Dominant point defects in doped cadmium telluride CdTe:Ge

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Quasi-chemical equations have been proposed for the formation of point defects (PD) and complexes thereof in germanium-doped cadmium telluride single crystals. Baric and temperature dependences of dominant PD and free charge carriers concentrations in CdTe:Ge have been obtained. Equilibrium constants for quasi-chemical equations of complex $(Ge_{Cd}^{+}V_{Cd}^{2-})^{-}$ formation have been determined as well as those for germanium transition from cation to anion sublattice of the main matrix. Results of the investigation have been explained by restricted solubility of the dopant under high temperature equilibrium of the PD. Dependence of germanium solubility in CdTe upon temperature and partial pressure of cadmium vapor have been calculated theoretically.

Предложены квазихимические реакции образования точечных дефектов и их комплексов в монокристаллах теллурида кадмия, легированного германием. Получены барические и температурные зависимости концентраций преобладающих точечных дефектов и свободных носителей заряда в CdTe:Ge. Определены константы равновесия квазихимических реакций образования комплексов $(Ge_{Cd}^{+}V_{Cd}^{2-})^{-}$ и перехода германия из катионной в анионную подрешетку основной матрицы. Результаты исследования объяснены ограниченной растворимостью примеси при условии высокотемпературного равновесия точечных дефектов. Теоретически рассчитаны зависимости растворимости Ge в CdTe от температуры и парциального давления паров кадмия.

Cadmium telluride investigations are challenged by its wide application range including non-linear optics, optical electronics, and radiation dosimetry [1]. CdTe has a broad set of physical and chemical properties, among which a large atomic number and band gap width, ability to the formation of *n*- and *p*-type semiconductors, broad range of the specific resistance values, high transparency in the IR region, etc. The doping of cadmium telluride with germanium results in increased temperature and radiation stability of the compound. In this case, electrical properties of doped samples remain unchanged after heating to 423 K and do not tend to change during a long time [2]. CdTe:Ge crystals are photorefractive [3, 4] and also have the highest light amplification coefficient without application of external electric field among all the semiconductors [5].

Directional change of the material electrical and optical properties requires the elucidation of the nature and behavior of the intrinsic and extrinsic (doping-induced) point defects (PD). There are many studies devoted to solution of this question [6–9]. In the study of Yatsunyk et al. [6], single crystals were grown using the vertical Bridgman method. The crystals were doped by introducing the calculated amount of germanium into previously synthesized CdTe (approximate germanium concentration in the sample was $2 \cdot 10^{18}$ cm^{-3}). Isothermal (873, 973, 1073 K) dependences of the free charge carrier (FCC) concentrations at different pressures of cadmium vapor and isobaric (10^2, 10^3, 10^4 Pa) dependences

Table. Quasi-chemical reactions of the intrinsic and extrinsic (dopant-induced) point defects formation in CdTe:Ge crystals annealed in Cd vapor and their equilibrium constants $K = K_0\exp(-\Delta H/kT)$ [11, 12]

#	Reaction equation	Equilibrium constant	K_0 (cm^{-3}, Pa)	ΔH (eV)
I	$0 \rightleftarrows e^- + h^+$	$K_i = np$	$5\cdot10^{39}$	1.50
II	$Cd^V \rightleftarrows Cd^0_{Cd} + V^{2+}_{Te} + 2e^-$	$K''_{Cd,V} = [V^{2+}_{Te}]\,P^{-1}_{Cd}$	$3\cdot10^{52}$	1.47
III	$Cd^V \rightleftarrows Cd^{2+}_i + 2e^-$	$K''_{Cd_i} = [Cd^{2+}_i]P^{-1}_{Cd}n^2$	$8\cdot10^{55}$	2.09
IV	$Cd^0_{Cd} + e^- \rightleftarrows V^-_{Cd} + Cd^V$	$K'_{Cd} = [V^-_{Cd}]P_{Cd}n^{-1}$	$1\cdot10^{-10}$	1.14
V	$Cd^0_{Cd} + 2e^- \rightleftarrows V^{2-}_{Cd} + Cd^V$	$K''_{Cd} = [V^{2-}_{Cd}]P_{Cd}n^{-2}$	$8\cdot10^{11}$	2.08
VI	$CdTe + e^- \rightleftarrows Te^-_i + Cd^V$	$K'_{Te_i} = [Te^-_i]P_{Cd}n^{-1}$	$4\cdot10^7$	1.19
VII	$Ge^-_{Te} + V^{2-}_{Cd} \rightleftarrows Ge^+_{Cd} + V^{2+}_{Te} + 6e^-$ $K'_{Ge} = [Ge^+_{Cd}][V^{2+}_{Te}]n^6[V^{2-}_{Cd}]^{-1}[Ge^-_{Te}]^{-1}$		$1\cdot10^{113}$	1.7
VIII	$[Ge_{tot}] = [Ge^+_{Cd}] + [Ge^-_{Te}]$			
IX	$n + [V^-_{Cd}] + 2[V^{2-}_{Cd}] + [Te^-_i] + [Ge^-_{Te}] = p + 2[Cd^{2+}_i] + 2[V^{2+}_{Te}] + [Ge^+_{Cd}]$.			

