Electrical properties of In or Ga-saturated CdTe crystals at high-temperature point defect equilibrium

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Abstract

High temperature Hall effect measurements between 873 and 1073 K in CdTe single crystals, heavily doped by In or Ga at maximal Cd partial vapor pressure were performed. The free electron density results were compared with respective values, obtained by numerical simulation, with satisfactory agreement. The analysis of experimental free electron density values at high-temperature point defect equilibrium allowed performing thermodynamic calculations ascertaining the position of the doubly negatively charged Cd vacancy donor in the CdTe band gap, lying at $\sim E_C - 0.8$ eV.

Keywords: CdTe; dopant solubility, electrical properties; point defect; energetic level

1. Introduction

The use of Indium as an important dopant in CdTe allows obtaining at various stoichiometric conditions and doping levels both low- and high-resistivity materials for practical use [1]. The electrical properties directly depend on the crystal's native/foreign point defect (PD) spectrum. That latter is formed and can be studied at high-temperature PD equilibrium conditions (HTDE, above ~ 700 K) using the Kröger's theory of quasi-chemical reactions between PDs (QCDR) in imperfect solids [2]. Such investigations were performed in CdTe<In(Ga)> single crystals, mostly in parallel with corresponding modeling by numerical simulation [3-6] calculating the free electron density in the crystal. Such computations are necessary to avoid enough laborious experiments if prompt evaluation of doped crystal's electric properties at various doping level, temperatures and stoichiometric relations is necessary. The comparison of the experimental and calculated data allows appreciating the adequacy of PD modeling, too. However the fore-quoted works deal exclusively with low or medium doped material, but for all that the dopant in the CdTe solubility temperature dependence was never taken into account. In addition, the peculiarity of these donor dopants consists in their ease of forming associates (A^-) with negatively charged native point defects. The arising associates play a decisive role in defining the crystal's electric properties. To purpose this problem free electron density temperature dependencies in heavily doped CdTe<In(Ga)> crystals should be

investigated, the respective activation energy considered. Assessing the nature of free electron generation at crystal heating allows obtaining new thermodynamic information.

Therefore the aim of this investigation was to: a) prepare In(Ga) saturated CdTe crystals; b) measure at HTDE their electric properties; c) compare the experimental values with the calculated ones by numeric simulation, taking into account the real solute dopant content at various temperatures; d) perform calculations in the framework of Kröger's quasi-chemical reactions formalism in order to obtain new thermodynamic knowledge concerning the behavior of PDs in CdTe.

2. Materials and methods

CdTe single crystal ingots were grown by the Bridgman vertical crystallization technique, using stoichiometric amounts of 6N-purity Cd and Te. The graphitized ampoules had a 25 mm diameter and a 10 cm length, were lowered with a 3 mm/hour rate. The temperature gradient in the crystallization zone was $\sim 4-5$ K/cm. The samples ($2.5 \times 2.5 \times 15$ mm³) were cut out from the middle part of ingots, then grounded, polished and etched in a bromine-methanol solution. The In- or Ga-doped crystals were prepared by the method of full saturation by these metals of the CdTe samples in vacuum (CdTe congruent sublimation conditions, what holds for equal quantities of Cd and Te in the vapor phase). At such conditions volatile metal tellurides are formed, they transport the dopant from the metallic source to the crystal,

followed by the dopant diffusion in the sample. Taking into account the known metals diffusion coefficient temperature dependence (obtained previously in our laboratory [7]), the necessary saturation time was calculated by use of the relation $x=2\sqrt{Dt}$, where “ D ” is the respective dopant diffusion coefficient at chosen temperature, “ t ” – the necessary saturation time and “ x ” – the half of the sample’s thickness. The real saturation time was taken with an excess of 25% and was equal to 4 weeks at 1123 K..

