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OPTICAL CHARACTERISTICS AND COMPOSITION OF $Cd_{1-x}Mn_xTe$ FILMS OBTAINED BY THE CLOSE SPACED SUBLIMATION TECHNIQUE

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Study of the optical properties of $Cd_{1-x}Mn_xTe$ films obtained by the close spaced sublimation technique was carried out. Measuring of the optical characteristics of the layers was performed by the spectrophotometric analysis method near the "red boundary" of the semiconductor photoactivity. This research allowed to obtain the spectrum distributions of the transmission $T(\lambda)$, reflection $R(\lambda)$ and absorption $\alpha(\lambda)$ coefficients of the films as well as estimate the band-gap energy of the compound. The values of the band-gap energy were used for determination of manganese concentrations in the films depending on the growth conditions.

Keywords: *$Cd_{1-x}Mn_xTe$ SOLID SOLUTION FILMS, TRANSMISSION COEFFICIENT, REFLECTION COEFFICIENT, WIDE BAND GAP, LAYER COMPOSITION.*

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1. INTRODUCTION

Semimagnetic $Cd_{1-x}Mn_xTe$ semiconductor is of a great interest due to the possibility of the creation on its basis of the magnetic field sensors, electro-luminescent and magneto-optical devices [1-3]. Lately, this material is also considered as an alternative one to the $Cd_{1-x}Zn_xTe$ solid solution for using in hard radiation detectors. Advantages of using of this semiconductor as a detector material are the following: very high resistivity; low coefficient of manganese segregation ($k \sim 1$) that allows to produce semiconductor layers with uniform volume distribution of impurities; possibility of the precise regulation of the band gap width (BG) of the solution due to the change in its composition (12-15 meV per 1 at.% of Mn in comparison with 6.7 meV/at.% of Zn), in this case it can be changed from 1.51 to 3.2 eV; small probability of the formation of tellurium precipitates, etc [3-4].

Publications [4-10] are devoted to the investigation of the properties of $Cd_{1-x}Mn_xTe$ bulk monocrystals. Films are studied much worse due to the complexity of the production, since pressures of the solution components are significantly different. In connection with this, thin layers of three-component compounds are mainly deposited by the laser [11] and flash [12] evaporation methods, high-frequency magnetron sputtering [13], which are characterized by high degree of the process non-equilibrium. As a result, such layers have low-quality fine dispersed structure that does not allow to use them in such devises as photodetectors and hard radiation detectors, solar cells, etc. In [14] $Cd_{1-x}Mn_xTe$ films are obtained by the hot wall method, which allows to deposit layers of multicomponent materials in quasi-equilibrium conditions. The authors have shown that this method can be effectively applied for the deposition of material layers with large difference of vapor pressures. However, optical and structural characteristics of such films were not studied.

To determine the influence of the physical and technological conditions of the condensation on the composition of $Cd_{1-x}Mn_xTe$ films deposited by the close spaced vacuum sublimation (CSVS) technique we study their optical characteristics. As it was shown earlier in [15-17], the CSVS method can be used to obtain high-quality films of A_2B_6 compounds, which are applicable for device using.

2. PRODUCTION TECHNIQUE AND FILM INVESTIGATION

Thin $Cd_{1-x}Mn_xTe$ films were obtained on the purified glass substrates in the vacuum device VUP-5M at the residual gas pressure in the chamber not more than $5\cdot10^{-3}$ Pa. Evaporation of the furnace-charge of semiconductor purity, which had $Cd_{0.7}Mn_{0.3}Te$ composition, was performed by the CSVS method. Evaporator temperature was changed in the range of T_e = 923-1073 K. Time of the layer condensation was usually equal to t = 8-10 min. Film thickness was measured by the interferometric method and was about d = 0.5-1.2 μm.

CdTe films were also obtained by the CSVS method from the furnace-charge of semiconductor purity. They were used as the standard while determining manganese composition in $Cd_{1-x}Mn_xTe$ solid solution using its BG E_g. It is well known that BG of this material depending on the manganese content is changed linearly from the values typical for CdTe to the values typical for MnTe. Substrate temperature during deposition of cadmium telluride films was T_s = 293-673 K. Evaporator temperature was equal to T_e = 893 K.