Index V — vapor; Cd_{Cd} — cadmium atoms in the site; Cd_i, Te_i — interstitial cadmium and tellurium atoms; V_{Cd}, V_{Te}, Ge_{Cd}, Ge_{Te} — vacancies and dopant atoms in both sublattices, respectively; e^- — electron; h^+ — hole; −, + — charge symbols.

at different temperatures were determined by six-probe conventional technique. The experimental results were compared to those for undoped CdTe single crystals. As revealed, at temperatures 873–1173 K and maximal values of cadmium vapor partial pressure, FCC concentrations were essentially the same both for samples of Ge-doped and undoped CdTe. A significant difference was observed in the isotherm slope. CdTe:Ge crystals showed significantly less slope, which decreased at temperature elevation. The fact was explained by amphoteric properties of germanium in CdTe. In the study of Panchuk et al., it has been proposed a model for germanium introduction into cadmium telluride. The model is based on assumption of $V^{2-}_{Cd} + Ge^+_{Cd} \rightleftarrows (Ge^+_{Cd}V^{2-}_{Cd})^-$ complex formation. These complexes are referred to have acceptor level characteristic of CdTe:Ge. Authors [7] had built approximated diagrams of high temperature equilibrium for the defects that describe only incompletely the crystal sublattice in particular, at the boundary of approximation areas. It was concluded that at low concentrations, germanium is located mainly in Cd sublattice, while at concentrations exceeding $5\cdot10^{18}$ cm^{-3} Ge substitutes equiprobably both Cd and Te atoms [8]. It should be noted that CdTe centers are not confirmed in experiment to date and stay as a model hypothesis. In [9], different data were obtained which form a basis for the statement that Ge atoms are located only in cadmium sublattice of the main matrix.

Despite of above-mentioned results, the questions regarding germanium nature and charge in cadmium telluride are today under discussion. In this work, some new data are presented on dominant PD and formation mechanisms thereof in CdTe:Ge crystals.

To analyze the state of defects in CdTe:Ge, of three models of quasi-chemical reactions describing formation of PD under high temperature annealing in cadmium vapor have been considered. The concentration of FCC and dominant PD under different technological conditions have been calculated theoretically taking into account the entire electroneutrality equation.

Model of isolated pointed defects. Equilibrium of the defects in CdTe:Ge crystals under high temperature annealing in cadmium vapor with amphoteric dopant action could been described in terms of Kroger theory [10] by quasi-chemical reactions (see Table). Application of action mass law to the quasi-chemical reactions (I–VII, see Table) makes in possible to obtain expressions for concentrations of intrinsic (1) and extrinsic (2) PD using equilibrium constants (K) of the reactions, cadmium vapor partial pressure P_{Cd}, total concentration of the

dopant $[Ge_{tot}]$ and electron concentration n:

$$[V_{Cd}^-] = K'_{Cd}n/P_{Cd}, \qquad (1)$$

$$[V_{Cd}^{2-}] = K''_{Cd}n^2/P_{Cd},$$

$$[Te_i^-] = K'_{Te_i}n/P_{Cd},$$

$$[Cd_i^{2+}] = K''_{Cd_i}P_{Cd}/n^2, \qquad (2)$$

$$[V_{Te}^{2+}] = K''_{Cd,V}P_{Cd}/n^2,$$

$$[Ge_{Te}^-] = \frac{[Ge_{tot}]}{(1 + K'_{Ge}K''_{Cd}/K''_{Cd,V}P_{Cd}^2 n^2)},$$

$$[Ge_{Cd}^+] = \frac{[Ge_{tot}]}{(1 + K''_{Cd,V}P_{Cd}^2 n^2/K'_{Ge}K''_{Cd})}.$$

