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First principles calculations of indium impurity-cadmium vacancy complex in CdTe

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First principles calculations are used to study stability of the complex formed by indium impurity and cadmium vacancy in CdTe. Formation energies and transition energy levels of the cadmium vacancy, indium impurity and their complex in different charge states are calculated using supercell method within density functional theory in the local density approximation. From the analysis of binding energy of the complex it is found that formation of the complex is favorable and the neutral and single charged states of the complex are stable. The studies of the formation energy as a function of the Fermi level show that interaction between the shallow indium impurity and cadmium vacancy results in the Fermi level pinning near the middle of the semiconductor band gap and leads to the formation of semi-insulating material.
Keywords: cadmium telluride, point defects, first principles calculations, formation energy.

Расчетами из первых принципов изучена стабильность комплекса, образованного примесью индия и вакансией кадмия в CdTe. Энергия образования и переходные энергетические уровни вакансии кадмия, примеси индия и их комплекса в различных зарядовых состояниях рассчитывались методом суперячейки в рамках теории функционала плотности с использованием приближения локальной плотности. Из анализа энергии связи комплекса установлено, что формирование комплекса является энергетически выгодным, причем стабильными являются нейтральный и однозарядный состояния комплекса. Изучение зависимостей энергий образования дефектов от положения уровня Ферми показывает, что взаимодействие мелкой примеси индия с вакансией кадмия приводит к закреплению уровня Ферми вблизи середины запрещенной зоны полупроводника и способствует образованию полуизолирующего материала.

Дослідження з перших принципів комплексу домішка індію-вакансія кадмію у CdTe. *І.М.Юрійчук, С.В.Солодін, П.М.Фочук.*

Розрахунками з перших принципів вивчено стабільність комплексу, утвореного домішкою індію та вакансією кадмію у CdTe. Енергія утворення та перехідні енергетичні рівні вакансії кадмію, домішки індію та їх комплексу у різних зарядових станах розраховані методом суперкомірки у рамках теорії функціоналу густини з використанням наближення локальної густини. З аналізу енергії зв'язку комплексу встановлено, що формування комплексу є енергетично вигідним, причому стабільними є нейтральний та однозарядний стани комплексу. Вивчення залежностей енергій утворення дефектів від положення рівня Фермі показує, що взаємодія дрібної домішки індію з вакансією кадмію обумовлює закріплення рівня Фермі поблизу середини забороненої зони напівпровідника і сприяє утворенню напівізоляційного матеріалу.

1. Introduction

Cadmium telluride crystals are widely used as materials for X-ray and gamma-radiation detectors, solar cells, photodetectors, etc. To provide large values of specific resistance required for operation of such devices, concentration of the charge carriers in the crystals at room temperatures should be sufficiently low. Due to considerable con-

centration of native defects and residual impurities, the large values of resistivity can be achieved by compensation among various native defects and impurities. For this purpose, alloying impurities of the third and seventh groups are used, in particular, indium, which, replacing cadmium, is a shallow donor and compensates deep acceptors (usually cadmium vacancies) [1–3].

Defect complexes with the third and seventh group impurities are characteristic features of CdTe defect system. In particular, indium impurity in cadmium telluride grown at the high tellurium pressure, forms an anisotropic complex $(In_{Cd}^{+}V_{Cd}^{2-})^{-}$ that shows the acceptor properties (A-center) with the energy level of $E_a = E_v + 0.14$ eV and compensates the shallow donor In^{+} (self-compensation) [2, 3]. The self-compensation phenomena in CdTe<In> were modeled theoretically using quasichemical defect reaction theory, which had a number of parameters taken from the experiment [2]. Experimental data are often ambiguous, so it is important to use theoretical models that could simulate the crystal defect system from a single point of view. At present, such a challenging problem can be solved reliably only with the use of the first principles calculations, that is, the calculations which do not use any experimental data. This method was used successfully to study stability of a number of point defects in semiconductors [4, 5]. Using the first principles calculations for the system of native defects and impurities in different charge states [7, 8], concentration of defects and the position of the Fermi level [8, 9], relaxation of atoms nearby the defect [10] were studied in CdTe. The anisotropic complex formed by the shallow impurities and cadmium vacancy was studied from the first principles in [11–13]. In the current paper we present the first principles calculations for the complex formed by indium impurity and cadmium vacancy. Calculated formation energies of the complex and its constituents are used to analyze the conditions which are necessary for obtaining the semi-insulating material.

