

Laser-induced Point Defects in CdTe:Mn Single Crystals Irradiated by IR Laser

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The electrical characteristics of CdTe:Mn *n*-type single crystals with an initial resistivity of 100 Ω cm (300 K), the dependence of the EPR spectra and low-temperature photoluminescence on the impurity concentration and temperature were studied. Manganese impurity localization in the crystal lattice and depth of impurity states are determined. No exchange interaction between the manganese ions is observed (with-in the concentration of introduced manganese $N_{Mn} \leq 5 \times 10^{18} \text{ cm}^{-3}$). Manganese occupies vacancies or replaces cadmium in the crystal lattice. The effect of IR laser radiation (with radiation quantum energy $\hbar\omega$ much lower than the band gap energy E_g and radiation power density W below the critical value) on the physical properties of *n*-CdTe:Mn single crystals is shown experimentally. It is established that variation of spectrum of point defects is due to interaction of the EH field of laser wave with inclusions of native components as well as background and specially introduced impurities.

Keywords: Semiconductors, Point defects, Impurities, CdTe, Laser interactions, Photoluminescence, Paramagnetic resonance, Conductivity, Optical transmittance.

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1. INTRODUCTION

Now CdTe and its solid solutions are the main materials for semiconductor detectors of X- and γ -radiation operating at room temperature [1-3] as well as passive elements in IR optoelectronics. Conduction of the above materials and mechanisms of charge carrier recombination (that determine their key parameters) depend on the concentration of uncontrolled background impurities and native defects as well as their spatial localization in crystal lattice. Recently a number of papers have been published that deal with an analysis of compensating effect of III and VII group elements and transition metals on CdTe conduction [4, 5] as well as effect of IR laser and neutron irradiation on impurity distribution in the undoped $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ ($0 \leq x \leq 0.04$) single crystals [6, 7]. At the same time, the relation between conduction and its temperature variation with concentration of residual impurities and native defects in specially undoped crystals still remains unexplained, because presence of background impurities and native defects is sufficient for the appearance of considerable concentration of complexes in the region of localization of native component inclusions. And the mechanism of interaction of IR laser radiation with CdTe single crystals and solid solutions based on them is still not completely understood.

The objective of the present work is investigation of the effect of IR laser radiation on behavior of background impurities, native defects and manganese impurity that determine the mechanisms of conduction, thermostimulated conductivity, optical absorption, EPR and low-temperature photoluminescence (LTPL). It is supposed that the radiation quantum energy $\hbar\omega$ is much less than the band gap energy E_g and radiation power density W_{cr} is below the damage threshold for CdTe single crystals doped with Mn ($N_{Mn} \leq 1 \times 10^{19} \text{ cm}^{-3}$).

2. PREPARATION OF MATERIALS

The following three procedures were used when studying CdTe ($N_{Mn} \leq 1 \times 10^{19} \text{ cm}^{-3}$) single crystals grown with the modified Bridgman method in the quartz carbon containers:

– procedure I: (Cd + Te) + Mn; Cd and Te were introduced into the stoichiometric ratio and manganese was added;

– procedure II: $\text{Cd}_{1-x} + \text{Mn}_x + \text{Te}$, in accordance with the ratio of components as in a solid solution;

– procedure III: CdTe + Mn, with manganese added into previously synthesized stoichiometric CdTe.

The chemical purity of the initial components was 6N. The single crystal plates of [111] orientation and 1-1.5 mm thick were cut out and subjected to bilateral chemical-mechanical polishing. Then the polished plates were cut into 1×10 mm samples (to study conduction and thermostimulated conductivity) and 5×10 mm samples (to study optical properties). The contacts for performing electrophysical studies were applied using chemical or thermal Au deposition.

3. ELECTROPHYSICAL AND OPTICAL PROPERTIES OF CdTe:Mn SINGLE CRYSTALS BEFORE AND AFTER IR LASER IRRADIATION

Contrary to undoped CdTe, the crystals grown to impurity concentrations $1 \times 10^{17} \leq N_{Mn} \leq 1 \times 10^{19} \text{ cm}^{-3}$ were of *n*-type in all procedures of growing and impurity introduction. Spreading of concentration and mobility of charge carriers over the ingot and plates as well as appearance of built-in CdTe-CdMnTe(MnTe) heterojunctions (due to non-uniform impurity distribution) were observed. This manifested itself as presence of photo-emf as well as the appearance of a large-scale potential relief (activation growth of mobility with temperature and

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anomalously low values of charge carrier concentration). These effects appeared most strongly in the single crystals grown using the procedures II and III. Therefore, we chose mainly crystals grown with the procedure I. The samples to be investigated were cut from the central plate parts rather than ingot periphery.

