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# Formation Energies of Native Point Defects in II–VI Crystals

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**Abstract**—The formation energies of point defects in II–VI crystals have been evaluated from Hall measurement results and calculated by a thermodynamic method and the extended Hückel method. The energies obtained by different techniques are in satisfactory agreement with each other and with data in the literature.

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## INTRODUCTION

The study of the physicochemical properties of crystals through modeling of their defect structure requires precise knowledge of the parameters of point defects: defect formation and ionization energies, changes in the vibrational frequencies of atoms around a defect, etc.

Such parameters were calculated in many theoretical and experimental studies [5–12], but the use of different models, calculational and those that are used to interpret experimental data, leads to considerable discrepancies between results obtained by different groups. Therefore, the ability to calculate defect formation energies is an important issue.

Quantum mechanics allows one to comprehensively explain any experimental data and predict the properties of a system. Accurate calculations can, however, be performed for only the simplest systems (atoms and molecules). In the case of complex systems, additional simplifications and certain approximations are needed, which often influences both calculated defect formation energies and materials parameters calculated using these values. Therefore, it is more reasonable in practical calculations to use experimentally determined point defect formation energies.

In this paper, the energies of point defect formation in CdTe crystals are calculated using electron and hole concentrations measured as functions of temperature and cadmium or tellurium vapor pressure in two-temperature anneals of crystals. To verify the adequacy of the results, formation energies are also calculated using the extended Hückel method (EHM) and a thermodynamic method (TM) proposed, respectively, by Ganina et al. [5–7] and Verner and Nichugovskii [8] for calculations of vacancy formation energies in III–V semiconductors.

## DETERMINATION OF POINT DEFECT FORMATION ENERGIES

A crystal–vapor system is at equilibrium during two-temperature annealing if the components of the system have the same chemical potential in the crystal (s) and vapor (g):

$$\mu_i^s = \mu_i^g, \quad i = \text{Cd, Te}. \quad (1)$$

The Gibbs energy of an imperfect crystal, needed to find  $\mu_i^s$  ( $\mu_i^s = dG^s/dN_i^s$ ), can be represented in the form

$$G = U_0 + \sum E_i [D] + nE_c - pE_v - T(S_n + S_p + S_k), \quad (2)$$

where  $E_i$  is a defect formation energy, which takes into account changes in the vibrational energy of the crystal;  $[D]$  is the concentration of defect species  $D$ ;  $E_c$  and  $E_v$  are the energies of the conduction band bottom and valence band top, respectively;  $S_k$  is the configurational entropy; and  $S_n$  and  $S_p$  are the entropies of the electrons in the conduction band and holes in the valence band.

The entropy was determined using Boltzmann's law:

$$S_k = k \ln \left( \prod W_j \right) = \sum k \ln (W_j) = \sum S_j, \quad (3)$$

where  $W_j$  is the thermodynamic probability of the  $j$ th sublattice. For a sublattice containing several different defect species and having a site density  $N_j$  and for the electrons and holes in the conduction and valence bands, the thermodynamic probabilities are

$$W_j = \frac{N_j!}{(N_j - \sum [D])! \prod [D]!}, \quad W_n = \frac{N_c!}{(N_c - n)! n!}, \quad (4)$$
$$W_p = \frac{N_v}{(N_v - p)! p!},$$

where

$$n = N_c \exp\left(\frac{\mu}{kT}\right), \quad p = N_v \exp\left(-\frac{\mu + E_g}{kT}\right), \quad (5)$$

$N_c$  and  $N_v$  are the densities of states in the conduction and valence bands, respectively,  $E_g$  is the band gap, and  $\mu$  is the chemical potential of electrons, which was determined from the electroneutrality condition:

$$N_c \exp\left(\frac{\mu}{kT}\right) - N_v \exp\left(-\frac{\mu + E_g}{kT}\right) = \sum Z[D^z]. \quad (6)$$

