

Ensemble of point defects in CdTe single crystals and films in the case of full equilibrium and quenching

V.V.Kosyak, A.S.Opanasyuk, I.Yu.Protsenko

Sumy State University, 2 Rimsky-Korsakov St., 40007 Sumy, Ukraine

The ensemble of point defects in CdTe undoped single crystals has been modeled. Two extreme cases were calculated: full equilibrium and quenching. Dependences of the point defect and free carrier concentrations on technological parameters of growing, post-growth annealing in Cd vapor, and the sample examination temperature have been studied. The growth conditions of single crystals and *n*- and *p*-type conductivity CdTe films were defined. The results obtained have been compared with experimental data. This made it possible to make conclusions concerning validity of the studied models and to propose additional experiments to make final choice between them.

Проведено моделювання ансамбля точечних дефектів в нелегированих монокристаллах і плівках теллурида кадмія. Розрахунки виконані для двох крайніх випадків — повного рівноваги і закалки дефектів. Отримані залежності концентрації власних дефектів, свободних носіїв заряду від технологічних параметрів вирощування, послеростового отжига в парах кадмія і температури дослідження образців. Определены условия изготовления монокристаллов и пленок CdTe *n*- и *p*-типа проводимости. Проведено сравнение полученных результатов с экспериментальными данными, что позволило сделать выводы относительно обоснованности рассмотренных моделей и предложить дополнительные эксперименты, позволяющие сделать окончательный выбор между ними.

A unique combination of physical properties in CdTe has drawn scientists' attention for a long time. The material is considered to be a promising one to produce a range of devices for semiconductor engineering, optoelectronics, microelectronics, solar power engineering, etc. [1,2]. However, complications in manufacturing of CdTe single crystals and films with programmable electrical and optical properties caused remarkable disappointment among the researchers. The only way to solve this problem is to synthesize layered cadmium chalcogenide with controlled ensemble of point defects (PDE), as it is just PDE that defines the structure-sensitive properties of the semiconductor. The method of quasi-chemical reactions (QR) [3] is often used at present to model PDE in CdTe and then to choose optimum physico-technologic parameters of growing and post-growth material treatment to obtain crystals with pre-specified properties.

De Noble was the first who has calculated theoretically PDE in cadmium telluride at high temperatures [4]. Later, numerous authors [5–11] used the QR method to model state of the defects in the undoped and doped material. Consideration of those works shows that initially, the researchers preferred the model where disordering of the material occurs according to Frenkel mechanism in the cadmium sublattice. At the same time, it was supposed that interstitial atoms appear in the course of crystal growth due to excess of cadmium, when vacancies appear due to excess of tellurium. This is a traditional model that is widely used when calculating PDE in the material [2, 3, 5]. The model developed by Chern presents an alternative point of view [6]. According to this model, interstitial atoms and vacancies appear either in cadmium or tellurium sublattice. Later, the existence of anti-

Table 1. Main models of CdTe defect structure

References	Types of defects								
	V_{Cd}^-	V_{Cd}^{2-}	Cd_i^+	Cd_i^{2+}	V_{Te}^+	V_{Te}^{2+}	Te_i^-	Te_{Cd}^{2+}	Cd_{Te}^{2-}
[1]	-	+	+	-	+	-	-	-	-
[2, 3]	+	+	+	-	-	-	-	-	-
[4, 5]	+	+	+	+	-	-	-	-	-
[6]	+	-	-	+	-	+	+	-	-
[9]	-		+	+	+	+	-	+	+
[10-12]	+	+	+	+	-	+	+	-	-
[13]	+	+	-	+	-	+	+	+	-
[14]	+	+	+	+	-	+	+	-	-
[16]	+	+	-	+	+	+	+	+	-

structural defects Te_{Cd}^{2+} in CdTe was supposed [12] and proved experimentally [13]. A more sophisticated model with antisite defects present in the material both in cadmium and tellurium sublattices is considered in [14]. The range of opinions concerning charge states of intrinsic defects and depth of occurrence of their energy levels in CdTe band gap (BG) is extremely wide [1-6, 12].

Last few years, a new period in research on CdTe defect structure is opened using a new method to calculate the PDE formation energy in semiconductors *ab initio*, i.e. basing on quantum-mechanical and thermodynamical parameters of atoms in the material [15]. This method made it possible to define the intrinsic defect ionization energy in CdTe and determine their charge state thereof [16]. We should note that even with the *ab initio* method, it is yet impossible to calculate the occurrence depth of energy levels in BG of the material as accurately as it is necessary. However, the model from [16] must be considered such one that reflects the real situation most adequately.

The basic models used to calculate PDE in CdTe are presented in Table 1. Considering the literature data, one can conclude that there is now no common opinion concerning the type and electric activity of defects in cadmium telluride. At the same time, experimental data are interpreted according to ideas of the PDE model in the material used by this or that scientist. The analysis is still more complicated due to the fact that in most of the works, PDE is modeled for the case of full equilibrium, while practical research is usually carried out on samples that are quenched to room temperature. As a rule, the presence of uncharged

defects is disregarded, what makes it more difficult to compare the calculated and experimental data.

Review of bibliography also proves that there is no data about PDE modeling in CdTe films. Still, there are numerous experimental works aimed at investigation of electro-physical properties of those objects, and the films themselves are widely used as base layers in various microelectronic devices. These are the reasons that determined the aims and objects of this work. Basing on conventional and the latest concepts of the nature of intrinsic defects in the material, we have modeled PDE state in cadmium single crystals annealed in cadmium vapor for two extreme cases: full equilibrium and quenching. The results obtained have been used to research the equilibrium of intrinsic defects in CdTe films deposited in various physical conditions. Refined data on QR constants were used in calculations. In our opinion, the comparison of the calculated results with experimental data will provide the final choice between the basic models of CdTe defect structure.