The In (Ga) dopant solubility temperature dependences at experimental $P_{Cd, max}$ conditions are given by the eq. (1, 2) [7] (actual up to the maximum solubility temperature of the CdTe-dopant solidus line).

$$S(In) = 5.9 \cdot 10^{21} \exp(-0.62 \text{ eV}/kT) \text{ at/cm}^3 \quad (1)$$

$$S(Ga) = 2.95 \cdot 10^{25} \exp(-1.12 \text{ eV}/kT) \text{ at/cm}^3 \quad (2)$$

So in the crystals were introduced considerable dopant quantities ($\sim 1 \cdot 10^{19}$ at/cm³ In and $\sim 3 \cdot 10^{20}$ at/cm³ Ga) at 1123 K. At that sole temperature all dopant atoms are solute in the CdTe lattice in conformance with eq. (1-2) occupying Cd sites and acting as electron donors. These quantities were sufficient to assure maximal dopant solubility values in the used in electrical measurements 873-1073 K temperature area. In that area the solute dopant amount (variable depending on the temperature) exists partly in form of electrical active extrinsic point defects, partly in the form of electrically inactive (neutral) second phase precipitates, which does not affect the Hall effect measurements but the free carrier mobility only.

The relation between the both dopant forms depends on the temperature and stoichiometric relations in the crystal only and is established automatically.

Six welded (tungsten wire) contacts were used to provide Hall effect measurements with data fixation in automatic mode [8]. The high-temperature “in situ” experiments (e.g. at HTDE) were carried out at each temperature (step ~ 10 K) in the 873-1073 K range at maximal Cd vapor pressure ($P_{Cd, max}$) to define the free electron density and their mobility temperature dependencies (Fig. 1 and 2).

3. Results and discussions

The free electron density temperature dependencies are represented in the investigated range by matching straight lines with a ~ 0.40 eV slope for both In- and Ga-doped material (fig. 1). This value as well the measured free electron densities are repeated in series of parallel experiments. As can be seen in fig. 1, the free electron density in both types of doped crystals is essentially higher (about one order of magnitude) than in undoped CdTe. The reason of this distinction lies in the high extrinsic donor (In/Ga) content (close to or exceeding $\sim 10^{18}$ at/cm³) in the

Fig. 1. Free electron density temperature dependence in undoped CdTe (lower line) and in saturated (table 2) by In (triangles) or Ga (squares) – upper line. Cd vapour pressure – maximal at each temperature

crystals. The difference arises because in undoped CdTe the electrons are provided by both regular V_{Te}^{2+} and interstitial Cd_i^{2+} native donors, whose content in heavily Ga(In) doped crystals is orders of magnitude lower. The latter follows from the Kröger’s QCDR theory: introducing of foreign donors reduces the content of the native donor PDs, concurrently raising the concentration of the native acceptor ones. On the contrary to pure CdTe, in donor-doped material the electrons are generated by both the donor dopant and associated point defects, comprising a double negatively charged native and another positively charged extrinsic PD (A^- associates, see below).

At the electric measurements the solute dopant content S in the crystal (Table 1, item 3) was always smaller as the introduced one during the saturation procedure (at 1123 K) due to lower experimental temperatures (1073 K or below) and the Cd vapor saturation. During the measurements the dopant solid solution in the crystal decays and the exceeding dopant quantities form precipitates in the matrix. The real solute dopant concentrations in the crystals at the three temperatures were calculated by use of equations (1,2) and shown in table 1 (item 3) and next used in computer modeling. In the same place are represented both the experimental free electron densities (item 4) and the calculated by computer modeling ones (item 5). The concentrations of the electronic and atomic PDs were obtained by numerical simulation. First by the iteration method at given $[In]_{total}$, stoichiometric conditions and temperature values the free electron density was established, and then by use of the appropriated equations [3-6] all PDs concentrations were calculated. Also shown are the average values for the experimental and simulated data (item 6) together with the calculated ensuing $[A^-]$ data (item 7) and the computed total $[In]$ or $[Ga]$ (item 8, see footnote in Table 1).

Let us consider these data. As can be seen in the table 1, the solute in the crystal In and Ga dopant contents (item

3) at identical conditions differ essentially – up to 20 times at various temperatures. However, both the experimental and calculated free electron densities are satisfactory close for both dopants..

