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Electrical properties of CdTe:P single crystals at low and high temperatures

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High-temperature (470-1170 K) properties of CdTe:P single crystals, grown by Bridgman technique, with an initial concentration of impurities in the melt 1×10^{19} at/cm³, were investigated by measuring of the Hall effect. Experimental results indicate that up to the temperature of ~700 K samples had p-type conductivity and above ~940 K – n-type one. Character of isothermal dependences of Hall constant strongly differs from the dependence of the undoped material due to the influence of impurities. Acceptor effect of phosphorus is observed up to 1170 K, it shows a high content of acceptor impurity form (P_{Te}). The low-temperature electric measurements data confirm the fact of phosphorus high solubility in CdTe. The results of IR microscopy indicate that the introduction of phosphorus into CdTe crystal resulted in almost complete elimination of second phase inclusions with size ≥ 1 μm , which are usually present in such material.

Keywords: cadmium telluride, phosphorus, Hall effect, point defects, high-temperature measurements.

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Introduction

CdTe crystals have interesting optical and electrical parameters that can be purposefully changed within a wide range by doping with various impurities. Due to this they are widely used in many microelectronic devices.

It was found that the introduction of such impurity as phosphorus into cadmium telluride provides crystal with high p-type conductivity due to the formation of shallow acceptor level [1, 2].

Arkadieva et al [2] investigated that phosphorus forms a shallow acceptor level $E_V + 0.05$ eV in CdTe. It is essential that in spite of the significant concentration of introduced acceptors ($\sim 10^{18}$ cm⁻³) the concentration of electrically active impurity turned out to be significantly lower ($\sim 10^{16}$ cm⁻³), which is explained by compensatory processes.

Hall studied the diffusion of phosphorus in CdTe [3]. Author believed that P is an acceptor on Te place and it is

compensated by donor defect, which is the interstitial cadmium Cd_i. Phosphorus diffusion in CdTe was measured as a function of annealing time and temperature in the 870-1100 K range. It was established that simple diffusion mechanism with an activation energy of 2 eV acted in the temperature range 870-1100 K, the surface concentration of phosphorus did not depend on the time of diffusion annealing and ranged from 1.5×10^{16} cm⁻³ at 870 K and 1×10^{18} cm⁻³ at 1100 K, and activation energy of dissolution of phosphorus was 1.3 eV. Hall also investigated the solubility of P in CdTe. It was 9×10^{19} at/cm³ at 1173 K and p_{Cd} (cadmium vapor pressure) = 8×10^5 Pa.

Agrinskaya [4] evaluated holes mobility ($\mu \sim 40$ -60 cm²/(V·s)), shallow acceptor concentration of the $[\text{P}_{\text{Te}}^-] = 5 \times 10^{17}$ cm⁻³, its ionization energy - 0.06 eV and compensation degree $N_d/N_a = 0.8$ by studying the photoluminescence, Hall effect measurements and optical absorption of CdTe crystals doped by phosphorus. The

optical ionization energy of P_{Te}^- centers was 0.07 eV. Annealing at 770 K (time and stoichiometric conditions were not specified, we can assume it was vacuum) resulted in P_{Te}^- decrease by almost an order of magnitude. Also the degree of compensation increased and the deep level $E_V+1.2$ eV appeared, which was explained by the formation of P complexes with donor defects as in [4], as well as by possible transition of part of P atoms with the acceptor state (P_{Te}^-) into the donor one (P_{Cd}^{3+}).

Selim and Kröger [5] found that phosphorus forms shallow acceptor level $E_V+0.035$ eV, for which the center P_{Te} or P_i is responsible, by annealing of CdTe:P crystals at high temperatures (970-1100 K) at p_{Cd} with subsequent quenching and Hall effect measurements (341-469 K). Phosphorus acts as an acceptor (P_{Te} and/or P_i) at high Cd vapor pressure and as a donor (P_{Cd}) at low p_{Cd} , forming neutral associates $(P_{Cd}P_i)^0$ or $(P_{Cd}2P_i)^0$. At high values of cadmium vapor pressure its own defects (Cd_i^{2+}) are involved in the process of self-compensation, at low p_{Cd} – impurity ones P_{Cd}^{3+} . Although these authors suggested the model of the defect structure of CdTe:P, but actually there are still no reliable evidences of its adequacy.

Chu and Bube [6] under similar to [5] processing conditions and measurements obtained close experimental results, within which it was concluded that in the CdTe:P samples at high Cd over pressure the shallow acceptors (P_{Te}) are compensated by their own donors Cd_i^{2+} , then as at lower p_{Cd} – by impurity ones P_{Cd}^{3+} . In CdTe:P samples there was only one mechanism of rapid diffusion caused by the phosphorus atoms, which were located at Cd nodes or interstitials.

By means of photoluminescence Molva and Saminadayar [7] studied the highly pure CdTe crystals of p-type, in which P^+ ions were implanted. It was found that P replaces Te atoms in CdTe sublattice. Energy level formed by it is situated in the forbidden gap at 68.2 meV above the top of valence band.

In [8] the diffusion of P (source - H_3PO_4) from the gas phase in CdTe was studied. In the layer up to 20 μm precipitates containing phosphorus were found. The diffusion coefficient of phosphorus $D_P = 5 \times 10^{-12} \text{ cm}^2 \times \text{s}^{-1}$ at 813 K was estimated.

