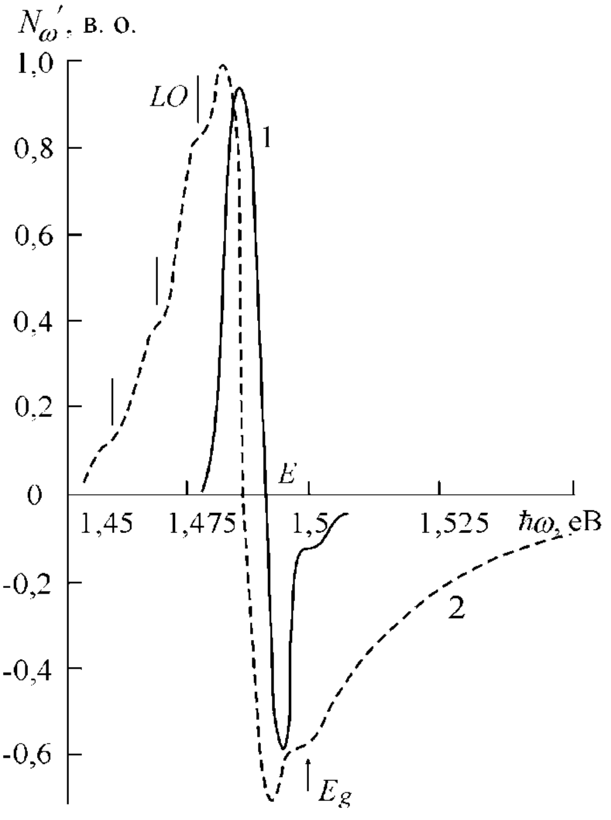

**Fig. 2.** Differential photoluminescence spectra of *CdTe:Mg* layers at different excitation levels: 1 – $L = 4 \cdot 10^{17}$ phot/s, 2 – $L = 10^{19}$ phot/s. $T = 300$ K.

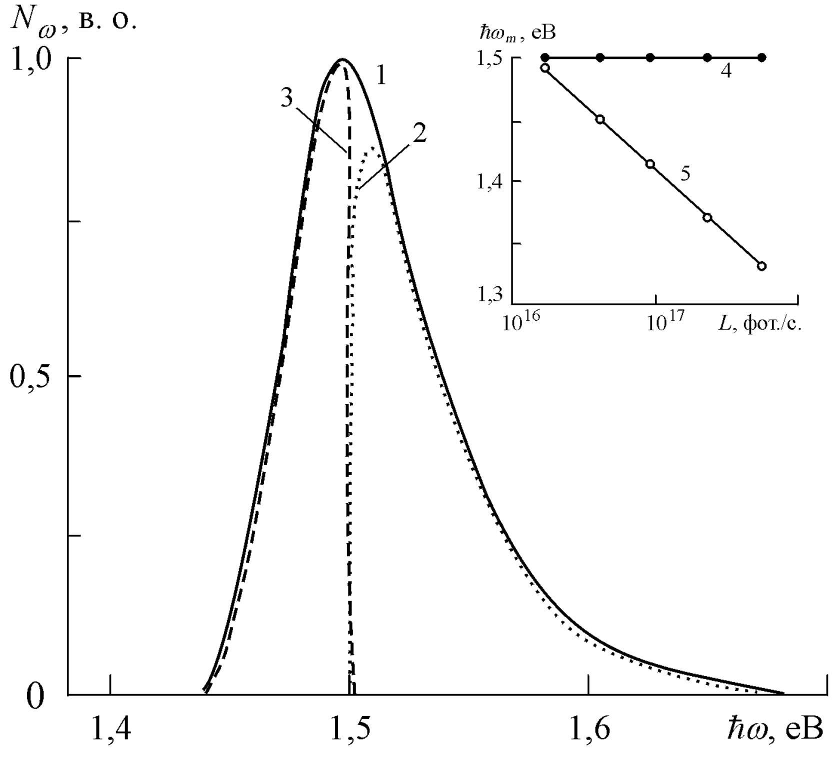

**Fig. 3.** Normalized spectra of photoluminescence and *CdTe:Ca* layers (1) and component bands of interband recombination (2) and exciton annihilation (3). The inset shows the dependence of the position of the maximum of the components of the emission bands of interband recombination (4) and exciton annihilation (5). $T = 300$ K.

the photon energy range of 1.45 - 1.7 eV can reach η = 7 - 8 %, in contrast to 0.1 % when doped with conventional donor and (or) acceptor impurities.