The chemical potential of a defect, which is equal to the chemical potential of a component with the plus sign for interstitials and with the minus sign for vacancies, was found by differentiating the Gibbs energy with respect to defect concentration:

$$\begin{aligned} \mu_D^s = & E_D - kT \ln\left(\frac{N_j - \sum[D]}{[D_i]}\right) \\ & + \left[ n\left(\frac{E_c}{kT} - \ln\left(\frac{N_c - n}{n}\right)\right) + p\left(\frac{E_v}{kT} + \ln\left(\frac{N_v - p}{p}\right)\right) \right] \\ & \times \frac{kTZ_{D_i}}{\sqrt{(\sum Z[D])^2 + 4N_c N_v \exp(-E_g/kT)}}. \end{aligned} \quad (7)$$

The chemical potential of the gas is given by [13]

$$\begin{aligned} \mu^g = & kT \ln P + \mu_0, \\ \mu_0 = & kT(-\ln(kT) + \ln(h^3/(2\pi mkT)^{3/2})), \end{aligned} \quad (8)$$

where  $m$  is the atomic or molecular mass.

In a single defect approximation, formula (1), where the chemical potential of a defect is given by Eq. (7) and that of the vapor, by Eq. (8), considerably simplifies, and one can obtain an expression for the defect formation energy as a function of defect density. We assume that the carrier concentration considerably exceeds the intrinsic concentration and is determined by one defect species. If the dominant defects are donors and, accordingly, the majority carriers are electrons, we obtain from (1)

$$\begin{aligned} \pm(kT \ln P + \mu_0) = & E_i - kT \ln\left(\frac{N_j}{[D_i]}\right) \\ & + n\left(E_c - kT \ln\frac{N_c}{n}\right) \frac{Z_i}{|Z_i[D]|}, \end{aligned} \quad (9)$$

$$\begin{aligned} E_i = & \pm(kT \ln P + \mu_0) \\ & + kT \ln\left(\frac{N_j}{[D_i]}\right) - n\left(E_c - kT \ln\frac{N_c}{n}\right) \frac{1}{[D]}. \end{aligned} \quad (10)$$

Similarly, we have for acceptors and holes

$$\begin{aligned} \pm(kT \ln P + \mu_0) = & E_i - kT \ln\left(\frac{N_j}{[D_i]}\right) \\ & + p\left(E_v + kT \ln\frac{N_v}{p}\right) \frac{Z_i}{|Z_i[D]|}, \end{aligned} \quad (11)$$

$$\begin{aligned} E_i = & \pm(kT \ln P + \mu_0) + kT \ln\left(\frac{N_j}{[D_i]}\right) \\ & + p\left(E_v + kT \ln\frac{N_v}{p}\right) \frac{1}{[D]}. \end{aligned} \quad (12)$$

Equations (9)–(12) take into account the relations  $N_c \gg n$ ,  $N_v \gg p$ , and  $N_j \gg [D]$ .

Using the electroneutrality condition for one predominant point defect species in the form  $Z[D] = n$  or  $|Z|[D] = p$ , and experimental  $n(T)$  data for donors and  $p(T)$  data for acceptors, we obtain

$$\begin{aligned} E_i = & \pm(kT \ln P + \mu_0) + kT \ln\left(Z_i \frac{N_j}{n(T)}\right) \\ & - Z\left(E_c - kT \ln\frac{N_c}{n(T)}\right), \end{aligned} \quad (13)$$

$$\begin{aligned} E_i = & \pm(kT \ln P + \mu_0) + kT \ln\left(|Z_i| \frac{N_j}{p(T)}\right) \\ & + |Z|\left(E_v + kT \ln\frac{N_v}{p(T)}\right). \end{aligned} \quad (14)$$

In calculating defect formation energies by formulas (13) and (14), we assumed that the predominant defect species in CdTe crystals annealed in cadmium vapor is either a doubly ionized tellurium vacancy [12] or a doubly ionized cadmium interstitial [12]. In tellurium-saturated CdTe, possible predominant defect species are singly or doubly charged cadmium vacancies [1–4] or tellurium interstitials [4, 14].

With previous experimental data [4], the calculated formation energies of predominant defects are

$$\begin{aligned} E_{V_{Te}} = & 3.75 + 0.0006T \text{ (eV)}, \\ E_{Cd_i} = & 2.27 - 0.0024T \text{ (eV)}. \end{aligned} \quad (15)$$

To calculate  $E_{Cd_i}$  and  $E_{V_{Te}}$ , we used experimental  $n(T)$  data for  $T > 900$  K and  $T < 900$  K, respectively, and a model proposed by Fochuk et al. [12].