2. Computational details

Density functional theory (DFT) calculations in the local density approximation (LDA) [4] were performed to study the point defects in CdTe. The defects were modeled in a supercell, consisting of the defect surrounded by a finite number of atoms of the host material, which was then repeated periodically throughout space. Removing one of the atoms from the supercell (near its center) a vacancy is simulated, and replacing one of the atoms with another, one can simulate an impurity. Density functional total energy calculations for the supercell with various defect configurations allow to find the defect formation energies.

We performed total energy calculations as implemented in the ABINIT code [14]. A plane wave projector augmented wave (PAW) scheme was used to represent the core electrons of Cd ($4d^{10}4p^{6}5s^{2}$) and Te ($5s^{2}5p^{4}$). The local density approximation of Ceperley and Alder as parameterized by Perdew and Zunger was used for the exchange-correlation functional. The electron wave functions were expanded in a plane-wave basis with cutoff energy of 410 eV, which was determined from a series of calculations with different cutoff energies. Brillouin zone integrations were performed using k-point grid set of (2×2×2) generated according to the Monkhorst-Pack scheme. Minimization of the total energy of the supercell was carried out taking into account the relaxation of the next to the defect atoms only, until all forces were below 10^{-5} Ha/Bohr. The accuracy of the supercell total energy calculations was not less than 0.02 eV.

Formation energy of a defect X^q in the charge state q in CdTe is defined as [5]

$$E_f(X^q) = E_{tot}(X^q) - E_{tot}(\text{CdTe}) - \\ - \sum_i n_i \mu_i + q(E_v + E_F + \Delta V), \quad (1)$$

where $E_{tot}(X^q)$ is the total energy derived from the supercell calculation containing the defect X^q and E_{tot}(CdTe) is the total energy of the defect-free supercell. The integer n_i indicates the number of atoms of type i (Cd, Te or impurity atoms) that were added to ($n_i > 0$) or removed from ($n_i < 0$) the supercell to form a defect. The chemical potentials of these atoms μ_i are the average energies of the atoms in the reservoir, with which atoms are being exchanged. The last term in (1) represents the change in the energy due to exchange of electron with the electron reservoir, the average energy of which can be identified with the electron chemical potential, or the Fermi level E_F, referenced to the valence band maximum E_v. Formation energy of the charged defect calculated with the small supercells could include errors due to finite-size of the su-

percell. Potential alignment correction ΔV takes into account these errors and it is the difference between the electrostatic potential of the most unperturbed point in the defect containing supercell and the same point in the defect-free supercell [15].

The chemical potentials of the atoms are regarded as variables that can vary within specific bounds which are determined by properties of the reservoir that the system exchanges with. The total energy calculations of a perfect supercell gives only the sum of the chemical potentials of the atoms: $E_{tot}(\mathrm{CdTe}) = \mu_{\mathrm{Cd}} + \mu_{\mathrm{Te}}$. However, the chemical potential of cadmium μ_{Cd} in CdTe can not be greater than the chemical potential of cadmium μ^0_{Cd} in elemental cadmium (metal with a hexagonal lattice), otherwise, in the process of CdTe growing, a phase with the less energy would be formed. The equilibrium growth conditions with the highest possible value of the cadmium chemical potential are Cd-rich conditions. Accordingly, the chemical potential of tellurium μ_{Te} in CdTe can not be greater than the chemical potential μ^0_{Te} of tellurium in elemental tellurium (semiconductor in the hexagonal modification). Conditions for which the maximum value of the tellurium chemical potential is ensured is the Te-rich conditions. Taking into account that the formation enthalpy for CdTe ΔH is determined as $E_{tot}(\mathrm{CdTe}) = \mu^0_{\mathrm{Cd}} + \mu^0_{\mathrm{Te}} + \Delta H$, one can obtain the bounds of the change in cadmium and tellurium chemical potentials:

$$\mu^0_{\mathrm{Te}} + \Delta H \le \mu_{\mathrm{Cd}} \le \mu^0_{\mathrm{Cd}}, \text{ and}$$
$$\mu^0_{\mathrm{Cd}} + \Delta H \le \mu_{\mathrm{Te}} \le \mu^0_{\mathrm{Te}}.$$

In order to test the cadmium and tellurium pseudopotentials we have studied some elastic and electronic properties of the bulk CdTe. To determine the CdTe formation enthalpy ΔH, we first calculated the total energy of CdTe compound, and then the energy of Cd atoms in elemental cadmium and the energy of Te atoms in the elemental tellurium were calculated with the same pseudopotentials and exchange-correlation functional. Calculated formation enthalpy for CdTe compound $\Delta H = -1.01$ eV is quite close to the experimental value of 0.96 eV [7]. Calculated CdTe band structure is in a good agreement with the experimental data as well. However, the band gap at Γ point is almost three times less than the experimental value. This is well-known drawback of