Sources of intense radiation based on *CdTe* were also obtained as a result of IVI doping with *Ca*. To do this, the initial substrates were processed by special annealing in aqua chemical solutions of calcium. The study of $\lambda$-modulated optical reflection $R'_{\omega}$ did not reveal the formation of a material of a different nature on the surface as a result of doping. This is evidenced by the band gap width $E_g$ = 1.50 eV defined by size $R'_{\omega}$ for *CdTe:Ca* and the parameters of the band structure, namely, the value of the spin-orbit splitting of the valence subband $\Delta_{so} \approx 0{,}90$ eV for *CdTe:Ca* [15].

IVI *Ca*-doped layers are also characterized by intense edge luminescence. Its quantum efficiency is $\eta$ ~ 15-20 %. Note that the radiation efficiency on the initial undoped *CdTe* crystals does not exceed 0.08 % [16].

The radiation of devices based on *CdTe* doped IVI *Ca* in the photon energy range $\hbar\omega \geq E_g$ is characterized by the independence of the position of the maximum $\hbar\omega_{m}$ on the excitation intensity *L*. The shape of the spectrum in this region also correlates well with the analytical expression (1). This indicates interband recombination. In the region $\hbar\omega \leq E_g$, radiation is also observed, indicating the second component. Its intensity varies according to the law $I \sim L^{1,5}$ and weakly depends on temperature [13, 15].

Such properties are characteristic of exciton luminescence in the case of inelastic exciton-electron interaction (Fig. 3). Its formation is due to the IVI, which forms a short-range potential [9, 11]. It is he who causes "short-range disorder" as a result of a slight local violation of the periodicity of the arrangement of atoms of the tetrahedral configuration [11, 14]. Accordingly, there is an increase in the half-width of exciton bands up to $\Delta\hbar\omega_{½} \sim kT$ (compared to classical bound excitons) and their temperature stability observed in the case of *CdTe:Ca* and *CdTe:Mg* under study. Also, the short-range potential predetermines a significant increase in the efficiency of exciton radiation up to $\eta \sim 15$ - 20 %, together with its weak temperature dependence. The latter makes it possible to observe it at $T \geq 300$ K [16].

Important for functional electronics are the results on obtaining photosensitive structures on the obtained *p–n* junctions. Special investigations carried out have revealed good agreement between the photosensitivity spectra and the characteristics given for edge radiation. The hole conductivity of the material is confirmed by measurements using a thermal probe, as well as studies of thermoEMF and CVC in a wide range of values.

## Conclusions

Thus, doping with isovalent impurities *Mg*, *Ca* predetermines the production of sources of intense radiation in the near-IR region based on *CdTe*. The isovalent nature of impurities contributes to the "cleansing" of background impurities, which cause nonradiative recombination, and also determines the formation of excitons bound to the IVI. The resulting radiation sources are characterized by intense radiation localized in the edge region of *CdTe* with a high quantum efficiency of $\eta \approx 7$-15%. According to the established optimal modes of diffusion and isovalent substitution, intense radiation is formed, which is determined by the interband recombination of free charge carriers and the dominant annihilation of excitons bound on isovalent impurities.

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# Світловипромінювачі на основі CdTe, легованого ізовалентними домішками

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Досліджено проблеми розроблення світловипромінювальних структур на основі *CdTe* із розширеним діапазоном робочих температур і радіаційно стійких параметрів. Встановлено оптимальні режими дифузії ізовалентних домішок *Mg* і *Ca*, визначено головні оптичні параметри і характеристики джерел випромінювання та отримано випромінювачі, висока квантова ефективність $\eta \approx 10 - 15\,\%$ яких визначається легуванням II-VI сполук ізовалентними домішками. Розроблено конструкцію приладів і виготовлено легуванням ізовалентними домішками *Mg, Ca* світловипромінювачі на основі *CdTe*, випромінювання яких визначається міжзонною рекомбінацією вільних носіїв заряду та домінуючою анігіляцією зв'язаних екситонів.

**Ключові слова:** світловипромінювачі, телурид кадмію, ізовалентна домішка, висока квантова інтенсивність.