The authors [9] found out that the main limiting factor in CdTe-based solar cells is the low doping ability of p-type for CdTe and, as a result, low open-circuit voltage (V_{OC}). Ji-Hui Yang and Wan-Jian Yin studied how to increase the density of holes by doping crystals with P and As impurities. The scientists discovered that p-type doping with both P and As impurity is self-compensating due to the formation of AX centers. However, although the high temperature resulted in a high hole density, rapid cooling was required to maintain the hole density and lower the Fermi level close to the valence band maximum (VBM) at room temperature. Through simulations, the scientists hypothesized that by cooling CdTe from high temperature to room temperature under low tellurium vapor pressure conditions and at an optimal dopant concentration of $10^{18}/\text{cm}^3$, P and As doping can lead to hole densities above 10^{17} cm^{-3} at room temperature and a decrease in the Fermi level within ~ 0.1 eV above the VBM. The obtained results are relevant for the purpose of increasing the V_{OC} and efficiency of CdTe solar cells.

Burst and Duenow [10] investigated the defect

structure of CdTe by annealing samples in a Cd or Te vapor atmosphere with and without doping impurities. When phosphorus was introduced as an impurity in a Cd vapor atmosphere, a lifetime of 30 ns with a hole density of 10^{16} cm^{-3} was achieved in monocrystalline and polycrystalline CdTe without $CdCl_2$ or Cu. It was established that doping CdTe with phosphorus is thermally stable, which is necessary for the development of solar cells based on CdTe. Burst and Duenow [11] also found that to increase the efficiency of CdTe solar cells, it is necessary to increase the open-circuit voltage above 900 mV. And this requires a high density of holes and a long life of charge carries.

Using first-principles calculations scientists Flores and Orellana [12] studied the defect structure and mechanisms of self-compensation in CdTe crystals doped with Phosphorus. They established that AX centers are not responsible for self-compensation mechanisms. In a Te vapor atmosphere, the P_i point defect has lower formation energy than the P_{Te} substitutional acceptor and acts as a compensating donor. And in the Cd vapor atmosphere, the limiting factor for p-type doping is the formation of complexes ($P_{Te}-V_{Te}$).

From the above it can be concluded that there is still no reliable model of phosphorus introduction into CdTe at this time. All previous measurements were carried out at room temperatures, which does not give a complete picture of the impurity behavior in CdTe. That's why the aim of our work was to investigate the influence of phosphorus on the electrical properties of CdTe single crystals at the first time in a high-temperature equilibrium in a wide range under the cadmium vapor pressure and to explain the obtained results based on Kröger's theory of quasi-chemistry reactions of defect formation [13].

I. Experimental method

Single-crystalline CdTe ingot, doped by phosphorus, was grown by Bridgman method. Cadmium and tellurium were taken in stoichiometric ratio, adding the calculated number of impurity. The initial amount of phosphorus in the melt was $1 \times 10^{19} \text{ at}/\text{cm}^3$. Samples for measurements were made in the shape of parallelepiped with the approximate dimensions $2.5 \times 2.5 \times 12 \text{ mm}^3$ by the standard method. All of them were grounded and polished by chemical- mechanical means. For high-temperature measurements the contacts (tungsten wire) were welded to the samples under the influence of an electric discharge. Measurements of electrical conductivity (σ) and Hall effect were performed/carried out by the method described in [14] in the temperature range of 470-1170 K in an atmosphere of cadmium vapor. For low-temperature measurements carried out using the method described in [15] ohmic contacts on samples were created by precipitation of gold from a solution of $HAuCl_4$. The morphology of the samples was investigated by IR microscopy. CL spectra were performed at 77 K.

II. Experimental results and discussion

For measurements several CdTe:P samples were

prepared. They were cut from different parts of the ingot in order to get samples with different phosphorus concentrations. The results obtained on samples with different g (g – position of the sample in the ingot, $g = 0$ – the beginning of the ingot, $g = 1$ – the end of the ingot) were similar, so in this article we give the data for one of them cut from the first half of the ingot.

Temperature dependence of carrier mobility for the sample P5Cd is shown in Fig. 1. The sample had possessed the hole conductivity up to ~ 700 K and the values of the charge carrier mobility were close to the hole mobility in undoped CdTe, which is shown as the dotted line "h⁺" [16]. After heating to ~ 820 K p-n-junction occurred and the conductivity type changed to electronic. With further temperature increase (above 920 K) the mobility began to decrease due to scattering of electrons on lattice oscillations. For the sample P5Cd charge carriers mobility at high temperatures is somewhat lower than for undoped CdTe (line "e⁻" [16]), which is explained by the presence of large number of impurity atoms.

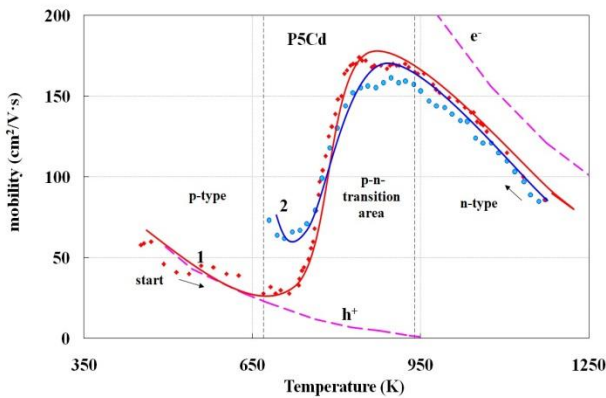


Fig. 1. Dependence of charge carrier mobility on temperature for the sample P5Cd at $p_{Cd,max}$ (1 – initial heating, 2 – cooling; dashed line – electrons and holes mobility in undoped CdTe [16]).

Isotherms of charge carrier concentrations for the sample P5Cd for $T < 1170$ K are located below the isotherms for undoped CdTe (Fig. 2). It is caused by the acceptor behavior of phosphorus. Impurity atoms bind free electrons, lowering their general concentration. These processes can be described by the following quasi-chemical processes.