Table 1. Free electron and point defect concentration temperature dependencies in CdTe<In(Ga)>

Indium				
1	T, K (experiment)	1073	973	873
2	$10^3/T, K^{-1}$	0.93	1.03	1.15
3	S(In), at/cm ³ (calc)	$7.1 \cdot 10^{18}$	$3.6 \cdot 10^{18}$	$1.8 \cdot 10^{18}$
4	[e ⁻], cm ⁻³ (exper.)	$2.5 \cdot 10^{18}$	$1.6 \cdot 10^{18}$	$1 \cdot 10^{18}$
5	[e ⁻], cm ⁻³ (model)	$2.6 \cdot 10^{18}$	$1.0 \cdot 10^{18}$	$9.1 \cdot 10^{17}$
6	[e ⁻], (aver.), cm ⁻³	$2.5 \cdot 10^{18}$	$1.3 \cdot 10^{18}$	$9.5 \cdot 10^{17}$
7	[A ⁻], cm ⁻³ (model)	$2.5 \cdot 10^{18}$	$1.2 \cdot 10^{18}$	$4.5 \cdot 10^{17}$
8	In(total), at/cm ³ *	$7.5 \cdot 10^{18}$	$3.7 \cdot 10^{18}$	$1.8 \cdot 10^{18}$

*Note: calculated In(total) = ([e⁻] + 2[A⁻])

Gallium				
1	T, K (experiment)	1073	973	873
2	$10^3/T, K^{-1}$	0.93	1.03	1.15
3	S(Ga), at/cm ³ (calc)	$1.6 \cdot 10^{20}$	$4.5 \cdot 10^{19}$	$9.8 \cdot 10^{18}$
4	[e ⁻], cm ⁻³ (exper.)	$2.5 \cdot 10^{18}$	$1.6 \cdot 10^{18}$	$1 \cdot 10^{18}$
5	[e ⁻], cm ⁻³ (model)	$1.6 \cdot 10^{18}$	$2.4 \cdot 10^{18}$	$1.3 \cdot 10^{18}$
6	[e ⁻], (aver.), cm ⁻³	$2.1 \cdot 10^{18}$	$2.0 \cdot 10^{18}$	$1.2 \cdot 10^{18}$
7	[A ⁻], cm ⁻³ (model)	$7.9 \cdot 10^{19}$	$2.0 \cdot 10^{19}$	$7.9 \cdot 10^{18}$
8	Ga(total), at/cm ³ *	$1.6 \cdot 10^{20}$	$6.0 \cdot 10^{19}$	$1.7 \cdot 10^{19}$

* Note: calculated Ga(total) = ([e⁻] + 2[A⁻])

As found in a multitude of investigations beginning with [2], at high temperatures In is incorporated in the CdTe lattice partly as the In_{Cd}⁺ PD and in part as the associate (In_{Cd}⁺ V_{Cd}²⁻)⁻ PD in conformity with the QCDR

The dopant mass balance equation for the In ionized dopant In_{Cd}⁺ PD (similarly for Ga), will be

$$\text{In}(\text{total}) = [\text{In}_{\text{Cd}}^+] + [(\text{In}_{\text{Cd}}^+ \text{V}_{\text{Cd}}^{2-})^-], \quad (4)$$

$$\text{or } \text{In}(\text{total}) = [\text{In}_{\text{Cd}}^+] + [\text{A}^-]$$

At that the approximated electro-neutrality condition will be

$$[\text{In}_{\text{Cd}}^+] = [\text{e}^-] + [\text{A}^-] \quad (5)$$

Combining (4) and (5) we obtain

$$\text{In}(\text{total}) = [\text{e}^-] + 2[\text{A}^-] \quad (6)$$

Assessing that PD equilibrium in doped CdTe, one can see, that raising in the crystal the In(total) doping level results according to (4) in an increase of both In_{Cd}⁺ and (In_{Cd}⁺ V_{Cd}²⁻)⁻ species. In spite of all this, the free electron density varies insignificantly only. Computer simulation results in the following data. If the dopant content is

