Photoelectrical and optical properties of $Cd_{1-x}Mn_xTe$ single crystals and thin films

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The optical absorption spectra at the fundamental absorption edge and the photoconductivity kinetics of $Cd_{1-x}Mn_xTe$ ($0 \leq x \leq 0.15$) at 78-300 K have been studied. Single crystals were grown by Bridgman method. They show an enhanced photoconductivity in the vicinity of fundamental absorption threshold. The binary compounds CdTe and MnTe can form a continuous row of $Cd_{1-x}Mn_xTe$ solid solutions (on CdTe crystal lattice) in the range $0<x<0.85$. At 293 K, the fundamental absorption red edge in crystals with $x \leq 0.05$ is determined by the exciton absorption. The fundamental absorption edge has the specific shape of crystals with high impurity levels density. The nature of optical transitions at the absorption edge was established from the spectral dependences of both optical absorption and photoconductivity. The energies of localized states in the band gap of $Cd_{1-x}Mn_xTe$ crystals and thin films have been determined.

1. Introduction

CdTe and MnTe crystals have attracted considerable attention of scientists working in both fundamental and applied research, thanks to a number of significant advantages. They are able to form solid solutions overall concentration range [1], are used as parent substances in semimagnetic superlattices preparation, besides they are suitable in investigating the effects related to Mn^{2+} centres, magnetic polarons characteristics etc. [2, 3].

$Cd_{1-x}Mn_xTe$ solid solutions crystallise based on the CdTe zincblende lattice in a wide concentration range; the lattice parameter, *a*, decreases linearly with concentration x, up to x=0.8.

The present paper reports on the study of the optical absorption and photoconductivity of $Cd_{1-x}Mn_xTe$ single crystals and thin films, in order to improve their efficiency in a series of technological applications concerning the quantum structures and photosensitive heterojunctions for the VIS spectral range.

2. Experimental

$Cd_{1-x}Mn_xTe$ compounds ($0 \leq x \leq 0.55$) have been synthesized from respective chemical component elements Cd (000), Te (extra U-V) and Mn (000). Single crystals with composition in the range x = 0; 0.50; 0.55; 0/70; 0.87; 0.95 have been grown by Bridgmann method. By using the emission spectral analyze of original crystals, the following impurities have been identified: Cu (~10^{-6} %), Fe, Mn, Cr, Ni (~10^{-5} %).

$Cd_{1-x}Mn_xTe$ thin films have been prepared by physical vapour deposition onto mica substrate, as well as by flash vaporization of the dispersed compound. $Cd_{0.5}Mn_{0.5}Te$ single crystals were used as a source.

The absorption and photoconductivity spectra have been recorded by using a spectrophotometric installation based on a monochromator with diffraction grating (1200 mm^{-1} and 600 mm^{-1}). The energy resolution provided by respective installation was of ~1 meV.

For the investigation of the optical properties samples with thickness in the range (1.50 - ~12) μm have been prepared. In photoconductivity measurements parallelepiped samples with dimensions $2.0 \times 4.0 \times 0.2$ mm^3 have been used. Cu and/or Al thin films vacuum evaporated (10^{-5} Torr) onto substrates have been used as electrodes.

3. Results and discussion

CdTe and MnTe can form a continuous row of $Cd_{1-x}Mn_xTe$ solid solutions. When x lays in the range $0 \leq x \leq 0.70$, their crystalline structure is of CdTe zincblende type, while for $0.70 \leq x \leq 1$, it is of β-MnTe type [4].

The electrical conductivity of $Cd_{1-x}Mn_xTe$ crystals at temperature ~78 K is of the order (10^{-12}-10^{-14}) $\Omega^{-1} \cdot cm^{-1}$, so that determination of the mobility in the low temperature range is not possible. The energy of the levels contributing in the electrical conductivity can be evaluated by analysing the experimental dependences $\sigma = f(10^3/T)$ by means of the relation [5]

$$\sigma(T) = \sigma_0 \cdot \exp(-\Delta E / 2kT), \qquad (1)$$

where σ_0 is a constant not depending on temperature, ΔE is the energy of the localized state (in the forbidden band),

k is the Boltzmann's constant, and T-the absolute temperature.

Fig. 1 shows temperature dependences of the electrical conductivity for $Cd_{1-x}Mn_xTe$ crystals with x in the range (0-0.5), in both dark (curves 1-7) and illumination (curves 1*-7*) conditions. The spectral range of the exciting radiation corresponds to the fundamental absorption band. As can be ascertained from Fig. 1, the experimental data are in good agreement with Eq. (1) for the composition range $0 \leq x \leq 0.5$. Except the case x=0.13, since at increasing temperature from 78 up to 350 K, the electrical conductivity increases by a factor of only ~1.5.

