A. Savitskjy, Ye. Nykonyuk, O. Parfenyuk, M. Ilashchuk, P. Fochuk, P.Feichuk

$Cd_{1-X}Zn_xTe$ Crystals Photoelectric Properties, Grown by High Ar Pressure

Chernivtsi National University,
2, Kotzyubynskiy Str., Chernivtsi, 58012, Ukraine ,
Phone: +380(372) 58-47-45; fax: +380(372) 55-18-05, e-mail: fochuk@chnu.cv.ua

Characteristics of CdTe and $Cd_xZn_{1-x}Te$ ($x \leq 0.2$) single crystals, grown by HPBM at different synthesis conditions and with Ar pressure of 60-120 atm in PHASE laboratory (CNRS, Strasbourg), were studied. At lower Ar pressure (60-70 atm) and preliminary synthesis with following overcharging in another ampoule it is possible to get low-resistance p-type crystals, similar to traditional Bridgman method. The semiinsulating CdTe and $Cd_xZn_{1-x}Te$ ($x \leq 0.2$) bouls can be grown (without overcharging) at Par > 120 atm. By photoelectrical measurements positions of 5 deep levels (0.5; 0.8; 0.93; 1.23; 1.42 eV) were determined. The bulk uniformity of semiinsulating crystals was worse.
Key words: semiconductors, crystal growth, deep levels, photoelectrical properties.

I. Introduction

Among semiconducting materials, suitable for production of ionization energy detectors, one of the first places belongs to CdTe and $Cd_xZn_{1-x}Te$. The large atomic number Z, high values of specific resistance ρ ($\sim 10^{10}$ Ohm×cm for CdTe and $\sim 10^{11}$ Ohm×cm for $Cd_xZn_{1-x}Te$ [1]) and $\mu\tau$ give the possibility to produce effective spectrometric sensors for α- and γ-radiation, which work at room temperatures on the base of these compounds.

During CdTe growth in closed volume from stoichiometric composition melt usually the crystals with large content of intrinsic acceptor defects (V_{Cd}) were obtained. That is why for producing of semiinsulating crystals doping by shallow donors (for example, Cl) is widely used. The comparison of CdTe spectrometric detectors characteristics, produced by different technologies (Bridgman method, vapour phase, THM), showed, that sensors, grown by THM, had possessed the best properties [2]. But this method is expensive and to grow the single crystals of large sizes is of great difficulty.

For such practical utilizations it is necessary to have in a disposal semiinsulating undoped uniform CdTe and $Cd_xZn_{1-x}Te$ single crystals. To obtain such crystals by traditional technology seems very problematic. Because of this, growth by Bridgman method under high pressure of inert gas (Ar) is promising [3]. It gives the possibility to produce material with intrinsic conductivity without additional doping. Following investigations had showed the structural uniformity and electrical properties sufficiently depended on growth equipment and heater element especially [4].

The goal of this work was to study electrical and photoelectrical properties of CdTe and $Cd_xZn_{1-x}Te$ ($x \leq 0.2$) single crystals, grown by HPBM under different technological conditions (synthesis, Ar pressure etc.).

II. Experiment

All ingots were grown by HPBM in the PHASE laboratory (CNRS, Strasbourg). The components used were 6N (Cd, Zn) and 5N (Te) of purity. The Ar pressure varied from 60 to 120 atm. The speed of ampoule lowering was 1.4 mm/hour. Two ways of synthesis were used: 1) the components in stoichiometric composition had been charged in a separate quartz ampoule and after synthesis the material was overloaded in a graphite container in HPBM growth equipment (note, these ampoules for synthesis had large free volume); 2) all components had been put at once in the container, after that synthesis and growth processes were realized in one step without overcharging.

The obtained crystals (up to 60 mm of length) consisted of large blocks. The contacts on specimens ($1.5\times1.0\times1.0$ mm^3) of low resistance and p-type conductivity were made by electroless deposition of Au from $HAuCl_4$ solution (with preliminary treatment of contact places by electric spark), of low resistance and n-

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Table.

Equilibrium properties of CdTe and $Cd_{1-x}Zn_xTe$ samples, grown by HPBM (300 K)[*].