Quasichemical description of PDE in CdTe single-crystals for the case of full equilibrium. In practice, the grown CdTe single crystals are usually annealed for a long time at 735 to 900°C in cadmium or tellurium vapor to obtain samples with pre-specified electrophysical properties. At present, two models of defects are considered to be the most valid and describe experimental results well enough. We used both of them to describe the equilibrium state of PDE in CdTe single crystals being annealed under cadmium overpressure. According to the model proposed in [2, 5], the intrinsic defects are supposed to appear according to the Frenkel

Table 2. Quasichemical reactions of defect forming and their thermodynamical parameters, $K = K_0 \cdot \exp(-\Delta H/kT)$ or $K = K_0 \cdot \exp(-\Delta E/kT)$.

№	Equation of reaction	Equilibrium constant	Thermodynamical parameters		
			$K_0, (\text{Pa}^{-1}, \text{Pa}, \text{cm}^{-3}, \text{cm}^{-6})$	$\Delta H, \Delta E, \text{ eV}$	
				[5,10]	[16]
Model of defects according to work [2,5]					
1	$\text{Cd}^{\text{G}} + \text{V}_{\text{I}}^0 \leftrightarrow \text{Cd}_{\text{I}}^+ + e^-$	$K_r \cdot P_{\text{Cd}} = R = n \cdot [\text{Cd}_{\text{I}}^+][\text{V}_{\text{I}}^0]^{-1} \approx n \cdot [\text{Cd}_{\text{I}}^+]$	10^{25}	-0.81	-0.81
2	$\text{Cd}_{\text{Cd}}^0 \leftrightarrow \text{V}_{\text{Cd}}^- + \text{Cd}_{\text{I}}^+$	$K_F = [\text{V}_{\text{Cd}}^-] \cdot [\text{Cd}_{\text{I}}^+]$	10^{25}	1.37	1.37
3	$\text{Cd}_{\text{I}}^0 \leftrightarrow \text{Cd}_{\text{I}}^+ + e^-$	$K_1 = [\text{Cd}_{\text{I}}^+] \cdot n \cdot [\text{Cd}_{\text{I}}^0]^{-1}$	$3.55 \cdot 10^{14} \cdot T^{3/2}$	0.02	0.02
4	$\text{Cd}_{\text{I}}^+ \leftrightarrow \text{Cd}_{\text{I}}^{2+} + e^-$	$K_2 = [\text{Cd}_{\text{I}}^{2+}] \cdot n \cdot [\text{Cd}_{\text{I}}^+]^{-1}$	$8.75 \cdot 10^{13} \cdot T^{3/2}$	0.21	0.20
5	$\text{V}_{\text{Cd}}^0 \leftrightarrow \text{V}_{\text{Cd}}^- + h^+$	$K_3 = [\text{V}_{\text{Cd}}^-] \cdot p \cdot [\text{V}_{\text{Cd}}^0]^{-1}$	$2.44 \cdot 10^{15} \cdot T^{3/2}$	0.05	0.20
6	$\text{V}_{\text{Cd}}^{2-} \leftrightarrow \text{V}_{\text{Cd}}^- + e^-$	$K_4 = [\text{V}_{\text{Cd}}^-] \cdot n \cdot [\text{V}_{\text{Cd}}^{2-}]^{-1}$	$8.75 \cdot 10^{13} \cdot T^{3/2}$		
7	$0 \leftrightarrow e^- + h^+$	$n \cdot p = K_i = f(T_p)$	$5 \cdot 10^{39}$	1.50	1.50
8	$n + [\text{V}_{\text{Cd}}^-] + 2 \cdot [\text{V}_{\text{Cd}}^{2-}] = p + [\text{Cd}_{\text{I}}^+] + 2 \cdot [\text{Cd}_{\text{I}}^{2+}]$				
Model of defects according to work [16]					
9	$\text{Cd}^{\text{G}} \leftrightarrow \text{Cd}_{\text{Cd}}^0 + \text{V}_{\text{Te}}^{2+} + 2e^-$	$K_8 = [\text{V}_{\text{Te}}^{2+}] \cdot n^2 \cdot P_{\text{Cd}}^{-1}$	$3 \cdot 10^{52}$	1.47	1.47
10	$\text{Cd}^{\text{G}} \leftrightarrow \text{Cd}_{\text{I}}^{2+} + 2e^-$	$K_9 = [\text{Cd}_{\text{I}}^{2+}] \cdot n^2 \cdot P_{\text{Cd}}^{-1}$	$8 \cdot 10^{55}$	2.09	2.09
11	$\text{Cd}_{\text{Cd}}^0 + e^- \leftrightarrow \text{V}_{\text{Cd}}^- + \text{Cd}^{\text{G}}$	$K_{11} = [\text{V}_{\text{Cd}}^-] \cdot n^{-1} \cdot P_{\text{Cd}}$	$8 \cdot 10^{11}$	2.08	2.08
12	$\text{CdTe} + e^- \leftrightarrow \text{Te}_{\text{I}}^- + \text{Cd}^{\text{G}}$	$K_{12} = [\text{Te}_{\text{I}}^-] \cdot n^{-1} \cdot P_{\text{Cd}}$	$4 \cdot 10^7$	1.19	1.19
13	$\text{Cd}_{\text{I}}^0 \leftrightarrow \text{Cd}_{\text{I}}^+ + e^-$	$K_1 = [\text{Cd}_{\text{I}}^+] \cdot n \cdot [\text{Cd}_{\text{I}}^0]^{-1}$	$3.5 \cdot 10^{14} \cdot T^{3/2}$	0.02	0.02
14	$\text{Cd}_{\text{I}}^+ \leftrightarrow \text{Cd}_{\text{I}}^{2+} + e^-$	$K_2 = [\text{Cd}_{\text{I}}^{2+}] \cdot n \cdot [\text{Cd}_{\text{I}}^+]^{-1}$	$8.75 \cdot 10^{13} \cdot T^{3/2}$	0.21	0.20
15	$\text{V}_{\text{Cd}}^0 \leftrightarrow \text{V}_{\text{Cd}}^- + h^+$	$K_3 = [\text{V}_{\text{Cd}}^-] \cdot p \cdot [\text{V}_{\text{Cd}}^0]^{-1}$	$2.44 \cdot 10^{15} \cdot T^{3/2}$	0.05	0.20
16	$\text{V}_{\text{Cd}}^{2-} \leftrightarrow \text{V}_{\text{Cd}}^- + e^-$	$K_4 = [\text{V}_{\text{Cd}}^-] \cdot n \cdot [\text{V}_{\text{Cd}}^{2-}]^{-1}$	$8.75 \cdot 10^{13} \cdot T^{3/2}$	0.70	0.80
17	$\text{V}_{\text{Te}}^+ \leftrightarrow \text{V}_{\text{Te}}^{2+} + e^-$	$K_{15} = [\text{V}_{\text{Te}}^{2+}] \cdot n \cdot [\text{V}_{\text{Te}}^+]^{-1}$	$8.75 \cdot 10^{13} \cdot T^{3/2}$	0.50	0.50
18	$\text{V}_{\text{Te}}^0 \leftrightarrow \text{V}_{\text{Te}}^+ + e^-$	$K_{\text{V}_{\text{Te}}} = [\text{V}_{\text{Te}}^+] \cdot n \cdot [\text{V}_{\text{Te}}^0]^{-1}$	$3.5 \cdot 10^{14} \cdot T^{3/2}$	0.40	0.40
19	$\text{Te}_{\text{I}}^0 \leftrightarrow \text{Te}_{\text{I}}^- + h^+$	$K_{\text{Te}_{\text{I}}} = [\text{Te}_{\text{I}}^-] \cdot p \cdot [\text{Te}_{\text{I}}^0]^{-1}$	$2.44 \cdot 10^{15} \cdot T^{3/2}$	0.80	0.80
20	$\text{Te}_{\text{I}}^- + \text{V}_{\text{Cd}}^{2-} \leftrightarrow \text{Te}_{\text{Cd}}^{2+} + 5e^-$	$K_{14} = [\text{Te}_{\text{Cd}}^{2+}] \cdot n^5 \cdot [\text{Te}_{\text{I}}^-]^{-1} \cdot [\text{V}_{\text{Cd}}^{2-}]^{-1}$	$2.5 \cdot 10^{82}$	3.76	3.76
21	$\text{Te}_{\text{Cd}}^0 \leftrightarrow \text{Te}_{\text{I}}^{2+} + 2e^-$	$K_{16} = [\text{Te}_{\text{I}}^{2+}] \cdot n^2 \cdot [\text{Te}_{\text{Cd}}^0]^{-1}$	$8.5 \cdot 10^{13} \cdot T^{3/2}$	0.40	0.40
22	$0 \leftrightarrow e^- + h^+$	$n \cdot p = K_i = f(T_s)$	$5 \cdot 10^{39}$	1.50	1.50