When dissolving impurity takes position of tellurium atoms in the lattice:



and then it is ionized



In total the concentration of charge carriers in the isotherms in Fig. 2 barely grows with p_{Cd} increasing and in most cases remains lower than $[e^-]$ in the undoped material. It should be noted that in the conditions of high-temperature equilibrium of defects the value of Hall constant (i.e. definition of the charge carriers value) is ambiguous under conditions of close presence of electrons

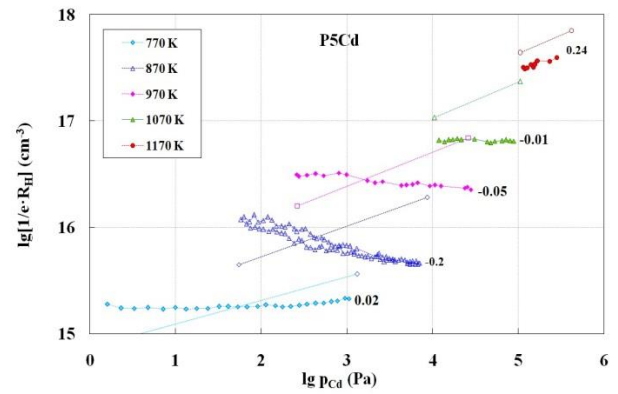


Fig. 2. The dependence of the Hall constant on cadmium vapor pressure for the sample P5Cd (dashed line – $[e^-]$ in undoped CdTe at corresponding temperatures, numbers – the slope lines for doped crystal).

and holes. To calculate the charge carrier concentration, we used the formula $n = \frac{1}{R_H \cdot e}$ (where n – the concentration of charge carriers, R_H – Hall constant, e – electron charge), which has meaning in terms of one type of carriers predominance. Perhaps at lower cadmium vapor pressure, when holes start to dominate, it is necessary to use the formula that takes into account both types of charge carriers. But you need to have reliable values of the holes and electrons mobility in the sample, which, unfortunately, are absent. At 770-1070 K (Fig. 2) isotherms for CdTe:P significantly differ from similar dependences for the undoped material. Experimental values of charge carrier concentration are the difference between the concentration of own donors and of acceptor impurity. Only at 1170 K the line of the doped material has a positive slope ($\gamma = 0.24$) and does not cross the isotherm of undoped CdTe. It means that in this case it is the prevalence of electronic conductivity, which is provided by a significant increase in own donors (Cd_i^{2+}) content with increasing of temperature as well as of p_{Cd} . Thus when $lg p_{Cd} = 5.1$ Pa the difference in values of the electrons concentration in undoped and doped materials is $\sim 2 \times 10^{17} \text{ cm}^{-3}$. It corresponds to approximate content of phosphorus acceptor in the crystal (at lower temperatures this content is less). From this it follows the conclusion about the growth of $[P_{Te}^i]$ when heated, which can be explained only by the increase of impurity solubility, which at lower temperatures is present in the crystal partly in the form of electrically inactive second phase, see Equation (1-2).

Fig. 3 shows the dependence of charge carrier concentration on temperature. In the beginning of measurements the holes concentration was $\sim 10^{17} \text{ cm}^{-3}$. The high value of $[h^+]$ indicates that the high content of phosphorus acceptor point defects, dissolved in the crystal matrix, tempered at relatively rapid cooling of the ingot after its growing (which corresponds to their estimated concentration at 1173 K, see. commentary to the Fig. 2). Such holes concentration remained at the level of $\sim 10^{17} \text{ cm}^{-3}$ up to 770 K. When heated to 870 K and excerpt at this temperature the conductivity of the sample with p-type for several hours transferred into bipolar and herewith the charge carriers concentration decreased by an order (to $\sim 10^{16} \text{ cm}^{-3}$). Further temperature increase above

~900 K leads to an increase of charge carrier concentration, generation of own donors is felt, whose contribution to the general $[e^-]$ always increases with temperature. For higher temperatures the electron density is lower than in undoped CdTe (dashed line). During slow cooling from this temperature high temperature equilibrium is set, content of dissolved impurity becomes equilibrium, charge carrier concentration logically lowers to values shown in Fig. 2. Cooling from 800 to 680 K caused slight rise of the charge carrier concentration (such results are typical when measuring the charge carrier concentration in the p-n junction), and further temperature decrease led to a decrease of charge carrier concentration to $\sim 5 \times 10^{13} \text{ cm}^{-3}$.

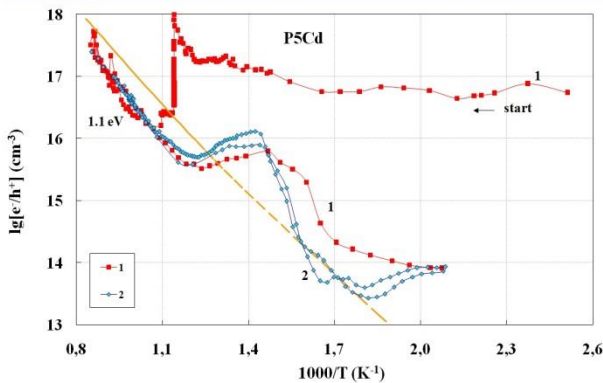


Fig. 3. Temperature dependence of charge carrier concentration for the sample P5Cd at $p_{\text{Cd,max}}$ (numbers – sequence of measurements, dashed line – $[e^-]$ in undoped CdTe, 1 – initial heating and cooling, 2 – second heating and cooling).

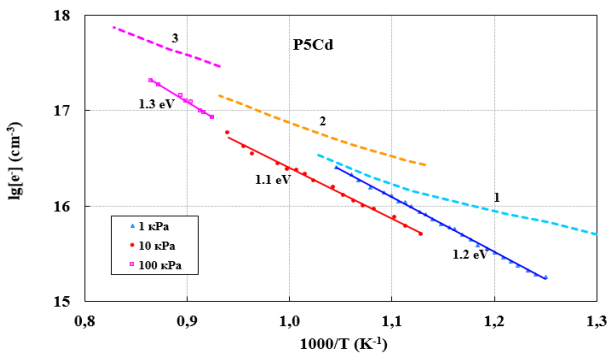


Fig. 4. Temperature dependence of the electron concentration for the sample P5Cd at different $p_{\text{Cd}} = \text{Const}$ (dashed line – $[e^-]$ in undoped CdTe at the corresponding cadmium vapor pressures: 1 – 1 kPa, 2 – 10 kPa, 3 – 100 kPa).

