Thermodynamic analysis of processes creating the defects in cadmium telluride crystals under conditions of high-temperature annealing

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Abstract. The defective structure of specifically undoped cadmium telluride crystals was researched using the theory of thermodynamic potentials. The calculated concentration of point defects and free charge carriers in the CdTe crystals, depending on technological factors of two-temperature annealing (annealing temperature T and partial pressure of cadmium P_{Cd} vapor). The dominant types of defects that determine the basic properties of the material n- and p-type conduction were determined.

Keywords: two-temperature annealing, thermodynamic potential, point defects, electrical properties, cadmium telluride.

1. Introduction

As the point defects determine basic properties of semiconductor materials, their characteristics can be studied by modeling their imperfect structure.

To calculate the equilibrium concentration of defects, the method of quasi-chemical reactions by Kreger is mainly used [1-8], empirically determined equilibrium constants K_0 and enthalpies for reactions of defects formation ΔH are being used in it. But considerable interest is caused by the works [9-11] where researches of point defects in the structure were performed using the theoretically determined energies of defects formation and change in the vibration frequency of atoms in the vicinity of the defect at its creation. The use of thermodynamic parameters of defects defined *ab initio* allows to calculate constants of equilibrium for the subsequent comparison with various experimental results. The latter often have considerable variations, especially in the cases when concentrations of a few dominant defects are close to each other. Also, this calculation is especially important for situations where constants are not determined or to do this in experiments is quite difficult.

Without regard, that in the works [9-11], with the use of theoretically determined parameters of defects [12], satisfactory accordance of the calculated and experimentally measured concentrations of charge carriers was obtained. But in our opinion, the parameters of some defects (energies of creation and energy of ionization) are not fully corresponding to experimental data, as it follows from the analysis presented in the work.

Thus, the problem to determine the influence of lattice disordering on properties of cadmium telluride crystals remains topical. The purpose of this work is to study the influence of two-temperature annealing technological condition on creation of the defect structure in crystals and their electric properties. To numerically calculate the equilibrium concentrations of point defects under conditions of high temperature annealing in vapors of components, we did not use any quasi-chemical formalism but instead the general thermodynamic equation of phase equilibrium in the heterogenic system.

2. Method of experiment

The crystals for investigations were grown by the Bridgman method. For a synthesis, we used the cadmium КД-0000 and tellurium – ТВ-4 (according to a certificate, content of basic substance was not less than 99.9999 % and 99.9997 %, accordingly), additionally cleaned by the method of zone melting. The concentration of non-controlled background impurities, as a rule, did not exceed $10^{-5} - 10^{-6}$ wt.% .

The high temperature measurements of the Hall effect were performed using the samples placed into a vacuum ampoule in a two-area stove, where the first area provided the temperature of samples, and the second one – temperature of Cd. Adjustment of both areas was carried out by a computer that received a signal from two thermocouples located, accordingly, near the sample and more cold end of ampoule, the temperature of which determined the pressure of Cd vapors. The accuracy of keeping the temperature was ±0.5 K. The temperature of both areas could be linearly changed within the wide interval of speeds, both when heating and cooling. Managing the whole commutation and taking the signals from all pairs of contacts and thermocouples was carried out by a computer and voltmeter.

3. Method to determine the equilibrium concentration of defects

The equilibrium concentrations of point defects in a crystal under two-temperature annealing are determined from the condition of equality of chemical potentials for every component in all phases of the system:

$$\mu_i^s = \mu_i^g, \text{ or } dG_i^s / dN_i^s = dG_i^g / dN_i^g, \quad (1)$$

where G^s, G^g and N^s, N^g are Gibbs thermodynamic potentials and concentrations of particles in a crystal and gas, accordingly; i – Cd, Te.

The Gibbs energy of crystal:

$$G = \sum (E + E_{vib})[D] + nE_c - pE_v - T(S_n + S_p + S_k), \quad (2)$$

where E is the energy of defect creation; F_{vib} is the free defect vibration energy; $[D]$ is the concentration of the defect D; n and p are concentrations of electrons and holes; E_c, E_v are energies of the conductivity band bottom of and top of the valence band, S_k is the configuration entropy, S_n and S_p are entropies of electrons in the conductivity band and holes in the valence band.