mechanism in cadmium sublattice only. The model comprises the following types of point defects: $(\text{Cd}_{\text{I}}^0, \text{Cd}_{\text{I}}^+, \text{Cd}_{\text{I}}^{2+}, \text{V}_{\text{Cd}}^0, \text{V}_{\text{Cd}}^-, \text{V}_{\text{Cd}}^{2-})$. The second model is based on calculations of intrinsic defect ionization energy in CdTe [16]. Its simplified variant was used in later works [8–11] to calculate PDE in the material. According to this model, the semiconductor may comprise a wide range of defects including vacancies, interstitials, and

antisite defects in different charge states $(\text{Cd}_{\text{I}}^0, \text{Cd}_{\text{I}}^{2+}, \text{V}_{\text{Te}}^0, \text{V}_{\text{Te}}^+, \text{V}_{\text{Te}}^{2+}, \text{V}_{\text{Cd}}^0, \text{V}_{\text{Cd}}^-, \text{V}_{\text{Cd}}^{2-}, \text{Te}_{\text{I}}^0, \text{Te}_{\text{I}}^-, \text{Te}_{\text{Cd}}^{2+})$.

The set of QR based on the model of defects presented in [2, 5] is shown in Table 2 (equations (1)–(8)). Equations (9)–(23) correspond to the alternative model of defects. The same table contains the values of thermodynamic parameters used to calculate the QR constants. The corresponding thermodynamic constants are taken from [3, 5,

8, 16]. Note that in [8], using an original procedure to optimize results of Hall effect measurements at high temperatures, K_0 , ΔH , ΔE values have been obtained that are likely to be the most reliable at present. In the modeling, we used two somewhat different sets of defect level energy values in the BG of the material. The missing constants K_0 or K were calculated as described in [3], with effective electron mass $m_n^* = 0.11 \cdot m_0$ and hole mass $m_p^* = 0.83 \cdot m_0$ [2, 5].