Isobaric dependences of the electron concentration are shown in Fig. 4. Isobars are straight lines, they all lie below the corresponding dependences for undoped CdTe, confirming the acceptor impurity behavior in the temperature range 700-1100 K. The results in Fig. 4 agree with the data of Fig. 2 for different charge carrier concentrations at different temperatures and cadmium vapor pressures.

Also, low-temperature ($T = 80\text{-}330 \text{ K}$) measurements of the Hall effect for CdTe doped with phosphorus (Fig. 5) were conducted. The slope of the temperature dependence of

electrical conductivity is $\sim 0.05 \text{ eV}$. It does not contradict to the value of phosphorus level according to literature data [2, 4, 5, 7].

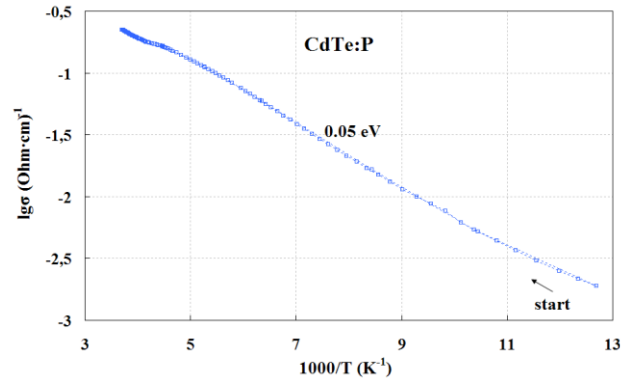


Fig. 5. Temperature dependence of electrical conductivity for the sample CdTe:P, $g = 0.55$.

The results of measurements of hole concentration at 300 K for samples with different values of g are shown in Fig. 6.

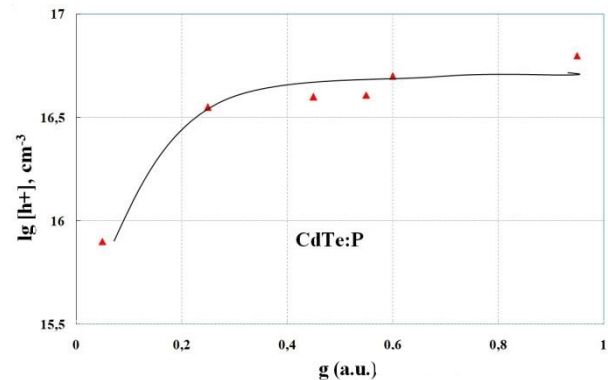


Fig. 6. The dependence of the hole concentration on the position of the sample in the ingot (g) at 300 K.

It is evident that their concentration increases from the beginning of the ingot to $g = 0.3$, and then it does not change until the end of the ingot. This explains why the electrical properties of samples with $g = 0.55\text{-}0.85$ are similar as noted above. The value of $[h^+]$ corresponds to the initial value in the beginning of measurements of temperature dependence of carrier concentration (Fig. 3) and is determined by the content of phosphorus acceptor point defects in CdTe crystal. The results of investigations of CdTe samples doped with phosphorus by the method of IR microscopy (Fig. 7) showed that in the beginning and the middle grown of the grown ingot precipitates were not visible, but at the end of the ingot they were present in significant numbers. Precipitates didn't have distinct/clearly defined shape and their sizes were in the range from 5 to 30 μm . The absence of inclusions in most part of the ingot confirms the high solubility of phosphorus in CdTe [3] and their presence only in the upper part of the ingot can be explained by the displacement of impurity to/into the end of the ingot. This allows to suggest that the distribution coefficient of phosphorus in CdTe is $k_{\text{segr}} < 1$.

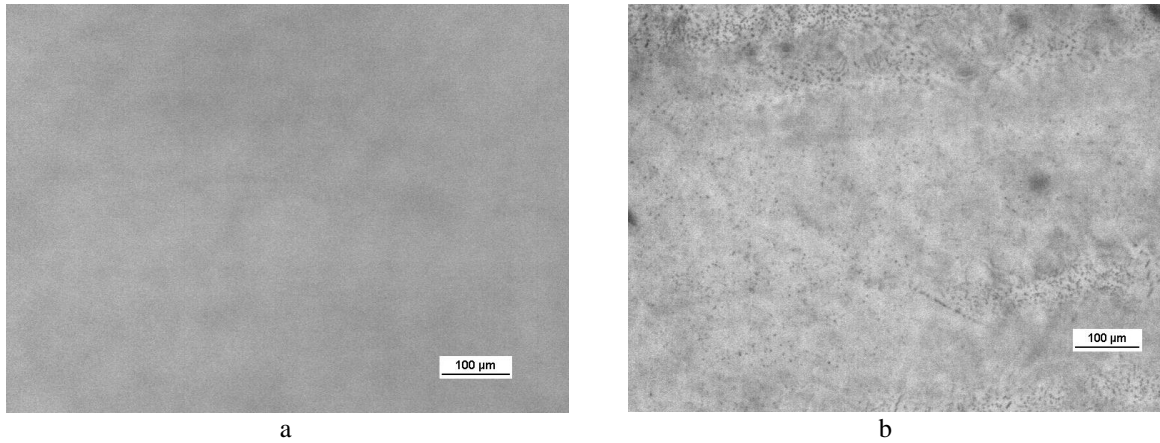


Fig. 7. Photomicrographs of CdTe:P in the infrared region of the spectrum (a – in the beginning and in the middle of the ingot, b – at the end of the ingot).