As can be seen in Fig. 1, in the low temperature range, the electrical conductivity weakly depends on temperature, indicating that levels with low ionization energy are present in studied crystals. In the case of As-doped CdTe and solid solutions with x in the range $0 \leq x \leq 0.05$, a localized state with an (ionization) energy of 15 meV is evidenced. Besides, in the case x=0.13, the charge carriers are thermally released from the level with an energy $\Delta E_A \leq 0.005$ eV.

The conductivity of the crystals with composition range $x \geq 0.3$ is much lower than in the case x=0.13 and slowly increases at increasing amount of MnTe in CdTe. At the same time, in the low temperature range ($T \leq 100$ K), the electrical conductivity weakly increases with temperature. The corresponding energies of localized states, as obtained from the slope of $\log\sigma = f(10^3/T)$ dependences, are listed in Table 1.

Table 1. Energy of localized states for $Cd_{1-x}Mn_xTe$ solid solutions, as determined from temperature dependences of dark electrical conductivity (E_1) and photoconductivity (E_2).

x	0	0.05	0.13	0.30	0.43	0.45	0.50
E_1, eV	0.015; 0.030; 0.060; 1.480	0.018; 0.060; 1.530	0.005; ~0.030	0.12	0.015; 0.920	0.165; 1.220; 1.920	0.520
E_2, eV	0.015; 1.480	1.530	0.030	0.110; 0.260	0.015; 0.200; 0.920	0.030; 1.920	0.033; 0.550

At temperatures over 200 K, a rapid increase of the electrical conductivity for the solutions in the range $0 \leq x \leq 0.5$ is registered, due to both ionization of deep levels and electron transitions between valence and conduction bands. As determined from the slope of the temperature dependence of electrical conductivity in the higher temperature domain, the width of the forbidden band for CdTe crystals doped with As (1 %) is equal to 1.48 eV. The obtained value is concordant with existing data [6].

The localized states in semiconducting materials can be determined by analysing the temperature dependence of the photoconductivity, σ_f, when the excitation is performed in a determined spectral range. In order to

elucidate the donor states in the case of $Cd_{1-x}Mn_xTe$ crystals, exciting photons with energy $h\nu \geq 0.30$ eV have been used.
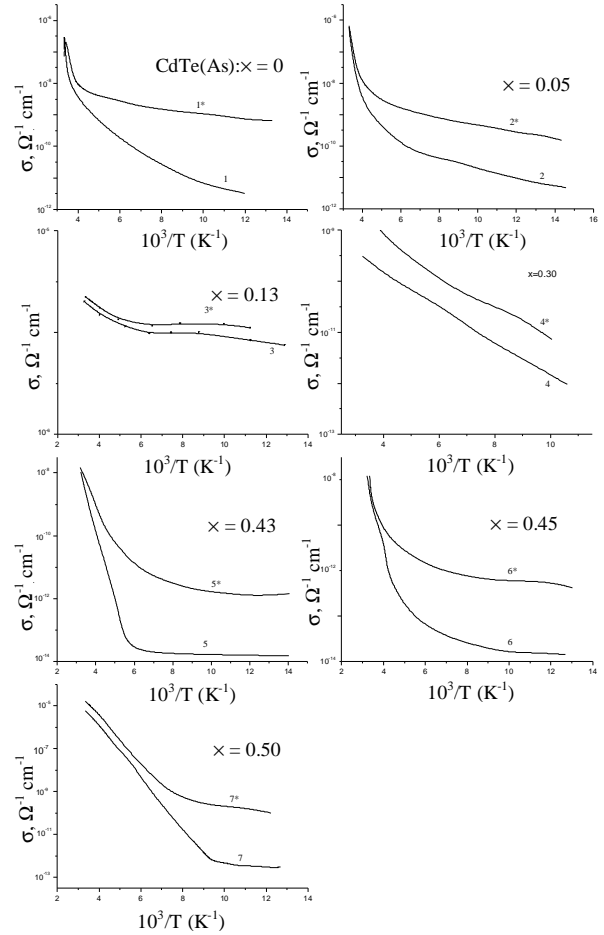

Fig. 1. Temperature dependence of electrical conductivity of $Cd_{1-x}Mn_xTe$ in dark (1-7) and illumination (1-7*) conditions.*

In the lower temperature domain, the electrical conduction of solid solutions with x = 0 and x = 0.05, in both dark and illumination conditions, is controlled by levels at 0.015 eV and 0.018 eV, respectively. The intermediary levels by 30 meV in CdTe (1 % As) and 60 meV in the case of solution with x=0.05 are ionized by the exciting photons. The energies of localised states for solid solutions in the range $0 \leq x \leq 0.5$, as determined from the slope of $\log\sigma_f = f(10^3/T)$ dependences, are presented in Table 1.

