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Technological conditions effect on structural perfection of $Cd_{1-x}Mn_xTe$ crystals

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Dependence of $Cd_{1-x}Mn_xTe$ crystals' quality ($0.02<x\leq0.55$) on synthesis duration and growing conditions, using the complementary X-ray diffraction methods, has been investigated. The obtained experimental results about the structural perfection and types of defects, their distribution and reasons of formation, allowed us to optimize the technological parameters of the perfect crystals' synthesis and growth.
Keywords: $Cd_{1-x}Mn_xTe$ solid solutions, X-ray topography, twins, crystal structure, Bridgman method.

Исследована зависимость структурного совершенства кристаллов твердых растворов $Cd_{1-x}Mn_xTe$ ($0,02<x\leq0,55$) от продолжительности синтеза и условий выращивания с использованием взаимодополняющих рентгеновских дифракционных методов. Экспериментально полученные результаты о структурном совершенстве кристаллов и типах дефектов, их распределении и причинах возникновения позволили оптимизировать технологические условия синтеза и выращивания совершенных кристаллов.

Вплив технологічних режимів на структурну досконалість кристалів $Cd_{1-x}Mn_xTe$. *В.П.Шафранюк, С.Г.Дремлюженко, С.В.Солодін, П.М.Фочук.*

Досліджено залежність структурної досконалості кристалів твердих розчинів $Cd_{1-x}Mn_xTe$ ($0,02<x\leq0,55$) від тривалості синтезу, а також від умов вирощування з використанням взаємодоповнюючих рентгенівських дифракційних методів. Експериментально одержані результати про структурну досконалість кристалів і типи дефектів, їх розподіл та причини виникнення дали можливість оптимізувати технологічні умови синтезу та вирощування досконалих кристалів.

1. Introduction

Cadmium telluride and solid solutions, based on it, for example, $Cd_{1-x}Mn_xTe$ (CMT), have a great perspective in photoelectronics, in particular, for γ-ray detectors manufacturing [1, 2]. One of the main reasons that limit their applications is a difficulty to obtain large and structurally perfect single crystals with reproducible and stable characteristics. The ensuring of these requirements is impossible without understanding the relationships between perfection of the crystal structure and growth conditions.

$Cd_{1-x}Mn_xTe$ crystals with x from 0.02 to ~0.55 are usually investigated (the most common content $x = 0.05$). The crystals with variable content (from this range) are used for different applications. For instance, for γ-ray detectors manufacturing the crystals with $x = 0.05–0.1$ are usually used [3]; for optical isolators — x=0.42–0.45 [4, 5]; for optical filters — the whole range of content.

It is known [6–10], nowadays that the $Cd_{1-x}Mn_xTe$ (x = 0.05; 0.1; 0.2) ingots with diameter of 25–30 mm and length of 8–13 cm are obtained. Solid crystalline materials have a real structure, which differs from an ideal (strictly ordered) by a presence of various defects. In CMT crystals, grown nowadays, it is observed rather high density of dislocations and inclusions of the second phase. In addition, there are significant amounts of twins and subgrains in these ingots. These defects especially reveal themselves in the crystals, grown by the Bridgman method [2, 7, 10–13], and to a lesser extent one can find them in the crystals, grown by the travelling heater method (THM) [12]. Typically, the Debye-Scherrer and Laue methods [11, 14] are used for structure studies, however information about direct X-ray methods is insufficient [6, 10]. However, such information would enable to improve the technology of perfect large CMT crystals growth with required parameters. Therefore, in this paper we present the CMT crystal structure researches by the following comprehensive and complementary methods: X-ray diffraction topography in the transmission mode (the Lang's method) [15] and in the reflection mode (the Berg-Barrett's method) to visualize the "growth" defects (twins, subgrains, dislocations, inclusions of the second phase); X-ray diffractometry (the Bond's method) to determine the lattice parameter; double-crystal spectrometry (DCS) [16] to determine the disorientation between grains. It should be noted that these methods not only make it possible to obtain the most complete information about the crystalline perfection of the material but also are expressive and nondestructive.

2. Experimental

CMT crystals ($0.02<x\leq0.55$) were prepared from synthesized raw materials (5N purity) in stoichiometric ratios. To prevent the interaction between Mn and walls of the a quartz ampoule, a synthesis of solid solutions was performed in a glassy-carbon container, placed in a vacuum container.

