Semiconductor Physics, Quantum Electronics & Optoelectronics. 1999. V. 2, N 4. P. 81-85.

PACS: 72.20, 78.30.A, F, 81.05.C, D, E, G, H

Crystals $Cd_{1-x}Zn_xTe$ – a promising material for non-cryogenic semiconductor detectors: preparations, structure defectness and electrophysical properties

L.V. Atroshchenko, S.N. Galkin, L.P. Gal'chinetskii, A.I. Lalayants, I.A. Rybalka, V.D. Ryzhikov, V.I. Silin, N.G. Starzhinskii

STC for Radiation Instruments, Concern «Institute for Single Crystals», NAS of Ukraine,
60 Lenin Ave.,310001 Kharkov, Ukraine.
Tel. (0572) 321379 fax (0572) 32130, E-mail:root@stcri.kharkov.ua

Abstract. Relationship between preparation conditions of the raw charge, crucible material, growth regimes and structure defectness and electrophysical properties of crystals $Cd_{1-x}Zn_xTe$ has been studied. The crystals were grown both from the raw material which had been pre-synthesized in quartz ampoules and from the raw material synthesized from the elements directly in the growth furnace. It is shown that the best values of electric resistivity ρ (up to 10^{11} Ohm·cm) and sensitivity to X-ray and gamma-radiation are obtained for crystals grown in crucibles of highly pure coal-graphite material from the pre-synthesized raw charge. Correlation has been established between values of ρ and crystal defectness: decrease of dislocation density by 10^4 times led to 10^7 times higher values of resistivity.
Concentration of dislocation etching pits regularly decreased with higher purity of the raw material and optimization of crystal preparation technology.

Keywords: preparation conditions, structure defectness, electric resistivity, dislocation density, semiconductor detectors.

Paper received 19.10.99; revised manuscript received 15.12.99; accepted for publication 17.12.99.

1. Introduction

Among semiconductor materials with wide band gap, much attention has been paid to CdTe and $Cd_{1-x}Zn_xTe$ as room-temperature detectors of X-ray and gamma-radiation. They have high atomic number (~ 50), high density (> 6 g/cm^3) and relatively high carrier mobility. It has been shown that formation of solid solutions CdTe-ZnTe is accompanied by broadening of the band gap, increase of resistivity (by more than an order of magnitude), and improved stability of spectral characteristics as compared with CdTe [1]. A general problem for semiconductor materials based on $A^{II}B^{VI}$ compounds is the difficulty of growing structurally perfect crystals characterized by high degree of chemical purity and stoichiometry. Requirements to the structural perfectness of crystals $Cd_{1-x}Zn_xTe$ are very high, because practically all their principal electrophysical and optical characteristics are strongly structure-dependent.

The present work was focussed on studying effects of preparation conditions of crystals $Cd_{1-x}Zn_xTe$ upon concentration of electrically active structural defects in this material and X-ray sensitivity of detectors made on its base.

2. Experimental procedure

We studied a set of crystals $Cd_{1-x}Zn_xTe$ (32 mm in diameter) grown by Bridgman method in vertical compression furnaces under inert gas (argon) pressure from 3.5 to 5.5 MPa. Crystal growth regimes are presented in Table 1.

In this work, crystals $Cd_{1-x}Zn_xTe$ were grown using raw materials pre-synthesized in a quartz ampoule, as well as those synthesized from elements (Cd,Zn,Te) directly in the growth equipment.

During growth of certain crystals (No. 9-12) gas samples were taken to analyze concentration of oxygen-containing impurities in the atmosphere of the growth furnace. Carbon oxide content at different growth stages varied from 0.1 to 3 vol. %. Concentration of oxygen and water vapor in the initial argon did not exceed $1\cdot10^{-3}$ vol. %. It could be concluded that in the growth furnace carbon oxide was formed from the air desorbed from the construction material, and its removal was necessary.

