

Study of the Conditions of CdTe and Cd_{1-x}Zn_xTe Crystal Growth

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Abstract

The present investigation describes the techniques for the production of initial substances of ultrahigh purity for the synthesis of CdTe and Cd_{1-x}Zn_xTe crystals for use in X-ray and γ -radiation spectrometry. The dependence of CdTe and Cd_{1-x}Zn_xTe ingot crystalline perfection on crystallization conditions have been noted. The characteristics of obtained crystals, *i.e.* energy resolution, half width of diffraction reflection curve, size and concentration of tellurium inclusions, transmittance in far infrared spectral region, *etc.*, correspond to those of the best CdTe and Cd_{1-x}Zn_xTe crystals synthesized by present.

INTRODUCTION

Cadmium telluride and CdTe-based solid solutions are used as a substrate material for Cd_xHg_{1-x}Te compounds epitaxy, as electrooptical modulators, and in solar elements. Besides, CdTe and Cd_{1-x}Zn_xTe are the most perspective materials for solving the problems of X- and γ -ray spectrometry.

Nevertheless, CdTe is not widely used in the listed areas at present. This is because the production of high-quality CdTe is not an easy task. The quality of the material should be understood not only as high structural perfection of crystal but also strictly definite optical, electrophysical and some other properties.

The majority of semiconductor crystal properties are known to be strongly influenced by the concentrations of residual background impurities. In particular, when obtaining CdTe of spectrometric quality, the purity of the material is of decisive significance. There is rather wide range of impurities that can have a harmful influence on detector operation. Therefore, the manufacture of CdTe from initial high-purity substances having not only low metal impurity contents but also small concentration of

gaseous and gas-forming impurities (oxygen, hydrogen, *etc.*) proves to be of interest and importance.

EXPERIMENTAL

High-purity initial materials were obtained according to original procedures using a complex of purification methods. The special technique of the preparation of quartz ampoules including repeated washing, drying, high-temperature annealing under vacuum allowed to minimize the influence of the container material impurities on initial cadmium, zinc and tellurium. High-purity tellurium was produced using chemical, distillation and crystallization methods of purification. The total impurities content of thus obtained tellurium was not more than 0.1 ppm, as the analysis showed. Cadmium and zinc were purified by repeated distillation through an oxide layer in dynamic vacuum and by other operations. The total content of residual impurities in purified cadmium and zinc was at a level of 0.1 and 0.5 ppm, respectively. The evacuation of impurity gases from the free volume of the ampoule after each

purification step allowed to minimize the concentrations of gaseous and gas-forming impurities till a level below 0.1 ppm. The dopant (CdCl_2) was also additionally purified by distillation and unidirectional crystallization.

To minimize the influence of impurities contaminating materials during weighing, the initial materials were loaded into the quartz ampoule in an air-tight box which allowed precise weighing of the components in an inert atmosphere. After loading the initial substances, the ampoule was connected to a vacuum system and sealed off under the vacuum of about $1 \cdot 10^{-3}$ Pa.

Since cadmium vapour pressure at the melting point of CdTe (1092 °C) exceeds 10 atm, the probability of explosion in the ampoule during the direct melting of components is high. Moreover, the higher the process temperature, the higher the rate of impurities diffusion from the walls of the quartz container. We developed an original technique permitting the synthesis at a temperature of 300–400 °C below the CdTe melting point. The developed technique excludes any possibility of depressurization of the ampoule and minimizes material contamination by impurities from container walls.

The synthesis was followed by crystallization from the gas phase repeated many times for additional purification of CdTe from gaseous impurities. The synthesis, purification and growing of crystal are concurrent in the same ampoule which allows to obtain the material of spectroscopic quality rapidly and at minimum costs.

$\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ and CdTe crystals have been grown both from stoichiometric melt according to Bridgman method and from solution in tellurium melt in the vertical three-zone furnace. In order to reveal dependence of crystalline perfection of the resulting ingots on the conditions under which $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ and CdTe are crystallized from the stoichiometric melt and from solution-melt with various tellurium concentrations, special experiments were performed. The important role of an axial temperature gradient near the crystallization front and the growth rate during the formation of $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ and CdTe ingots was revealed. Since the crystallization from Te-enriched melt involves constant enrichment of the liquid phase with tellurium, the rate of crystallization, *i. e.* the growth rate,

decreases if the ampoule is immersed in an ordinary manner without simultaneous cooling of the whole furnace [1]. This results in more than 200-fold change in the crystallization rate by the end of growth period while the ampoule is moved down at a constant rate. Besides, the crystallization front shifts with respect to a selected point in the furnace. These factors can worsen crystal quality. Therefore, the knowledge of an exact dependence of rate of solution-melt cooling on growth rate, composition and container shape is necessary.