The synthesis was performed according to the existed phase diagram of CdTe–MnTe system. The melt maximum temperature during the synthesis was about 1400 K, which was sufficient to melt the high-temperature solid phases in the melt. After the synthesis, the crystals were grown by the vertical Bridgman technique (temperature gradient at the solid-melt interface was 10÷15 K/cm, growth rate — 2 mm/h). In our experiments we used both a conventional and modified setup described elsewhere [17]. After finish of the melt solidification the ingot was in situ annealed at ~1173 K for 48 h and finally cooled down to the room temperature at the rate of 20 K/h. As we know a disturbance of monotonic container movement with the melt has a negative influence on as-grown crystal structure, therefore in the modified setup the disturbance was eliminated due to a movement of a large heater along the stationary container (ampoule). To stabilize the movement of the heater its weight was balanced by two counterpoises. In addition, the heater was connected with a fixed system of damping rollers. It was found that crystals, grown by the movable heater usage, had more perfect structure comparing with the ones, grown by the conventional Bridgman setup.

The grown CMT ingots were oriented in (111) and (110) planes. The ingots were cut into plates with 1 mm thickness, mechanically grinded and polished on both sides. The final treatment of the samples was chemical etching in 5 % $Br–CH_3OH$ solution for 1 min to remove the damage layer. To reveal the grain structure, twins and surface defects it was applied the Berg-Barrett's method using symmetric (111), (220) and asymmetric reflections from crystallographic planes (113), (331), (400), (511). In this method it was used a fine-focus X-ray tube BSM-1 with the focus dimensions of ~50 μm, that made it possible to obtain a high-resolution of ~0.5 μm. Topograms in the transmission mode were obtained by using the Lang's method with MoK_α-radiation at X-ray machine URT-1. The integral evaluation of the crystal perfection and disorientation between grains were carried out by DCS method; the lattice parameter distribution along ingot's axial and radial directions was determined by the Bond's method with the high-resolution (±0.00002 nm).

3. Results and discussion

A typical topogram from a perfect crystal in the Berg-Barrett's method is depicted on positive as two parallel near light stripes, which are the areas of the Cossel's cone $K\alpha_1$ and $K\alpha_2$-lines of characteristic radiation of K_α-series.

In Fig. 1 there are represented the series of X-ray topograms, obtained by the Berg-Barrett's method for $Cd_{0.95}Mn_{0.05}Te$ crystals, grown in a conventional Bridgman setup (synthesis duration was varied from 10 h to 70 h).

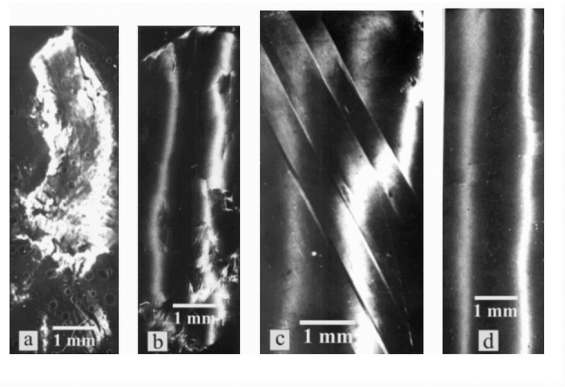

Fig. 1. X-ray topograms of $Cd_{0.95}Mn_{0.05}Te$ crystals grown from the charge, that had been synthesized at duration τ: a) τ = 10 h, b) τ = 30 h, c) τ = 40 h, d) τ = 70 h. (CuK_α-radiation, reflection from crystallographic planes (333) .

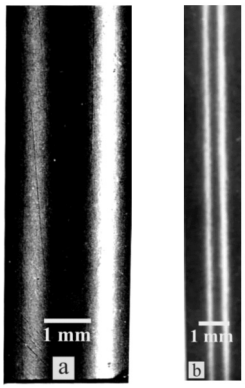

Fig. 2. X-ray topograms of $Cd_{0.95}Mn_{0.05}Te$ crystals, grown in the optimal conditions. CuK_α-radiation, a, b — reflection from crystallographic planes (333) and (111), respectively.

Analysis of the topograms indicated, that the crystals, grown from the synthesized mixture during 10 h and 30 h, possessed an ideal structure warping resulting in presence of the grains structure and lattice parameter gradient. Distortion and shift of the Cossel's lines can be explained by irregularity of crystallization and Mn impurity distribution along the ingot's axial and radial directions during the growth process leading to the crystal's deformation. The distortion of the crystal structure was represented in the topograms as reflections' overlap from different parts of the sample as well as a splitting of certain lines of doublet in several lines, that often formed closed circuits.