In Fig. 2 typical spectral dependences of photoconductivity at room temperature (293 K) for solid solutions with x=0, 0.30, 0.43 and 0.50 are illustrated.
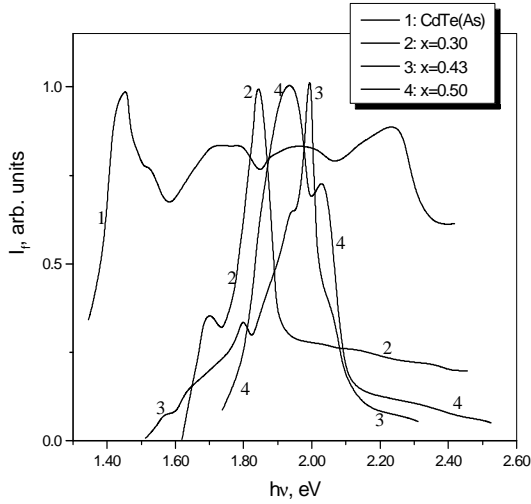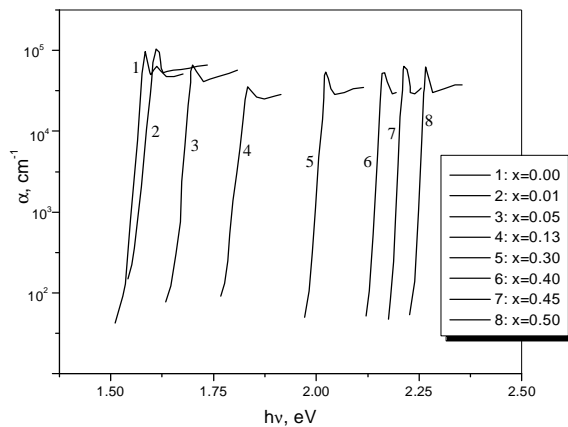
Fig. 2. Photoconductivity spectra of $Cd_{1-x}Mn_xTe$.

Fig. 3. Spectral dependence of the absorption coefficient of $Cd_{1-x}Mn_xTe$ at T=78 K.

The photoconductivity spectrum of undoped CdTe crystals at temperature 293 K consists of an outlined maximum, localised at the fundamental absorption edge, whose energy position, of 1.50 eV, identifies with the compound's bandgap at room temperature [6]. As can be seen in Fig. 2 (curve 1), the spectral dependence of photosensitivity for CdTe crystals doped with As (1 %) is quite complex and contains an outer predominant band peaked at 1.46 eV, a weaker line positioned at 1.53 eV, as well as a continuum laying up to 2.30 eV. The particularity by 1.53 eV agrees with the bandgap value of CdTe at 293 K and so, can be interpreted as the generation of non-equiiulibrium charge carriers as a result of optical transitions between extremities of the valence and conduction bands in the center of Brillouin zone (Γ point). The maximum at 1.46 eV, characteristic only to CdTe(As) crystals, can be assigned to optical transitions between As acceptor level by ~70 meV toward the top of the valence

band, and the conduction band. A similar structure of photoconductivity spectrum is registered for solid solution with x=0.3, but the outer band is significantly reduced as compared to previous case. The particularities of the photoconductivity spectrum for the above solid solution are localised at 1.71 eV and 1.85 eV. The first particularity (by 1.71 eV), positionned at a lower energy as compared to the fundamental absorption edge at this temperature, equal to 1.84 eV [7], is conditionned by an impurity level localised at ~0.13 eV above the valence band, which controls the electrical conductivity at temperatures close to room temperature.
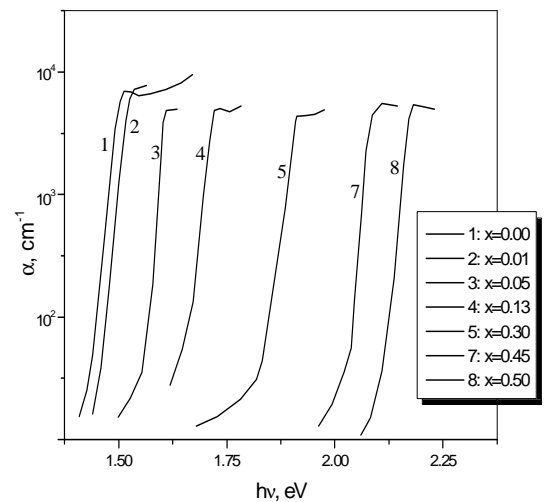

Fig. 4. Spectral dependence of the absorption coefficient of $Cd_{1-x}Mn_xTe$ at T=293 K.