Fig. 8 shows the comparison among the CL spectra of CdTe:P crystals ($g = 0.05$) as-grown and annealed under different stoichiometric conditions (Cd-pressure, Te-pressure, vacuum) and slow cooled (1 K/min) after annealing. The main feature visible in the spectra is the presence of an emission band centred at $E = 1.53$ eV, in addition to the NBE emission centred at $E = 1.56-1.57$ eV, as a function of the sample analysed. In the literature it was reported that phosphorus creates an acceptor level at about 30-50 meV above the valence band [2, 5]. If these data are right we can attribute this CL band ($E = 1.53$ eV) to a transition involving the acceptor level related to phosphorus doping. Another interesting feature is the absence of the CL band at $E = 1.35$ eV in the spectrum acquired on the Te-annealed sample (the spectrum acquired on the quenched sample is absolutely similar).

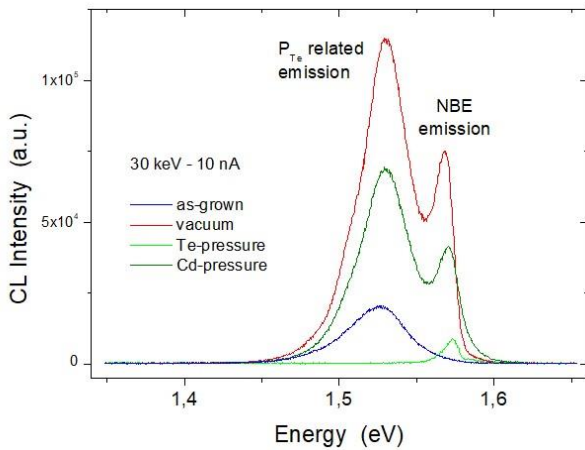


Fig. 8. CL spectra of CdTe:P crystals ($g = 0.05$).

On the contrary all the as-grown samples (as you can see in fig. 9) does not show the NBE emission. All the as-grown samples, independently on the position in the ingot, show only a broad CL emission centred at $E=1.52/3$ eV. The exact emission energies of the different bands obtained by deconvolution are summarized below: for $g = 0.05$ $E = 1.527$ eV, for $g = 0.55$ $E=1.523$ eV, for $g = 0.95$ $E = 1.521$ eV.

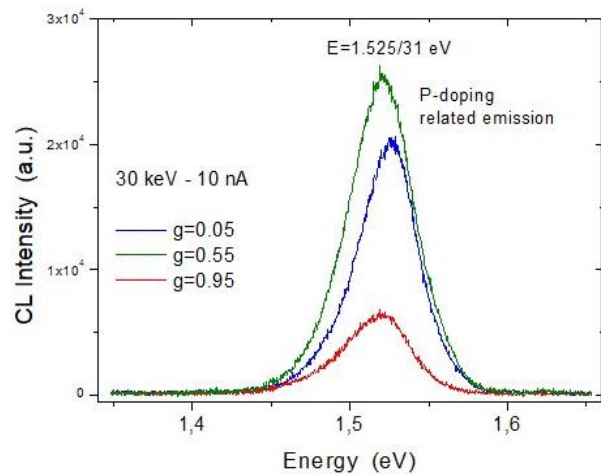


Fig. 9. CL spectra of CdTe:P crystals with different position in ingot (1 – $g = 0.05$, 2 – $g = 0.55$, 3 – $g = 0.95$).

This very small shift supports our opinion that this band is the same in all the samples and is due to the same transition. This emission has the same origin of that observed in the vacuum and Cd-annealed samples and is due to a transition involving the P-acceptor related level. You can observe strong differences in the CL intensity among the 3 samples. This result is not reliable, because all the samples are highly inhomogeneous and the CL intensity can change of 50% moving from a region to another (see Fig.11).

The main feature observed in monoCL images (Fig. 10) is the alternate of bright and dark regions, which relative dimensions change respect to the sample analysed. In particular the sample cut from $g = 0.05$ position in the ingot shows the bright areas with the biggest dimensions (several hundreds of microns), while the samples cut from $g = 0.55$ and $g = 0.95$ ingot positions show bright regions of reduced dimensions (down to few tenth of microns). By observing deeply the images of the samples cut from $g = 0.55$ and $g = 0.95$ ingot positions, it is possible to observe a bright shadow underneath the small bright spots. Taking into account that the CL spectra show one band only, we suppose that the bright areas

represent regions of higher radiative recombination efficiency respect to the dark ones. If our supposition, that the observed CL band is related to the P-doping, is right, the monoCL images give a direct evidence of the in-plane non-homogeneous distribution of the doping.

Fig. 11 shows monochromatic images at $E = 1.53$ eV

on the as-grown samples (P-doping related emission). The images are characterized by an alternate of bright and dark regions, as you can observe for example in the case of $g = 0.55$ as-grown sample. In this case we observe bright regions of about $100 \mu\text{m}$ in diameter surrounded by dark regions. The luminescence intensity inside the bright

