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Optically induced change of photoelectric properties of CdMnTe crystals

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To study the optically induced transformation of the point defect system under strong ans weak excitation from the intrinsic absorption $h\nu \geq E_g$, photoelectric and electric properties of semiconductor solid solutions $Cd_{1-x}Mn_xTe$ ($x = 0.08 \div 0.1$) have been studied at 78 and 300 K. It has been found that the weak optical excitation ($h\nu \sim 2$ eV) under simultaneous fast chilling down to 78 K results in a dramatic drop of the photocurrent and increase of the crystal dark resistance by more than a decimal order. The crystal photosensitivity is recovered in part by ultrasonic annealing or after a prolonged exposure at room temperature. A possible mechanism of that effect is discussed associated with the photoinduced ionization of manganese ions. The pulse laser irradiation ($\lambda = 694$ nm, $\tau_L = 20$ ns) at an under-threshold power results in photosensitization of the $Cd_{1-x}Mn_xTe$ crystals not only in the irradiation zone but also in the control region.

С целью исследования оптически индуцированной трансформации системы точечных дефектов в условиях сильного и слабого возбуждения из области собственного поглощения $h\nu \geq E_g$ изучались фотоэлектрические и электрические свойства полупроводниковых твердых растворов $Cd_{1-x}Mn_xTe$ ($x = 0.080 \div 1$) при $T = 78$ К и $T = 300$ К. Было обнаружено, что в результате слабого оптического возбуждения ($h\nu \sim 2$ эВ) при одновременном быстром охлаждении до $T = 78$ К происходит катастрофическое падение фототока и рост темнового сопротивления кристаллов более чем на порядок. Фоточувствительность кристаллов частично восстанавливалась в результате ультразвукового отжига или после длительной выдержки при комнатной температуре. Обсуждается возможный механизм наблюдаемого эффекта, связанный с фотоионизацией ионов марганца. Обработка импульсным лазерным излучением ($\lambda = 694$ нм, $\tau_L = 20$ нс) допороговой мощности приводила к фотоочувствлению кристаллов $Cd_{1-x}Mn_xTe$ не только в зоне облучения, но и в контрольной области образцов.

The II–VI semiconductor compounds doped with iron group ions (Fe, Mn, Co, Ni, etc.) make a class of prospective materials for thin-film electroluminescent devices, active laser media and gates, fast-acting light receivers, semi-insulating substrates, magnetically sensitive low-dimensional quantum structures, etc. [1–6]. The nanoscale engineering provide a strict dosing up to the controlled arrangement of magnetic ions within one nanoscale formation, thus offering new possibilities in practical application of such semiconductors. That is why the interest in study of such compounds is ever increasing. At the same time, the semi-magnetic semiconductors are of great interest from the standpoint of fundamental problem solution in the physics of solids, due to specific structure features of the 3*d* shell in transition elements. For example, $Cd_{1-x}Mn_xTe$ solid solutions are convenient models to study the magnetic and magneto-optical properties, dynamics of spin system in magnetic ions, relaxation mechanisms of inter-

band and intracenter electron excitation, as well as stimulated defect formation processes [3–7].

The possibility to vary the Mn^{2+} cation concentration in the $Cd_{1-x}Mn_xTe$ matrix volume from several hundredth per cent to tens per cent allows to consider manganese in the solid solution as an impurity or as a component and to change the material properties respectively. It is to note the intense studies of $Cd_{1-x}Mn_xTe$ solid solutions at $x > 0.4$, since it is just such compounds where the competition between the band and intracenter channels of emissive recombination becomes apparent clearly, the latter channel being predominant [4]. However, $Cd_{1-x}Mn_xTe$ demonstrates some properties of interest, e.g., photomemory, also at low manganese concentrations in the matrix [8, 9] although such works are few in number. In this connection, the purpose of this work is to study the properties of $Cd_{1-x}Mn_xTe$ semiconductor solid solutions at $x = 0.08 \div 0.1$ under weak and strong optical excitation from the intrinsic absorption region, $h\nu \geq E_g$.