Besides, the grown crystals contained twins, which were reflected in the topograms as the displaced Cossel's lines (Fig. 1c). The pronounced twinning was observed in the CMT crystals with $0.2<x\leq0.35$ composition similarly to the results in paper [7]. It should be noted that the tendency to twinning was much weaker at $0.35\leq x\leq0.55$.

The CMT solid solutions crystals with $x\leq0.05$, that were synthesized during 70 h, possessed a more perfect structure, as evidenced by separation of the topograms doublet in the topogram (Fig. 1d).

Obtaining the large single crystals depends on the ampoule shape. The highest yield of ones was observed after the ingots' growing in the double wall quartz ampoule (diameter 50–60 mm) with flat bottom and heat sink in the center of the ampoule bottom [18]. At the ampoule movement in the furnace cold part a nucleation was occurred at the point, where the heat sink was attached. The further growth continued in the melt that surrounded the nucleation point. Thus influence of the ampoule walls on the crystal, that stressed it, was eliminated, and thereby the crystal structure was improved. In Fig. 2 there are shown the topograms, which were typical for $Cd_{0.95}Mn_{0.05}Te$ crystals, grown in such ampoules at optimal growth conditions. These topograms showed that crystals have the high structural perfection since there was observed a clear separation of doublets $K\alpha_1$ and $K\alpha_2$ for different reflections, confirming the absence of macrostresses, grains, twins and other defects.

For these crystals there were determined the full width of half maximum (FWHM) values of the rocking curves for (111) crystallographic plane reflection by applying the DCS method $(n, -m)$ — Si(220). Quantitative structural perfection degree estimation for investigated crystals was performed by comparing the experimentally obtained FWHM values of the rocking curves θ_{exp} with the theoretically calculated ones θ_{theor}. The latter was defined by FWHM lines of a monochromator (Si) θ_M and a sample θ_s as well as a dispersion of the instrument $D^2\Delta\lambda^2$:

$$\Theta_{theor} = (\theta^2_M + \theta^2_s + D^2\Delta\lambda^2)^{1/2}. \qquad (1)$$

Contribution of the FWHM rocking curve for the perfect crystal is determined by the formula:

$$\Theta_{cr} = \frac{2 \cdot C \cdot X_h}{\sin2\theta}, \qquad (2)$$

where $C = 1$, for σ-polarization; $C = \cos2\theta$, for π-polarization, X_h — the Fourier crystal component.

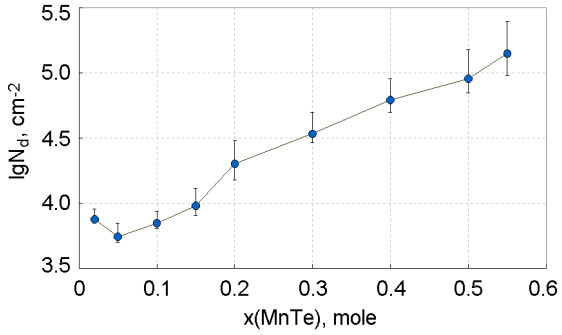

Fig. 3. Dependence of dislocations density on MnTe content in $Cd_{1-x}Mn_xTe$ solid solutions crystals grown in modified facility by the vertical Bridgman technique with synthesis duration ~70 h.

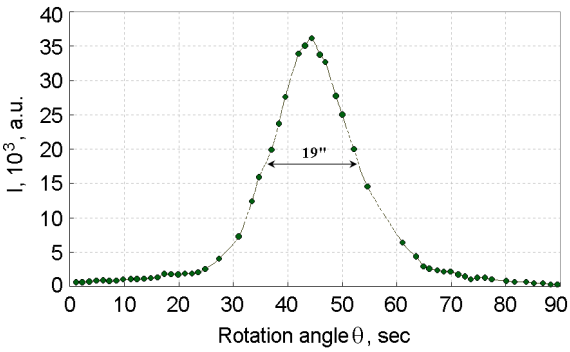

Fig. 4. X-ray diffraction rocking curve for $Cd_{0.95}Mn_{0.05}Te$ single crystal obtained using (220) reflection, CuK_α-radiation.