Basing on relations for defect concentrations (1, 2) and taking into account the material balance (VIII, Table) and electroneutrality (IX, Table) conditions, an equation for determination of electron concentration can be derived:

$$An^6 + Bn^5 + Cn^4 + Dn^3 - \qquad (3)$$
$$- En^2 - Fn - G = 0,$$

$$A = 2K''_{Cd}K''_{Cd,V}P_{Cd}^2,$$

$$B = K''_{Cd,V}P_{Cd}^2(K'_{Cd} + K'_{Te_i} + P_{Cd}),$$

$$C = 2K'_{Ge}K''^2_{Cd} + [Ge_{tot}]K''_{Cd,V}P_{Cd}^3,$$

$$D = K'_{Ge}K''_{Cd}(K'_{Cd} + K'_{Te_i} + P'_{Cd}) - $$
$$- K_i K''_{Cd,V}P_{Cd}^3,$$

$$E = P_{Cd}^2(2K''_{Cd,V}P_{Cd}^2(K''_{Cd_i} + K''_{Cd,V}) + $$
$$+ [Ge_{tot}]K'_{Ge}K''_{Cd}),$$

$$F = K_i K'_{Ge}K''_{Cd}P_{Cd},$$

$$G = 2K'_{Ge}K''_{Cd}P_{Cd}^2(K''_{Cd_i} + K''_{Cd,V}).$$

Concentration of the current carriers n_X is determined experimentally from Hall effect as

$$n_X = n - p = n - K_i n^{-1}. \qquad (4)$$

From equations (3) and (4), we have calculated dependence of the Hall current carrier concentration on cadmium vapor partial pressure (Fig. 1, curve *1*). It has been observed a divergence between experimental and calculated data: electron concentrations are lower than those predicted by the model.
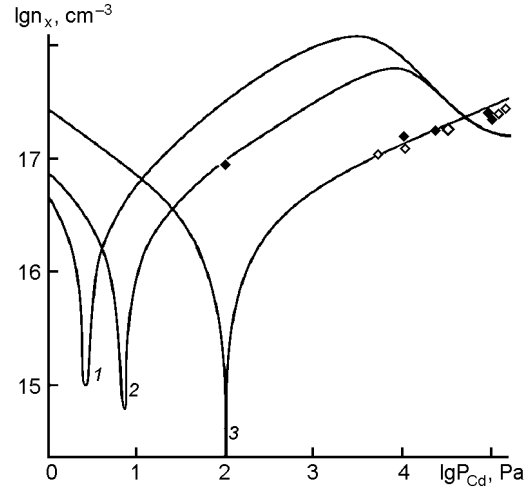

Fig. 1. Baric dependences of free charge carrier concentration in the CdTe:Ge (*1*, *2*, ♦) and CdTe (*3*, ◊) crystals at annealing in cadmium vapor. Solid lines: calculation: *1*, model of isolated defects; *2*, model of associative centers; *3*, undoped cadmium telluride. $[Ge_{tot}] = 2 \cdot 10^{18}$ cm^{-3}, $T = 1073$ K. Experimental data are taken from [6].

Model of associative centers. The decrease of calculated FCC concentrations at low partial pressures of cadmium vapour can be provided by consideration of the acceptor complexes of germanium dopant with cadmium vacancy $(Ge_{Cd}^+V_{Cd}^{2-})^-$:

$$Ge_{Cd}^+ + V_{Cd}^{2-} \rightleftarrows (Ge_{Cd}^+V_{Cd}^{2-})^- \equiv A_{Ge}^-, \qquad (5)$$

$$K'_p = [A_{Ge}^-][Ge_{Cd}^+]^{-1}[V_{Cd}^{2-}]^{-1},$$

$K_p' = 6 \cdot 10^{23}\exp(1.15/kT)$. The material balance equation will take the form:

$$[Ge_{tot}] = [Ge_{Cd}^+] + [Ge_{Te}^-] + [A_{Ge}^-]. \qquad (6)$$

Electroneutrality condition is determined as:

$$n + [V_{Cd}^-] + 2[V_{Cd}^{2-}] + [Te_i^-] + [Ge_{Te}^-] + [A_{Ge}^-] = $$
$$= p + 2[Cd_i^{2+}] + 2[V_{Te}^{2+}] + [Ge_{Cd}^+]. \qquad (7)$$