The crystals of $Cd_{1-x}Mn_xTe$ semiconductor solid solution ($x = 0.08 \div 0.1$) were grown by Bridgman technique in inclined rotating ampoules, thus favoring the material homogenization during growth. Manganese was introduced into raw blends as a Cd-based ligature. All the samples showed photosensitivity at room temperature, had n-type conductivity and resistivity of 5 to 25 kΩhm·cm. The strong excitation was realized by a ruby laser ($\lambda \approx 694$ nm) at passive quality modulation of the optical resonator on plane-parallel mirrors, thus providing the light pulse duration at the half-height not exceeding $\tau_L \approx 20$ ns. The crystals were laser treated in normal conditions at room temperature in single pulse regime as well as in that of dose dependence, $KW_0\tau_L$ where K is the number of pulses in the dose; $W_0 = 2$ MW/cm^2, the power density in single pulse. The light in the irradiation area was focused into a spot of about 4 mm in diameter. The surface area adjacent to the irradiated one was used as a control and protected against the laser radiation (LR) by a metal screen or a thick layer of black varnish. To realize the weak excitation, the samples were illuminated with "red" light from a MDR-3 monochromator at $\lambda \sim 620$ nm. A standard procedure was used to measure the stationary photoconductivity for high-ohmic samples with

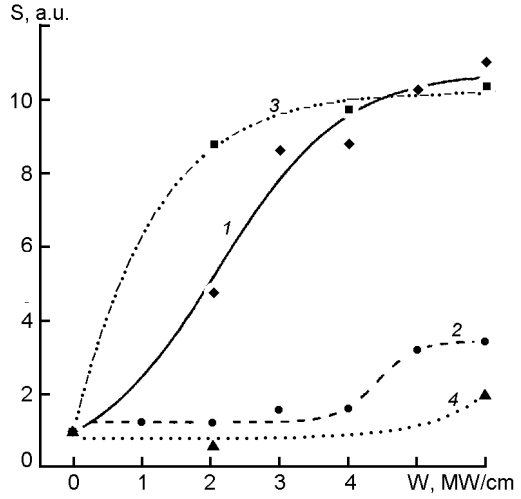

Fig. 1. Dependence of integral photosensitivity on the pulse LI intensity for: $Cd_{0.9}Mn_{0.1}Te$ in the irradiation zone (*1*), the same in control area (*2*); CdTe:Mn (*3*), and undoped CdTe (*4*).

synchronous detection in the constant field regime [10]. The spectral distribution of photosensitivity in the $\lambda = 700 \div 900$ nm range was measured prior to and after the laser treatment; the sample dark resistance was controlled, too.

The pulse laser irradiation (pulse LI) of the $Cd_{1-x}Mn_xTe$ solid solution crystals ($x = 0.08$ to 0.1) resulted in a significant increase in the photoelectric current and in dark resistance. A typical dependence of the integral photosensitivity on the irradiation intensity for $Cd_{0.9}Mn_{0.1}Te$ is presented in Fig. 1 (curve 1). It is to note that the parameters mentioned become changed not only in the area of the direct laser beam interaction with the crystal but also in the control area (Fig. 1, curve 2), that is, the laser long-range action effect was observed. The weak excitation ($h\nu \sim 2$ eV) under simultaneous chilling down to $T = 78$ K resulted in the photoconductivity "quenching", the crystal photosensitivity falling down to the noise level. The dark resistance increased considerably. Neither re-heating up to room temperature nor the subsequent pulse LI treatment resulted in the photosensitivity recovery. The dark resistance of the samples at 300 K became increased more that by one order, e.g., from 5 to 80 kΩhm·cm. The crystal photosensitivity was recovered in part after ultrasonic annealing or a prolonged storage at room temperature (up 1 month) being essentially an annealing at 300 K. The preliminary treat-

ment of the initial samples with at least two laser pulse at $W = 2$ MW/cm^2 prevented the effect described above.

It is obvious that the photosensitivity of a semiconductor crystal depends on the recombination center concentration therein and on the completion extent of those centers. The critical part in the recombination processes is played by the composition and state of the system of point and extended defects [10]. The weak optical excitation results mainly in the recharging or ionization of the existing local centers, i.e., in the state changes of the crystal lattice defects connected thereto. Under strong excitation, however, the corporative effect of factors accompanying pulse LI results in generation of new defects; that effects no doubt the crystal properties. Let us consider the possible mechanisms of the effects observed in $Cd_{1-x}Mn_xTe$ crystals under weak and strong optical excitation.