The  $E$  values calculated for a cadmium vacancy and tellurium interstitial in tellurium-saturated cadmium telluride using previous experimental data [9] are

$$\begin{aligned} E_{V_{Cd}} = & 3.66 + 0.0005T \text{ (eV)}, \\ E_{V_{Cd}^{2-}} = & 4.31 + 0.0004T \text{ (eV)}, \end{aligned} \quad (16)$$

$$\begin{aligned} E_{Te_i} = & 1.78 - 0.0019T \text{ (eV)}, \\ E_{Te_i^{2-}} = & 2.80 - 0.0023T \text{ (eV)}. \end{aligned} \quad (17)$$

To calculate  $E_{\text{Te}_i}$  and  $E_{V_{\text{Cd}}}$ , we used experimental  $p(T)$  data for  $T > 1000$  K and  $n(T)$  data for  $T < 1000$  K, respectively, and a model proposed by Prokopiv et al. [4].

The calculated defect formation energies (Table 1) take into account the defect ionization energies and changes in free vibrational energies. At  $T = 0$  K, the calculated energies are the sums of the formation and ionization energies of neutral defects. Note that the formation energies of neutral donors are lower than the calculated energies by the magnitude of the ionization energy, and those of acceptors are higher by the magnitude of the defect ionization energy [4].

To analyze the calculated energies in greater detail, we calculated the formation energies of neutral vacancies using the EHM [5–7] and TM [8]. The calculation results for II–VI compounds are presented in Table 2.

## RESULTS AND DISCUSSION

To compare the formation energies obtained here for ionized defects with data for neutral defects in the literature, their ionization energies should be taken into account. Interstitial cadmium produces shallow donor levels ( $\varepsilon_1 = E_c - 0.02$  eV [11] and  $\varepsilon_2 = E_c - 0.17$  eV [15]), and tellurium vacancies produce a shallow and a deep level ( $\varepsilon_1 = E_c - 0.035$  eV [14] and  $\varepsilon_2 = E_c - 0.34$  eV [15]).  $V_{\text{Cd}}^-$  ( $\varepsilon_1 = E_c - 0.05$  eV [16]) and  $\text{Te}_i^-$  ( $\varepsilon_1 = E_c - 0.15$  eV [14]) also act as shallow donors. Thus, the formation energies of neutral defects differ little from those calculated here.

The formation energies obtained here for  $\text{Cd}_i$  and  $V_{\text{Te}}$  agree well with those reported by Su-Huai and Zhang [10] and Fochuk et al. [12], which can be considered evidence for the adequacy of the present results. At the same time, the most likely formation energy of cadmium vacancies is  $\approx 3.2$ – $3.6$  eV, which was also used in earlier defect structure models [3] and is close to the value reported by Nobel [11] ( $\approx 3.2$  eV). The value obtained here for interstitial tellurium is very close to the 1.48 eV reported by Berding [9] (Table 1).

It is also worth pointing out that the formation energy obtained by Berding [9] for interstitial cadmium is a factor of 2 lower in comparison with other calculations, but it differs little from the value used by Grill et al. [3] in defect system modeling. At the same time, Sakalas [17] estimated the formation energy of interstitials using the formula  $E = zE_g/2$  ( $z$  is approximately equal to the valence of the atom), which yields 1.6 eV for  $E_{\text{Cd}_i}$ , at  $T = 0$  K, that is, well below the values obtained here and previously [10, 12]. Thus, the  $\text{Cd}_i$  formation energy may be lower than the value obtained by us.

The formation energies of cadmium and tellurium vacancies derived from Hall effect measurements cor-

**Table 1.** Calculated defect formation energies for CdTe

Energy, eV				Source
$V_{\text{Cd}}$	$\text{Cd}_i$	$V_{\text{Te}}$	$\text{Te}_i$	
3.66 ( $V_{\text{Cd}}^-$ )	2.27 ( $\text{Cd}_i^{2+}$ )	3.75 ( $V_{\text{Te}}^{2+}$ )	1.78 ( $\text{Te}_i^-$ )	This work
4.31 ( $V_{\text{Cd}}^{2-}$ )			2.80 ( $\text{Te}_i^{2-}$ )	
3.44	0.76; 1.10	5.56	1.48; 0.85	[9]*
2.67	2.04; 2.26	3.24	3.52; 3.41	[10]*
	2.1 ( $\text{Cd}_i^{2+}$ )			[12]

\* Neutral defects.