Expressions for the extrinsic defect concentrations are as follows:

$$[Ge_{Cd}^+] = K'_{Ge}K''_{Cd}[Ge_{tot}] \times$$
$$\times (K'_{Ge}K''_{Cd}(K'_p K''_{Cd}n^2/P_{Cd} + 1) +$$
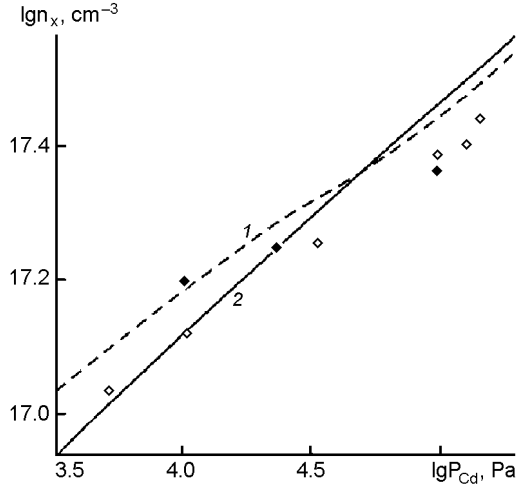$$+ K''_{Cd,V}P_{Cd}^2 n^2)^{-1},$$

Fig. 2. Baric dependences of free charge carrier concentration in the CdTe:Ge (1, ♦) and CdTe (2, ◊) crystals at annealing in cadmium vapor (model of associative centers). $Ge_S = 6 \cdot 10^{16}$ cm^{-3}, $T = 1073$ K. Experimental data are taken from [6].

Fig. 3. Temperature dependences of free charge carrier concentration n_x in CdTe:Ge at P_{Cd}, Pa: 10^2 (1, ●), 10^3 (2, ■), 10^4 (3, ♦). ●, ■, ♦ — experiment [6], solid lines — calculation according to the restricted dopant solubility model.

$$[Ge_{Te}^-] = K''_{Cd,V}[Ge_{tot}]P_{Cd}^2 n^2 \times$$
$$\times (K'_{Ge}K''_{Cd}(K'_p K''_{Cd}n^2/P_{Cd} + 1) +$$
$$+ K''_{Cd,V}P_{Cd}^2 n^2)^{-1},$$

$$[A_{Ge}^-] = K'_{Ge}K'_p K''^2_{Cd}[Ge_{tot}]n^2 \times \qquad (8)$$
$$\times (P_{Cd}(K'_{Ge}K''_{Cd}(K'_p K''_{Cd}n^2/P_{Cd} + 1) +$$
$$+ K''_{Cd,V}P_{Cd}^2 n^2))^{-1}.$$

Substituting the relations (1) and (8) into the electroneutrality condition (7) makes it possible to obtain an equation for determination of electron concentration as a function of equilibrium constants (K) for reactions describing defect formation, cadmium vapor partial pressure (P_{Cd}) and the dopant content $[Ge_{tot}]$.

The model of defect subsystem which takes into account the acceptor associates $(Ge_{Cd}^+ V_{Cd}^{2-})^-$ provides a good agreement with experiment at $P_{Cd} \sim 10^2$ (Fig. 1, curve 2), unlike the isolated PD model. Within the range of cadmium partial pressure 10^2 Pa $< P_{Cd} < 10^5$ Pa, the FCC concentration is observed to increase at initially. This concentration achieves a maximal value at $P_{Cd} \sim 10^4$ Pa, then it starts to decrease till the value corresponding to undoped cadmium telluride. The latter effect is not observed in experiment. Hence, within the range of cadmium vapor saturation, the model describes the experimental results inadequately. Perhaps this is connected with that
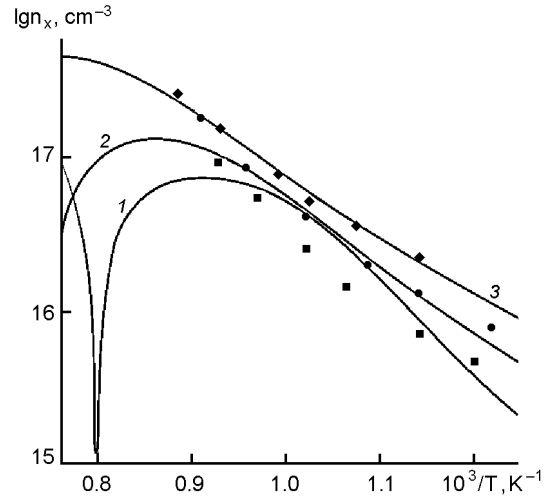
the model does not take into account the restricted solubility of the dopant. Theoretical analysis indicates that at 1073 K, germanium solubility in cadmium telluride is $Ge_S \sim 10^{17}$ cm^{-3} (Fig. 2) [12].