Measurement of the optical characteristics of condensates was carried out using spectrophotometer SF-26 in the wavelength range λ = 700-1000 nm. Spectral dependences of the reflection $R(\lambda)$ and transmission $T(\lambda)$ coefficients were obtained. To measure the spectra $R(\lambda)$ we used the add-on PZO-2, which provided double reflection of light from the surface of experimental samples taking into account its reflection from the check sample. Calculation of the reflection coefficient (in percents) was performed by the formula $R = 10\sqrt{B}$, where B is the scale reading of measuring ammeter. Calculation of the optical constants of material was realized using the software environment Maple 7.

3. RESULTS AND DISCUSSION

Complexity of film production from the furnace-charge of $Cd_{1-x}Mn_xTe$ solid solution is connected with the features of evaporation of A_2B_6 compounds. As it is well known, they are evaporated with dissociation by the formula [15]

$$AB(solid\ phase) = A(gaseous\ phase) + 1/2\,B_2(gaseous\ phase)\,. \qquad (1)$$

As a result, gaseous phase contains both the cadmium and manganese atoms and tellurium molecules. Pressure of saturated vapor of separate components in gaseous phase can be determined by the formula

$$\lg P = -A/T_e + B - C\lg T_e - DT_e \, , \tag{2}$$

where *A, B, C, D* are the known (from handbooks) constants given in Table 1 [15, 18]

Table 1 *– Constants used in calculations of vapor pressures [15, 18]*

Material	Cd		Te		Mn	CdTe
	solid phase	liquid phase	solid phase	liquid phase	solid phase	solid phase
T, K	298-594.3	594.3-1040	298-723	723-1263	298-1517	768-1000
A	5924	5406	9232	6016	15400	9761
B	10.049	11.35	19.667	6.402	12.408	6.57
C	−0.172	−0.975	−2.100	0.400	−0.369	–
D	$-0.642\cdot10^{-3}$	–	$-2.308\cdot10^{-3}$	–	$-0.739\cdot10^{-3}$	–

In the case of three-component vapor, pressure above the substrate (without taking into account the transport phenomena) is defined by correlation [19]

$$P = P(\text{Cd}) + P(\text{Mn}) + P(\text{Te}_2) =$$
$$= \alpha_0(\text{Cd})P(\text{Cd})N(\text{Cd}) + \alpha_0(\text{Mn})P(\text{Mn})N(\text{Mn}) + \alpha_0(\text{Te}_2)P(\text{Te}_2)N(\text{Te}_2) \, , \tag{3}$$

where P(Cd), P(Mn), $P(\text{Te}_2)$ are the pressures of saturated vapor of the compound components; α_0(Cd), α_0(Mn), $\alpha_0(\text{Te}_2)$ are the coefficients of inverse accomodation of the corresponding atoms, which are equal to the ratio of the number of atoms recondensed from the substrate surface to the number of atoms collided with the substrate; N(Cd), N(Mn), $N(\text{Te}_2)$ are the molar fractions of the corresponding solution components. At low substrate temperatures coefficients α_0 are closed to 1 that simplifies further calculations.

Corresponding calculations of the pressure of saturated vapor of the components of $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ compound performed for the cases, when they are in liquid and solid states (these estimated values of P are found to be out of the chosen temperature range), are shown in Fig. 1. For comparison, vapor pressure of CdTe compound is represented in the same figure.

As seen from Fig. 1, cadmium pressure for traditional temperatures of CdTe evaporation (T_e = 893-1015 K [15-17]) exceeds substantially tellurium pressure, and the latter, in turn, exceeds manganese pressure. Thus, during evaporation of three-component furnace-charge one should expect tellurium depletion of the films and, to an even greater degree, manganese depletion in comparison with the furnace-charge. Only at T_e = 1260 K tellurium and manganese pressures are equal. Thus, to obtain films with large Mn content it is necessary to increase evaporator temperature that, in turn, leads to the deflection of condensation conditions from equilibrium and decrease in the crystalline quality of the films.

So, one should choose optimal evaporation temperatures, which, on the one hand, provide necessary Mn content in condensates and, on the other hand, allow to obtain qualitative $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ films. Thus, analysis of the vapor pressures of the components of three-component compound allowed to choose evaporation temperatures of the furnace-charge, which are used in this work

T_e = 923-1073 K. In this case, substrate temperature was low in order to prevent re-evaporation from the substrate T_s = 423 K.