The laser irradiation of CdTe crystal is known to result in a depletion of Cd atoms of its near-surface layer [11], that is, the pulse LI action causes an increased concentration of acceptors, N_A, i.e., cadmium vacancies V_{Cd} being the photosensitivity centers for the material. It is quite logical to suppose that a similar effect may be observed at the pulse LI of $Cd_{1-x}Mn_xTe$ solid solutions. In fact, consideration of diffusion flows of the point defect out of the interaction area between the substance and the radiation indicates that the flow caused by the vacancy concentration gradient and directed from the crystal surface towards its depth. Fig. 2 presents the resulting flow J as well as the components thereof as functions of the incident radiation power W; those are calculated for $Cd_{1-x}Mn_xTe$ basing on expressions given in [12].

It is to note that the photosensitivity increase effect in $Cd_{1-x}Mn_xTe$ as well as in CdTe:Mn (Fig. 1, curve 2) amounts 1 to 2 orders and exceeds considerably the sensitization effect of undoped cadmium telluride (Fig. 1, curve 4), the LR intensity being the same. This seems to be associated with increased concentration of photosensitivity centers due not only to Cd exit out of sites and evaporation but also to displacement of manganese atoms out of cadmium sites. (Manganese is distributed almost statistically in the matrix lattice during the growth forming individual defects of Mn^{2+}_{Cd} type as well as clusters of 1 to 2 μm size). A similar effect of the interstitial

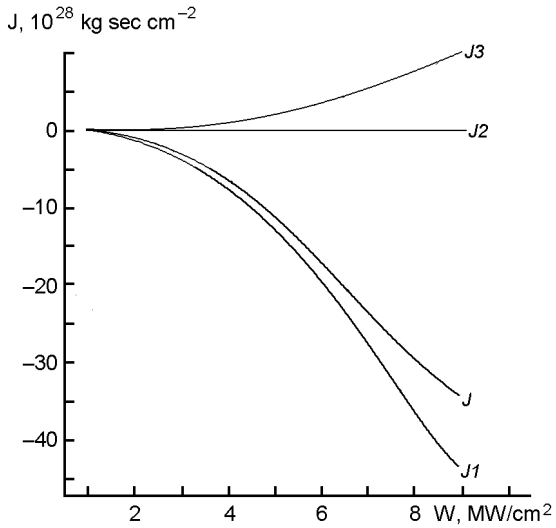

Fig. 2. Diffusion flow of Cd vacancies as a function of the incident radiation power W calculated for a $Cd_{1-x}Mn_xTe$ crystal. The total flow $J(W) = J1 + J2 + J3$ consists of the flow J_1 due to the vacancy concentration gradient; J_2 one due to the crystal straining; and J_3 one due to the temperature gradient. The sign at J value indicates the flow direction (minus, towards the crystal bulk; plus, towards the surface).

manganese concentration rise was observed under laser irradiation of PbTe(Se):Mn crystals and is confirmed by ESR examination [13, 14].

The exit of manganese ions out of the sites is evidenced also by the fact of the composition change of $Cd_{1-x}Mn_xTe$ solid solutions (decrease of x) found by us for the samples irradiated with pulses >4 MW/cm^2 and resulting in a shift of the intrinsic photoconductivity maximum towards longer wavelengths. That shift indicates, first of all, a narrowing of the band gap E_g of the solid solution determined using the expression [15, 16]

$$E(\Gamma_6) - E(\Gamma_8) = E_g(0) - 4.3 \cdot 10^{-4}T + 1.592x,$$

where $E_g(0) = 1.606$ eV is the CdTe band gap at $T = 0$ K. The calculated E_g values for various compositions and temperatures coincided with those determined in experiment at the intrinsic absorption edge and at the half-height of the "red" photoconductivity boundary. The E_g shift resulting from pulse LI corresponds to x decrease by 1 or 2 %. This effect is observed both in the irradiated and protected sample surface areas.

The dark resistance increase in irradiated crystals is due to decrease of the effective concentration of the major equilibrium carriers $n = N_D - N_A$ caused by the increased concentration of V_{Cd} and N_t traps, the increase seems to exceed that of the donor states. Since the concentration of major carriers, and thus that of filled traps, falls, the minor carrier lifetime, τ_R, increases ($\tau_R = 1/\gamma_R n$, γ_R being the recombination coefficient; n, the major carrier concentration [10]), the crystal photosensitivity becomes higher. The deterioration of fast recombination s-centers could be supposed also.