In the set of equations used to calculate PDE in the material, equations (1), (9)–(12) describe the cadmium vapor-intrinsic defects equilibrium; reactions (2)–(6), (13)–(21), the intrinsic structural defects equilibrium in the solid phase; (7), (22), stimulation of chalcogenide intrinsic conductivity; (8), (23) are equations of semiconductor electric neutrality. In these expressions V_{Te} , V_{Cd} , denote tellurium and cadmium vacancies, respectively; Te_i , Cd_i , interstitials; Te_{Cd} , antisite defect (tellurium in cadmium site); e^- , h^+ electrons and holes, respectively, n , p being the concentrations thereof; P_{Cd} , partial pressure of cadmium in the course of sample annealing; ΔH , ΔE , the defect forming enthalpy and ionization energy, respectively; k , the Boltzmann constant; T_s temperature of single crystal annealing. Index G corresponds to atoms in vapor phase. The joint solution of the sets of equations (1)–(8) and (9)–(23) for the first and second models, respectively, makes it possible to define all types of defects concentration for the case of full equilibrium using QR constant K and partial pressure of cadmium vapor P_{Cd} or temperature of sample annealing T_s .

Conductivity and charge carrier concentration in cadmium telluride samples are measured mostly at temperatures close to room one, though single crystals themselves are grown at higher temperatures. As a result, the real PDE state in the semiconductor corresponds to their partial equilibrium at some intermediate temperature. The higher cooling rate of the samples is, the closer is the final concentration of defects to the equilibrium at the single crystal growing temperature. In this case, the comparison of calculated data with experimental ones is more adequate, if PDE state in the material is described by means of the model of partial equilibrium or quenching [3].

We used the following reasoning to calculate the concentration of defects for the quenching case. If the samples are quenched

quickly enough, the PDE that appears in CdTe at high temperature is frozen. However, the quenching does not influence the equilibrium balance of electrons and holes. As a result, all the electrons and holes recombine at a low enough temperature, and the intrinsic defects capture excessive free carriers and become neutral. To take these processes into account, one should add to the set of quasi-chemical reactions describing full equilibrium state additional equations that characterize the constancy of total concentration of charged and neutral vacancies and interstitial atoms in the material in the course of quenching. In this case, the intrinsic defect concentration depends on the measurement temperature T_0 , that does not coincide as a rule with the temperature of single crystal growing or annealing, T_s .

Additional equation for the first model of defects is the following:

$$[Cd_i^+] + [Cd_i^{2+}] + [Cd_i^0] = [Cd]_{tot} = f(T_s), \quad (1)$$

$$[V_{Cd}^-] + [V_{Cd}^{2-}] + [V_{Cd}^0] = [V_{Cd}]_{tot} = f(T_s), \quad (2)$$

with $[Cd]_{tot}$, $[V_{Cd}]_{tot}$ standing for total defect concentration in samples in full equilibrium.

For the second model of defects, the following ratios are to be added to equations (3) and (4):

$$[Te_i^-] + [Te_i^0] = [Te_i]_{tot} = f(T_s), \quad (3)$$

$$[V_{Te}^+] + [V_{Te}^{2+}] + [V_{Te}^0] = [V_{Te}]_{tot} = f(T_s). \quad (4)$$

Solution of the sets of equations enlarged in such a way makes it possible to calculate the PDE concentration in quenched samples depending on technological parameters of growing and temperature of crystal investigation. Note that we get an over-defined set of equations, i.e. the number of equations exceeds that of unknown defect concentrations. The reason is that some of the equations are interrelated.

Fig. 1 shows the numerical calculation results of PDE and free carriers concentration in cadmium telluride depending on P_{Cd} for the cases of full equilibrium and quenching using models 1 and 2. When the partial equilibrium model was used, the temperature of sample investigation was assumed to be equal to room one ($T_0 = 293$ K). Fig. 2 presents the respective dependences in coordinates $N \cdot 10^3 / T$, assuming that chalcogenide was formed under ex-