Spectral dependences of the reflection $R(\lambda)$ and transmission $T(\lambda)$ coefficients from $Cd_{1-x}Mn_xTe$ films obtained at different evaporation temperatures of the furnace-charge are shown in Fig. 2a, b. For comparison, in this figure (Fig. 2c, d) we present the measurement results of the optical characteristics of CdTe films. As seen from the figure, studied two-layered structures glass-$Cd_{1-x}Mn_xTe$ film are characterized by sufficiently high reflection coefficient (Fig. 2b), which is equal to 12-17% and increases with λ. This is conditioned by weakly expressed relief of low-temperature condensates and reflectivity of their surface.

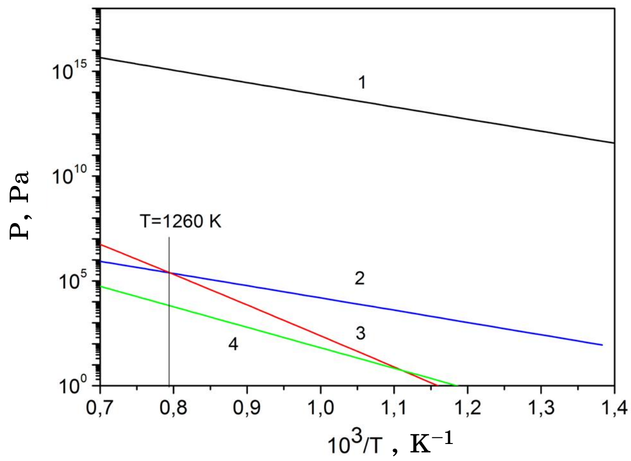

Fig. 1 *– Pressures of saturated vapor of Cd (1), Te (2), Mn (3) and CdTe (4) at different temperatures*

Transmission spectra of $Cd_{1-x}Mn_xTe$ films obtained at different regimes of condensation have the same behavior (see Fig. 2a). At the radiation wavelengths more than λ ~ 720-730 nm (at the energies less than the BG of the material) the substantial increase in the transmission coefficient of condensates occurs. In this wavelength range the transmission coefficient of the films is 50-60% in some cases. The maximums and minimums of intensity connected with the radiation interference in thin layers of chalcogenide (as it was already noted, their thickness was small and equal to $d \leq 1.2$ μm) are observed both on $R(\lambda)$ and $T(\lambda)$ dependences. Interference peaks observed on these spectra indicate the uniformity of investigated films in area.

To determine the optical BG E_g of $Cd_{1-x}Mn_xTe$ solid solution and CdTe we have used the following correlation, which is true for direct band gap semiconductors [20]:

$$\alpha h\nu = A(h\nu - E_g)^{1/2}, \quad (4)$$

where A is some constant, which depends on the effective mass of the charge carriers in the material; $h\nu$ is the energy of an optical quantum; α is the absorption coefficient of the material.