For reflections from crystallographic planes (111), (220), (422), (400), (311) of the perfect CdTe crystal the theoretical value of FWHM rocking curve respectively was equal to ~ 25, 17.5, 16.3, 12.3 and 13.6 seconds. For real crystals the FWHM was $\theta_{exp} > \theta_{theor}$ due to the presence of structural defects and micro-stresses. For broadening of the rocking curves $\Delta\theta$ the density of dislocation N_d was calculated, which was a quantitative assessment of the crystal perfection:

$$N_d = \Delta\theta^2/9.42 \cdot b^2, \qquad (3)$$

where $\Delta\theta = (\theta^2_{exp} - \theta^2_{theor})^{1/2}$, b — the Burgers vector.

Resulting from the calculation the average dislocations density in CMT crystals was lying within $5{\cdot}10^3 \div 10^5$ cm^{-2} (Fig. 3). The rocking curve (Fig. 4) for monocrystalline sample $Cd_{0.95}Mn_{0.05}Te$, which prepared from the middle of the ingot, was obtained using (220) reflection. This ingot was grown using modified facility by the Bridgman technique. The small difference (~1.5 seconds) between the theoretical value of the rocking curve for the reflection from crystallographic plane (220) of the ideal CdTe crystal and the result obtained for $Cd_{0.95}Mn_{0.05}Te$ indicates a sufficiently high structural perfection of the crystal. The dislocation density estimated from the rocking curve is in within $5 \div 6{\cdot}10^3$ cm^{-2}.

It was established that amount of the different structural defects depended on Mn content and initially was reduced at $x = 0.01 \div 0.05$, and in the sequel increased at $x > 0.15$. It can be concluded that small Mn addition within a few percents lead to a the more perfect structure comparing with CdTe, as evidenced by a clear separation of $K\alpha_{1,2}$-doublet and the absence of the low-angle grains boundaries and twins on the topograms. The improving of the crystal structural perfection confirms the known fact that under formation of ternary solid solutions a configuration of homogenous region undergoes the significant changes (compared to the binary compounds that form them) and it is a function of the solid solutions composition. Therefore, one of the effective way to reduce concentration of the point defects in the crystal is an incorporation of isovalent Mn impurity in small quantities ($x < 0.1$).

To better understanding the dislocation structure of the most perfect CMT crystals we applied the Lang's method for thin (120–220 μm) samples, where $\mu t < 1$, where μ — linear absorption coefficient, t — thickness of the crystal (120–220 μm). Experimental topograms were obtained by the Lang's method, using the reflection from planes $(\bar{2}20)$ and $(20\bar{2})$ at scanning along diffraction vectors $\bar{g}$ (Fig. 3). In the topograms the dislocations manifest themselves as lines with the high intensity and regions with the low intensity correspond to twins. There was also clearly visible the dislocation network and the high intensity lines of certain orientations which correspond to slip bands. On the crystal edges the pendulum fringes were observed, it is due to wedge-shaped crystal's edge, resulting in the etching effect.

Presence of the pendulum fringes evidenced the high quality of the crystal, in which the dislocations density did not exceed 10^4 cm^{-2}.

The most dislocations have the Burgers vector $b = a/2$ in [110] direction which are located in {111} planes or dislocation with $b = a/2$ in [101] direction. As a result of the studies it was found that basic struc-

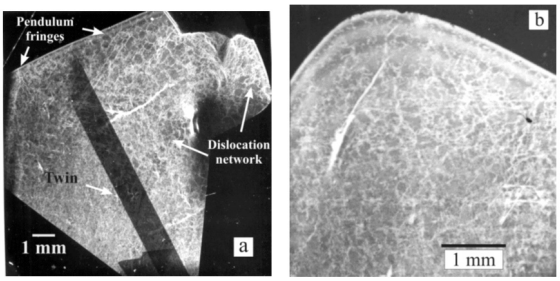

Fig. 5. X-ray topograms of $Cd_{0.95}Mn_{0.05}Te$ crystals obtained by the Lang's method, a — (220) reflection, b — (202) reflection.

tural defects in $Cd_{0.95}Mn_{0.05}Te$ single crystals were the low-angle boundaries, twin lamellae and dislocations with the Burgers vector of type $a/2$ [110] and $a/2$ [101].