Quality and uniformity of the properties and structure of the grown crystals was determined by several independent

Table 1. Conditions and results of experiments of $Cd_{1-x}Zn_xTe$ crystal growth

Experiment №	Raw charge	Material of crucible	Growth rate, mm/hour	Melt evaporation, %	R,Ohm·cm
1	3N	Graphite	5	7.5	-
2	- // -	- // -	3	9	-
3	- // -	- // -	3	9	-
4	- // -	- // -	2.8	4.5	-
5	- // -	Pyrographite, thermal expansion coefficient $< 5 \cdot 10^{-6}\ K^{-1}$	2.8	-	-
6	Cd+Zn+Te Qualification 6N, synthesis in autoclave	- // -	1.54	0.7	10^3
7	- // -	- // -	1.54	0.9	10^3
8	- // -	- // -	1.35	1	10^4
9	- // -	- // -	1.35	1	10^4
10	$Cd_{0.8}Zn_{0.2}Te$ Qualification 6N, synthesis in quartz ampoule	- // -	2.6	1	10^5
11	- // -	- // -	3	1.9	10^9
12	- // -	- // -	2.6	0.7	10^{10}
13	Cuts of 1-5 crystals	- // -	2.6	3.5	10^{10}
14	$Cd_{0.8}Zn_{0.2}Te$ Qualification 6N, synthesis in quartz ampoule	- // -	2.6	-	$5 \cdot 10^{10}$

methods: selective chemical etching on dislocations, IR microscopy, IR spectroscopy, measurements of resistivity and gamma-sensitivity. The etching agent used for detection of dislocations in crystals $Cd_{1-x}Zn_xTe$ was the same as that commonly used for CdTe crystals and had the following composition [2]: 10 ml (10 ml of conc. HNO_3 + 20 ml H_2O + 4g $K_2Cr_2O_7$) + 10 mg $AgNO_3$.

Studies of crystals in IR spectral region (0.75-1.2 μm) were carried out in transmitted light using a MIK-4 microscope (amplifications from 44^x to 1200^x). Measurements of resistivity ρ were carried out using samples of $5\times5\times2$ mm^3 after chemical etching and application of contacts on the 5x5 mm^2 area. Gamma- and X-ray sensitivity of detectors based on crystals $Cd_{1-x}Zn_xTe$ were studied using radionuclides Cs-137 and Am-241, as well as X-ray sources IRI and RAPAN-200 (U = 20-200 kV, $I \le 5$ μA). Elemental analysis of the raw material and crystals grown from it was carried out using a VRA-30 X-ray fluorescent spectrometer with accuracy of ± 0.4 at.%.

3. Results and discussion

To obtain structurally perfect crystals by Bridgman method, one should minimize negative effects of the atmosphere in the growth furnace, crucible material, variations of the elemental composition due to thermal dissociation, as well as of possible contamination of the crystal by construction materials.

Accounting for peculiar features of the $A^{II}B^{VI}$ crystal growth by this method, the crucible material should meet the following requirements:

- thermal stability up to 1500 K;
- non-wettability by the $Cd_{1-x}Zn_xTe$ melt;
- chemical inertness with respect to $Cd_{1-x}Zn_xTe$ and the initial elemental components;
- thermal expansion coefficient of the crucible material should be lower than that of the crystal;
- low gas penetrability;
- high mechanical strength.

At present, boron nitride is often considered as a promising material in this respect [3]; however, the use of this material is limited by its high cost.

To work out the main technological regimes, we carried out a set of crystal growth experiments in graphite crucibles 25 mm in diameter (No. 1-5, Table 1).

For growth of crystals No. 6-14 32 mm in diameter (Table 1) we used crucibles of highly pure coal-graphite material with thermal expansion coefficient not more than $5.7 \cdot 10^{-6}$ K^{-1}. The use of such material allowed to decrease the carry-over of the raw charge due to melt evaporation from 9% to 0.7% as compared with the graphite crucibles. It was also possible to avoid crystal deformation during cooling, and the crystal could be easily removed from the crucible.

To study the effects of the raw charge composition upon composition and electrophysical properties of crystals $Cd_{1-x}Zn_xTe$, three kinds of raw materials for charge were used.

At the first stage of working out of the growth regimes (crystals No. 1-5) raw material of 3N qualification was used. In this crystals, we analyzed only the melt evaporation and the degree of structural perfection, which was not high.