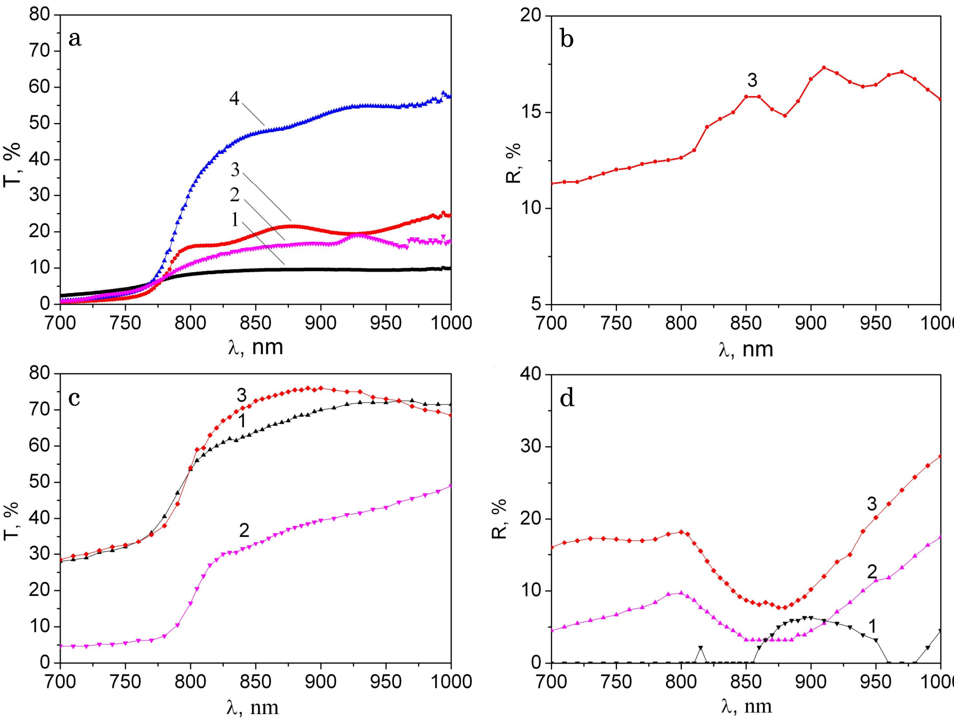

Fig. 2 – *Transmission spectra (a) of $Cd_{1-x}Mn_xTe$ films obtained at T_s = 423 K and different T_e, K:* 923 *(1)*, 973 *(2)*, 1023 *(3)*, 1073 *(4) and reflection spectra (b) at T_e* = 1023 *K. Transmission (c) and reflection (d) spectra of CdTe films, T_e* = 893 *K; T_s, K:* 473 *(1)*, 573 *(2)*, 673 *(3)*

As it follows from this correlation, extrapolation of the linear part of the figure $(\alpha h\nu)^2 - h\nu$ on the energy axis allows to determine the BG of semiconductors. Absorption coefficients of $Cd_{1-x}Mn_xTe$ solid solution and CdTe films at different lengths of the incident radiation necessary for E_g calculation were obtained using the reflection and transmission spectra and correlation [4, 21]

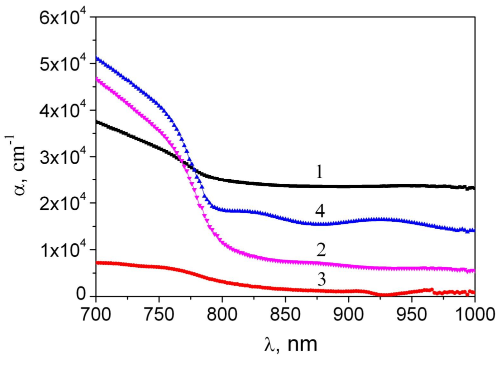

Fig. 3 – *Absorption spectra of $Cd_{1-x}Mn_xTe$ films obtained at T_s = 423 K and different T_e, K:* 923 *(1);* 973 *(2);* 1023 *(3);* 1073 *(4)*

$$\alpha = -\frac{1}{d}\ln\left(\frac{1}{R^2}\left(-\frac{(1-R)^2}{2T}+\sqrt{\frac{(1-R)^4}{4T^2}+R^2}\right)\right). \quad (5)$$

As calculations show, absorption coefficient of the obtained $Cd_{1-x}Mn_xTe$ films in the radiation energy band more than the BG was usually equal to $\alpha = (1\text{-}5)\cdot 10^4$ cm^{-1} (see Fig. 3). These values are closed to those observed for pure cadmium telluride $\alpha = (2\text{-}5)\cdot 10^4$ cm^{-1}.

In Fig. 4 we present the dependences $(\alpha h\nu)^2 - h\nu$, which were used for the determination of the BG of $Cd_{1-x}Mn_xTe$ and CdTe. As seen from the figure, these dependences in the energy band close to the photoelectric threshold are approximated by the straight lines, whose intersections with the energy axis allow to determine E_g. In the case of pure CdTe it was equal to $E_g = 1.52$-1.53 eV, and solid solution had the BG $E_g = 1.46$-1.57 eV. The corresponding results of E_g determination for the investigated $Cd_{1-x}Mn_xTe$ samples are represented in Table 2.