To better understanding how Mn atoms affect on the structure of the CMT solid solutions at fixed "x", in this paper the dependence of a lattice parameter along the ingot's axial and radial directions was determined by the Bond's method. It was revealed that the lattice parameter in the radial direction almost didn't change in the CMT crystals, grown by using the optimized technique. Along the axis it was revealed the slight lattice constant gradient. For instance, for $Cd_{0.975}Mn_{0.025}Te$ ingot it was equal to ~0.00042 nm/cm (Table) or 0.04 %, that is uniformity of Mn distribution along the ingot is lying within $x = 0.025 \pm 0.001$.

Thus, the long-term synthesis ($\tau \geq 70$ h) ensures not only the improving the crystal structure (Fig. 2), but also even distribution of the Mn impurity inside an ingot.

4. Conclusions

It was established, that quality of the obtained crystalline grains depended on the synthesis duration of $Cd_{1-x}Mn_xTe$ solid solutions, and accordingly the uniformity of Mn distribution in the solid solution. The results showed that after long-term synthesis ($\tau \geq 70$ h) the manganese was almost uniformly distributed in the bulk. The obtained results about structural perfection of the crystals and type of the defects, their distribution and reasons of formation, obtained by the X-ray methods, made it possible to optimize the synthesis and growth conditions of the perfect $Cd_{1-x}Mn_xTe$ crystals. $Cd_{0.95}Mn_{0.05}Te$ ingots grown in the optimal conditions using the modified growth facility and the double wall quartz ampoule with flat bottom and heat sink in the center of the ampoule bottom were the most perfect.

Table. Lattice parameter a dependence along with $Cd_{0.975}Mn_{0.025}Te$ ingot's length

l, mm	a, nm
10	0.64774
20	0.64770
25	0.64768
30	0.64766
35	0.64765
40	0.64763
45	0.64760
50	0.64758
55	0.64755
60	0.64750

References

1. L.Davydov, P.Fochuk, A.Zakharchenko et al., *IEEE Trans. Nucl. Sci.*, **62**, 1779 (2015).
2. A.Hossain, G.D.Gu, A.E.Bolotnikov et al., *J. Nucl. Instr. Methods A*, **781**, 33 (2015).
3. K.Kim, G.Jeng, P.Kim et al., *J. Appl. Phys.* **114**, 063706 (2013).
4. H. Guerrero, J.L.Escudero, E.Bernabeu, *J. Appl. Phys.*, **74**, 3459 (1993).
5. A.E.Turner, R.L.Gunshor, S.Datta, *Appl. Optics*, **22**, 3152 (1983).
6. J.Zhang, W.Jie, T.Wang et al., *J. Cryst. Growth*, **306**, 33 (2007).
7. J.Zhang, W.Jie, L.Wang, L.Luan, *Cryst. Res. Technol*, **45**, 7 (2010).
8. K.H.Kim, A.E.Bolotnikov, G.S.Camarda et al., *Mater. Res. Soc. Symp. Proc.*, **1341 (2011).**
9. Y.Du, W.Jie, T.Wang et al., *J. Cryst. Growth*, **318**, 1062 (2011).
10. U.N.Roy, G.S.Camarda, Y.Cui et al., *J. Cryst. Growth*, **437**, 53 (2016).
11. M.Azoulay, A.Raizman, R.Weingarten, H. et al., *J. Cryst. Growth*, **128**, 588 (1993).
12. R.Triboulet, A.Heurtel, J.Rioux, *J. Cryst. Growth*, **101**, 131 (1990).
13. S.B.Qardi, E.F.Skelton, A.W.Webb, *Physica*, **139 & 140 B**, 341 (1986).
14. G.Babonas, R.R.Galazka, G.Pukinskas, A.Sileika, *Phys. Stat. Sol. (b)*, **154**, 389 (1989).
15. G.S.Camarda, N.M.Abdul-Jabbar, S.Babalola et al., *Proc. SPIE*, **6706**, 670605 (2007).
16. S.Stoupin, Z.Liu, S.M.Heald, D.Brewe, M.Meron, *J. Appl. Cryst.*, **48**, 1734 (2015).
17. Ye.S.Nikoniuk, Z.I.Zakharuk, A.I.Rarenko et al., *J. Nano- and Electron. Phys.*, **7**, 04054 (2015).
18. Z.I.Zakharuk, A.I.Rarenko, E.V.Rybak et al., *Phys. Chem. Solid State*, **8**, 25 (2007).