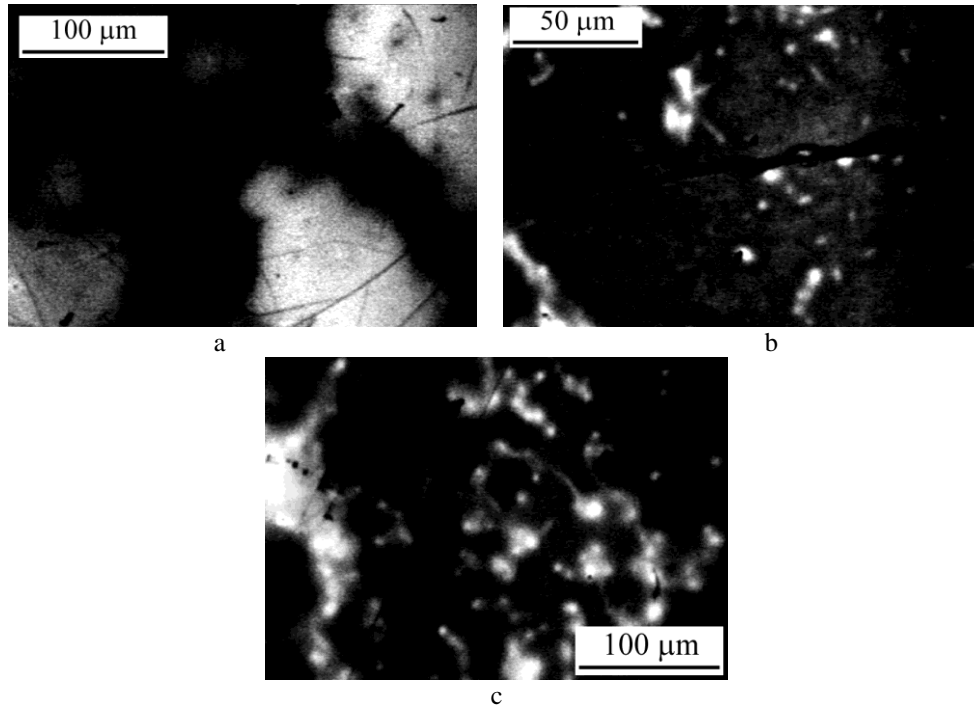


Fig.10. MonoCL images of surface of CdTe:P crystals at the maximum of the P-doping related CL band (a – $g = 0.05$ at $E = 1.526$ eV, b – $g = 0.55$ at $E = 1.526$ eV, c – $g = 0.95$ at $E = 1.521$ eV).

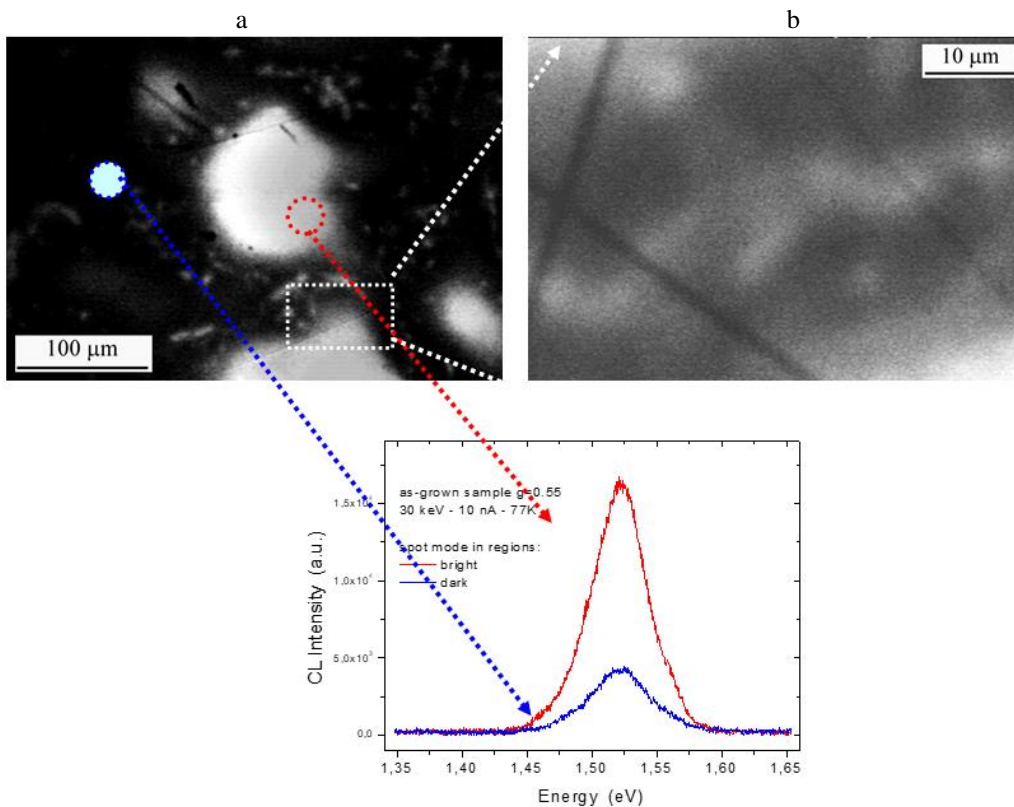


Fig. 11. CL spectra of CdTe:P crystals ($g = 0.55$) for different parts of the sample (1 – light regions, 2 – dark regions);
a - section of the surface of the sample at a magnification of $100 \mu\text{m}$,
b - selected fragment from the surface area **a** at a magnification of $10 \mu\text{m}$).

regions is quite homogeneous, but the in dark ones it is possible to observe a not uniform contrast (as you can see in fig. 11b)

The comparison of the CL spectra acquired inside the bright and dark regions respectively, is shown in the fig. 11. It's clear that the only feature is a strong reduction of the CL intensity in the dark regions, with respect to the bright ones. This means that the dark regions are simply zones of reduced luminescence efficiency. Since the only CL emission we observe in this sample is that related to the P-doping, this could be an indication of a non-homogeneous distribution of the doping inside the crystal. We observed a similar behavior in the others as-grown samples (caught from $g = 0.05$ and $g = 0.95$ position) but the dimensions of the bright regions are different.

Discussion

IR microscopy (Fig. 7) shows that the first half of CdTe:P ingot has not inclusions, they appear only at the end of the ingot (5-30 μm). In all samples cut from different parts of the ingot, on the monochromatic surface images there was observed alternation of light and dark areas, which are zones with different luminescence intensity, that indicates the inhomogeneous radial distribution of Phosphorus in ingot.