Summation was performed over all sublattices and all defects in each sublattice. Energies of singly and doubly ionized defects were determined using the formulas:

$$E_1 = E_0 - \frac{Z}{|Z|}\varepsilon_1, \quad E_2 = E_0 - \frac{Z}{|Z|}(\varepsilon_1 + \varepsilon_2), \quad (3)$$

where E_0 is the energy of creation of a neutral defect; Z is the charge state of the defect; ε_1, ε_2 are the first and second levels of defect ionization.

A change of the free vibration energy at defect creation was determined using the formula [13]:

$$F_{vib} = \pm(3kT\ln(T_\theta/T) - kT) + x \cdot 3kT\ln(\omega/\omega_0). \quad (4)$$

T_θ is the Debay temperature, x is an amount of atoms changing the frequency of intrinsic vibrations from ω_0 to ω.

The entropy was determined by the Boltzmann law:

$$S_k = k\ln\left(\prod W_j\right) = \sum k\ln\left(W_j\right) = \sum S_j, \quad (5)$$

where W_j is the thermodynamic probability of j sublattice. For a sublattice with several different types of defects:

$$W_j = \frac{J!}{(J - \sum[D])! \cdot \prod[D]!}, \quad (6)$$

where J is the concentration of knots where defects can appear.

For electrons and holes, thermodynamic probabilities are evened:

$$W_n = \frac{N_c!}{(N_c - n)!n!}, \quad W_p = \frac{N_v!}{(N_v - p)!p!}, \quad (7)$$

where

$$n = N_c \exp(\mu/kT), \quad p = N_v \exp(-(\mu + E_g)/kT), \quad (8)$$

N_c, N_v is the density of states in the conductivity band and in the valence band, accordingly, E_g is the bandgap energy, μ is the chemical potential of electrons determined from the equation of electro-neutrality:

$$N_c \exp(\mu/kT) - N_v \exp(-(\mu + E_g)/kT) = \sum Z \cdot [D^z]. \quad (9)$$

The chemical potential of defect, which equals to the chemical potential of component taken with the sign "+" or "–" depending on the type of defects, was determined by differentiation of the Gibbs energy with regard to the concentration of defects.

$$\mu_{D_i}^s = E_{D_i} - kT \cdot \ln\left(\frac{J - \sum[D]}{[D_i]}\right) +$$

$$+ \left[n\left(\frac{E_c}{kT} - \ln\left(\frac{N_c - n}{n}\right)\right) + p\left(\frac{E_v}{kT} - \ln\left(\frac{N_v - p}{p}\right)\right)\right] \times$$

$$\frac{kT \cdot Z_{D_i}}{\sqrt{\left(\sum Z[D]\right)^2 + 4N_c N_v \exp\left(-E_g / kT\right)}}. \quad (11)$$

The chemical potential of gas [14]:

$$\mu^g = kT\ln P + \mu_0. \quad (12)$$

In the case of monoatomic gas Cd:

$$\mu_0 = kT\left[-\ln(kT) + \ln\left(h^3 / (2\pi mkT)^{3/2}\right)\right]. \quad (13)$$

For diatomic gas Te$_2$:

$$\mu_0 = kT\left[-\ln(kT) + \ln\left(h^3 / (2\pi mkT)^{3/2}\right) + \ln(h^2 / 8\pi^2 IkT) + \ln(h\nu / kT)\right]. \quad (14)$$

Here, m is the mass of atom or molecule, $I = ml^2$ is the moment of molecule inertia, l is the inter-kernel distance in the molecule, ν is the internal frequency of molecular vibrations.