№	Ingot	Compo-sition, x	Sample position in ingot	Conduc-tivity type	ρ, Ohm×cm	Mobility, $cm^2/V×s$	Level position ΔE, eV	Ar pressure, atm.	Notes
1	KTC-01-P	0.04	0.22	p	$2.6*10^2$	64	-	60	a
2	KTC-01-P	0.04	0.50	p	$2.4*10^1$	74	0.12	60	a
3	KTC-01-P	0.04	0.87	p	$1.4*10^1$	68	0.12	60	a
4	HPHZ-44	0.1	0.15	p	$6.3*10^1$	70	0.14	70	a
5	CZT-70-15	0.1	0.4	(p) n	$9.1*10^9$			120	b
6	B-2	0.2	0.75	p	$2.2*10^9$	22	0.76	120	b
7	HPc4-KT	0.0	0.55	n	$2.8*10^9$	790	0.78	120	b
8	KT-PS-98	0.0	0.8	p	$1.1*10^1$	75	0.11	60	b

a – preliminary synthesis; b – synthesis + growth
[*] samples' nomination in the text are the same as in Table 1.

type – by In melting in H_2 atmosphere, on semiinsulating samples – by Cu deposition from $CuSO_4$ water solution.

The temperature dependences of Hall coefficient RH and conductivity σ were measured with the use of direct current. The spectral dependence of photoconductivity (PC) and PC infrared (IR) quenching in the 80-300 K temperature range were investigated.

III. Results and discussion

The equilibrium characteristics of investigated specimens are shown in Tabl. 1. The crystals were of low resistance and semiinsulating and possessed p- or n-type conductivity. Low-resistance p-type crystals (samples 1-4, 8; Fig. 1) were characterized by such parameters: the ionization energy of working acceptor level $E_C = 0.11$-0.14 eV; the acceptor concentration $[A] = (0.7$-$1.4)\times10^{16}$ cm^{-3}. The scattering centers concentration (N_i), determined from temperature dependence of mobility μ_H, was equal to $(0.8$-$2.7)\times10^{17}$ cm^{-3}. The comparison of samples' parameters, cut from different parts of ingot, had shown their close values, indicating good crystals uniformity. They were analogical to common Bridgman crystals. The acceptors most likely had a complex nature $(D^+V_{Cd}^{2-})^-$, where D^+ were uncontrolled impurities of IIIA group elements on Cd sites or VIIA group elements – on Te sites. In different crystals the ionization energy varied a little and correlated with ionization centers concentration: at N_i increasing the E_a value decreased. The samples 4 and 8 demonstrated high hole density,
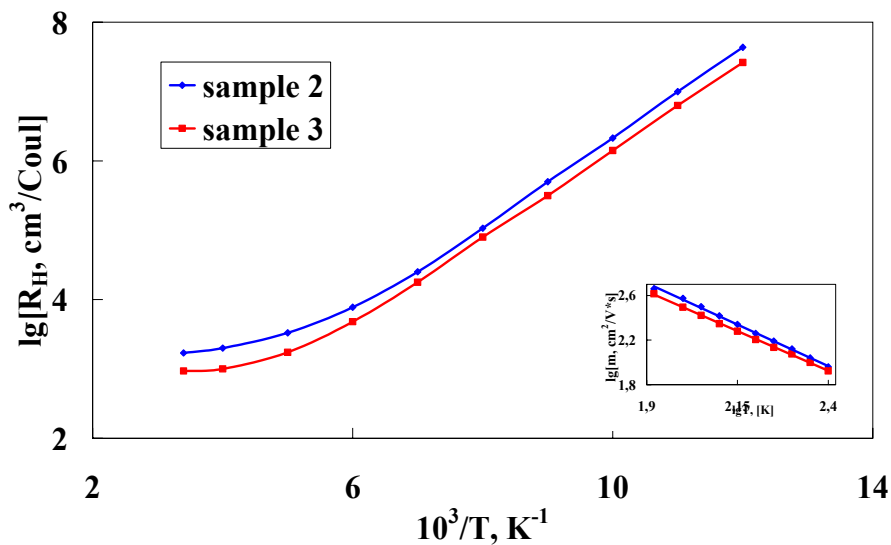