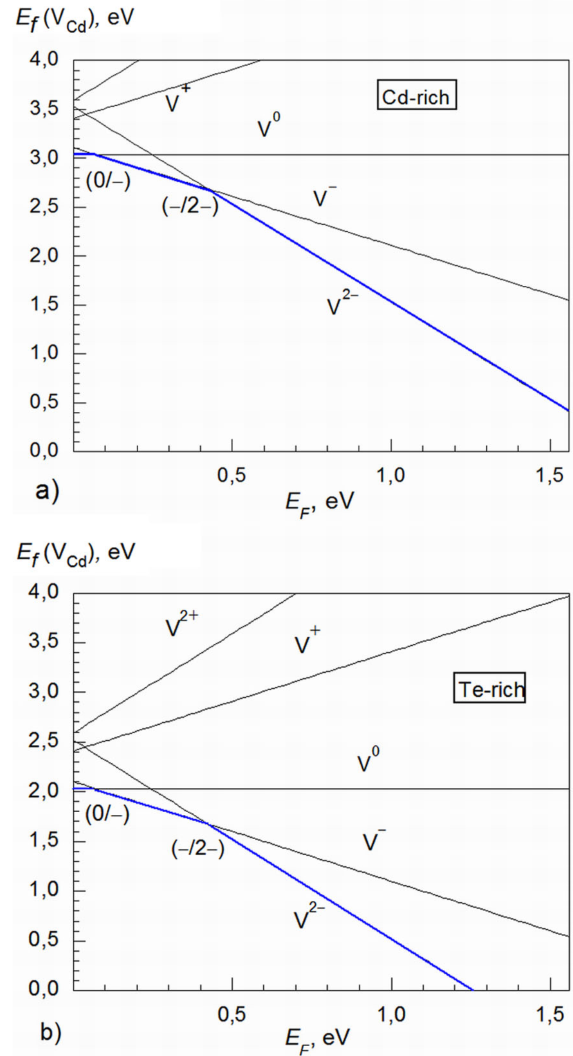


Fig. 1. Formation energies of cadmium vacancy in CdTe as functions of the Fermi level in Cd- and Te-rich conditions.

DFT in the LDA approximation, which can be taken into account by the scaling of the theoretically calculated band gap to the experimental one [16]. Calculated lattice parameter of CdTe $a = 6.42$ Å is close to the experimental value $a = 6.48$ Å (the deviation is less than 1 %). Somewhat smaller values of the lattice parameter compared to the experimental ones are typical for the LDA calculations.

3. Results and discussion

Calculations of the defect formation energies were performed using a 64-atom cubic cell with the theoretically calculated lattice parameter. To simulate a defect in the charge state q, a certain number of electrons was added to $(q < 0)$ or removed from $(q > 0)$ the supercell into the electron reser-

Table. Formation energies and transition energy levels of cadmium vacancy, indium impurity and their complex in CdTe

Defect	E_f, eV (Cd-rich)	E_f, eV (Te-rich)	$E(q_1/q_2)$, eV			
			$E(+/2+)$	$E(+/0)$	$E(0/-)$	E(−/2−)
V_{Cd}^0	3.04	2.03	–	–	$E_v + 0.07$	$E_v + 0.42$
In_{Cd}^0	2.30	1.32	–	$E_c + 0.12$	–	–
$(V_{Cd}In_{Cd}^0)$	3.51	1.49	–	–	$E_v + 0.17$	–

voir, whose average energy is the Fermi level. Since it is impossible to take into account more than one defect in the supercell method, the Fermi level in such approach is a parameter. A stable charge state of the defect is the energetically most favorable charge state for a given location of the Fermi level in the bad gap of the semiconductor. As follows from (1), the dependence of formation energy of the defect in charge state q on the Fermi level is linear. The slope of the dependence is determined by the sign and value of the charge state.

Calculated formation energies of cadmium vacancy in CdTe as functions of the Fermi level for two limiting cases — cadmium and tellurium rich conditions are presented in Fig. 1. As follows, the vacancy may be in three charge states: V_{Cd}^0, V_{Cd}^-, V_{Cd}^{2-}. Other charge states (for example V_{Cd}^+ or V_{Cd}^{2+}) are energetically unfavorable. The charge states are successively changing from V_{Cd}^0 up to V_{Cd}^- and V_{Cd}^{2-} with increasing of the Fermi level position from the valence band maximum. The formation energy of the negatively charged cadmium vacancies decreases with the capture of the electron, that is, V_{Cd}^- vacancy, as well as V_{Cd}^{2-} vacancy shows acceptor properties.