Thus, we got the system of equations of the type $\pm\mu_{D_i}^s = \mu_i^g$ allowing to find the equilibrium concentration of defects, which was solved by minimization of the quadratic function from deficiencies $\left(\pm\mu_{D_i}^s - \mu_i^g\right)$ [15]:

$$L_{\min} = \Sigma\left(\pm\mu_{D_i}^s - \mu_i^g\right)^2. \qquad (15)$$

The co-ordinates of a function minimum $L_{\min}$ are the equilibrium values of defect concentrations at the set pressure P and temperature T. To find concentrations of electrons and holes, we used formulas (8) where the chemical potential of electrons was determined using the formula (10).

Vacancies and intersticial atoms of Cd and Te such as V_{Cd}, V_{Te}, Cd_i, Te_i were considered as the main atomic defects. Each of these defects can be in three charge states: neutral, singly or doubly charged. Thus, $L_{\min}$ is a function of twelve variables.

The parameters of point defects that are used in calculations are shown in Table.

4. Energies of defects creation and energy of their ionization

Energies of defects creation are expected *ab initio* in the works [12, 16]. The main difference in calculations between these works consists in the choice of bases functions. In [12] we used a base built on the atomic functions of waves with $l \le 5$, and in [16] calculation was performed on the base of flat waves. The use of different bases was stipulated by the fact that the obtained energies of defects creation considerably differ between themselves. To calculate them, we used values determined in the work [16] (Table), because majority of them differ a little from energies of creation, which we obtained in experimental [6] and calculation works [9-10].

Table. Parameters of point defects in CdTe crystals.

	V_{Cd}	Cd_i	V_{Te}	Te_i
E, eV	2.67 [16]	2.04 [16]	3.24 [16]	3.41 [16]
ε_1, eV	$E_v+0.05$ [2]	$E_c-0.016$ [17]	$E_c-0.01$ [19]	$E_v+0.15$ [2]
ε_2, eV	$E_v+0.8$ [12]	$E_c-0.17$ [18]	$E_c-0.34$ [18]	$E_v+0.57$ [16]
x	4	5	4	5
ω/ω_0	3.75	0.25	1.60	0.15

Difficult and ambiguous is the task to determine a position of energy levels of defects in the bandgap of CdTe. Information of different authors strongly differs between itself [1, 2, 12, 16–27].

For the vacancy of cadmium, from data of different authors the first level of ionization makes $E_v+(\approx 0.06)$ eV [2, 21, 23, 24] or $E_v+(\approx 0.15$-$0.20)$ eV [1, 12, 16]. The experimentally observed level $E_v+(\approx 0.06)$ eV is one of the most intensive, and authors related it to the first charge state of the cation vacancy. The level of $E_v+(\approx 0.15)$ eV is also observed experimentally [20], but not in all samples and with a less intensity. Calculations give for the first charge state of the cation vacancy the values 0.2 eV [12] and 0.15 eV [16]. In the work [2], the level $E_v+0.15$ eV is added to the first charge state of intersticial tellurium atom. Besides, the energy of ionization close to 0.15 eV can belong to some complexes and impurity atoms [16]. The second charge state of cadmium vacancy lies within the limits 0.6–0.8 eV [1, 12, 27]. But in the work [23], it was found that this level is by 0.47 eV higher than the top of the valence band. As the accuracy of determination of positions inherent to energy levels by quantum-mechanic methods is not high, in our calculations we used respective values of ionization energies observed experimentally. For the vacancy of cation, we used the values 0.05 and 0.8 eV according to the first and second charge states. There is a little information about the position of ionization levels for the inersticial tellurium atom. We used the value 0.15 eV that was also used by Chern [2] for the first level and 0.57 eV for the second level of ionization. The value 0.57 eV was obtained in calculations [16]. The level with the ionization energy close to this value (0.583 eV) was fixed in the work [24], and in opinion of the authors belongs to the intersticial atom of tellurium.

There are no large divergences between the values of ionization energies for the intersticial cadmium atom that were offered by different authors. The levels of $E_c-(\approx 0.02)$ eV and $E_c-(\approx 0.2)$ eV that are observed in the material [17, 18] were attributed by the authors according to the first and second charge states of intersticial cadmium atom. The calculation [12] gives approximately the same results, which confirms that these values can be considered as the first and second ionization levels of Cd_i. For the vacancy of tellurium, there are a few variants of energy levels location in the forbidden gap [2, 12, 16, 25, 26]. We considered that the ionization energies of the tellurium vacancy are $E_c-0.01$ eV and $E_c-0.34$ eV according to the first and the second levels.