The cases of solution-melt crystallization in conical and cylindrical sections of the ampoule were considered. For both cases, we obtained the dependence of crystallization front temperature on time from the beginning of growth. It is necessary to know this dependence in order to maintain constant crystal growth rate. For the crystallization in a cylindrical section of the ampoule, this dependence may be easily obtained in an evident form:

$$T = T_{\text{CdTe}} - \left[\frac{1}{T_{\text{melt}} - T_0} - \frac{\rho S V_{\text{cr}} t}{\text{Const} \cdot M} \right]^{-1} \quad (1)$$

Here: t – current time, h; M – a charge mass, g; ρ – CdTe density, g/cm^3 ; S – cross-section of the ampoule, cm^2 ; V_{cr} – crystallization rate, cm/h ; T_0 – the starting temperature of programmed cooling of solution-melt, °C; T_{melt} – melting point of solution-melt, °C; T_{CdTe} – melting point of stoichiometric CdTe, °C; Const – a constant dependent on the liquidus shape.

Similarly, as well as in the case of crystallization in a cylindrical section (1), we can write the equation permitting us to find the dependence $T(t)$ for crystallization in a cone which corresponds to a constant crystallization rate. At first the inverse function $t(T)$ may easily be defined in terms of the following formula, then $T(t)$ may be obtained:

$$t = [4V_c(M/(\pi\rho))^{1/3}(H/(12\Phi))^{2/3}/V_{\text{cr}}] \times \int_{\Delta T} i(T)[g(T) - g(T_0)]^{2/3} dT \quad (2)$$

Here: V_c – cooling rate, °C/h; T – current temperature, °C; H – height of the cone, cm; Φ – diameter of the cone base, cm; $i(T)$ – temp function (the rate of solid phase fraction changing *versus* temperature) [1]; $g(T)$ – the dependence of the

fraction of crystallized CdTe on temperature [1]. Evident forms of $i(T)$ and $g(T)$ depend on how the liquidus shape is approximated.

The prescribed furnace cooling mode was supported with a microprocessor programmed temperature regulator "Proterm 100". The calculated cooling curve was divided into some linear plots.

The quality of Cd_{1-x}Zn_xTe and CdTe crystals was tested using optical microscopy. A special device was designed on the basis of an ordinary optical microscope and overhead "Uniscan" scanner (Novosibirsk) to study materials transparent in near infrared spectral region [2]. The scanner was fixed at the draw-tube of the microscope with a special adapter so that the linear image sensor was located in the plane of the real image formed by the microscope lens.

The optical resolution of the system allows us to observe the defects with a size of about 1 μm . Using this device we studied the features of the entrapment of Te inclusions in the crystals grown under different conditions.

RESULTS AND DISCUSSION

It was found that the monocrystallinity of the resulting ingots is not affected by the starting temperature of programmed cooling of the solution-melt within a wide temperature range. In the region of solid phase formed before the beginning of programmed cooling and at the very beginning of cooling, large Te inclusions with a faceted edge were usually observed. This edge of an inclusion was oriented in the direction of crystal growth. CdTe ingots in the range were, as a rule, monocrystalline.

It was found that with the axial temperature gradient of 0.4–0.6 $^{\circ}\text{C}/\text{mm}$, irrespective of growth rate, CdTe ingots contain large Te inclusions visible to the unaided eye, concentrated near the axis of the ingot. With the gradient more than 1.2 $^{\circ}\text{C}/\text{mm}$, large inclusions are absent. With the gradient of the order of 1.5–1.8 $^{\circ}\text{C}/\text{mm}$, the contents of inclusions with a size more than 10 μm do not exceed $5 \cdot 10^3 \text{ cm}^{-3}$, and their distribution is close to uniform.

It was stated that doping with chlorine does not result in any noticeable modification of concentration of inclusions and their sizes.

When CdTe crystals are grown from stoichiometric melt, the total content of inclusions is less than in the case of growth from solution-melt. The modes of high-temperature annealing of CdTe were determined experimentally that allowed to remove all the inclusions with sizes more than 1 μm (which was the opti-

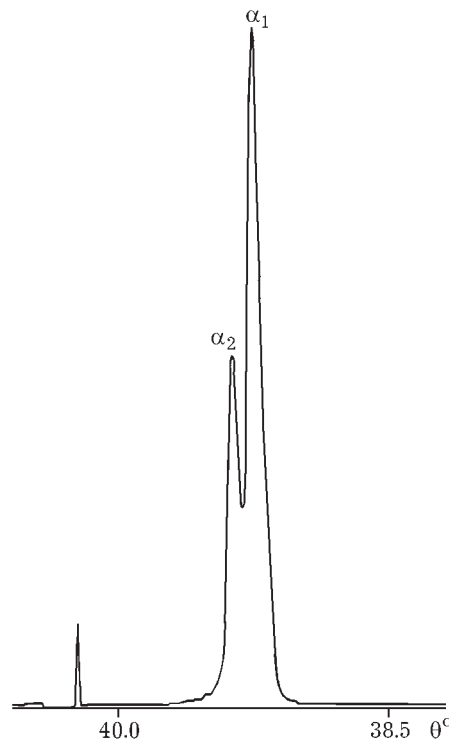


Fig. 1. X-ray diffraction patterns of the sample under investigation.