Low-temperature Hall effect measurements (100-300 K) for all samples have showed hole concentration at $\sim 5 \times 10^{16} \text{ cm}^{-3}$ (Fig. 12).

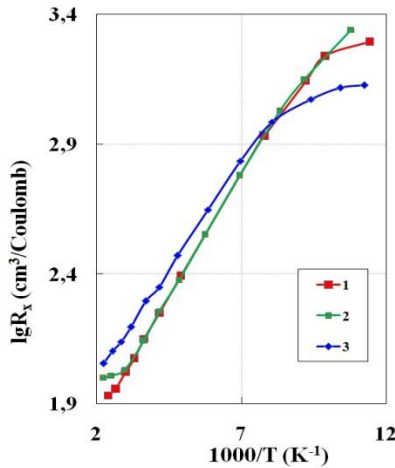


Fig. 12. Hall constant R_H temperature dependence in CdTe:P samples. 1 – $g = 0,25$; 2 – $g = 0,45$; 3 – $g = 0,85$.

Only at the beginning of the ingot, this value was 5-6 times lower. The position of the acceptor level $E_a = E_v + 0.016 \text{ eV}$ (Table 1) was determined. With a high impurity concentration the phenomenon of self-compensation appears and calculations show that the concentration of impurity donor [D] and acceptor [A] are $\sim 2 \times 10^{18} \text{ cm}^{-3}$ (Table 1).

Fig. 12 shows the temperature dependence of Hall coefficient R_H for three samples from different parts of the ingot.

The ionization energy was calculated on a straight section of $\lg(R_x T^{3/2}) = f(10^3/T)$ dependence in accordance with the equation (3):

$$\frac{p(p+[D])}{[A]-(p+[D])} = \frac{N_V}{g} \exp\left(\frac{E_a}{kT}\right) \quad (3)$$

where g is the degeneration factor at the top of the valence band (VB), $g = 4$, N_V is the density of states in the VB, p is the concentration of holes in the VB.

$$N_V = 2(2\pi m_p kT/h^2)^{3/2} \quad (4)$$

$$m_p^* = 0.63m_0 \quad (5)$$

$$E_g = (1.6 - 4 \times 10^{-4})eV \quad (6)$$

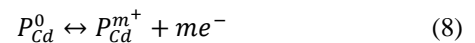
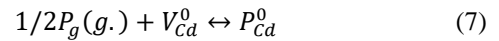
Hence, taking into account $[h^+]_{\text{sat}}$ (concentration of holes in conditions of saturation), the concentrations of [D] and [A] were calculated.

The table shows that with the increasing of value g , and, consequently, the acceptor concentration in the sample, the transition temperature (T_{trans}) increases to the conductivity on the impurity band (see Table 1).

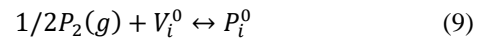
Under the cadmium vapor pressure above $\sim 850 \text{ K}$ samples possessed n-type conductivity. The charge carrier concentrations at all temperatures are significantly lower than for undoped CdTe, that testifies to the mainly acceptor impurity effect.

Where the phosphorus concentration is low (beginning of the ingot, $k_{\text{segr}} < 1$), impurity atoms replace Tellurium atoms, showing the acceptor behavior. The wide band at 1.53 eV , which is observed in the PL and CL spectra, is caused by the acceptor P_{Te} .

In the case when the dopant concentration is high (the ingot end) the phosphorus not only replaces tellurium atoms, but also the cadmium atoms or is in the interstices, showing amphoteric behavior, as mentioned in Selim and Kröger article [5]:



where “m” is the ionization degree of P_{Cd} .



The high-temperature Hall effect measurements and PL and CL data show it.

Table 1.

Calculated results of doped CdTe:P crystals' parameters

No	The position of the sample in the ingot (g)	$[h^+]$, cm^{-3} (T = 300 K)	$[h^+]_{\text{sat}} = [A]-[D]$, cm^{-3}	E_A^0 , meV	$[D] = [A]$, cm^{-3}	T_{trans} , K
1.	0.25	5.4×10^{16}	6×10^{16}	16	1.6×10^{18}	115
2.	0.45	5.3×10^{16}	8×10^{16}	16	2.2×10^{18}	122
3.	0.85	4.0×10^{16}	6×10^{16}	13	2.5×10^{18}	135