5. Results and discussions

Using the deduced formulas, we performed calculation of dependences for concentrations of point defects and free charge carriers in CdTe on the temperature T and partial pressure of cadmium vapors P_{Cd} under two-temperature annealing. The results have been presented in Figs 1 to 4. As it is obvious from Figs 1 and 2, the theoretically determined concentration of electrons n describes experimental data satisfactorily, which testifies to adequacy of the accepted model.

According to the calculation, at low pressures of cadmium vapors P_{Cd} at two-temperature annealing, material should possess *p*-type conductivity. When annealing, the increase in P_{Cd} results in diminishing the hole concentration, thermodynamic *p-n* transition and obtaining the material with the *n*-type conductivity (Fig. 2).
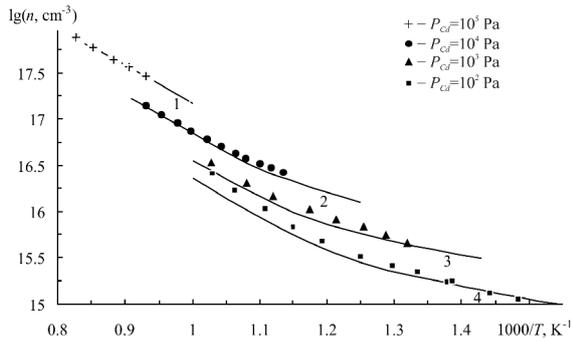
Fig. 1. Dependence of the electron concentration on the annealing temperature T at the partial pressures of cadmium vapor P_{Cd}. Lines – calculation, points – experiment: $1 – 10^5$, $2 – 10^4$, $3 – 10^3$, $4 – 10^2$ Pa.
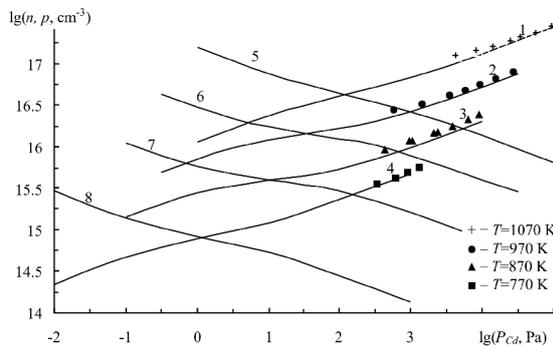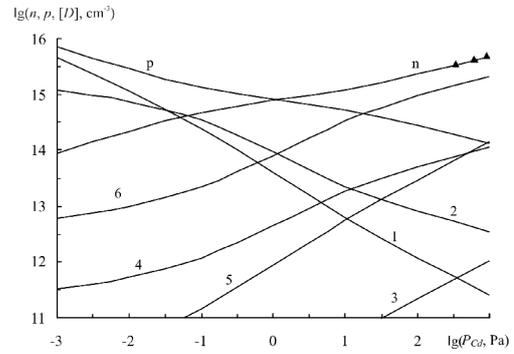

Fig. 2. Dependence of electron n and hole p concentrations on the partial pressure of cadmium vapor P_{Cd}. Lines – calculation, points – experiment. For n: $1 – 1070$, $2 – 970$, $3 – 870$, $4 – 1070$ K; for p: $5 – 1070$, $6 – 970$, $7 – 870$, $8 – 770$ K).

There are two temperature intervals in material of n-type conductivity, within the limits of which different defects prevail (Fig. 3). Up to the temperature $T \approx 900$ K, the dominant donor is the doubly ionized vacancy of tellurium V_{Te}^{2+} (Fig. 3a). At the temperatures $T > 900$ K, the doubly ionized interstitial atom of cadmium Cd_i^{2+} prevails (Fig. 3b). These results are in accord with other works [2, 6].

