

Fundamental absorption edge in thin films of Cd_{1-x}Mn_xTe solid solutions

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The absorption spectra in the domain of the fundamental absorption band of Cd_{1-x}Mn_xTe solid solutions in thin films prepared by discrete ("flash") evaporation of synthesized single crystals and by physical vapor deposition (using Cd_{0.5}Mn_{0.5}Te as source material) are investigated. The chemical composition of Cd_{1-x}Mn_xTe films deposited by "flash" evaporation is close to CdTe, while by physical vapor deposition solid solutions with low Mn content result. The optical gap of Cd_{1-x}Mn_xTe films prepared by discrete evaporation is equal to ~2.0 eV and 2.13 eV at temperatures 293 K and 78 K, respectively.

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1. Introduction

The binary compounds CdTe and MnTe can form a continuous row of Cd_{1-x}Mn_xTe solid solutions, with x in the interval 0 ≤ x ≤ 1 [1]. For composition range 0 ≤ x ≤ 0.7, the structure of respective ternary compounds is based on CdTe crystal lattice (zinc-blende type). In this range, the lattice parameter slowly decreases from 6.48 Å (x=0) to 6.40 Å (x=0.7), while the optical bandgap is seen to increase from 1.5 eV to ~2.4 eV [2, 3]. Own to these features, as well as to their magneto-optical properties, Cd_{1-x}Mn_xTe solid solutions are utilized in the technology of various nanoelectronic devices (heterojunctions, quantum holes structures with reduced dimensionality etc.) [4,5].

During film deposition of multicomponent semiconducting compounds by thermal evaporation, dissociation in components often takes place. The presence of a great number of atoms in the vaporized compound leads to formation of a large scale of compositional and structural defects, which engender a series of energy levels in the forbidden band of as-deposited film.

In our previous paper [6] we have report on the existence and characteristics of the photomagnetic effect in CdTe films.

In the present paper, we investigate the optical properties (the fundamental absorption threshold) of Cd_{1-x}Mn_xTe thin films prepared by discrete ("flash") evaporation into vacuum and physical vapor deposition.

2. Experimental

In the deposition process of Cd_{1-x}Mn_xTe films, Cd_{0.5}Mn_{0.5}Te single crystals, grown by Bridgman method in a two-zone furnace, have been used as source material. They were synthesized by their chemically pure component elements, in stoichiometric proportions.

The films under study have been prepared by two methods: discrete evaporation of Cd_{0.5}Mn_{0.5}Te single crystals with grain dimensions d < 15 μm, and physical

vapor deposition. In both methods, substrate temperature (T_s) has been varied, so that single crystalline films have been obtained. Mica (muscovit) plates with high decomposition temperature (~900 K) have been used as substrates. For discrete evaporation of Cd_{0.5}Mn_{0.5}Te single crystals, a wolfram crucible with temperature ~1700-1750 K has been used. The substrate temperature was maintained at ~680 K.

In the case of physical vapor deposition, single crystalline blocks of Cd_{0.5}Mn_{0.5}Te with linear dimensions ~3-5 mm have been used as source materials. The source temperature laid in the range (1020-1050) K, while the substrate was maintained at temperatures between 860 K and 930 K. In this temperature range, single crystalline thin films with mirrored faces have been obtained.

As determined by an interferometric method, the film thickness ranged between 0.10 and 8.00 μm. Besides, for the vaporization process, the samples have been cut from single crystalline blocks with thickness in the range (0.1-3.00) μm and polished faces.

The optical transmission and reflexion spectra, T(hν) and R(hν) respectively, at temperature 78 K and 293 K, have been recorded by a spectrophotometric equipment based on a diffraction grill monochromator (600 mm⁻¹), with a spectral resolution ~0.5 meV, in the domain (1.30-2.50) eV.

The absorption coefficient, α, at wavelength λ has been calculated by taking into account the multiple reflexion of incident radiation on sample faces, as well as the interference in plan-parallel layers, using the equation [7,8]:

$$T = \frac{(1-R)^2 + 4R \sin^2 \psi}{e^{-\alpha d} - R^2 e^{-\alpha d} - 2R \cos 2(\varphi + \psi)}, \quad (1)$$

where d is the sample thickness, T and R represent the transmission and reflexion factors respectively, and the quantities φ, ψ are expressed by

$$\varphi = \frac{4\pi nd}{\lambda}, \quad \psi = \arctg\left(\frac{2k}{n^2 + k^2 + 1}\right), \quad (2)$$

