

Z.I. Zakharuk, A.I. Rarenko, E.V. Rybak, M.L. Koval'chuk, I.M. Yuriychuk
Peculiarities of CdTe, CdMnTe and CdZnTe Single Crystal Crystallization

*Yuriy Fedkovych Chernivtsi National University, 2 Kotsjubynskiy Str., Chernivtsi 58012, Ukraine
Tel. +380-372-584893, e-mail: microel@chnu.cv.ua*

The influence of crystallization conditions on CdTe, Cd_{1-x}Mn_xTe, Cd_{1-x}Zn_xTe single crystal structures is investigated. An optimal form of the ampoule for various size crystal growth is determined. It is shown that using crystallization heat of the material, placed between the walls of special form ampoule, one can change the shape of solid-melt interface.

Keywords: CdTe, solid solutions, growth, single crystal, crystallization, solid-melt interface.

Стаття поступила до редакції 23.07.2006; прийнята до друку 10.10.2006.

The unique properties of CdTe make it an ideal material for numerous applications [1]. It can exhibit both n and p types of conductivity, which makes diode technology and field effect transistors possible, and it can exhibit a semi-insulating state as well. CdTe based semimagnetic semiconductor – CdMnTe, displays extremely exciting properties. CdTe is a component of the CdHgTe ternary alloy, one of the major industrial materials for infrared detection. CdZnTe is used as a substrate for the epitaxial deposition of HgCdTe layers. Despite considerable progress in CdTe, CdZnTe, CdMnTe crystal growth, a problem of reproducible obtaining of specific size single crystals is solved only partially [2-5]. Reproducible growth of single crystals is caused by crystallization conditions and peculiarities of nucleation center formation. The influence of these processes on CdTe, CdZnTe, CdMnTe crystal structures is investigated in the present paper.

Single crystals CdTe, Cd_{1-x}Mn_xTe (0.02 ≤ x ≤ 0.55), Cd_{1-x}Zn_xTe (0.02 ≤ x ≤ 0.2) were obtained from stock prepared from stoichiometric charges of source components. Elementary substances (N6 pure cadmium, N6 pure tellurium and N6 pure manganese) were additionally purified by vacuum distillation method and finally cadmium and tellurium were purified by zone melting method. The ends of purified ingot after multiple zone melting passes are enriched in with impurities, thus their rediffusion into purified ingot take place. Contaminated ends of the ingot should be removed. For this purpose we have developed a device which design is presented in the Fig.1. The device provides melting-down of the material and discharge of the ingots ends enriched in with impurities. Such device have been used for purification of Cd, Te and CdTe.

At growing of Cd_{1-x}Mn_xTe solid solutions the

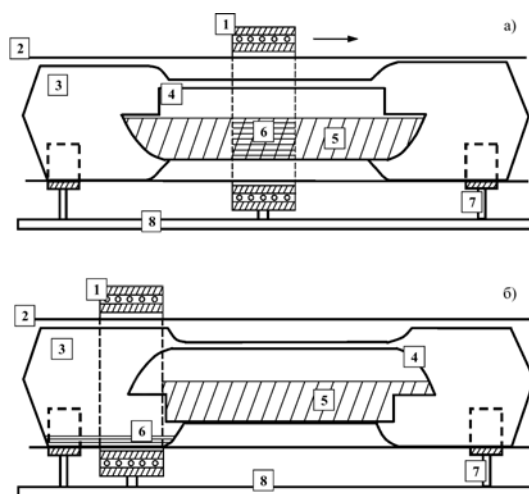


Fig.1. Design of the device for Cd and Te purification: a) purification position; b) position at discharge of the ingot end. 1 – zone heater, 2 – tube, 3 – ampoule, 4 – container, 5 – purified material, 6 – melt, 7 – holder, 8 – support.

interaction of the mixture with graphitized coating and a material of the container sometimes takes place. Therefore long-term synthesis, in particular for large manganese concentration, is very difficult. The main cause of interaction of the mixture with a material of the container is residual oxides, which are present on the surface of initial components. Synthesis of the alloys in hydrogen atmosphere is not a solution of the problem, because hydrogen does not reduce manganese oxides. Furthermore, hydrogen itself dissolves in the alloy, changing materials properties. Therefore, growing of Cd_{1-x}Mn_xTe single crystals was carried in glass-

graphitized containers, which did not interact with Mn and its oxides. In order to charge the components into the container we have developed an ampoule of special form (Fig. 2a), comprising a fused tube that enters the glass-graphitized cup. After long-term synthesis of the mixture the single crystals were grown by Bridgman method (temperature gradient at solid-melt interface – $10 \div 15$ K/cm, growth rate – 2 mm/hour).