The spectral dependence of the solid solution with x=0.43 (curve 3) is characterised by a prevailing maximum at ~1.97 eV, a shoulder at 2.07 eV and slowly decreases at decreasing photon energies below 1.90 eV. If one supposes that the particularity by 2.07 eV is due to the photogeneration of non-equilibrium charge carriers as a result of band-to-band optical transitions, then the peak by 1.97 eV can be associated to an impurity level localised at ~100 meV above the valence band, that can be evidenced by analysing the temperature dependence of photoconductivity.

Two impurity bands, well outlined, peaked at 1.94 eV and 2.05 eV are present in the spectral dependence of photoconductivity for the solid solution with x=0.5. These band are located at higher wavelengths as compared to the red absorption edge, which at temperature 293 K corresponds to a bandgap of ~2.20 eV. Consequently, both bands are of impurity nature, and the energies of respective levels are 0.26 and 0.15, respectively. As can be found in Fig. 1, the level by 0.26 eV is in good agreement with that of 0.28 eV, which determines the thermal activation of both dark electrical conductivity and photoconductivity in temperature range T≥150 K.

Figs. 3 and 4 illustrate the spectral dependences of the optical absorption for the solid solutions in the range

$0 \leq x \leq 0.5$ at temperatures 78 K and 293 K, respectively. As a characteristic feature of the absorption spectrum of respective solid solutions at low temperatures, an outlined absorption edge is present, which displaces in function of sample composition, x. In the higher wavelengths domain, a series of maxima clearly evidences, that can be associated to the absorption accompanied by formation of free excitons. The exciton absorption at 78 K is manifest by a narrow band localised in the vicinity of the fundamental absorption threshold. As can be observed in Fig. 3, the absorption coefficient in the exciton line maximum (n=1) is weakly decreasing at increased amount ao MnTe in CdTe. At the same time, an increase of the average width of the exciton line contour for compositions $0 \leq x \leq 0.13$ is registered. When the amount of MnTe in CdTe is further increased, the dynamics of the exciton line change is seen to reverse: the peak absorption increases, and the width of the line n=1 decreases.

With a precision up to the exciton binding energy, equal to ~7 meV, one can admit that the energy position of the exciton (n=1) line peak indicates the bandgap of the respective solid solution [8]. In Fig. 5 the dependence of this energy on the sample composition, x, is presented. As can be found in these figure, the width of the forbidden band in solid solutions of $Cd_{1-x}Mn_xTe$ linearly increases with the amount of MnTe in CdTe. This dependence is also characteristic to other solid solutions of different binar compounds [9]. A small deviation from the Vegard law is registered in the solutions with compositions in the vicinity of CdTe, when MnTe concentration is under 5 %. Probably, in these solutions a part of Mn and Te ions fills up the Cd and Te native defects in CdTe, while another part participates in the formation of the solid solution itself. At increasing sample temperature from 78 K to 293 K, the thermal coefficient of the fundamental absorption edge of $Cd_{1-x}Mn_xTe$ solid solutions varies from 2.8×10^{-4} K^{-1}, for x=0.01, to 4.6×10^{-4} K^{-1}, for x=0.13.

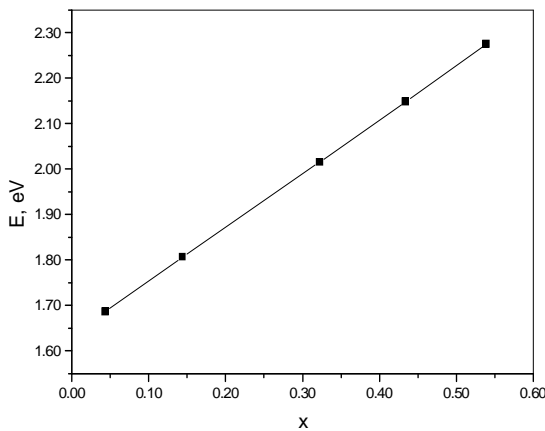As can be seen in Figs. 3 and 4, in the vicinity of the exciton absorption red edge, the dependence $\alpha(h\nu)$ can be described by the Urbach rule [10]:

$$\alpha = \alpha_0 \cdot \exp\left[-\frac{\sigma(\hbar\omega_0 - \hbar\omega)}{kT} \right], \qquad (2)$$

where α_0, ω_0 and σ_0 denote some energy parameters, characteristics to respective material. A similar $\alpha(h\nu)$ dependence can be experimentally obtained if the impurity atoms or defects present in the crystal create strong internal electric fields or distort locally the sample crystalline lattice, respectively. These factors are little influenced by temperature, since they are related to lattice transformations.