$2.5 \cdot 10^{19}$ at/cm³, the lg[e⁻] is equal to $3.2 \cdot 10^{18}$, when it increases to $5 \cdot 10^{19}$ then $3.4 \cdot 10^{18}$ (calculated for Ga at 1073K). So the dopant content rises by 100%, whereas the [e⁻] by 7% only. Thus the greater is the dopant content in the crystal, the relatively smaller is the share of free electrons in the concentration of the negative charged dominant PDs. All this is caused by the peculiarities of the dopant self-compensation effect [2-6]. By use of eq. (6) were calculated the obtained by numerical simulation solute quantities In(total) and Ga(total) at various temperatures. At that we should take into account, that at computer modeling the entropy and enthalpy values of the associates forming QCDR (3) are known for the In-associate only [3]. Therefore in modeling calculations the latter value was tentatively used to obtain the content of the Ga-containing associate, too. This assumption came true and is supported by the identical structure of the outer electronic shell of their atoms and relatively close covalent radii values of the two elements: 0.130 and 0.155 nm for Ga and In respectively.

In general the solubility values satisfactory correspond to that calculated (compare items 3 and 8) what confirms the suitability of the used PD spectrum model.

During all high-temperature experiments the In-containing crystals possessed n-type conductivity (Fig. 2).

Fig. 2. Electron mobility temperature dependence in In-doped CdTe crystal. Dashed lines – similar dependencies in undoped CdTe for electrons (n) and holes (p) [5].

However the electron mobility values were essentially smaller compared to undoped CdTe assuming free carrier phonon scattering (fig. 2, upper dashed line), evidently due to the high dopant content accounting the decay of its solid solution in the CdTe crystal. At cooling the saturated at 1123 K crystal releases excessive dopant quantities forming precipitates, which embarrass the electron flow, affecting the electron mobility. As seen in fig. 2, the discrepancy between the experimental electron mobility values and the theoretical ones in undoped CdTe is temperature-dependent. At low one the discrepancy is large (plenty of precipitates), but considerably decreases at higher ones (few precipitates due to higher dopant solubility), all this according to the solidus line position in

the CdTe-dopant state micro-diagram [7]. For the Ga-doped CdTe crystal, the situation is identical.

Now we consider the temperature dependence of the free electron density in dopant-saturated CdTe (fig.1). Here the main question arises: what donor PD ensures the free electron density increase with rising temperature? We should take into account that both impurities are shallow donors, fully ionized even under room temperatures. Let us analyze the case of In, noting that the native donor point defect concentrations are negligible relative to [In] and [Ga].

The approximate electro-neutrality equation for our situation arises from eq. (5):

$$[e^-] \approx [In_{Cd}^+] - [(In_{Cd}^+ V_{Cd}^{2-})^-].$$

In In-doped CdTe at experimental (high) temperature conditions the charged Cd vacancies V_{Cd}^- and V_{Cd}^{2-} and isolated In_{Cd}^+ donors, as well as the A^- associates are dominant, see PD structure model in [6].

As other (minority) atomic PDs can not act as donors, the electron generation to the conduction band can be assured by the sole probable V_{Cd}^{2-} PD via the following subsequent reactions at temperature rising:

It should be taken notice that advancing of reaction (7) does not change the electron balance in the crystal, solely reaction (8).

The mass action law for reactions (7)-(8) is:

$$\frac{[In_{Cd}^+][V_{Cd}^{2-}]}{[A^-]} = B_1 \exp\left(-\frac{\Delta H_A}{kT}\right) \quad (9)$$

$$\frac{[e^-][V_{Cd}^-]}{[V_{Cd}^{2-}]} = B_2 \exp\left(-\frac{\Delta E_v}{kT}\right) \quad (10)$$

Multiplying (9) by (10) we obtain

$$\frac{[In_{Cd}^+][V_{Cd}^-][e^-]}{[A^-]} = B_1 B_2 \exp\left(-\frac{\Delta H_A + \Delta E_v}{kT}\right) \quad (11)$$

Taking into account the mass balance equation (4) eq. (11) turns into (12)

$$[V_{Cd}^-][e^-] = \left(\frac{[In_{tot}]}{[In_{Cd}^+]} - 1\right) B_1 B_2 \exp\left(-\frac{\Delta H_A + \Delta E_v}{kT}\right) \quad (12)$$

The V_{Cd}^- concentration we calculate as:

$$[V_{Cd}^-] = \frac{K_{11}[e^-]}{P_{Cd}} \quad (13)$$

where K_{11} – is the equilibrium constant of the reaction:

$$K_{11} = B_3 \exp\left(-\frac{\Delta H_{11}}{kT}\right) \quad (15)$$

where ΔH_{11} – is the reaction (13) enthalpy.