**Table 2.** Neutral vacancy formation energies (eV) calculated using the EHM [5–7] and TM [8]

II–VI	ZnS	ZnTe	CdS	CdTe
EHM	5.56, 4.33	4.08, 2.81	5.22, 4.00	3.65, 2.54
$E(V_A)$ , $E(V_B)$ ( $D$ )	8.23, 7.86	4.39, 5.01	6.79, 6.52	3.72, 4.44
$E(V_A)$ , $E(V_B)$ ( $E_{\text{at}}$ )	6.75, 6.38	3.71, 4.32	5.31, 5.04	3.12, 3.84

relate with the values obtained by the EHM and TM (Table 2).

In contrast to Verner and Nichugovskii [8], who proposed a thermodynamic method for evaluating vacancy formation energies, we determined the energy of bond breaking upon vacancy formation not by using the difference between the enthalpies of sublimation and formation from elements under standard conditions but by setting it equal to the atomization energy,  $E_{\text{at}}$ , of the compound [18] or the bond energy,  $D$  [19], like Ganina et al. [5–7] (Table 2).

It is worth noting that the enthalpies of monovacancy formation calculated by two different techniques agree well (Table 2), especially in the case of metal vacancies (Table 2). The enthalpies of chalcogen vacancy formation calculated by different techniques differ by more than 1 eV, which is essential for modeling the defect structure of crystals using these values. One possible reason for this is that some of the assumptions made in the above theory are not true. In particular, the assumption that  $sp^3$  hybridization persists for chalcogen vacancies may be invalid in the EHM because the nearest neighbors of a chalcogen vacancy are metal atoms. The energy of bond formation around a vacancy may also differ markedly from that proposed by Verner and Nichugovskii [8] (equal to the energy of melting of pure elements). Like in the EHM, it is reasonable to assume that uncertainty will be higher for metals that have delocalized, nondirectional metallic bonds in elemental form. An important point for II–VI compounds is to evaluate the effective atomic charges needed for TM calculation [8], which

determine the Coulomb energy because the concept of effective charge itself in crystals with nonionic bonding is rather ambiguous and its meaning depends significantly on the determination technique [19].

The TM [8] allows one to determine not only formation energies but also the bond strain around a vacancy. Our calculations indicate however that the strain is not high enough to produce significant changes in defect formation energies. For example, a vacancy in cadmium telluride changes the distance between its nearest and second neighbors by  $\approx 0.04 \text{ \AA}$ , which leads to changes in vacancy formation energy by a value of the same order.

Note that strain is often neglected in calculations, in particular in the EHM [5–7]. It is also worth pointing out that unionized and ionized defects may differ significantly (both quantitatively and qualitatively) in strain [20].

## CONCLUSIONS

We calculated the formation energies of vacancies and interstitials in CdTe using experimentally determined electron and hole concentrations as functions of annealing temperature and cadmium vapor pressure in two-temperature anneals.

Using the semiempirical Hückel method and a thermodynamic method, we calculated the enthalpies of formation of metal and chalcogen monovacancies in ZnS, ZnTe, CdS, and CdTe.

The strain around neutral vacancies was shown to have little effect on the formation energy of such defects.

The defect formation energies calculated by different techniques are in satisfactory agreement with each other and with data in the literature and can be used to evaluate defect densities in semiconductors.