Table 2 – *Results of the determination of the BG and $Cd_{1-x}Mn_xTe$ film composition using different published data*

Sample	T_e, K	T_s, K	E_g, eV	x_1 [11]	x_2 [13]	x_3 [12]	x_4 [22]	x_5 [22]
1	923	423	1.456	−0.0547	−0.0587	−0.0622	−0.0015	0.0022
2	973	423	1.480	−0.0364	−0.0397	−0.0444	0.0169	0.0202
3	1023	423	1.561	0.0251	0.0246	0.0156	0.0791	0.0806
4	1073	423	1.565	0.02812	0.0278	0.0185	0.0821	0.0836

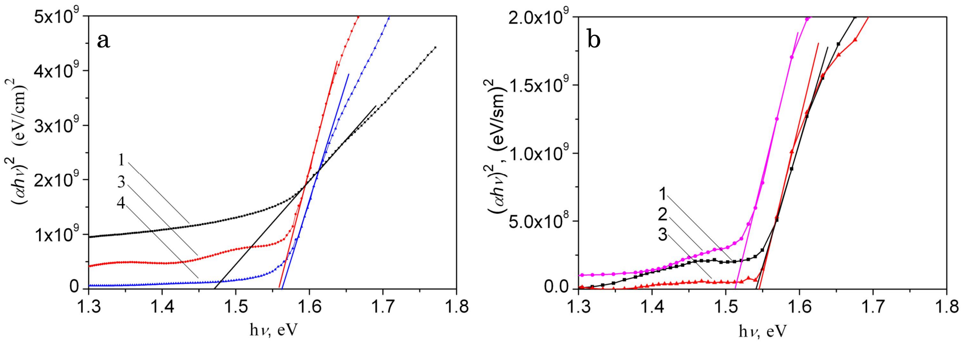

Fig. 4 – *Determination of the optical BG of $Cd_{1-x}Mn_xTe$ and CdTe films. Films of solid solution are obtained at T_s = 423 K and different T_e, K: 923 (1), 1023 (3), and 1073 (4) (a); CdTe films at T_e = 893 K; T_s, K: 473 (1), 573 (2), and 673 (3) (b)*

Henceforth, experimentally obtained values of the BG of the material were used to determine the manganese content in $Cd_{1-x}Mn_xTe$ solid solution by the known dependences (E_g - x). For this, the following expressions were taken from the published data [11-13, 22]:

$$E_g = 1.528 + 1.316x\,, \quad (6)$$

$$E_g = 1.53 + 1.26x\,, \quad (7)$$

$$E_g = 1.54 + 1.35x\,, \quad (8)$$

$$E_g = 1.458 + 1.303x\,, \tag{9}$$

$$E_g = 1.453 + 1.34x\,. \tag{10}$$

We have to note that correlation (6) was obtained as a result of piezo-modulation investigations of the reflection from $Cd_{1-x}Mn_xTe$ condensates, and expression (7) – as a result of ellipsometer study. Two last correlations are obtained by the optical measurements of the transmission coefficient of the films with the following determination of the BG using 50% value of this coefficient.

Dependences (E_g - x), which correspond to the correlations (6)-(10), are shown in Fig. 5. The values of x determined from these dependences by the experimentally found values of E_g are generalized in Table 2.

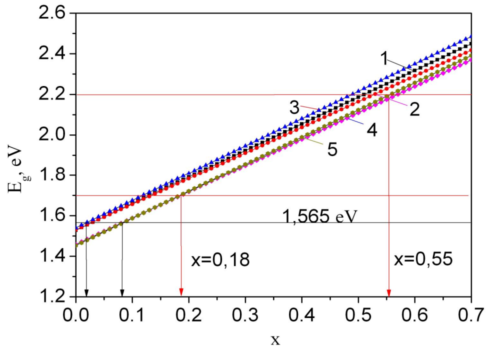

Fig. 5 – *Dependence of the BG E_g of $Cd_{1-x}Mn_xTe$ compound on the manganese content x. The following published data was used: correlation (6) – 1 [11]; (7) – 2 [13]; (8) – 3 [12]; (9), (10) – 4, 5 [22]*

As seen from Table 2, usage of the dependences (E_g - x) cited by different authors [11-13, 22] leads to slightly different values of manganese content in the studied films. Sometimes these values have even negative value that is not physical. This can be connected with the fact that besides of the main reason, i.e. manganese content, the BG of a triple compound (as well as cadmium telluride) is defined also by the crystalline size, film thickness, content of uncontrolled isovalent impurities in material, first of all, oxygen [23-24]. This leads to the discrepancy of E_g values represented in different works. Nevertheless, the most exact values of x, in our opinion, were found using expressions (6)-(8), since the BG of cadmium telluride (which is used in these correlations) is closed to that we have obtained for CdTe film samples: E_g = 1.52-1.53 eV. That is, the studied films, most likely, contain 2-4% of manganese.