The point defect formation in the area of direct laser radiation interaction with a semiconductor crystal is known to occur in the frame of the electron-strain-thermal (EST) model [17]. According to that model, the laser radiation excites the crystal electron subsystem. The relaxation energy of the excited states heats the lattice while the inhomogeneous spatial distribution of the concentration and thermal fields causes straining the near-surface layer of the semiconductor material resulting in decrease of the point defect formation energy in the laser-modified area.

The property changes of the crystals under study in the local LR action area agrees satisfactorily with the EST model [18]. The revealed laser long-range effect evidences a substantial role of non-thermal pulse LI factors. For the samples studied, the maximum diffusion path of heat and non-equilibrium charge carriers from the LR focusing area to the control one during the time τ_L does not exceed several micrometers [18]. Thus, those factors cannot cause the long-range effect. At the same time, it is known that, due to photothermal stress relaxation, the surface acoustic waves are generated in the irradiation region, which transfer to the distant zone an energy sufficient to stimulate the transformation of the crystal impurity and defect composition. The interaction of such a wave with the crystal intrinsic defects in the long-range effect zone occurs by excitation of the metastable accumulations of the defects, that causes a structure re-building in the regions of increased defect concentration as well as is accompanied by annihilation of the defects and gettering thereof to extended runoffs, as well as by generation of secondary elastic wave sources [19]. According to our estimations, the surface acoustic wave generates a pressure up to $2 \div 3$ MPa in the crystal control area ($\leq$4 mm) and a surface shift up to 5 nm [20], that can be a cause of the point center concentration change outside the focusing area and of the material property changes.

The effect of a dramatic photosensitivity drop under a weak optical excitation and simultaneous cooling has been observed in $Cd_{1-x}Mn_xTe$ and CdTe:Mn solid solutions while being absent in undoped CdTe. That is why we associate it with the manganese atoms presence in the crystal matrix. The ground manganese state d^5 is localized within the valence band of $Cd_{1-x}Mn_xTe$ [21–24]. In the crystal field, the d state of Mn cation is split into doublet e^2 (Γ_{12}) and triplet t^3 (Γ_{15}). The configuration of Mn ground state can be writtes as $[Mn^{2+},d^5,e^2_+\ t^3_+e^0_-]$ or $^6A_1$ [21].

The optical excitation may result both in the atom ionization to Mn^{2+} and in intraatomic transitions $d \rightarrow d^*$ (e.g., from the orbital t_+ to the lowest unoccupied orbital e_- $[Mn^{2+},d^5,e^2_+\ t^3_+e^0_-] \rightarrow [Mn^{2+},d^4,e^2_+\ t^2_+e^1_-]$, $^6A_1 \rightarrow {}^4T_1$). These transitions do not result, however, in the photosensitivity changes; that is why those will not be considered. The donor-like transition may result in ionization of the manganese atom e_+ orbital that corresponds to the $[Mn^{2+},d^5,e^2_+t^3_+\ e^0_-] \rightarrow [Mn^{3+},d^4,\ e^1_+t^3_+e^0_-]$ transition. There is, however, no hybridization of e^2 (Γ_{12}) cationic state and t^3 (Γ_{15}) anionic one, therefore, the e-symmetry states remain undisturbed [21]. In spite of interaction between cationic (Te and anionic (Mn) states of t_2-symmetry and strong p-d hybridization, the probability of t_+ orbital ionization ($[Mn^{2+},d^5,e^2_+t^3_+\ e^0_-] \rightarrow [Mn^{3+},d^4,\ e^2_+t^2_+e^0_-]$) is also low, since the manganese ground state is localized lower that the valence band top [26]. At the same time, the valence band electron (e.g., from the p-state of Te) transition to the lowest unoccupied orbital of manganese ($[Mn^{2+},d^5,e^2_+t^3_+e^0_-] \rightarrow [Mn^{1+},d^6,\ e^2_+t^3_+e^1_-]$) is highly probable (the model proposed by van Allen [25]). This transition is responsible for the peaks near 2 eV in luminescence [21, 27] and photoconductivity [28] spectra of $Cd_{1-x}Mn_xTe$ crystals.