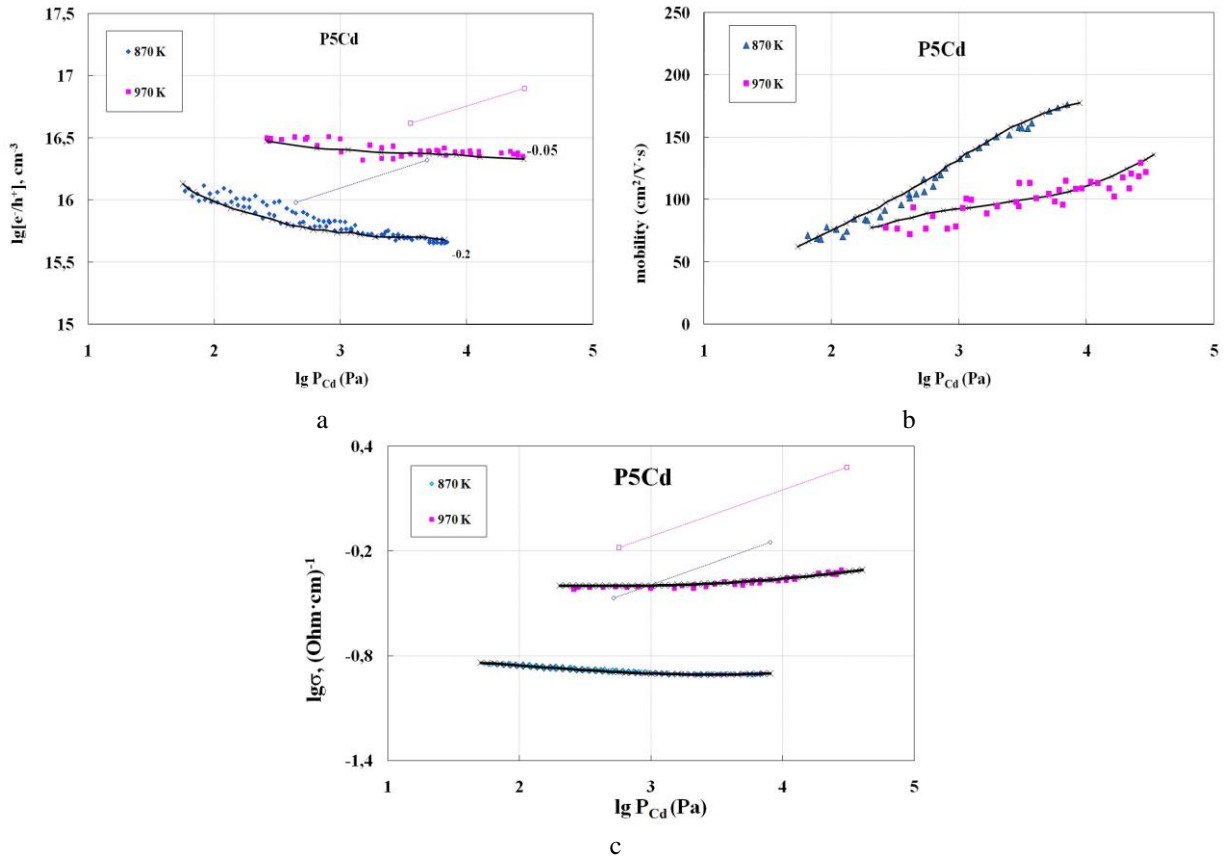
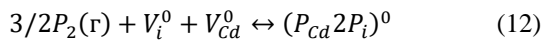
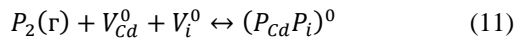


Fig. 13. Pressure dependence modeling of carrier concentration (a), the charge carrier mobility (b) and conductivity (c) at 870 and 970 K for the sample P5Cd.

For sample annealed at $p_{Cd,max}$, there is a small band displacement caused by the acceptor center P_{Te} into the region of lower energies, and also it is observed the lower PL intensity, indicating that the annealing in the atmosphere of cadmium vapor creates more of defects and therefore bandgap decreases.

According to [5] the formation of associates between impurity defects is possible, which leads to the charge carrier compensation:



In contrast to other acceptors in CdTe, the phosphorus solubility at high temperatures are fairly high, it allows to create low ohmic material with high hole mobility.

Modeling

Experimental measurement of high-temperature Hall effect crystal CdTe:P showed a very weak dependence of carrier concentration on p_{Cd} in a wide range of cadmium vapor pressure, especially at low temperatures. We conducted a simulation of pressure dependence of concentration and mobility of charge carriers and conductivity at 870 and 970 K for the P5Cd sample (Fig.13). The modeling took into account the presence of all inherent defects and defects caused by the presence of phosphorus impurities – P_{Te} and P_i . Numerical values of constants and enthalpies for defect formation reactions were taken from the work of Selim and Kröger [5].

Theoretical calculations based on modeling the existence of internal source of phosphorus (probably phosphorus precipitates), characterized by chemical potentials $\mu R(T, P_{Cd})$. This source supplies the electrically active P_{Te} shallow acceptors in Te sublattice and compensates intrinsic donors formed at appropriate temperatures. The simulation results are in good agreement with the experimental data, taking into account the additional shallow acceptor level (P_i) with a concentration of $8 \times 10^{16} \text{ cm}^{-3}$.

Conclusions

With the help of high- and low-temperature Hall effect measurements of single CdTe:P crystals grown by Bridgman method it was found that the acceptor action of phosphorus is observed in a wide temperature range from 77 to 1170 K. This indicates on high content of acceptor point defect P_{Te} , which is located at ~ 0.05 eV above the top of valence band. In an atmosphere of cadmium vapor the samples possess p- type conductivity up to the temperature of ~ 700 K, above 940 K the conductivity becomes of n-type due to increasing of own donor concentration (Cd_i^{2+}). Isothermal dependences of the Hall constant for CdTe:P and undoped CdTe differ significantly, which is caused by the influence of the impurity. Using IR microscopy it was investigated that phosphorus has high solubility in CdTe crystals and its introduction practically don't leads to creation of inclusions second phase.

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Електричні властивості монокристалів CdTe:P при низьких та високих температурах

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Досліджено властивості монокристалів CdTe:P, які були вирощені методом Бріджмена із розплаву з початковою концентрацією домішок 1×10^{19} ат/см³, при високих температурах (470-1170 К) за допомогою вимірювання ефекту Холла. Аналіз експериментальних результатів показує, що до температури близько 700 К зразки мали р-тип провідності, а вище 940 К – n-тип. Ізотермічні залежності константи Холла суттєво відрізняються від аналогічних залежностей для нелегованого матеріалу через вплив домішок. Акцепторна дія фосфору спостерігається до 1170 К завдяки високому вмісту акцепторної домішкової форми (P_{Te}). Результати низькотемпературних електричних вимірювань доводять, що домішка фосфору володіє високою розчинністю в кристалах CdTe. За допомогою ІЧ-мікроскопії встановлено, що при введенні фосфору в CdTe практично зникають включення другої фази завбільшки близько 1 мкм, що завжди спостерігаються в даному матеріалі.

Ключові слова: кадмій телурид, фосфор, ефект Холла, точкові дефекти, високотемпературні вимірювання.