Advantage of the correlation (10) is the following: it allows for the whole array of experimental data E_g to obtain positive values of x, though, probably, with some small systematic error (on the level of some percents). Therefore, we have used it for further additional calculations.

We should note that usage of all known dependences (E_g - x) allows to reveal a tendency to the increase in manganese concentration in condensates with the increase in the evaporation temperature of the furnace-charge, as it should be according to the analysis of the pressure-temperature dependences (see Fig. 1).

Data obtained based on the analysis of the optical characteristics of the samples is confirmed by the investigation results of film composition by the EDAX method. Peaks from manganese were observed on the corresponding spectra together with the peaks which belong to cadmium and tellurium. Here, manganese concentration in condensates was about 2-4%. Coincidence of the data obtained by the optical method and method of the X-ray spectroscopic microanalysis implies that manganese with cadmium telluride forms a solid solution and is not exuded as precipitates in crystalline volume or along the grain boundaries.

We note, dependences presented in Fig. 5 allow to predict the manganese content in layers of $Cd_{1-x}Mn_xTe$ promising for application as a detector material. We remind that during detector operation at room temperature, material with E_g ~ 1.60 eV is necessary, and at higher temperatures – with E_g ~ 1.70-2.20 eV [3, 4]. These values of the BG correspond to the material with x = 0.05-0.06 and x = 0.18-0.55 (Fig. 5). Thus, films obtained at high evaporator temperatures T_e = 1073 K with the manganese content of x = 0.02-0.04 (Table 2), but thicker, can be used as the base material of detectors operating at room temperature. Moreover, they are promising as absorbing layers of thin-film solar converters, since can be obtained with n-type conductivity that provides better charge carrier mobility in material [1, 2].

Based on the investigation results, we present (x - T_e) and (E_g - T_e) dependences (see Fig. 6), which allow to determine in the first approximation the evaporator temperature (at low substrate temperatures when one can neglect re-evaporation of the material) necessary to obtain $Cd_{1-x}Mn_xTe$ films with the required for the instrument application BG and manganese content.

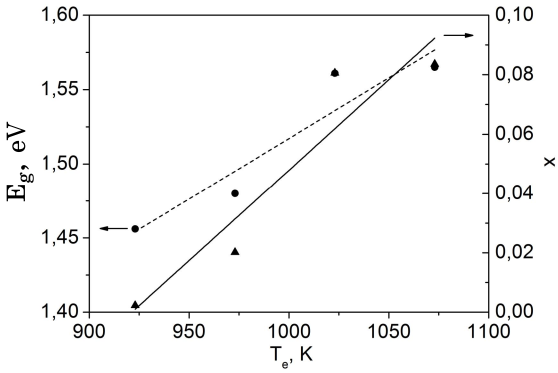

Fig. 6 – *Dependence of the BG E_g and manganese content x of $Cd_{1-x}Mn_xTe$ triple compound in the films on the evaporation temperature T_e of the material*

These dependences can be analytically written as follows:

$$E_g = 0.701 + 8.16 \cdot 10^{-4} T_e , \quad (11)$$

$$x = 6.09 \cdot 10^{-4} T_e - 0.561 . \quad (12)$$

4. CONCLUSIONS

In the work, the component pressures of $Cd_{1-x}Mn_xTe$ compound are calculated and the evaporation temperatures, which are necessary to obtain films

with small (some percents) and large manganese concentration, are estimated. At the low substrate temperature (T_s = 423 K), when re-evaporation processes of the substance can be neglected, and at different evaporator temperatures (T_e = 923-1073 K), from the furnace-charge with $Cd_{0.7}Mn_{0.3}Te$ composition thin films of this compound are obtained by the CSVS method. Spectral dependences of the reflection $R(\lambda)$ and the transmission $T(\lambda)$ coefficients of the obtained films are investigated and the BG of the material, which is equal to E_g = 1.46-1.57 eV, is defined. Using published data about the dependence of the BG of $Cd_{1-x}Mn_xTe$ compound on the manganese content, concentration of this element in the samples is determined. It is established that the manganese content in the films is equal to x = 0.02-0.04 and it increases with the increase in the evaporation temperature of the furnace-charge. This data is confirmed by the investigation results of film composition by the EDAX method. Analytical dependences, which allow to predict in the first approximation the film composition and the BG of the material by the known evaporation temperature, are obtained.

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