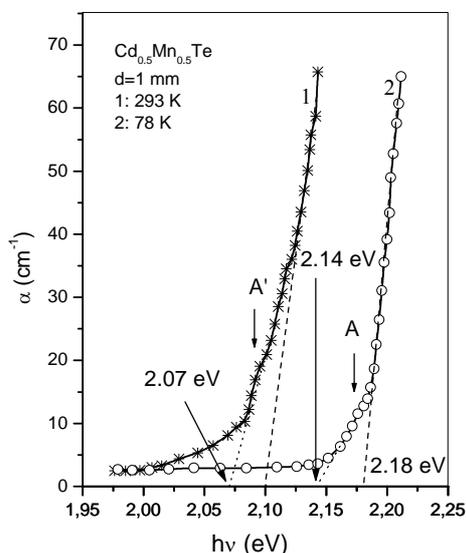


Fig. 1. The absorption spectrum of $Cd_{1-x}Mn_xTe$ single crystals at 293 K (curve 1) and 78 K (curve 2).

with n and k denoting the reflexion and extinction index, respectively. The term $\cos 2(\varphi + \psi)$ has been neglected in the case of thicker samples ($d \gg \lambda$).

3. Results and discussion

We have examined the fundamental absorption edge of as-prepared $Cd_{1-x}Mn_xTe$ thin films, as well as of their source material.

Fig. 1 shows the absorption spectra, at temperatures 78 K and 293 K, of $Cd_{0.5}Mn_{0.5}Te$ single crystals. The optical energy gap at temperatures 293 K and 78 K, as determined by extrapolation to zero ($\alpha=0$) of the linear portion of $\alpha(h\nu)$ dependence, was found as 2.10 eV and 2.18 eV, respectively. At the same time, for absorption coefficients $\alpha < 8 \text{ cm}^{-1}$ at 78 K and $\alpha < 20 \text{ cm}^{-1}$ at 293 K clearly evidences the presence of an absorption band which may be of impurity nature (A and A', respectively). Since holes are the majority charge carriers in these crystals [9], one can admit that respective absorption particularities are produced by electron transitions from the nonionized acceptor level into the conduction band. The acceptor level is localized at $\sim 30 \text{ meV}$ for $T=293 \text{ K}$ (difference between 2.10 and 2.07 eV), and at $\sim 40 \text{ meV}$ for $T=78 \text{ K}$ (difference between 2.18 and 2.14 eV), above the valence band.

In Fig. 2, a typical wavelength-modulated absorption spectrum of $Cd_{0.5}Mn_{0.5}Te$ single crystals, at 78 K, is illustrated. The sample thickness was $d=870 \text{ }\mu\text{m}$. As can be easily observed, in the energy range (2.18-2.22) eV, optical direct transitions take place between the top of the valence band and the bottom of the conduction band, in the center of the Brillouin zone (analogous to CdTe, the

structurally equivalent compound). The material bandgap, determined as the energy value for which $dI/I_0 d\lambda=0$, is equal to 2.20 eV (Fig. 2), by 20 meV larger than the corresponding value calculated from the absorption spectrum (Fig. 1). The spectral branch beginning in the point B and laying in the lower energy domain, is probably due to the impurity absorption (the band A peaked at 2.152 eV in Fig. 1, evidenced in relatively thick single crystals).

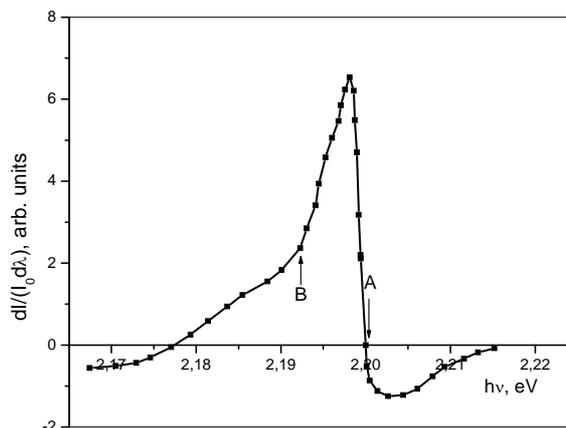


Fig. 2. Absorption spectrum (λ -modulated) of $Cd_{0.5}Mn_{0.5}Te$ single crystals ($d \approx 0.87 \text{ mm}$) at 78 K.