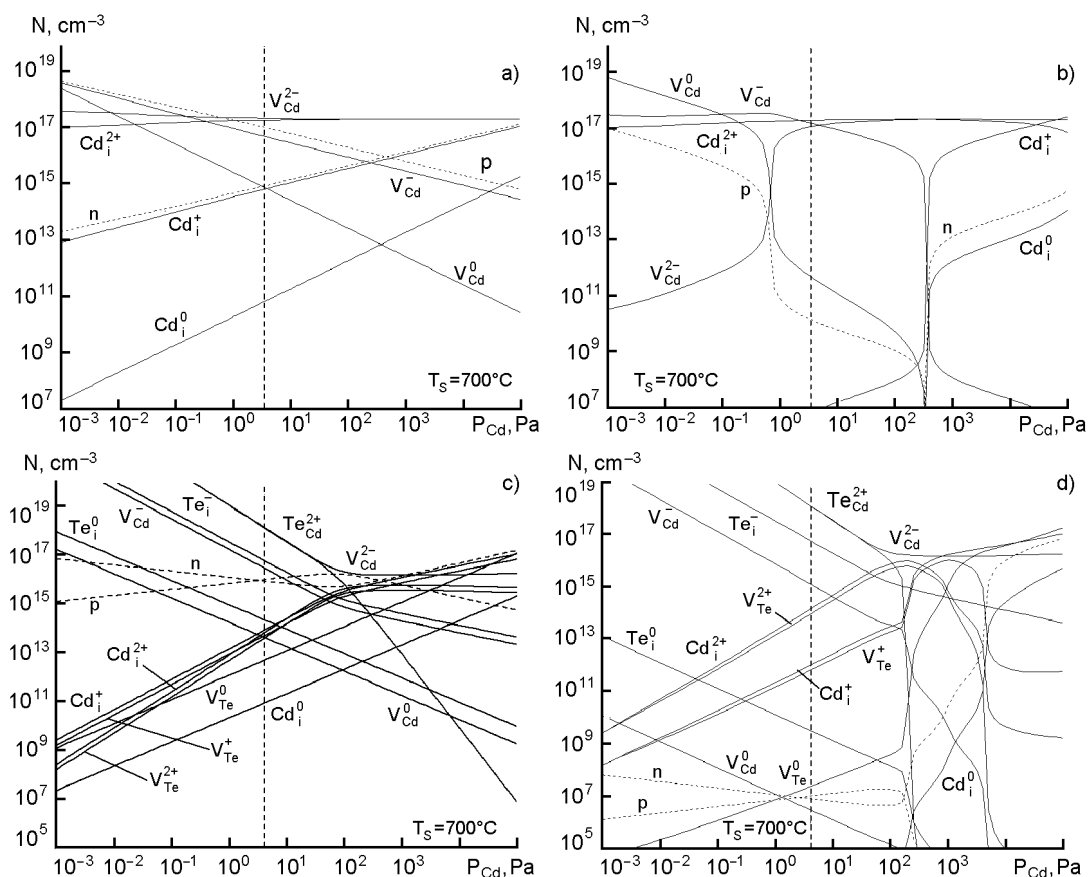


Fig. 1. Concentration of intrinsic point defects and free charge carriers at different partial pressures of cadmium vapor at the temperature of CdTe single crystal annealing. The first model of defects: full equilibrium (a); quenching (b). The second model of defects: full equilibrium (c); quenching (d).

cess cadmium pressure P_{min} . The Hall concentration of charge carriers is the main parameter of cadmium telluride determined experimentally. Therefore, we calculated dependence of this value on P_{Cd} in the course of the material annealing basing on $n_H = n - p$ ratio, where $p = K_i/n$. The corresponding dependences for various PDE models and cooling rates are shown in Fig. 3a. The same Figure displays the experimental measuring results of the Hall carrier concentration in chalcogenide according to the data in [16]. Finally, critical pressure of the material annealing causing the conductivity type inversion in the semiconductor was determined, the results are presented in Fig. 4. The second model was used to define dependences that are taken as an example. The same Figure shows dependences of Hall charge carrier concentration on cadmium pressure for the cases of full equilibrium and quenching of CdTe at various annealing temperatures.

Where possible, we got analytical dependences of defect concentration on technological parameters and compared corresponding values with the calculated results.

Quasi-chemical description of PDE in CdTe films in cases of full equilibrium and defect quenching. When investigating the defect formation processes in thin films, we considered the two extreme cases: full equilibrium and defect quenching, the same way as with single crystals. The calculations were carried out for the same alternative models of defects used above. We considered the case of layer deposition by means of semiconductor and cadmium co-evaporation from two separate sources. It is possible to change cadmium vapor pressure over the substrate through a wide range of values by changing the temperature of the additional source. The modeling was carried out for evaporator temperature T_e and substrate temperature T_s usually used when cadmium telluride films are condensed.

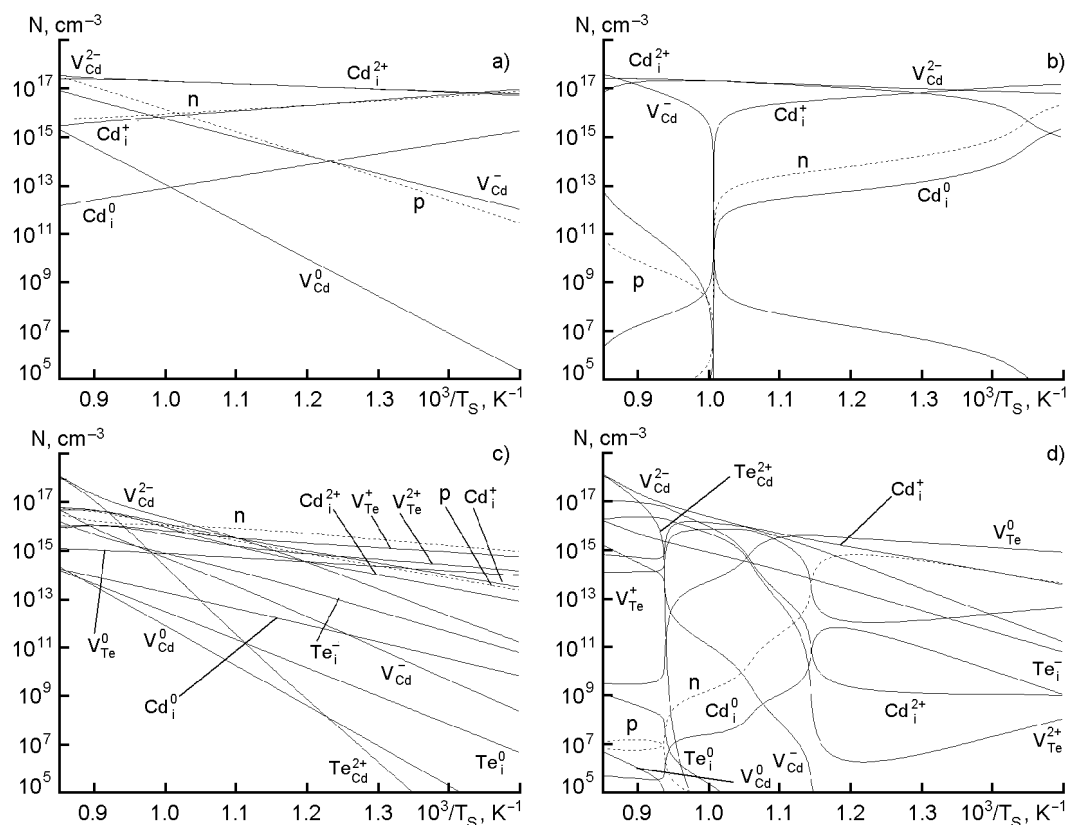


Fig. 2. Concentration of intrinsic point defects and free charge carriers at different temperatures of CdTe single crystal annealing at $P_{Cd} = 60$ Pa. The first model of defects: full equilibrium (a); quenching (b). The second model of defects: full equilibrium (c); quenching (d).