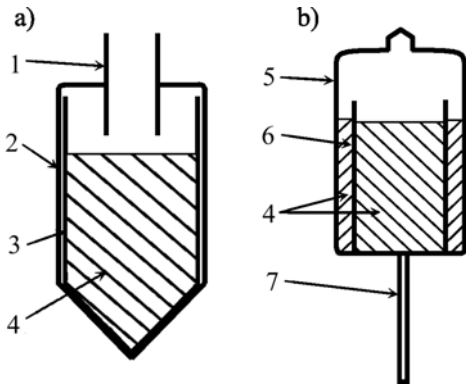


Fig.2. Ampoules for single crystal growth: a) CdMnTe, b) CdTe, CdZnTe. 1 – fused quartz tube, 2 – quartz ampoule, 3 – glass-graphitized cup, 4 – ampoule charge, 5 – external ampoule, 6 – fused internal ampoule, 7 – light conductor.

For growing of large single crystal by Bridgman method a form of the bottom of an ampoule, where crystals growth starts, is very important. The crystals were grown in quartz ampoules with various form of the bottom: a cone, a hemisphere, a flat bottom with light or heat conductor in the center, and also in an ampoule with the system of neckings. The diameter of the ampoules lies within $14 \div 60$ mm.

We have found that for perfect single crystals growing the choice of optimum form of the ampoule depends on its diameter. For crystals less than 20 mm in diameter the best single crystals reproducibility is obtained if ampoules with the system of neckings is used, for crystals of $20 \div 30$ mm in diameter – at the use of ampoules with a cone bottom. For crystal growing of $30 \div 60$ mm in diameter the best results gives the use of a flat bottom with long light or heat conductor. It is worth to note that the use of ampoules with the system of neckings resulted in obtaining the crystals with strained lattice. In ampoules of $20 \div 30$ mm in diameter with two types of bottoms (cone and flat bottom with heat conductor) we have got the crystals with less defects. Yield of single crystal material in ampoules with flat bottom with heat conductor was the highest. At the use of such ampoules the reproducible growing of large single crystals is possible only under precise temperature control of the bottom of the ampoule in order to prevent overheating of the melt at the growth beginning. At the initial stage of the growth the bottom of the ampoule must be at a temperature that not exceeds the melting temperature more than on $5-8^{\circ}\text{C}$. The appearance of nucleation centers on ampoule walls is eliminated in this

case, and the seed is formed in the center of the bottom, where temperature is lowered due to the presence of heat conductor.

We have studied the distribution of dislocations on the section of single crystal in dependence on ampoule diameter. For ampoules of 25 mm in diameter the distribution was uniform, for single crystals grown without twinnings in ampoules more than 26 mm in diameter the dislocation density was greater on the edges of the ingot. For single crystals more than 40 mm in diameter a dislocation pile-up and stacking fault were usually observed in the center of the ingot. When twins and blocks are present the structural defects more often forms aggregate of defects near their boundaries, and the distribution of dislocation in the volume of the single crystal is more uniform and dislocation density is less.

Distribution of temperature on the solid-melt interface has a complicated form, however, in most cases, except for the initial crystallization stage, the interface is concave toward the crystal. This is because the walls of the ampoule are cooling down faster and heat removal, both convection and light, takes place from the walls of the ampoule largely.

We suggest to level the solid-melt interface by warming up the ampoule walls with the heat of crystallization of the material placed outside the ampoule where growth takes place. We have carried out experiments on growing of single crystals in containers with double walls (Fig. 2b). Quartz glass was inserted in a quartz ampoule. In lower part of the ampoule a tube of greater diameter was welded to the wall of less diameter. The synthesized material was loaded in amount sufficient for filling the volume of the lesser ampoule and space between walls. For filling this space the cuts were done in upper part of lesser ampoule, through which the melt was introduced into the space between ampoules. Heat of crystallization of the material between walls heated the wall of internal ampoule and increased the temperature in external part of the ampoule that resulted in smoothing of solid-melt interface.

To determine an optimum relation between ampoules diameters let us consider a simple model of single crystal growth from the melt [6]. An ampoule of radius r is inserted into an ampoule of greater radius R (Fig.3). The material is crystallizes in the ampoule of lesser radius as well as in the gap between ampoules. Maximum crystallization rate is achieved in the case when latent crystallization heat is fully conducted into the solid phase. Then crystallization rate is determined by temperature gradient on melt-solid interface and depends on material density ρ , thermal crystal conductivity K and latent crystallization heat L :

$$\left(\frac{dx}{dt}\right) = \frac{K}{\rho L} \left(\frac{dT}{dx}\right). \quad (1)$$

If we assume that crystallization heat is fully conducted into the ingot and dissipated from the surface of the ampoule of radius R , than maximum crystallization rate in the ampoule of radius r in the case when temperature gradient in the melt is absent is given by [6]:

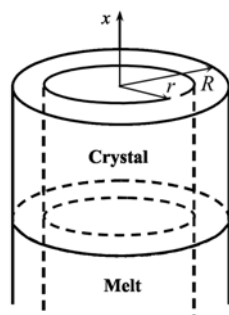


Fig. 3. To the calculation of crystallization process in the ampoule with double walls.