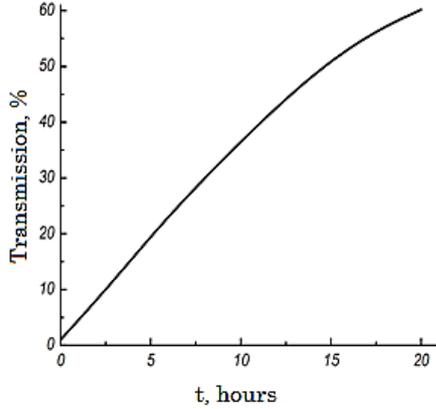


Fig. 1 – Dependence of optical transmission τ of CdTe:Mn single crystals at $\lambda = 10 \mu\text{m}$ on time t of action of IR laser radiation

The concentration of charge carriers in the samples did not show explicit dependence on the concentration of introduced Mn and was $1.2 \times 10^{14} \leq n \leq 3.0 \times 10^{15} \text{ cm}^{-3}$, with mobility $750 \leq \mu_{295 \text{ K}} \leq 1100 \text{ cm}^2/\text{V}\cdot\text{s}$ as impurity concentration changed by over three orders of magnitude. Variation of electron mobility with impurity introduction indicates change in mechanism of charge carrier scattering and, as a result, variation of resistivity not only because of compensation of native defects. In this case, the activation energies of defects were determined from the experimental dependences $\lg(R_H T^{3/2}) = f(10^3/T)$. They were $E_{D1} \leq 0.02 \text{ eV}$ for shallow donors and $E_{D2} \leq 0.36 \text{ eV}$ for deeper donor centers (whose density of states was much lower than that for E_{D1}). After interaction of IR laser radiation with a number of crystals, it was found that the type of crystal conductivity is not changed; the resistivity at $T = 300 \text{ K}$ increases by four orders of magnitude. The mobility of charge carriers is $\mu_{295 \text{ K}} = 1.2 \times 10^3 \text{ cm}^2/\text{V}\cdot\text{s}$ and does not depend on impurity concentration. In this case, optical transmission for crystals at $10 \mu\text{m}$ increases from 4 % to 64 % and spectral transmission region of crystals increases from $3 \mu\text{m}$ to $20 \mu\text{m}$ (Fig. 1). These results indicate (i) homogenization of CdTe:Mn crystals, (ii) improvement of their crystal structure and (iii) variations of mechanisms of CdTe:Mn absorption of IR radiation. Before irradiation in that spectral region, the main absorption mechanism was absorption by free charge carriers and precipitates of native components whose concentration decreases with IR laser irradiation time.

It is known that in perfect CdTe single crystals the predominant mechanism of charge carrier scattering at $T > 100 \text{ K}$ is that by optical phonons, so the mobility of charge carriers varies with temperature as $T^{3/2}$. In turn, the effective densities of states in the conduction band ($N_c = 2(m_n^* k T / 2\pi\hbar)^{3/2}$) and in the valence band ($N_v = 2(m_p^* k T / 2\pi\hbar)^{3/2}$) are proportional to $T^{3/2}$ (m_n^* and m_p^* are the effective masses of electron and hole, re-

spectively). Then the temperature dependence of resistivity $\rho = 1/(en\mu_n + ep\mu_p)$ is the exponential function of temperature (μ_n and μ_p are the electron and hole mobilities, respectively), and dependences $\rho(T)$ in coordinates $\ln(\rho)$ on $1000/T$ (presented by straight lines) can be used to determine activation energy ΔE of material conduction (Fig. 2).

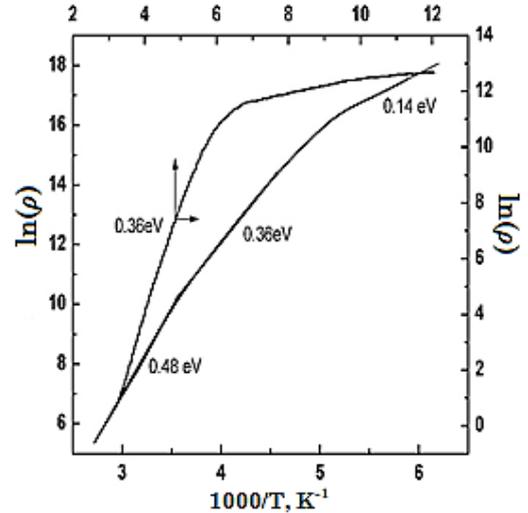


Fig. 2 – Dependence of resistivity on temperature ($\ln\rho$ versus $1000/T$): upper curve – before IR laser irradiation of CdTe:Mn, lower curve – after irradiation for 21 hours at $W = 20 \text{ W}\cdot\text{cm}^{-2}$