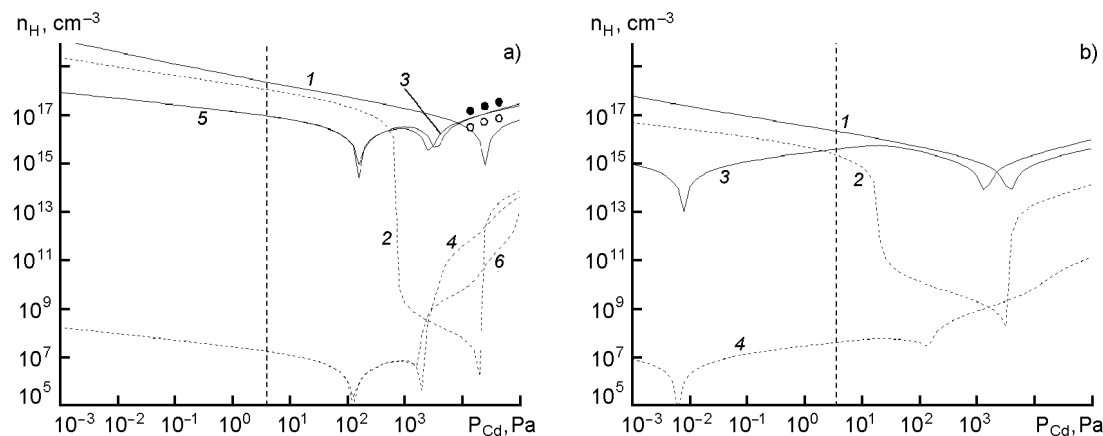


Fig. 3. Hall concentration of free charge carriers at different partial pressure of cadmium vapor (a) calculated for a single-crystal, model of defects [5]: full equilibrium (1), quenching (2); model of defects [16]: full equilibrium (3, 5), quenching (4, 6). To calculate curves 3 and 4, the set of constants [5, 10] is used; for curves 5 and 6, the set [10, 16]. $T_s = 900^\circ\text{C}$. $T_0 = 293^\circ\text{C}$. Experimental data denoted by points. (b) calculated for films, model of defects [5]: full equilibrium (1), quenching (2); model of defects [16]: full equilibrium (3), quenching (4). $T_e = 700^\circ\text{C}$. $T_s = 500^\circ\text{C}$.

In this case, to describe the full equilibrium state of PDE in CdTe films, the QR sets presented in Table 2 can be used, however, two new relations are to be added

thereto. The first of them describes evaporation of the compound at the evaporator temperature T_e and takes into account the compound dissociation at its transition

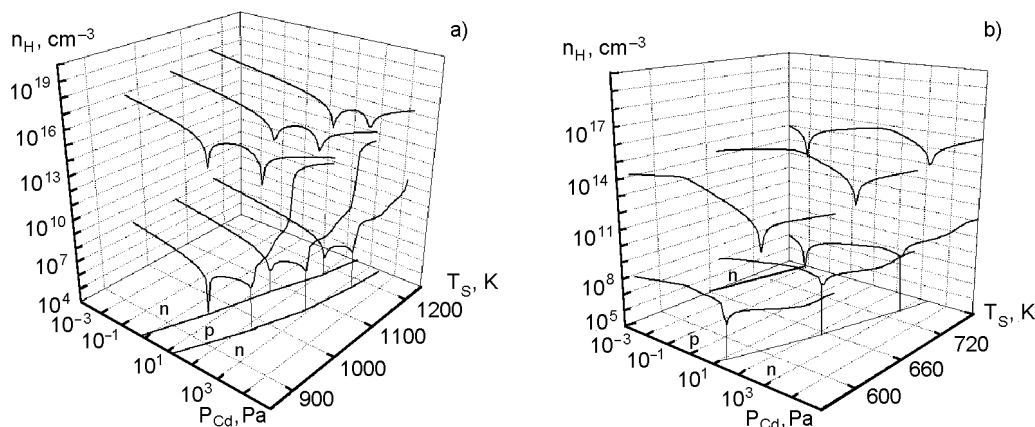
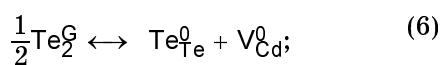
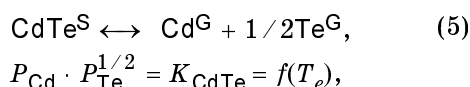


Fig. 4. Critical pressure of cadmium vapor corresponding to inversion of CdTe conductivity type at various temperatures T_s : (a) single crystals, (b) films. $T_e = 700^\circ\text{C}$. Model of defects [16]. Hall concentrations of charge carrier for the case of full equilibrium and quenching at different P_{Cd} are also shown.

from the solid phase (S) into vapor (G). The second equation describes equilibrium in the tellurium vapor-condensate system when intrinsic defects appear in CdTe film at the deposition (substrate) temperature T_e



$$\frac{[\text{V}_{\text{Cd}}^0]}{P_{\text{Te}_2}^{1/2}} = K_{\text{Te}_2} = f(T_s).$$

The joint solution of the QR set enlarged in such a way made it possible to define dependences of concentrations of intrinsic defects, free charge carriers, Hall charge carriers on P_{Cd} for various physico-technological conditions of layer condensation (T_s and T_e). These results are presented in Figs. 3b, 4b, and 5a, c. The defect concentration calculated for the full equilibrium basing on the above-mentioned methods are used to determine the corresponding parameters in CdTe films subjected to quenching. These dependences are shown in Figs. 5b, d. In all the figures, the vertical dotted line marks the P_{min} position.