The Cd vapor pressure temperature dependence is given by [11]

$$P_{Cd} = B_4 \exp\left(-\frac{H(Cd)}{kT}\right) \quad (16)$$

Combining (11), (12), (14) and (15), we obtain:

$$[e^-] = \left[B \left(\frac{[In_{tot}]}{[In_{Cd}^+]} - 1\right)\right]^{1/2} \exp\left(-\frac{\Delta H_A + \Delta E_v - \Delta H_{11} + H(Cd)}{2kT}\right) \quad (17)$$

$$\text{where } B = \frac{B_1 B_2 B_4}{B_3}$$

Though B and $\left(\frac{[In_{tot}]}{[In_{Cd}^+]} - 1\right)$ are somewhat temperature

dependent, we assume as a rough approximation that the expression in the square brackets is almost temperature independent. In consequence for the overall process activation energy (17) we obtain:

$$E_a = \frac{\Delta H_A + \Delta E_v - \Delta H_{11} + H(Cd)}{2} \text{ (eV)}, \quad (18)$$

From where the V_{Cd}^{2-} donor ionization energy ΔE_v can be calculated:

$$\Delta E_v = 2E_a - \Delta H_A + \Delta H_{11} - H(Cd) \quad (19)$$

The ΔE_v value was calculated using the following data: $E_a = 0.4$ eV (experiment), $\Delta H_A = 0.92$ eV [3], $H(Cd) = 1.05$ eV [8], $\Delta H_{11} = 2.08$ eV [9,10],

But for all that the experimental E_a value (0.4 eV) should be discussed. Generally speaking, the slope of the $\lg[e^-] - 10^3/T$ dependence gives valuation data only, as it does not take into account that in a donor-compensated material $[e^-]$ is proportional to $T^{3/2} \exp(-\Delta E_v/kT)$. As in our case $[e^-] \approx B^{1/2} \exp(-\Delta E_v/kT)$, the $\lg[e^-]$ (which is proportional to $T^{3/4}$) versus $10^3/T$ dependence gives the 0.34 eV normalized slope. In consequence $E_a = 0.34$ eV.

Final calculations using (13) give:

$$\Delta E_v = 2 \times 0.34 - 0.92 + 2.08 - 1.05 = 0.79 \text{ eV} \quad (20)$$

Consequently the V_{Cd}^{2-} donor level is located at $\sim E_C - 0.8$ eV

in the CdTe gap. The position of the V_{Cd}^{2-} acceptor PD in the CdTe gap, obtained by different optical and electrical methods [11-17] lies in the $(E_v + 0.43 \text{ eV}) - (E_C - 0.06 \text{ eV})$ range. So our value, obtained by an alternative method satisfactorily fits in that area.

The obtained ΔE_v value should be adequate under the assumption that at elevated dopant content the foreign donors do not substantially interact one with the other by forming dopant bands in the gap. Another necessary assumption – the absence of considerable possible displacement of the A^- associate components at such doping level what can affect the associate formation enthalpy ΔH_A and consequently the ΔE_v value. If these

assumptions match, the obtained ΔE_v seems to be sufficiently grounded.

4. Conclusions

In saturated by In or Ga CdTe crystals free electron density measurements at high-temperature point defect equilibrium resulted in a matching straight-line temperature dependence with the 0.40 eV slope for both dopants. The respective data for both In- or Ga-doped crystals were very close although the real solute amounts of the both dopants in the material were different at identical temperatures. That was clarified by the analysis of the peculiarities of the dopant self-compensation process by comparison of the experimental electron density data with the values obtained by numeric simulation taking into consideration the known In(Ga) in CdTe solubility data.

An alternative calculation method of the V_{Cd}^{2-} donor energetic level location in the CdTe gap by use of both high-temperature electrical measurements results and Kröger's quasi-chemical reactions in solids thermodynamical formalism was developed. These computations resulted in the ~0.8 eV ionization energy of the V_{Cd}^{2-} donor, thus locating its energetic level at $\sim E_C - 0.8$ eV in the CdTe gap.

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