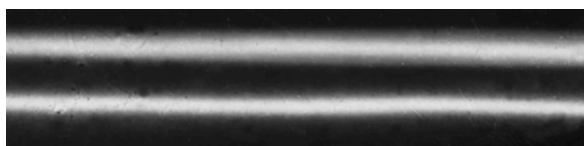


Fig.4. Typical X-ray topogram of the ends of the samples grown in the ampoule with double walls. Reflection of CuK-radiation, (111) surface, x10 magnification.

$$\left(\frac{dx}{dt}\right)_r = \frac{1}{\rho L} \sqrt{\frac{2\sigma K T_m^5 R}{3r^2}}, \quad (2)$$

where σ – Stephan-Boltzmann's constant, T_m – temperature of the melt. Same suggestions for

crystallization process in the gap between ampoules gives the expression for the maximum crystallization rate of the material between walls:

$$\left(\frac{dx}{dt}\right)_R = \frac{1}{\rho L} \sqrt{\frac{2\sigma K T_m^5 R}{3(R^2 - r^2)}}. \quad (3)$$

During growing the rates (2) and (3) should be equal, so one can obtain rough estimate of the relation between ampoule radiuses: $R = \sqrt{2}r$. The gap between walls is $h = R - r = (\sqrt{2} - 1)r$, thus for internal ampoules of 14÷60 mm in diameter the value of the gap between ampoules lies within 3 ÷ 12 mm.

Using the ampoules with double walls the large CdTe, CdZnTe, CdMnTe single crystals with good electrohysical parameters were obtained. Mobility of charge carriers in grown crystals at liquid nitrogen temperatures was more than order greater than mobility at room temperatures, it means that concentration of residual impurities was low. X-ray studies showed that the structure of the single crystals was perfect (Fig. 4).

Захарук З.І. – старший науковий співробітник;
Раренко Г.І. – старший науковий співробітник;
Рибак Є.В. – науковий співробітник;
Ковальчук М.Л. – аспірант кафедри;
Юрійчук І.М. – асистент кафедри.

- [1] R. Triboulet. Fundamentals of the CdTe sythesis // *J.Alloys and Compounds*, 371(1-2), pp. 67-71 (2004).
- [2] R. Triboulet. Solid-state recrystallization: a promising technique for the growth of semiconductor materials // *Cryst.Res.Technol.*, 38(3-5), pp. 215-224 (2003).
- [3] S. Hassani, A. Lusson, A. Tomson-Carli, R. Triboulet. Seed-free growth of (111) oriented CdTe and CdZnTe crystals by solid-state recrystallization // *J.Cryst.Growth*, 249(1-2), pp. 121-127 (2003).
- [4] M. Zha, A. Zappetini, F. Bissoli, L. Zanotti, V. Corregidor, E. Dieguez. Boron oxide encapsulated Bridgman growth of hogh-purity high-resistivity cadmium telluride crystals // *J.Cryst.Growth*, 260, pp. 291-297 (2004).
- [5] M. Funaki, T. Ozaki, K. Satoh, R. Ohno. Growth and characterization of CdTe single crystals for radiation detectors // *Nucl.Instrum Methods.A.*, 436, pp. 120-126 (1999).
- [6] S.A. Medvedev, *Introduction to semiconductor materials technology*. Vyshaya Schkola, M. 504 p. (1970) (In Russian).

З.І. Захарук, Г.І. Раренко, Є.В. Рибак, М.Л. Ковальчук, І.М. Юрійчук
Особливості кристалізації монокристалів CdTe, CdMnTe і CdZnTe

*Чернівецький національний університет ім. Ю.Федьковича, вул.Коцюбинського, 2,
 Чернівці, Україна, 58012, E-mail: microel@chnu.cv.ua*

В роботі розглянуто вплив умов кристалізації на структуру кристалів CdTe, Cd_{1-x}Mn_xTe, Cd_{1-x}Zn_xTe. Показано, що використовуючи теплоту кристалізації матеріалу, який кристалізується між подвійними стінками ампули, можна змінювати форму границі між рідкою і твердою фазами. Визначена оптимальна форма ампули для одержання монокристалів різної величини.