At the second stage (crystals No. 6-9) elementary Cd, Zn, Te of 6N qualification were used as raw charge after appropriate purification. It was established that, during synthesis of the charge from elements directly in the growth furnace, there was chemical interaction with the crucible and other construction parts made of carbon, yielding CTe, CTe_2, CdC, ZnC and similar compounds. These caused contamination of the melt by reaction products and to the presence of carbon-containing inclusions in the crystal structure, as well as to high concentration of growth dislocations, low optical uniformity and decreased values of ρ (Table 1).

Typical microstructure of crystals grown from the raw charge synthesized from the elements directly in the growth furnace is shown in Fig. 1a. On the cross-section normal to the growth direction (orientation is arbitrary) there are non-uniformly distributed dark etching figures in the shape of isoscales triangle or trapezium. This is in full agreement with the scheme of theoretically constructed configuration of dislocation etching pits in crystals CdTe [2]. Purity of the material (nature and amount of admixtures) has a decisive influence upon formation of etching figures, i.e., the process of selective etching of the surfaces of the studied crystals is related to segregation of admixtures or the Cottrell atmosphere on dislocations. The obtained etching figures appear to be growth dislocations decorated with admixtures. In areas of their highest concentration, density of etching figures reached $\sim 4 \cdot 10^5$ cm^{-2}. We also observed small inclusions of spherical shape, concentration of which reached $\sim 5 \cdot 10^6$ cm^{-2}; their nature remained unclear.

By means of IR microscopy, in such crystals $Cd_{1-x}Zn_xTe$ inclusions of elongated shape were detected, which were orientated along the growth direction. Their size could reach 0.8-1 mm.

We have determined that the best values of resistivity (up to 10^{11} Ohm·cm) and sensitivity to X-ray and gamma-radiation are obtained in crystals grown from the raw charge which had been pre-synthesized in quartz ampoules. Typical microstructure of crystals grown from the raw charge which had been pre-synthesized in quartz ampoules is shown in Fig. 1b. Large ρ values allow to increase the electric field and to decrease charge collection time, or to decrease the leakage current and the accompanying noise.

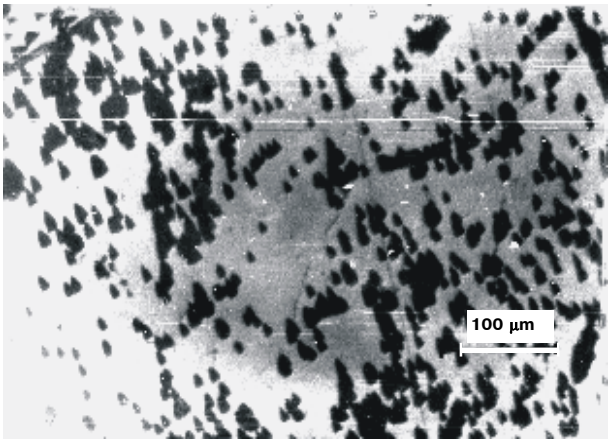

Fig. 1a. Cross-section microstructure for a crystal grown from the raw materials synthesized from the elements directly in the growth furnace.

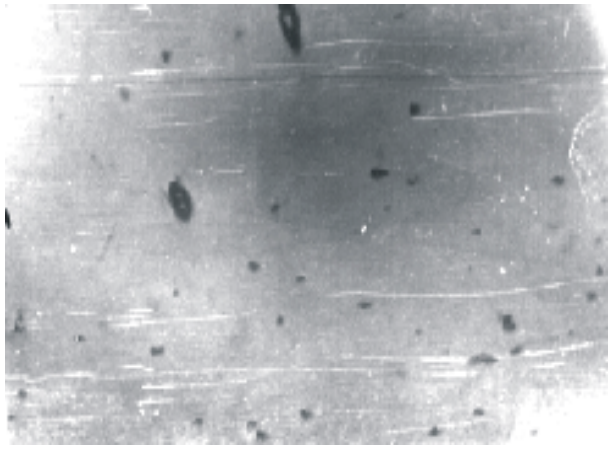

Fig. 1b. Cross-section microstructure for a crystal grown from the raw charge which had been pre-synthesized in quartz ampoules.