Fig. 1. Temperature dependences of Hall coefficient and mobility (inset) for low-resistive $Cd_xZn_{1-x}Te$ single crystals (sample 2 and 3).
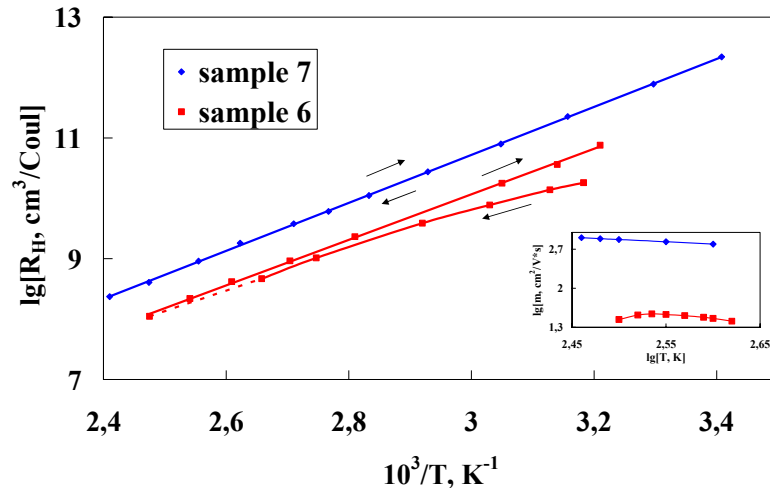
Fig. 2. Temperature dependencies of Hall coefficient and mobility (inset) for semiinsulating Cd$_x$Zn$_{1-x}$Te (sample 6) and CdTe (sample 7) single crystals.
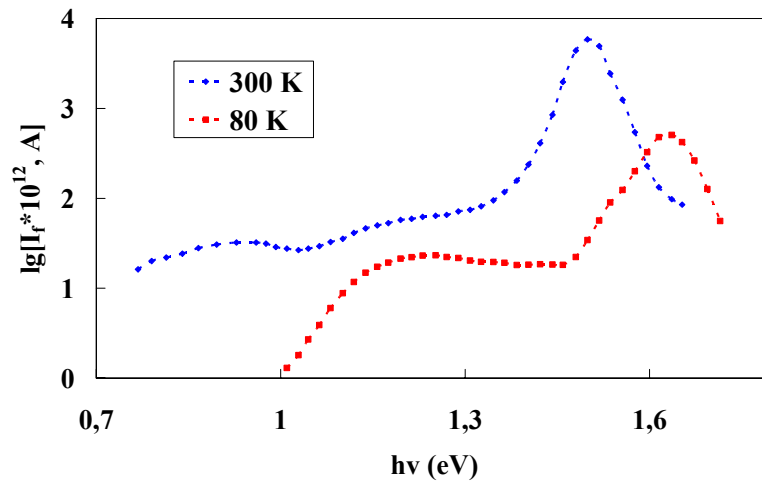

Fig. 3. Spectral dependencies of photoconductivity for Cd$_{0.9}$Zn$_{0.1}$Te crystal (sample 5).

what is rarely found in crystals grown by traditional Bridgman method.

From R$_H$ temperature dependences in semiinsulating crystals (Fig. 2) it had been established their conductivity was determined by deep levels in the middle of the gap: E$_V$+0.76 eV (sample 6) and E$_C$-0.78 eV (sample 7). For sample 5 the inversion of the R$_H$ sign had been observed, what made impossible ΔE and μ_H defining. Temperature dependence of μ_H (Fig. 2, inset) had shown that the mobility of Cd$_{0.8}$Zn$_{0.2}$Te sample was small and practically did not depend on temperature. The μ_H = f(lgT) dependence in sample 7 showed the main role of lattice vibrations in the scattering processes.

The optical transmission measurements at λ = 2-20 μm had no structure. They demonstrated the high values (T = 60%) in crystals 5 and 7; in crystal 6 the transmission was less (T ~ 55%).

Comparing the resistance ρ of the crystals with their producing conditions it was seen that low-resistance p-type CdTe in the most cases had been received using preliminary synthesis in a separate quartz ampoule. The reasons could be: presence of large free volume at synthesis process, what resulted in crystal formation with

Te excess and consequently to considerable V$_{Cd}$ concentrations; possibility of foreign impurity transition from quartz to the melt; insufficient pressure of inert gas (60-70 atm.) during growth, because low-resistance CdTe (sample 8) also had been obtained when synthesis and growth processes had been taking place in the same container.

All semiinsulating crystals had been grown at sufficiently high Ar overpressure and without overloading. At such conditions stable undoped semiinsulating material with high mobility μ_H (sample 7) was obtained.

Small μ_H values and the slope change in R$_H$ temperature dependence at repeated investigations in sample 6 (Cd$_{0.8}$Zn$_{0.2}$Te) showed that the system of intrinsic and foreign point defects had not reached the equilibrium thermodynamic state during growth. The structure defects concentration was essential. Like this in [4,5] other authors had determined in HPBM crystals a big amount of ZnTe precipitates and an inhomogeneous Zn distribution both along the ingot and in perpendicular direction to crystal growth.