In our case, the absorbed "red" light energy (about 2 eV) is quite sufficient to provide the $Mn^{2+} \rightarrow Mn^{1+}$ transition. The recharged manganese ion gives rise to a state with $3d^6$ configuration that splits in the crystal field into two levels, $^5T_2$ and ^5E. The study results of electron absorption spectra of $Cd_{1-x}Mn_xTe$ evidence the electron

capturing onto the ^5E state localized within the band gap (E_V+1.569 eV) and is considered as a hydrogen-like acceptor [26]. It is quite probable that the dramatic drop of dark current (the dark resistance increase) and photocurrent described here resulting from the weak optical excitation of $Cd_{1-x}Mn_xTe$ crystals under simultaneous cooling is associated just with the involvement of the new acceptor-like level (the ^5E excited state of manganese ion) in the generation/recombination process and in conductivity.

It is to note also a possibility of the stress redistribution in the crystal at fast chilling and thus formation of potential barriers hindering the fast return of the defect system to the equilibrium state after the external action is over. Formation of defect complexes involving the excited manganese atom is also possible. In both cases, an annealing is able to accelerate the relaxation, that was observed in experiments. In general, the long-term relaxation is typical of the material under study. The persistent photoconductivity in $Cd_{1-x}Mn_xTe$:In,Ga crystals can be an example [8, 9]. Since the pulse LI of $Cd_{1-x}Mn_xTe$ crystals causes, along with an enrichment in cadmium vacancies, the Mn atom exit out of the crystal lattice sites and gettering thereof, e.g., with manganese clusters, the formation probability of acceptor states $Mn^{1+}(^5E)$ in a sufficient amount and the involvement thereof in the generation/recombination process is lowered sharply. As a consequence, the crystal retains the photosensitivity both at room temperature and in liquid nitrogen.

Thus, a substantial change in electric and photoelectric properties of $Cd_{1-x}Mn_xTe$ semiconductor solid solutions ($x = 0.08 \div 0.1$) has been found to result from both strong and weak optical excitation. While the pulse LI results in a considerable increase of $Cd_{1-x}Mn_xTe$ photosensitivity, the weak excitation from the intrinsic absorption region $h\nu \geq E_g$ under simultaneous fast chilling causes the photosensitivity drop down to the noise level. The observed dramatic photosensitivity drop is associated, in our opinion, with ionization of manganese ions $[Mn^{2+},d^5,e^2_+t^3_+\ e^0_-] \rightarrow [Mn^{1+},d^6,\ e^2_+t^3_+e^1_-]$ and involvement of the new acceptor-like level in the generation/recombination process and in conductivity. The laser long-range effect has been first revealed in $Cd_{1-x}Mn_xTe$ solid solution crystals ($x = 0.08 \div 0.1$). This effect evidences a substantial part played by non-thermal pulse LI action on the semiconductor and it is to be taken into account when solving the applied tasks basing on the supposition of the local action of coherent light.

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Оптично індукована зміна фотоелектричних властивостей кристалів CdMnTe

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З метою дослідження оптично індукованої трансформації системи точкових дефектів в умовах сильного і слабкого збудження з області власного поглинання $h\nu \geq E_g$ вивчалися фотоелектричні та електричні властивості напівпровідникових твердих розчинів $Cd_{1-x}Mn_xTe$ ($x = 0.08 \div 0.1$) при $T = 78$ К і $T = 300$ К. Виявлено, що в результаті слабкого оптичного збудження ($h\nu \sim 2$ еВ) при одночасному швидкому охолодженні до $T = 78$ К відбувається катастрофічне падіння фототока, а темновий опір кристалів підвищується більш ніж на порядок. Фоточутливість кристалів частково відновлювалася в результаті ультразвукового відпалу або після тривалої витримки при кімнатній температурі. Обговорюється можливий механізм ефекту, що спостерігається, пов'язаний із фотоіонізацією іонів марганцю. Обробка імпульсним лазерним випромінюванням ($\lambda = 694$ нм, $\tau_L = 20$ нс) допорогової потужності приводила до росту фоточутливості кристалів $Cd_{1-x}Mn_xTe$ не тільки в зоні опромінення, але й у контрольній області зразків.