It was established by analyzing the $\rho(1/T)$ dependences that action of IR laser radiation leads to reduction of electron concentration in single crystals due to formation of a number of deep donor centers with different densities of states in the forbidden band of CdTe:Mn. The energy levels of these centers are determined (see Fig. 2). It is unlikely that the centers nature is related to the paramagnetic impurity Mn (see below). Most likely it is determined by the presence of background impurities that become electroactive due to their interaction with the native components in the crystal lattice after their dissociation in the \mathbf{EH} field of IR laser wave.

4. EPR IN CdTe:Mn

The EPR spectra were registered over the wide temperature range (20-300 K) with the Varian E-12 setup. At high temperatures, the spectrum consists of six isotropic lines of hyperfine structure with the half-width $\Delta H = 30 \text{ Oe}$ that become narrower to $\Delta H = 10 \text{ Oe}$ as temperature decreases.

Six lines in the EPR spectra are due to the interaction of $3d^5$ -electrons of the Mn^{2+} ion with the native nuclear momentum $I = 5/2$ of the ^{55}Mn isotope. The half-width of the EPR lines is due to the presence of Mn^{2+} ions at the lattice points and interstitial Mn^{2+} ions. In this case, the spin Hamiltonian constants are characterized by the following values:

$$g = 2.0090 \pm 0.0005, \quad A = (59.9 + 0.2) \times 10^{-4} \text{ cm}^{-1}.$$

Here g is the factor of spectroscopic splitting and A is the constant of hyperfine interaction with Mn^{55} nucleus. Earlier it was noted that as temperature decreases, the

satellites appear near each of the six narrower lines of hyperfine structure $\Delta H \sim 10$ Oe (Fig. 3). They are due to superhyperfine interaction of $3d^5$ -electrons of Mn^{2+} with nuclear moments of the ^{125}Te and ^{123}Te isotopes ($I = 1/2$) of the first coordination sphere with natural content of 6.57 % and 0.85 %, respectively. The EPR spectrum of CdTe:Mn single crystals at $T = 20$ K is characterized by the following constants of spin Hamiltonian:

$$g = 2.010 \pm 0.0005,$$

$$A = (61.16 \pm 0.2) \times 10^{-4} \text{ cm}^{-1},$$

$$a_{Te} = (12.20 \pm 0.2) \times 10^{-4} \text{ cm}^{-1},$$

where a_{Te} is the superhyperfine interaction constant. It should be noted that a Mn^{2+} ion at the CdTe lattice point (lattice of zinc blende structure) will be surrounded by four Te ions of the first coordination sphere.

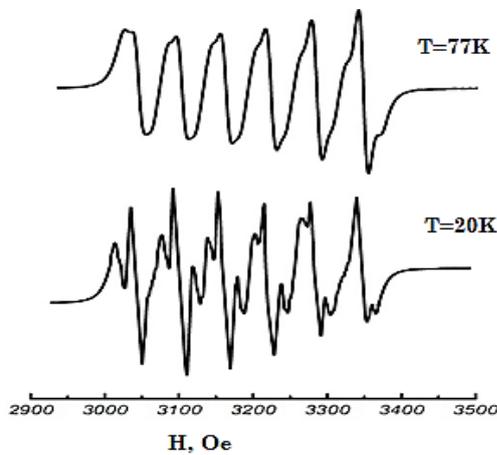


Fig. 3 – EPR spectra of Mn^{2+} ions in CdTe:Mn at temperatures of 77 K and 20 K

There were no qualitative changes in the EPR spectra after interaction with IR laser radiation, and the spin Hamiltonian parameters remained the same. Only a slight increase of intensity of EPR lines was observed. This indicates growth of concentration of EPR active centers in the CdTe crystal lattice and confirms presence of a small part of uncharged manganese impurity in inclusions or complexes with native defects and background impurities. In this case, however, it is necessary to take into account an increase of skin layer thickness since resistivity grows by several orders of magnitude in the course of irradiation.

5. LOW-TEMPERATURE PHOTO-LUMINESCENCE (LTPL) OF CdTe:Mn SINGLE CRYSTALS

The CdTe:Mn samples of (111) orientation were used to investigate IR laser action on them. Just before measuring LTPL the single crystals were splitted along the (110) cleavage planes. Laser-stimulated "annealing" of samples was performed under the natural conditions. The temperature of the crystals studied at laser "annealing" did not exceed 470 K.