Model of the restricted dopant solubility. When developing the model of CdTe:Ge defect structure, it is taken into account that a fraction of the dopant atoms may form precipitates Ge_p. Increase of temperature T or decrease of cadmium vapor partial pressure P_{Cd} may result in dissolution of precipitates with subsequent transition of the dopant into solid solution. The transition can be described by such reactions:

$$Ge_p^0 + V_{Cd}^{2-} \rightleftarrows Ge_{Cd}^+ + 3e^-, \qquad (9)$$
$$Ge_p^0 \rightleftarrows Ge_{Te}^- + V_{Cd}^{2-} + 3h^+.$$
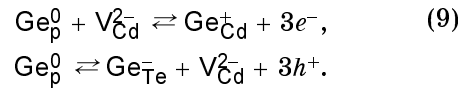
In this case, the material balance equation is:

$$[Ge_{tot}] = [Ge_p] + Ge_S, \qquad (10)$$

where $[Ge_{tot}]$ is the dopant total concentration in CdTe; Ge_S, germanium solubility in the compound.

$$Ge_S = [Ge_{Cd}^+] + [Ge_{Te}^-]. \qquad (11)$$

Electroneutrality condition of the material is defined as:

$$n + [V_{Cd}^-] + 2[V_{Cd}^{2-}] + [Te_i^-] + [Ge_{Te}^-] = \qquad (12)$$
$$= p + 2[Cd_i^{2+}] + 2[V_{Te}^{2+}] + [Ge_{Cd}^+].$$
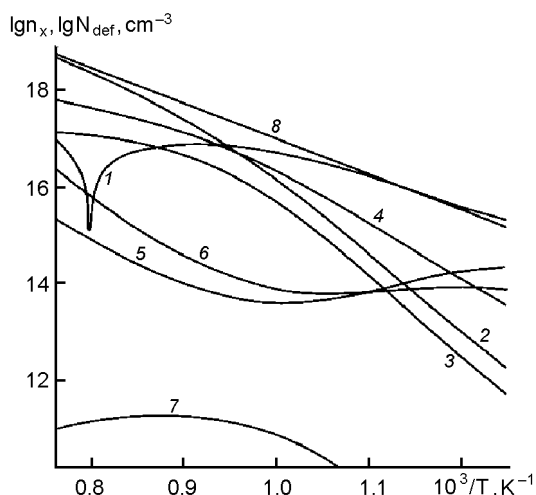
Fig. 4. Temperature dependences of point defect and free charge carrier concentrations in CdTe:Ge (the restricted dopant solubility model): *1*, n_x; *2*, $[V_{Cd}^-]$; *3*, $[V_{Cd}^{2-}]$; *4*, $[Te_i^-]$; *5*, $[V_{Te}^{2+}]$; *6*, $[Cd_i^{2+}]$; *7*, $[Ge_{Te}^-]$; *8*, $[Ge_{Cd}^+]$. $P_{Cd} = 10^2$ Pa.
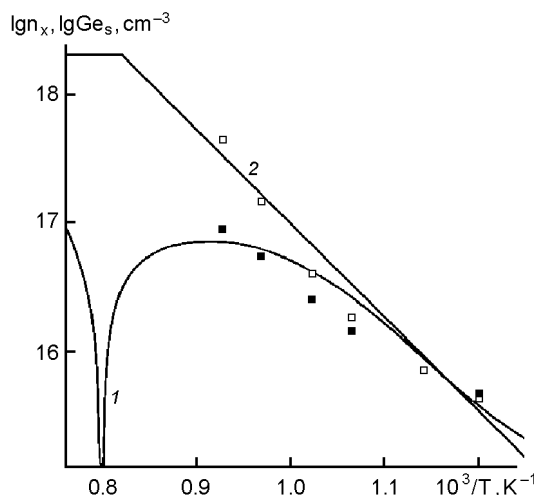

Fig. 5. Temperature dependences of free charge carrier concentration n_x (*1*, ■) and germanium solubility Ge_S (*2*, □) in CdTe:Ge (the restricted dopant solubility model). ■ — experiment [6], □ — calculation according to (14). $P_{Cd} = 10^2$ Pa.