Fig. 2 shows the output signal of the $Cd_{1-x}Zn_xTe$ based detectors as a function of the dose rate of X-ray radiation ($E \sim 100$ keV) and the bias voltage U_b (curves 1-3). It was found that X-ray sensitivity of detectors of this type are proportional to ρ and U_b, and at $U_b = 200$ V X-ray sensitivity is by an order of magnitude higher as compared with scintielectronic detectors based on ZnSe(Te) that is one of the best scintillators (curve 4). These data show that detectors based on $Cd_{1-x}Zn_xTe$ are very promising for their current mode applications in introscopic and dosimetric systems of high sensitivity.

Average growth dislocation density in these crystals did

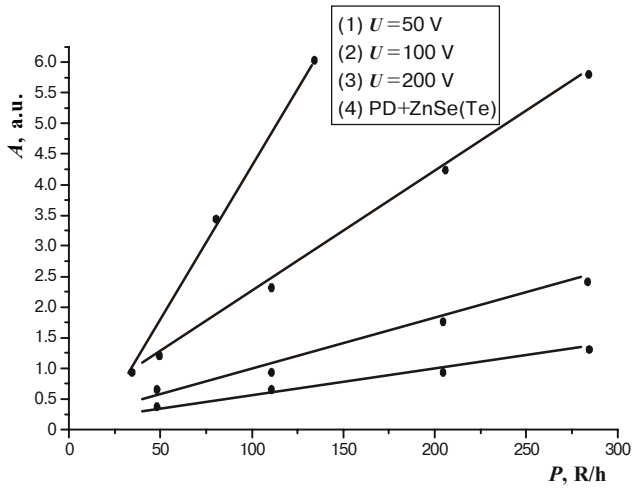

Fig. 2. Output signal, A, as function of dose rate, P, of X-ray radiation for detectors based on $Cd_{1-x}Zn_xTe$ (1-3) and a scintielectronic detector of «scintillator-photodiode» type (4).

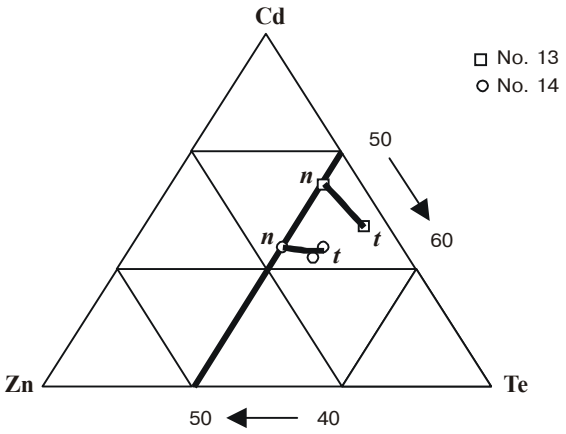

Fig. 3. Composition of the grown crystals $Cd_{1-x}Zn_xTe$ (No. 13 and No. 14) on the ternary diagram of state Zn-Cd-Te.

not exceed $2 \cdot 10^{-2}$ cm^{-2}, and inclusions of extra phases were not observed. A correlation was found between values of ρ and defectness of the crystals. When growth dislocation density decreased by 10^4 times, ρ became 10^7 times higher. Dislocations in all studied crystals detected by selective chemical etching were decorated, which suggested that these were due to the presence of admixtures. Concentration of dislocation etching pits regularly decreased with higher purity of the raw material and optimization of the growth technology.

The composition of crystals was uniform up to 0.4-0.5 from the ingot «nose». Zn content in the «nose» part of the ingot was 5-12% higher than in the initial mixture of the components. Similar deviations of composition of crystals $Cd_{1-x}Zn_xTe$ were observed in [4,5].

Besides, X-ray fluorescent analysis data (Table 2 and Fig. 3) show that only composition from the «nose» part of the ingots belongs to the quasibinary section CdTe – ZnTe of the ternary diagram of state.