The LTPL spectra were investigated at liquid helium temperature (4.2 K) on cleaved (110) planes. Excitation was made by Ar or He-Ne lasers at wavelengths

$\lambda = 488.0$ nm and $\lambda = 632.0$ nm, respectively. The radiation was analyzed with an MDR-23 grating monochromator. The focus was on investigation of LTPL lines in the three characteristic spectral regions of luminescence: (i) bound exciton (at a neutral A^0X acceptor and at a neutral D^0X donor), (ii) donor-acceptor emission (DA) and (iii) low-energy region (A- or D-centers).

Inessential LTPL changes were in the (ii) and (iii) spectral regions. But in the exciton (i) spectral region, as can be seen from Fig. 4, the intensity of exciton lines A^0X and A^0X' on a neutral acceptor dropped considerably, while that on a neutral donor D^0X increased because of action of IR laser radiation. In addition, attention is drawn to a minor shift of exciton bands into the violet spectral region, since introduction of manganese impurity results in increase of band gap energy E_g of CdTe:Mn single crystals. A decrease of intensity of semistructured transition lines is observed in the conduction band-acceptor transition (DA + BA) region. This indicates reduction of concentration of shallow acceptor impurities and increase of the $h\nu = 1.5771$ eV line intensity that may be related to an exciton at a deeper neutral donor.

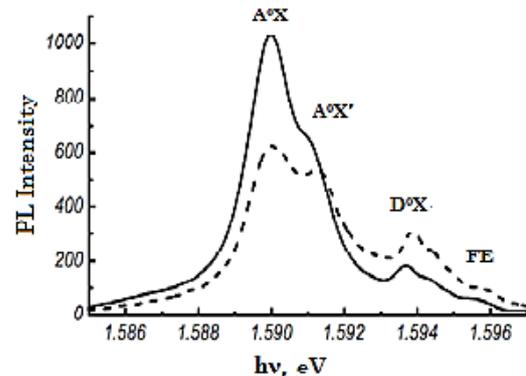


Fig. 4 – The spectra of exciton region of CdTe:Mn LTPL. Full curve – before interaction, broken curve – after interaction of IR laser radiation with CdTe:Mn for 15 hours

6. DISCUSSION

Changes in the system of intrinsic and impurity point defects that are present in the crystal in different charge states [8, 9], their concentration, spatial localization, as well as a change in the bandgap of CdTe and its solid solutions, occur after purposeful doping with one or another impurity from the melt, vapor phase or implantation followed by thermal annealing. The concentration of metal and chalcogen vacancies under cadmium telluride growth temperatures is high due to low formation enthalpies and varies significantly along the length of the ingot from 10^{18} down to 10^{15} cm^{-3} beyond the crystallization zone [10, 11], which corresponds to the concentration of uncontrolled background impurities. The behavior of impurities in the crystal has a complex distribution pattern with formation of $M_i\text{-Te}$ complexes that will be stable in the matrix of the main lattice (CdTe), if their bond strength is higher or equal to that of the matrix [12, 13].

The bulk changes in the crystal under the action of laser radiation ($h\omega \ll E_g$) are possible if the crystals before irradiation have internal sources of one or an-

other intrinsic or impurity component, which is activated by laser IR radiation and leads to the appearance of point defects or forms a complex with intrinsic defects. The mechanism of laser-stimulated migration of impurities in the crystal in the transparency region of a matrix, when being exposed to laser radiation, is complex. The effectiveness of this interaction depends on the nature of crystalline complexes, their concentration, size, local density and laser radiation parameters [14]. The inclusions are characterized by a significant dispersion in size of $10^{-2} \leq R_{\text{inc}} \leq 100 \mu\text{m}$ and geometric shape as well as irregular distribution in the crystal matrix. Therefore, crystals always contain regions with a distance d between them, for which the condition $R_{\text{inc}+d} \ll \lambda/n$ is satisfied, where λ is the laser wavelength, n is the refractive index of the crystal [15].