The calculation results of PDE state in CdTe single crystals using the first model (Figs. 1a, b, 2a, b) made it possible to establish that such a type of the point defects in the material as cadmium interstitials with charge states Cd_i^+ and Cd_i^{2+} prevail in cadmium high pressure range while in low pressure one, the structure-sensible proper-

ties of the semiconductor are defined by the V_{Cd}^- and V_{Cd}^0 vacancies. The charged cadmium interstitials are shallow state donors and the charged vacancies are acceptors, therefore, when P_{Cd} becomes lowered during the chalcogenide annealing, concentration of electrons in the material decreases, and as a consequence, the material conductivity type is changed (Fig. 3a, curve 1). As P_{Cd} decreases in the cadmium low pressure range, the CdTe conductivity rises because of increased holes concentration.

Quenching of single crystal samples results in considerable change of PDE state in the semiconductor (Figs. 1b, 2b). As a consequence, the material resistance increases in some range of cadmium pressure by almost eight orders (Fig. 3a, curve 2). The pressure values and P_{Cd} range where the material becomes semiconductive are defined by the material annealing temperature. As T_s goes down, the cadmium pressure range enlarges and shifts to lower P_{Cd} range. Besides, in $n_H - P_{\text{Cd}}$ dependence (Fig. 3a, curve 2), a pressure range is observed where the material conductivity does not decrease so considerably (by 2–3 times as compared to equilibrium state of defects). But the task to grow in this range CdTe crystals of high conductivity by providing intrinsic charged defects is still complicated.

The results we got basing on the second model of intrinsic defects in chalcogenide (Figs. 1c, d; 2c, d) are of great interest. As the calculations show, in the high cadmium pressure range, the structure-sensible properties of single crystals are defined by Cd_i^+ and Cd_i^{2+} and interstitial atoms, while in the low pressure range, $\text{V}_{\text{Cd}}^{2-}$ and $\text{Te}_{\text{Cd}}^{2+}$

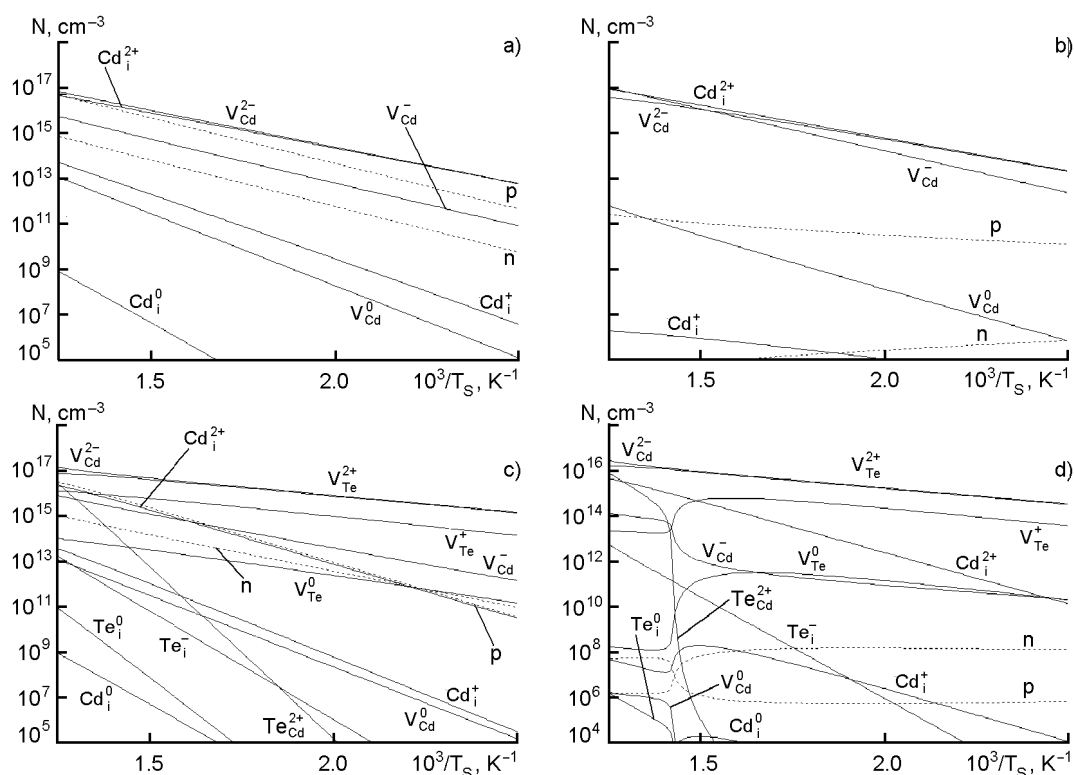


Fig. 5. Intrinsic point defects concentration in CdTe film at various substrate temperatures T_s . The first model of defects: (a) full equilibrium; (b) quenching. The second model of defects: (c) full equilibrium; (d) quenching. $T_e = 700^\circ\text{C}$, $P_{\text{Cd}} = 60$ Pa.

defects are dominating in CdTe. At the same time, the concentration of the latter defects increases very quickly as P_{Cd} decreases, and goes beyond the bounds of the material homogeneity region. The region of solid solutions existence within the investigated temperature range makes up 10^{19} to 10^{20} cm^{-3} . This fact evidences that tellurium precipitates may be formed in the semiconductor, obtained at $P_{\text{Cd}} < 10^{-1}$ to 10^2 Pa (depending on T_s). Note that the alternative model of defects, as well as the first one, predicts the change of conductivity type from n to p -type as P_{Cd} decreases (Fig. 3a, curves 3, 5). The corresponding values of cadmium critical pressures increase as the material annealing temperature rises. The pressures at which conductivity type of the semiconductor is changed, predicted by the two models, are close enough. The same concerns CdTe conductivity in high P_{Cd} region. Most of the experimental data are obtained in this very region, therefore it is rather difficult to make a choice between the two models. The reason is that both of them describe experimental data well enough, but better coincidence is observed in the data

(Fig. 3a), obtained on the basis of the second model.