## REFERENCES

1. Fochuk, P., Grill, R., and Panchuk, O., The Nature of Point Defects in CdTe, *J. Electron. Mater.*, 2006, vol. 35, no. 6, pp. 1354–1359.
2. Kosyak, V.V. and Opanasyuk, A.S., Calculation of Fermi Level Location and Point Defects Ensemble in CdTe Single Crystals and Thin Films, *Semicond. Phys. Quantum Electron. Optoelectron.*, 2007, vol. 10, no. 3, pp. 95–102.
3. Grill, R., Franc, J., and Höschl P. Semi-Insulating Te-Saturated CdTe, *IEEE Trans. Nucl. Sci.*, 2005, vol. 52, no. 5, pp. 1925–1931.
4. Prokopiv, V.V., Fochuk, P.M., Gorichok, I.V., and Vergak, E.V., Thermodynamics Analysis of Defects Created Processes in the Crystals of Cadmium Telluride in the Conditions of High Temperature Annealing, *Semicond. Phys. Quantum Electron. Optoelectron.*, 2009, vol. 12, no. 13, pp. 412–416.
5. Ganina, N.V., Shmugurov, V.A., and Fistul', V.I., Quantum-Chemical Determination of the Enthalpy of Formation of Monovacancies in Semiconductors, *Fiz. Khim. Tverd. Tila*, 2004, vol. 5, no. 3, pp. 430–435.
6. Ganina, N.V., Shmugurov, V.A., and Fistul', V.I., Quantum-Chemical Determination of the Enthalpy of Formation of Monovacancies in III–V Semiconductors, *Fiz. Khim. Tverd. Tila*, 2004, vol. 6, no. 1, pp. 94–95.
7. Ganina, N.V., Shmugurov, V.A., and Fistul', V.I., Enthalpy of Formation of Antisite Defects in III–V Compounds, *Fiz. Khim. Tverd. Tila*, 2006, vol. 7, no. 2, pp. 271–273.
8. Verner, V.D. and Nichugovskii, D.K., Formation Energy of Metal Vacancies in Gallium Arsenide and Indium Antimonide, *Fiz. Tverd. Tela* (Leningrad), 1973, vol. 15, pp. 2012–2013.
9. Berding, M.A., Native Defects in CdTe, *Phys. Rev.*, 1999, vol. 60, no. 12, pp. 8943–8950.
10. Su-Huai, W. and Zhang, S., Chemical Trends of Defect Formation and Doping Limit in II–VI Semiconductors: The Case of CdTe, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2002, vol. 66, paper 155 211.
11. Nobel, D., Phase Equilibria and Semiconducting Properties of Cadmium Telluride, *Philips Res. Rep.*, 1959, vol. 14, pp. 361–492.
12. Fochuk, P.M., Panchuk, O.E., and Shcherbak, L.P., The Nature of Predominant Point Defects in CdTe Crystals: Cd-Rich Region, *Fiz. Khim. Tverd. Tila*, 2004, vol. 5, no. 1, pp. 136–141.
13. Rumer, Yu.B., *Termodinamika, statisticheskaya fizika i kinetika* (Thermodynamics, Statistical Physics, and Kinetics), Moscow: Nauka, 1972.
14. Chern, S.S., Vydyanath, H.R., and Kroger, F.A., The Defect Structure of CdTe: Hall Data, *J. Phys. Chem. Solids*, 1975, vol. 14, no. 1, pp. 33–43.
15. Bobrova, E.A., Klevkov, Yu.V., Medvedev, S.A., and Plotnikov, A.F., A DLTS Study of Deep Levels in the Band Gap of Textured Stoichiometric *p*-CdTe Polycrystals, *Semiconductors*, 2002, vol. 36, no. 12, pp. 1341–1346.
16. Parfenyuk, O.A., Ilashchuk, M.I., Ulyanitskii, K.S., et al., Electrical Properties and Low-Temperature Luminescence of Si-Doped CdTe Crystals, *Semiconductors*, 2006, vol. 40, no. 2, pp. 143–147.
17. Sakalas, A., *Tochechnye defekty v poluprovodnikovykh soedineniyakh* (Point Defects in Compound Semiconductors), Vilnius: Mokslas, 1988.
18. Medvedev, S.A., *Vvedenie v tekhnologiyu poluprovodnikovykh materialov* (Introduction to Semiconductor Materials Technology), Moscow: Vysshaya Shkola, 1970.
19. Harrison, W., *Electronic Structure and Properties of Solids*, San Francisco: Freeman, 1980.
20. Lany, S., Ostheimer, V., Wolf, H., and Wichert, Th., Vacancies in CdTe: Experiment and Theory, *Phys. B*, (Amsterdam, Neth.), 2001, vols. 308–310, pp. 958–962.