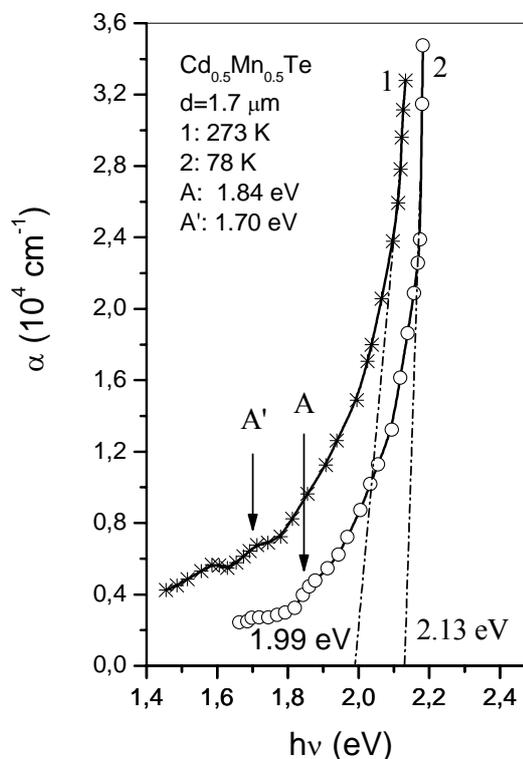


Fig. 3. Absorption spectrum, $\alpha(h\nu)$, for a $Cd_{0.5}Mn_{0.5}Te$ film on mica.

The absorption spectra of films deposited onto mica substrate at temperature 680 K, by discrete evaporation of $Cd_{0.5}Mn_{0.5}Te$ crystals, are presented in Fig. 3. The absorption edge, approximated by extrapolation of linear

portion of $\alpha(h\nu)$ dependence to $\alpha=0$, is localized at 1.99 eV and 2.13 eV for temperatures 293 K and 78 K, respectively. As can be ascertained from Fig. 3, in the absorption spectrum of Cd_{1-x}Mn_xTe solid solutions in thin films prepared by discrete evaporation, a particularity in form of threshold is evidenced, located at ~ 1.70 eV (the point A', T=293 K) and 1.84 eV (the point A, T=78 K). The impurity acceptor levels responsible for these absorption bands are located at ~ 0.30 eV above the top of the valence band. At decreasing temperature from 293 K to 78 K, the width of the forbidden band increases by ~ 0.13 eV, while the position of the acceptor level is practically unchanged.

Fig. 4 presents a typical absorption spectrum, wavelength-modulated, for films prepared by discrete vaporization of Cd_{0.5}Mn_{0.5}Te single crystals. The experimental curve was registered at 78 K, for a film with thickness $d=1.53 \mu\text{m}$. As can be easily found, the energy range of the $dI/I_0d\lambda(h\nu)$ curve for thin films is significantly larger than in the case of single crystals. This fact indicates presence of an important number of defects, which, according to the Urbach's rule [10], lead to an exponential decrease of the absorption coefficient in the energy range $h\nu < E_g$. The absorption edge of Cd_{1-x}Mn_xTe solid solutions is due to optical direct transitions accompanied by formation of free excitons [9]. As one can see from Fig. 4, the energy of excitons in the state $n=1$, determined by the position of the point A, is equal to 2.15 eV, at T=78 K. By comparing Figs. 3 and 4, it is found that the optical bandgap is by 20 meV lesser than the energy required for exciton formation. At this point it is relevant to mention that in Cd_{1-x}Mn_xTe solid solutions, the line of free excitons, evidenced in the photoluminescence (PL) spectra at temperature 78 K, is displaced towards lower energies by ~ 20 meV with respect to the characteristic maximum from reflexion spectra [11]. It's natural to admit that with linear dependence of the lattice constant of Cd_{1-x}Mn_xTe solid solutions on x , a linear dependence of the optical bandgap on composition x [12,13] is also valid for them and can be written as

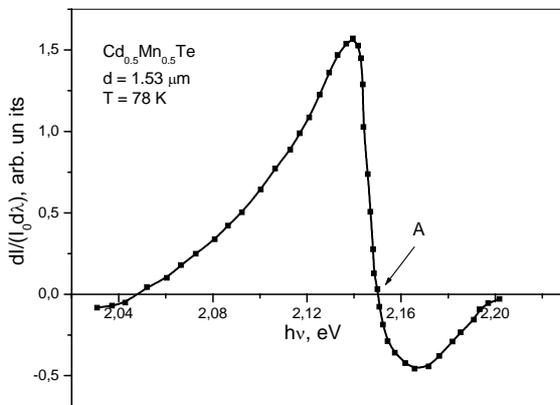


Fig. 4. Absorption spectrum, λ -modulated, of thin films ($d = 1.53 \mu\text{m}$) prepared by discrete evaporation of Cd_{0.5}Mn_{0.5}Te single crystals (T=78 K).