IR transmission spectra of some of the studied crystals are presented in Fig. 3. It is shown that for crystals of high electric conductivity absorption by the free carriers can be observed, which is characterized by a featureless spectrum described by the λ^p law ($1.5 < p < 3.5$). For crystals of low electrical conductivity absorption on the free carriers is not observed. Absorption in the 2000- 3800 cm^{-1} region can apparently be ascribed to the valence vibrations of hydroxyl groups as well as to CO– groups. For crystals grown from the raw material that had been pre-synthesized in quartz ampoules, optical transmittance in the 500-1500 cm^{-1} region was not less than 66%.

Our studies have shown that, for 60 keV gamma-radiation (Am-241), the signal-to-noise ratio in these crystals was 1/3-1/4 at the bias voltage of 200 V. The lifetime of carriers multiplied by their mobility (a value that determines, alongside with the resistivity, the ability of the detector material to maintain and to enable the detection of ionizing charges) was not less than $8 \cdot 10^{-5}$ cm^2/V.

Table 2. Results of chemical analysis of content of the main components in crystals $Cd_{1-x}Zn_xTe$ over the ingot length.

N	Number of crystal	Content of element,at. % Cd	Zn	Te
1.	13 (nose)	46.97	2.99	50.04
2.	13 (2)	46.32	3.00	50.68
3.	13 (3)	46.58	2.92	50.50
4.	13 (tail)	40.80	2.81	56.39
5.	14 (nose)	40.74	8.98	50.28
6.	14 (2)	38.52	8.74	52.74
7.	14 (tail)	41.92	5.64	52.44

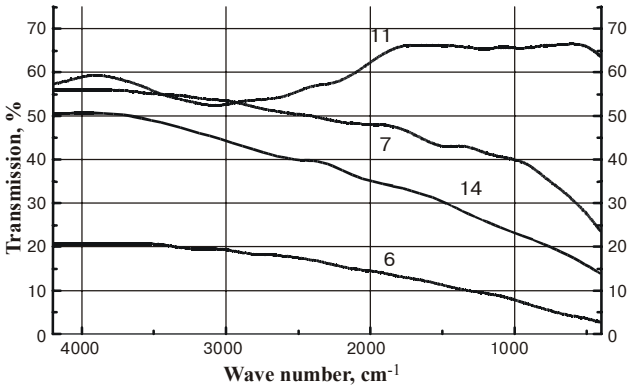

Fig. 4. IR transmission spectra of crystals $Cd_{1-x}Zn_xTe$.

Conclusions

Results of our studies show that the use of Bridgman method under pressure is a promising way to obtain crystals $Cd_{1-x}Zn_xTe$ with high values of electrophysical parameters and high sensitivity to ionizing radiation, even for crystals of small diameter. Synthesis of raw charge in this case should be carried out in quartz ampoules under vacuum.

Acknowledgments

The authors are grateful to Dr.V. Kutniy and Dr.A. Rybka for their having taken part in discussion of the results of this work.

This work was carried out with financial support of the Lawrence Livermore National Laboratory.

References

1. F.P. Doty, J.E. Butler et al.Properties of CdZnTe crystals grown by a high pressure Bridgman method// *J. Vac. Sci. Technol*. **10**. N4, pp.358-363, 1992.
2. M. Jnoue, J. Teramoto, S. Takayanagi. Etch pits and polarity in CdTe crystals// *J. Appl. Phys*. **33**. N8, pp.2578-2582, 1962.
3. H.F. Glass, A.J. Socha, C.L. Parfeniuk, D.W. Baccen. Improvements in production of CdZnTe crystals grown by the Bridgman method // *J. Crystal Growth*. 184/185, p.1035, 1998.
4. Atsuko Ebina, Kasuyuki Saito, Tadashi Tacahashi. Crystals grown of $ZnCd_{1-x}$ Te solid solution and their optical properties at the photon energies of the lowest band-gap region// *J. Appl. Phys*. **44**. N 8(2), pp.3659-3662, 1973.
5. J. Karniewich, T. Majchrak. The directional solidification of $Zn_xCd_{1-x}Te$ from tellurium solvent// *In book: 6 Int. Conf. for Crystal Growth*, Moscow, **B 3**, p.311, 1980.