At the temperatures $T < 1000$ K, the dominant acceptor in material of p-type is the singly charged cadmium vacancy V_{Cd}^- (Fig. 3a). With the growth of temperature, the concentration of interstitial tellurium atoms grows quicker than the concentration of cadmium vacancies, and at the temperatures $T > 1000$ K interstitial tellurium atom Te_i^- determines the p-type of material conductivity (Fig. 3b).

The complicated defect structure in the crystals CdTe is observed at maximal pressure of cadmium vapors. At the temperatures of $T < 900$ K, the dominant donor defect is the vacancy of tellurium V_{Te}^{2+}, and at higher temperatures it is the interstitial cadmium atom Cd_i^{2+}. At the temperatures $T > 1100$ K, the concentrations of singly ionized interstitial cadmium

atoms Cd_i^+ are comparable with the concentrations of Cd_i^{2+}. Therefore, to interpret experimental dependences at $T > 1100$ K it is necessary to take into account the existence of interstitial cadmium atom in two charge states: Cd_i^+ and Cd_i^{2+}.

a)
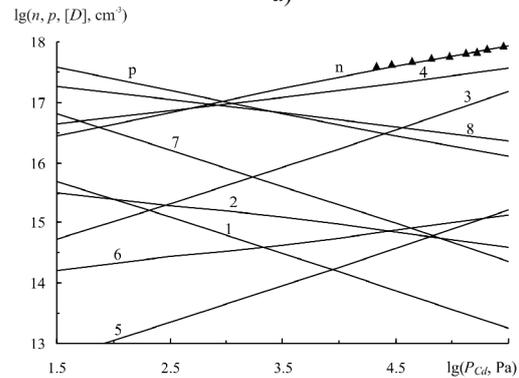
b)

Fig. 3. Dependence of point defects [D], electron n and hole p concentrations on the partial pressure of cadmium vapor P_{Cd}. Lines – calculation, points – experiment. $1 – V_{Cd}^-$, $2 – V_{Cd}^{2-}$, $3 – Cd_i^+$, $4 – Cd_i^{2+}$, $5 – V_{Te}^+$, $6 – V_{Te}^{2+}$, $7 – Te_i^-$, $8 – Te_i^{2-}$. (a – $T = 770$ K; b – $T = 1170$ K.)
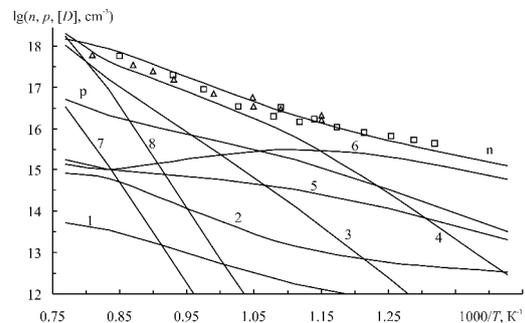

Fig. 4. Dependence of point defects [D], electron n and hole p concentrations on the annealing temperature at the maximal pressure of cadmium vapor P_{Cd}. Line – calculation, points – experiment. $1 – V_{Cd}^-$, $2 – V_{Cd}^{2-}$, $3 – Cd_i^+$, $4 – Cd_i^{2+}$, $5 – V_{Te}^+$, $6 – V_{Te}^{2+}$, $7 – Te_i^-$, $8 – Te_i^{2-}$.

6. Conclusion

Using the method of thermodynamic potentials, we described the processes of defects creation in the crystals of CdTe depending on the technological parameters (temperatures T and partial pressure of cadmium vapors P_{Cd}) of the two-temperature annealing. The concentrations of atomic point defects and free charge carriers were calculated as dependent on T and P_{Cd}.

Also determined are the ranges of prevailing donor and acceptor defects that determine the type of material conductivity.

For all the explored values of annealing temperatures 670–1200 K and partial pressures of cadmium vapors P_{Cd} 10^1–10^5 Pa, the dominant defects are charged.

The results obtained in the work can be used by specialists in the field of device designing and physicists-experimenters with the purpose to establish optimum parameters of after-growth annealing for preparation of crystals with the electrophysical properties set in advance.

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