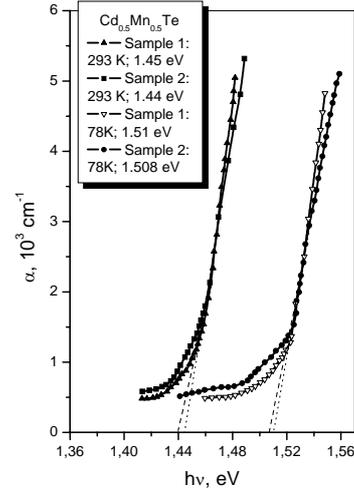


Fig. 5. Absorption spectra $\alpha(h\nu)$ for Cd_{0.5}Mn_{0.5}Te films prepared by physical vapor deposition for substrate temperatures $T_s=883$ K (sample 1) and 893 K (sample 2). In legend temperature, T (K), and optical gap, E_{go} (eV), are indicated.

$$E_g = 1.54 + 1.35x. \quad (3)$$

By using the above equation, the composition of films deposited onto mica by discrete evaporation of Cd_{0.5}Mn_{0.5}Te single crystals can be determined. As resulted value is $x \approx 0.45$.

In Fig. 5 the absorption spectra of Cd_{0.5}Mn_{0.5}Te films prepared by physical vapor deposition are presented. For substrate (mica) temperatures between 870 K and 930 K, single crystalline films with mirrored faces are obtained. As can be seen in the last figure, the substrate temperature weakly influences the shape of the absorption spectrum in the vicinity of the fundamental absorption edge. The absorption coefficient is seen to change more markedly with temperature only for values less than 2000 cm^{-1} . At increasing substrate temperature, the slope of $\alpha(h\nu)$ curve slowly decreases at high temperatures and is seen to increase at temperatures above 910 K. The shift of the absorption curves from Fig. 5 is mainly due to the decrease of the absorption coefficient at increased deposition-temperatures. Since the optical bandgap is determined by the linear segment of $\alpha(h\nu)$ curve (Fig. 5) for absorption coefficients in the range $(2-5) \times 10^3 \text{ cm}^{-1}$, one can admit that the fundamental absorption edge is formed by direct electron transitions between the valence and the conduction bands, and it is not of impurity nature. By extrapolating $\alpha(h\nu)$ curve to $\alpha=0$, the optical gap was found as ~ 1.45 eV at 293 K and ~ 1.51 eV at 78 K. Since the slope of $\alpha(h\nu)$ depends on the crystallization temperature of respective compounds, the dependence of the optical gap, E_g , on the substrate temperature (T_s) can be determined, which is illustrated in Fig. 6. As can be found, the optical bandgap of Cd_{1-x}Mn_xTe films, grown onto mica from vapor phase, depends on the substrate temperature and at room temperature decreases from 1.45 eV to 1.44 eV for increasing temperature from 880 K to 893 K. At substrate temperatures over 895 K, the optical gap increases with temperature. The width of the forbidden

band reaches its minimum at a substrate temperature ~ 890 K in both cases, 78 K and 293 K.

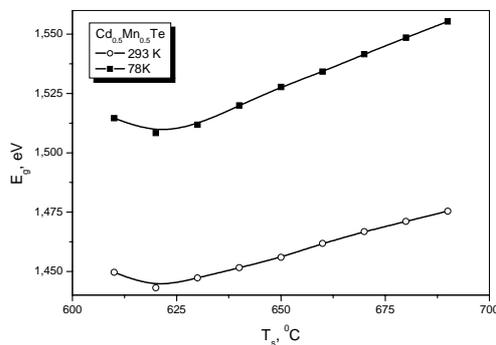


Fig. 6. Dependence of the optical gap on the vapor phase deposition temperature for films prepared from $Cd_{0.5}Mn_{0.5}Te$ single crystals.

Fig. 7 shows the absorption spectra, λ -modulated, of $Cd_{1-x}Mn_xTe$ ($x=0.5$) films prepared by physical vapor deposition onto mica, for two substrate temperatures, 890 K (curve 1) and ~ 930 K (curve 2). From this figure, the width of the forbidden band was found as 1.575 eV at temperature 78 K and it is by 15 meV lesser as compared to the corresponding value of CdTe [14].