The dependence (2) can be also found experimentally when the absorption edge is produced by free excitons interacting with optical phonons of energy $h\nu_{ph}$. In this case, the parameter σ depends on temperature and phonon energy according to [11]

$$\sigma = \sigma_0 \frac{2kT}{\hbar\omega_{ph}} th\left(\frac{\hbar\omega_{ph}}{2kT} \right). \qquad (3)$$

In the above equation, the parameter σ_0 is independent on temperature and is inversely proportional to the constant of exciton-phonon interaction [11].

By analysing the dependence $\log\alpha = f(h\nu)$ for different sample temperatures in the range (78-293) K, the dependences $\sigma(x)$ and $\sigma(T)$ for $Cd_{1-x}Mn_xTe$ solid solutions have been determined. For investigated samples, σ is seen to decrease at decreasing sample temperature. Thus, for the composition x=0.01, when temperature is decreased from 293 K to 78 K, the coefficient σ decreases from 1.91 to 1.04. Besides, σ value at a fixed temperature, T=293 K, decreases from 1.98 to 1.64, at increasing compositions, x, between 0 and 0.13; at further increase of x, σ weakly increases up to 1.71, for x=0.5.

As registered decrease of σ at a fixed temperature for increasing concentrations $0 \leq x \leq 0.13$ can be explained by both amplified exciton-phonon interaction and increase of respective phonon average energy. Probably, in the present case, the second factor is decisive, since in CdTe-MnTe solid solutions the average energy of the normal vibrations is increased together MnTe amount in CdTe. At further increase of MnTe weight (x>0.13), the exciton-phonon interaction weakens, which is indirectly related to the reduction of the exciton band halfwidth in the absorption spectra at T=78 K (clearly illustrated in Fig. 3).

By analysing $\sigma(T)$ dependences the parameter σ_0 has been determined overall composition range and found to range between 0.65 and 0.85. In this way, we can conclude that in both pure CdTe crystals and $Cd_{1-x}Mn_xTe$ solid solutions ($0 \leq x \leq 0.5$) the interaction exciton-phonon is strong at temperatures $T \geq 78$ K. In the case of CdTe, these results are in good agreement with reported data [11].

Fig. 5. Energy of the exciton line as a function of x for $Cd_{1-x}Mn_xTe$ at T=78 K.

4. Conclusions

$Cd_{1-x}Mn_xTe$ solid solutions have been synthesized from their chemical components. The concentration of the impurity atoms (Cu, Fe, Ni, Mg, Cr) was under 10^{-5} % at. The single crystals with composition in the range $0 \leq x \leq 0.5$ have been grown by Bridgmann method, from which parallelepipedic samples have been prepared for optical, electrical and photoelectrical measurements. Cu and Al thin films vacuum evaporated have been used as electrodes.

The electrical conductivity of $Cd_{1-x}Mn_xTe$ solid solutions for $0 \leq x \leq 0.5$ in both dark and illumination (in the domain of the fundamental absorption band) conditions has been investigated. The domain of the spectral photosensitivity has been determined, as well as the energies of localised levels contributing in the electrical and photoelectrical properties of respective compounds.

The photoconductivity of investigated solid solutions is interpreted in the frame of the semiconductor model with two recombination localised levels, differing by both energy and effective cross-section of electron trapping by holes localised on these levels.

The fundamental absorption edge of $Cd_{1-x}Mn_xTe$ crystals ($0 \leq x \leq 0.5$) is formed by free excitons, whose energy as a function of x comply the Vegard's rule. At increasing temperatures from 78 K to 293 K, the red edge of the fundamental absorption band displaces toward lower energies. The thermal coefficient of the bandgap lies in the range $(2.8\text{-}4.6) \times 10^{-4}$ K^{-1}.

In the vicinity of the red exciton absorption edge, $\alpha(h\nu)$ dependence is determined by the exciton-phonon interaction and for the composition range $0 \leq x \leq 0.5$, the Urbach rule is verified. The exciton-phonon interaction constant slowly decreases with increasing x in the investigated range.

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