Expressions for the extrinsic defect concentrations are as follows:

$$[Ge_{Te}^-] = Ge_S / (1 + K'_{Ge} K''_{Cd} / K''_{Cd,V} P_{Cd}^2 n^2),$$

$$[Ge_{Cd}^+] = Ge_S / (1 + K''_{Cd,V} P_{Cd}^2 n^2 / K'_{Ge} K''_{Cd}).$$

$$(13)$$

Substituting the relationships for defect concentration (1, 13) into the electroneutrality condition (12), we can obtain an equation for calculation of the value of dopant solubility Ge_S for every experimental dot (n, P_{Cd}, T) obtained from high temperature measurements of the Hall effect. That calculated value of dopant solubility will provide the specified electron concentration n:

$$Ge_S = \qquad (14)$$

$$= -\left(\sum_i z_i [D_i]\right) \frac{K'_{Ge} K''_{Cd} + K''_{Cd,V} P_{Cd}^2 n^2}{K'_{Ge} K''_{Cd} - K''_{Cd,V} P_{Cd}^2 n^2},$$

where $[D_i]$ — concentrations of intrinsic PD (reactions (1)); z_i, charge of the defects. The obtained values for germanium solubility Ge_S have been approximated by exponential dependences:

for $P_{Cd} =$ $\qquad (15)$

$= 10^2 Pa - Ge_S = 3 \cdot 10^{23} \exp(-1.29/kT),$

for $P_{Cd} = 10^3 Pa - Ge_S = 10^{22} \exp(-1.04/kT),$

for $P_{Cd} = 10^4 Pa - Ge_S = 6 \cdot 10^{21} \exp(-0.98/kT).$

The theoretically calculated FCC concentrations agree well with experimental data for investigated annealing temperature range (Fig. 3). At cadmium vapor partial pressures P_{Cd} of 10^2 to 10^4 Pa and annealing temperatures of 800 to 1300 K, the temperature dependences of the FCC concentration are similar to each other. The electron concentration increases with increasing annealing temperature till a certain value and then drops sharply while at low cadmium vapor partial pressures ($P_{Cd} \sim 10^2$ Pa), even the conductivity type inversion of the material takes place and a further increase of the hole concentration. Results of theoretical analysis indicate that high annealing temperatures ($T = 1100-1300$ K) result in intensification of vacancy V_{Cd}^- and interstitial tellurium atoms Te_i^- generation processes. Those prevail over the extrinsic defects in that region and account for the material conductivity p-type within this temperature range (Fig. 4). The change of two-charge donor PD concentration of Cd_i^{2+} and V_{Te}^{2+} in the material within broad range of annealing temperatures is insignificant.

The calculated values for germanium solubility within a certain annealing temperature interval are lower than experimental values of electron concentration, that is caused by predominance of intrinsic PD over extrinsic ones in the material under above-mentioned conditions (Fig. 5). At increasing cadmium vapor partial pressure,

this annealing temperature interval increases, while germanium solubility decreases.

It should be noted that for all investigated values of technological annealing factors, germanium concentration in tellurium sublattice $[Ge_{Te}^-]$ is by 3–8 orders lower than that in cadmium sublattice $[Ge_{Cd}^+]$. Therefore, the Hall concentration of charge carriers n_X in crystals is controlled mainly by doping centers $[Ge_{Cd}^+]$ and intrinsic PD.

To conclude, a model of quasi-chemical reactions has been proposed for the defect formation with account of restricted germanium solubility. This model describes adequately the defect subsystem CdTe:Ge at high temperature annealing in cadmium vapor. Dependences of free charge carrier concentrations and dominant point defects upon technological conditions (annealing temperature and cadmium vapor partial pressure) have been calculated. It has been established that within the annealing temperature range of 800 to 1250 K, and partial pressure of cadmium vapor P_{Cd}, of 10^2 to 10^4 Pa, germanium is located mainly in cadmium sublattice, what account for the electron conductivity of the material. Temperature dependences of Ge solubility in CdTe at different partial pressures of cadmium vapor have been determined.

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Домінуючі точкові дефекти у легованому телуриді кадмію CdTe:Ge

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Запропоновано квазіхімічні реакції утворення точкових дефектів і їх комплексів у монокристалах телуриду кадмію, легованого германієм. Одержано баричні та температурні залежності концентрацій переважаючих точкових дефектів і вільних носіїв заряду в CdTe:Ge. Визначено константи рівноваги квазіхімічних реакцій утворення комплексів $(Ge_{Cd}^+V_{Cd}^{2-})^-$ та переходу германію з катіонної підгратки в аніонну основної матриці. Результати дослідження пояснено обмеженою розчинністю домішки за умови високотемпературної рівноваги точкових дефектів. Проведено теоретичний розрахунок розчинності Ge в CdTe у залежності від температури і парціального тиску пари кадмію.