To determine the energy level spectra, located in the gap, photoelectric characteristics of 2 semiinsulating
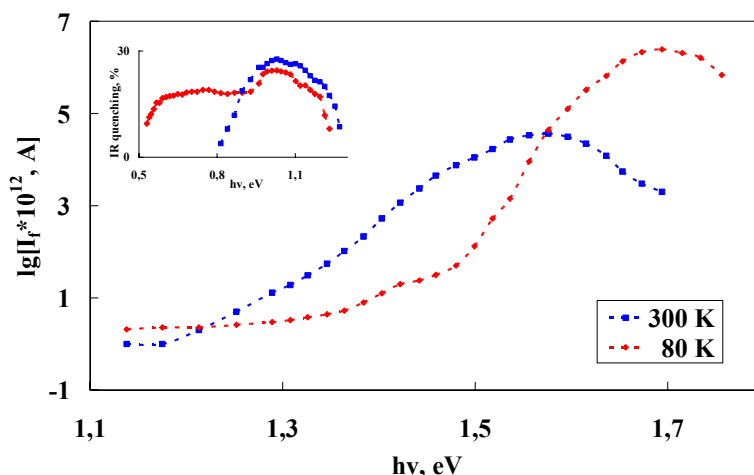
Fig. 4. Spectral dependences of photoconductivity and IR quenching (inset) for $Cd_{0.8}Zn_{0.2}Te$ crystal (sample 6).

$Cd_xZn_{1-x}Te$ crystals were studied.

It was noted for sample 5 ($Cd_{0.9}Zn_{0.1}Te$) that its photosensitivity had diminished with temperature decrease (Fig. 3). In experimental PC dependences at room temperature 2 bands of dopant PC with the maximum at 0.93 and 1.23 eV were observed. When temperature decreased the 0.93 eV band disappeared, but the intensity of 1.23 eV band increased. The high energy maximums were due to PC at intrinsic absorption. PC IR quenching was absent.

The photosensitivity of $Cd_{0.8}Zn_{0.2}Te$ crystal (sample 6) was higher (Fig. 4). Long-wave PC boundary in this case shifted to the high energy side comparing with previous sample. In the spectral PC dependences one dopant peak only, with the maximum at 1.42 eV, clearly expressed at 80 K, was observed. It was typical to observe IR quenching of PC [6] in these crystals (Fig. 4, inset). The positions of two slow recombination levels ($E_1 = 0.8$ eV and $E_2 \approx 0.5$ eV) were determined from the long-wave boundary of spectral dependence of PC IR quenching.

The found in this work deep level defect positions were close to defect energy, obtained in $Cd_xZn_{1-x}Te$ crystals, grown by HPBM [7]. It is necessary to carry out

a lot of investigations to define the nature of such deep centers. Most probably they are due to residual impurities, but not to intrinsic point defects, because the concentration of the latter is small in the case of HPBM. It can be mentioned, that by help of CdTe doping by IV group elements and elements with 3-d incomplete level, deep levels, located in the energy region near 0.4-0.9 eV [8] are introduced in the crystal.

IV. Conclusions

At last it can be noted that the properties of CdTe and $Cd_xZn_{1-x}Te$ single crystals, grown by HPBM, strongly depend on the inert gas pressure and peculiarities of synthesis conditions. The investigated low-resistance CdTe and $Cd_xZn_{1-x}Te$ samples of p-type conductivity were similar to obtained by the traditional Bridgman method. The uniformity of semiinsulating crystals was worse. The deep levels in the gap probably belong to foreign impurities.

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А. Савицький, Є. Никонюк, О. Парфенюк, М. Ілащук, П. Фочук, П. Фейчук

Фотоелектричні властивості кристалів Cd$_{1-x}$Zn$_x$Te, вирощених під високим тиском Ar

Чернівецький національний університет,
вул. Коцюбинського 2, Чернівці, 58012, Україна
Тел: +380 (372) 58-47-45; факс: +380 (372) 58-48-43, E-mail: fochuk@chnu.cv.ua

Вивчені характеристики монокристалів CdTe та Cd$_x$Zn$_{1-x}$Te (x ≤ 0,2), вирощених методом HPBM (high pressure Bridgman method) при різних умовах синтезу і тиску Ar 60-120 атм. в лабораторії PHASE (CNRS, Strasbourg). При низьких тисках Ar (60-70 атм.) і попередньому синтезі з наступним перезавантаженням в іншу ампулу можна отримати низькоомні кристали p-типу, подібні до одержаних класичним методом Бріджмена. Напівізолюючі кристали CdTe та Cd$_x$Zn$_{1-x}$Te (x ≤ 0,2) можуть бути вирощені (без перезавантаження) при тиску Ar, вищому за 120 атм. З фотоелектричних вимірювань були визначені 5 глибоких рівнів (0,5; 0,8; 0,93; 1,23; 1,42 еВ). Однорідність злитку у випадку напівізолюючих кристалів була гіршою.