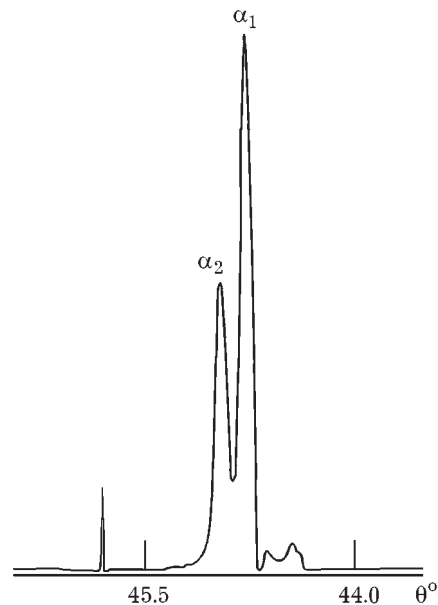


Fig. 2. X-ray diffraction patterns of the standard LiF sample. $N_d = 10^3 \text{ cm}^{-2}$.

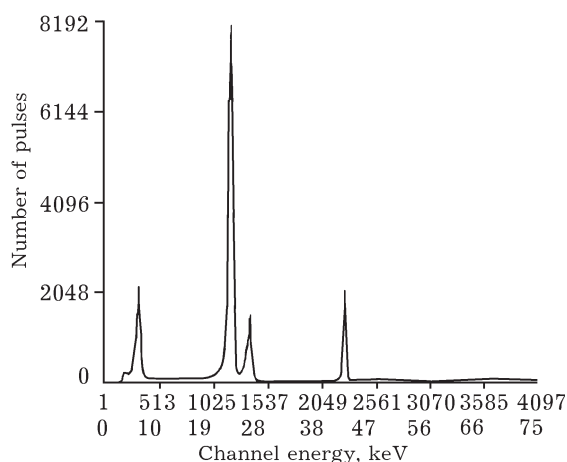


Fig. 3. The spectra of γ -quanta of ^{55}Fe , ^{109}Cd , ^{241}Am isotopes. Detector temperature is -37°C .

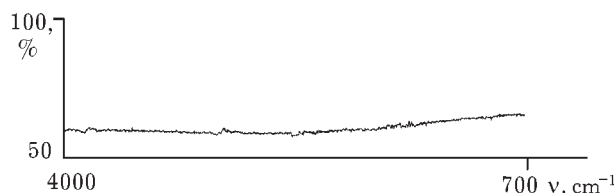


Fig. 4. IR transmittance of the CdTe sample.

cal resolution of the microscope) from the bulk of the sample.

We also studied the dependence of properties and structural perfection of $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ and CdTe crystals on growth conditions, doping and heat treatment.

Monocrystalline CdTe samples were investigated with X-ray device [3] for the purpose of evaluating the lattice perfection. The measurements carried out with a goniometer and diffraction reflection curves of $\text{CuK}\alpha_1$ showed that the half-width of diffraction reflection curves ($\Delta\omega_{1/2}$) is rather small, namely, 1.8–2.4' in various points and different CdTe samples (Figs. 1 and 2). Since the diffraction reflection curves were measured not according to the standard scheme of a two-crystal spectrometer, the presence of lattice defects was evaluated by comparing with well-known standard LiF, Ge and diamond crystals. The half-width of diffraction reflection curves of a 200 $\text{CuK}\alpha_1$ reflex of LiF crystal with the dislocation density of $N_d = 10^3 \text{ cm}^{-2}$ is $\Delta\omega_{1/2} = 1.8'$. For low-dislocational ($N_d = 10^1\text{--}10^2 \text{ cm}^{-2}$) crystals of Ge and diamond

(reflex 111 $\text{CuK}\alpha_1$) $\Delta\omega_{1/2}$ is 1.7 and 1.8', respectively. It can be concluded on the basis of the comparisons with the above-mentioned values that N_d of CdTe crystals does not exceed the level of 10^4 cm^{-2} .

X-ray investigation and the measurements of the charge-carriers' mobility multiplied by their lifetime ($\mu\tau$) have shown close values of $\Delta\omega_{1/2}$ and $\mu\tau$ for the crystals obtained under different conditions. For the crystals grown from a solution-melt with different doping degrees, $\mu\tau$ changes by a factor of 2–3, and specific resistance ρ by an order of magnitude. The crystals obtained are characterized with high spectrometric quality. The energy resolution does not exceed 1.5 keV for γ -quantum line of the isotope ^{241}Am for the best samples, and 0.57 keV for ^{55}Fe line (Fig. 3). In the case of crystal growth from stoichiometric melt, it was not possible to obtain a material of spectrometric quality.

Infrared transmission spectra were investigated. The increase of transmittance in far infrared region (Fig. 4) was revealed which is likely to be due to the presence of inclusions that are not resolved through optical microscope.

CONCLUSION

Thus, a technique is developed to prepare $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ and CdTe crystals of spectrometric quality. By studying such characteristics of the crystals as energy resolution, half-width of diffraction reflection curves, size and concentration of Te inclusions, transmittance in infrared region, we have demonstrated that the crystals thus grown correspond to the best crystals obtained by present.

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