The electric field in inclusion E_{inc} , if take into account the field of dipole moments that are induced by an external wave in inclusions, will be equal by the order of magnitude to the electric field of laser wave E_L , which is $E_L \approx 10^2 \text{ V cm}^{-1}$ for applied laser power densities. For inclusions with dimensions smaller or equal to the electron free path $l \sim 10^{-6} \dots 10^{-5} \text{ cm} \geq R_{\text{inc}}$, an absorption cross-section can be described by the expression [14]:

$$\sigma_{\text{inc}} = 64/411 (E_F/\hbar\omega)^2 S_{\text{inc}}. \quad (1)$$

For metallic inclusions, the Fermi energy E_F is about several electronvolts, and if one takes $E_F = 5 \text{ eV}$, and laser quanta energy $\hbar\omega = 0.117 \text{ eV}$, than $\sigma_{\text{inc}}/S_{\text{inc}} \approx 3 \cdot 10^2$. In this case, the inclusion temperature change is

$$\Delta T_{\text{inc}} = \sigma_{\text{inc}} \cdot W/3 \cdot K \cdot R_{\text{inc}}, \quad (2)$$

where W is the laser power density, K is the semiconductor crystal thermal conductivity. Our estimations have shown that for $R_{\text{inc}} = 100 \text{ \AA}$ and $W = 50 \text{ W/cm}^2$, the inclusion temperature exceeds the CdTe sample temperature by $\Delta T_{\text{inc}} \approx 25 \text{ K}$.

The temperature gradient of the inclusion – matrix system is the cause of the mass transfer of the components that make up the inclusion to the region of the crystal adjacent to the inclusion, which leads to the filling of vacancies and a change in their electrophysi-

cal and optical properties.

In this case, the equilibrium state is achieved by rearrangement of the lattice through relaxation of local vibrations of atoms surrounding the defect. Such a short-term occurrence and disappearance of intense local vibrations upon the introduction of atoms (activated state) from inclusion into a cold matrix significantly increases the probability of not only moving a defect, which does not require thermal activation energy, but also the appearance of new point defects.

The concentration of laser-stimulated defects in this case will depend, first of all, on the power density and wavelength of laser radiation. In the activated state, the \mathbf{EH} field of the laser wave promotes the drift of inclusion atoms in its vicinity to the equilibrium state in sites of the CdTe crystal lattice. The proposed model is tentative to a certain degree.

We did not perform special experiments to investigate the inclusion density dependence on the time of their interaction with IR laser radiation. However, experimental facts of changing the bandgap of CdMnTe, the observed increase in the crystal transparency and carrier mobility up to the theoretical limit can be considered as indirect evidence of the disappearance of inclusions.

7. CONCLUSIONS

Interaction of IR laser radiation with CdTe:Mn single crystals leads to redistribution in bulk of inclusions of native components, complexes, impurities and intrinsic defects that are in the crystals. This changes the electrophysical, optical and structural properties of the crystals. The redistribution and generation of defects in the field of the laser IR wave occurs in the bulk, which manifests itself as an increase in the optical transmittance from $\tau \approx 0.04$ in the spectral region $2.5 \leq \lambda \leq 23 \mu\text{m}$, virtually, to the theoretical limit $\tau \approx 0.64$, which is determined by the absorption by free carriers. As a consequence, such crystals become more suitable for optoelectronic applications as compared with original ones. In addition, such technique may be prospective for nondestructive material properties control by the transformation of the defect subsystem.

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ГЧ лазерно-індуковані точкові дефекти в монокристалах CdTe:MnС.В. Пляцко¹, Ю.С. Громовий¹, О.М. Стрильчук¹, Л.В. Рашковецький¹, З.І. Захарук²¹ *Інститут фізики напівпровідників імені В.С. Лашкарьова НАН України, Київ, Україна*² *Чернівецький національний університет імені Ю. Федьковича, Чернівці, Україна*

Досліджено електричні характеристики монокристалів CdTe:Mn *n*-типу провідності з початковим питомим опором 10 Ом·см (300 К), залежність спектрів ЕПР і низькотемпературної фотолюмінесценції від концентрації домішки і температури. Визначено глибина залягання домішкових рівнів, локалізація домішки марганцю в кристалічній решітці. Показано, що в межах концентрації введеного марганцю $N_{Mn} \leq 5 \cdot 10^{18} \text{ см}^{-3}$ обмінної взаємодії між іонами марганцю не спостерігається, марганець займає вакансії або заміщає кадмій в ґратці. Експериментально показано вплив ГЧ лазерного випромінювання з енергією кванта випромінювання $\hbar\omega$ значно меншою ширини забороненої зони E_g і щільністю потужності випромінювання W нижче критичної на фізичні властивості монокристалів *n*-CdTe: Mn. Встановлено, що зміна в спектрі точкових дефектів відбувається в результаті взаємодії **EH** поля лазерної хвилі з включеннями власних компонентів, фонових і спеціально введених домішок.

Ключові слова: Напівпровідники, Точкові дефекти, Домішки, CdTe, Лазерна взаємодія, Фотолюмінесценція, Парамагнітний резонанс, Провідність, Оптичне пропускання.