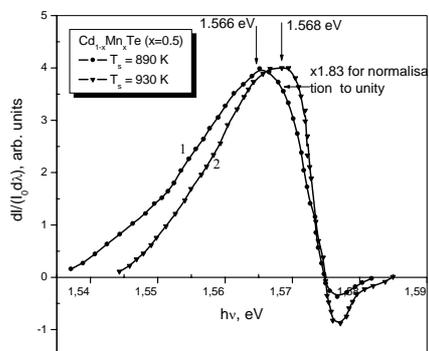


Fig. 7. Absorption spectrum, λ -modulated, for $Cd_{0.5}Mn_{0.5}Te$ films, vapor deposited.

By analysing Figs. 1 and 7, one can state that $Cd_{1-x}Mn_xTe$ films prepared by physical vapor deposition, have different chemical composition from that of the source material ($Cd_{0.5}Mn_{0.5}Te$ single crystals). The width of the forbidden band (of as-prepared films) is close to the respective value of CdTe single crystalline films. As was stated in [14], the energy gap of CdTe films vapor phase deposited from CdTe single crystals is equal to 1.59 eV at 78 K and 1.54 eV for $T = 293$ K. Consequently, the vapor phase of $Cd_{0.5}Mn_{0.5}Te$ is preponderantly composed of CdTe; MnTe, in little amounts, creates localised states which, in turn, produce a red shift of the absorption threshold with respect to the absorption edge of the initial crystals.

4. Conclusions

The optical gap of $Cd_{0.5}Mn_{0.5}Te$ single crystals, as determined by extrapolation of $\alpha(h\nu)$ experimental curve to $\alpha=0$, is equal to 2.10 eV and 2.18 eV, at temperatures 293 K and 78 K, respectively. The energy of the impurity acceptor levels, is equal to about 2.09 eV at 293 K, and 2.15 eV at 78 K. The energy of the optical transitions leading to exciton (in the state $n=1$) formation in $Cd_{0.5}Mn_{0.5}Te$ single crystals, as determined from the absorption spectrum, wavelength-modulated, at temperature 78 K, is equal to ~ 2.20 eV.

The optical gap of $Cd_{1-x}Mn_xTe$ films prepared by discrete evaporation of $Cd_{0.5}Mn_{0.5}Te$ fragments, is equal to ~ 2.0 eV and 2.13 eV at temperatures 293 K and 78 K, respectively. Based on the linear dependence of the optical gap of $Cd_{1-x}Mn_xTe$ solid solutions on temperature, was established that by discrete evaporation of compound with $x=0.5$, the obtained composition of deposited films was not $x=0.5$, but $x \approx 0.45$. The optical gap of single crystalline $Cd_{1-x}Mn_xTe$ films, grown onto mica from vapor phase, depends on the substrate temperature and reaches its minimum at $T_s \sim 890$ K at both temperatures, 78 K and 293 K.

References

- [1] D. E. Aspnes, Phys. Rev. **147**, 554 (1966).
- [2] I. N. Odin, M. V Chukichev, M. E. Rubina, Inorg. Mater. **39/4**, 345 (2003).
- [3] P. V. Jukovskii, Ya. Partyka, P. Vengerek, FTP **35/8**, 937 (2001) (in Russian).
- [4] R. Meyer, M. Dahl, G. Schaack et al, Solid State Commun. **96**, 271 (1995).
- [5] X. C. Zhang, S. K. Chang, A. V. Nurnikko, Solid State Commun. **56/3**, 255 (1985).
- [6] G. G. Rusu, M. Rusu, M. Caraman, J. Optoelectron. Adv. Mater. **7(2)**, 811(2005).
- [7] T. S. Moss, G. J. Burrell, B. Ellis, Semiconductor Opto-Electronics, Butterworth, London (1973).
- [8] Yu. I. Uchanov, Optičeskie Svoistva Poluprovodnikov, Nauka, Moskva (1977) (in Russian).
- [9] D. Todoran, M. Caraman et al, Sci. Annals USM, Phys.-Maths. Series, 187 (2001).
- [10] F. Urbach, Phys. Rev., **92**, 1324 (1953).
- [11] V. F. Agekian, Fan Zing, FTP **18/10**, 1859 (1984) (in Russian).
- [12] V. P. Jukovskii, Ya. Partyka, P. Vengerek et al, FTP **35/8**, 937 (2001).
- [13] J. Diouri, J. P. Lascaray, R. Triboulet, Solid State Commun. **42/3**, 231 (1982).
- [14] Iuliana Caraman, P. Gashin, C. Rotaru, Mihaela Rusu, Phys. Low-Dim. Struct. **7/8**, 1 (2001).

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