A characteristic feature of the model of defects [16] is an additional change of CdTe conductivity from p to n -type in low cadmium pressure area (Fig. 3a, curves 3, 5). These technological conditions correspond to the material annealing under excessive tellurium pressure. The antisite defect being a donor appears as the interstitial atom Te_i substitutes V_{Cd} . This causes formation of the n -type conductivity material in this region. This is possible because this defect formation enthalpy $\Delta H_{\text{Te}_{\text{Cd}}} = 3.76$ eV is lower than that of cadmium vacancy formation $\Delta H_{\text{V}_{\text{Cd}}} = 4.75$ eV. We should mention that in [13], n -type conductivity CdTe was observed in experiment to be formed at annealing in chalcogenide vapor, but chlorine doped material was used. The authors [11] who also used chlorinated semiconductor have obtained similar results proceeding from the model somewhat simpler than the present one. The results of modeling prove that similar effect must be observed as well in the undoped material annealed under excessive tellurium pressure. In our opinion,

similar investigations are of importance today and should help to determine the real defect structure of cadmium telluride.

When the samples are quenched, the semiconductor PDE changes considerably (Fig. 3a, curves 4, 6), and as a result, CdTe takes insulating properties within almost the whole range of investigated cadmium vapor pressures. The conductivity of chalcogenide turns out to be lower than it is predicted in the first model (Fig. 3a, curve 2). It should be noted that dependences of PDE concentration and free charge carriers on P_{Cd} (Fig. 3a, curves 3, 5, 4, 6) were not changed considerably as different data sets on energy of point defects in cadmium telluride were used. This proves that our calculations are highly reliable and correspond to the real situation. The PDE state in films is similar to that in single crystals. The temperature of film growing defines to a great extent the pressure at which the semiconductor conductivity is changed from p - to n -type. As T_s grows, the critical pressure of conductivity inversion increases, though the character of the free carrier concentration change remains almost the same. The second model of defects predicts, as well as in single crystals, that it is possible to get the n -type conductivity chalcogenide in the very low cadmium pressure region ($P_{\text{Cd}} < 10^{-2}$ Pa) (Fig. 3a, curves 3, 4) and high condensation temperatures (Fig. 4b). At temperature $T_s < 400^\circ\text{C}$, it is impossible to get electron material under high tellurium pressure throughout the whole range of P_{Cd} changes (Fig. 3b, curve 4). In the case of film quenching, by analogy with single crystals, the conductivity decreases by 6–9 orders (Fig. 3b, curve 2). According to the first model, the region where the layers have half-insulating properties, is wider (Fig. 3b, curve 2) in comparison with single crystals (Fig. 3a, curve 2). According to the second model, the film conductivity is decreased more considerably, it is observed throughout the whole range of the investigated P_{Cd} values (Fig. 3b, curve 4).

In conclusion, the QR method has been used to model PDE in CdTe single crystals and films for the cases of high temperature defects equilibrium and quenching at annealing under excessive cadmium pressure. We used two models of defects, which are considered to be the most valid at present. The nature of dominating defects in the material of n - and p -type conductivity has been determined. The calculations have shown that both models give close enough values of charge carrier concentration in the mate-

rial within high cadmium pressure region and predict inversion of chalcogenide conductivity from p to n -type as P_{Cd} increases. At the same time, the model of defects given in [16] shows that the n -type conductivity chalcogenide exists in the region of low cadmium pressure. Experimental observations of changes of the undoped material conductivity during annealing under excessive tellurium pressure have to give evidences in favor of this theory or deny it. Quenching of the samples formed under excessive cadmium pressure in a wide range of P_{Cd} causes considerable decrease of cadmium telluride conductivity. This effect is more pronounced in the case of films. On the one hand, this makes it possible to get easily cadmium chalcogenide with semi-insulating properties, which is a promising material as a base layer for γ -detectors instead of chlorine doped CdTe. On the other hand, this reduces opportunities to regulate the material conductivity by changing its stoichiometry. As a result, it is difficult to get layers of cadmium telluride with high conductivity, a promising material in the field of solar energy, for example.

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Ансамбль точкових дефектів у монокристалах та плівках CdTe у випадках повної рівноваги та гартування

В.В.Косяк, А.С.Опанасюк, І.Є.Проценко

Проведено моделювання ансамблю точкових дефектів у нелегованих монокристалах і плівках телуриду кадмію. Розрахунки виконано для двох крайніх випадків — повної рівноваги і загартування дефектів. Одержано залежності концентрації власних дефектів, вільних носіїв заряду від технологічних параметрів вирощування, післяростового відпалу у парах кадмію і температури дослідження зразків. Визначено умови виготовлення монокристалів і плівок CdTe *n* і *p*-типу провідності. Проведено порівняння отриманих результатів з експериментальними даними, що дозволило зробити висновки щодо обґрунтованості розглянутих моделей і запропонувати додаткові експерименти, які дозволяють зробити остаточний вибір між ними.