The Fermi level position in the band gap for which the charge state of the impurity changes from q_1 to q_2, is the transition level energy $E(q_1/q_2)$. The transition levels values correspond to thermal ionization energies of the defect, which are observed experimentally. Calculated transition level (0/−) for the single charged cadmium vacancy referenced to the valence band maximum is $E(0/-) = E_v + 0.07$, hence the ionization energy of V_{Cd}^- is of 0.07 eV. For the double charged vacancy we have $E(-/2-) = E_v + 0.42$ eV. The calculated ionization energies are in a good agreement with the known experimental data, which suggest two acceptor vacancy levels in the following bounds $E(0/-) = E_v + 0.05 \div 0.2$; $E(-/2-) = E_v + 0.47 \div 0.8$ eV [17]. The formation energies of the defects in the neutral charge state and the energy of the transition levels are presented in Table. Note, that the accuracy of the formation energies and transition energy levels calculations in the model is of 0.1−0.2 eV.

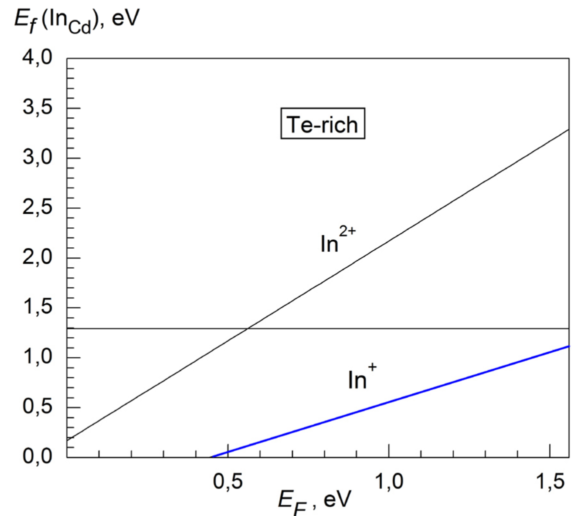
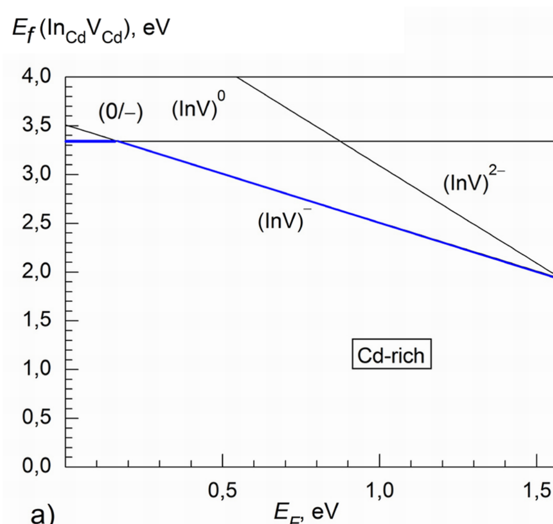


Fig. 2. Formation energies of indium impurity in CdTe as functions of the Fermi level in Te-rich condition.

The formation energies of indium impurity in different charge states in CdTe (Te-rich conditions) as functions of the Fermi level are presented in Fig. 2. The calculations show that two charge states In_{Cd}^+ and In_{Cd}^{2+} are stable, moreover the single charged state has lower formation energy. Thus, for indium impurity it is favorable to get rid of electrons, that indicates the donor nature of the impurity. The transition level $E(0/+) = E_c + 0.12$ eV is located outside the bandgap, but is within the error of the calculations.

Modeling of indium impurity-cadmium vacancy complex have been performed by removing one cadmium atom from the supercell and replacing one cadmium atom in the neighboring site by indium atom. The



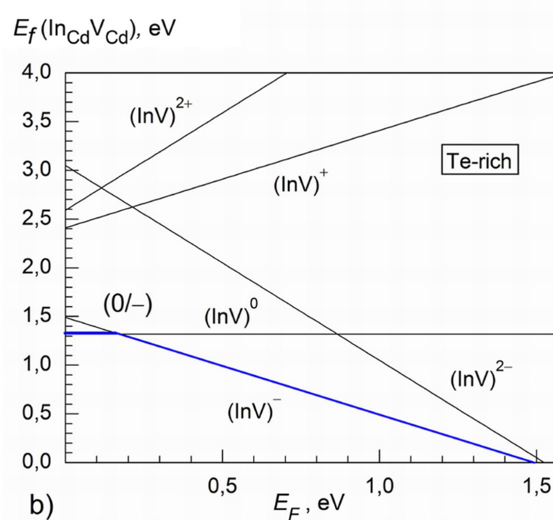
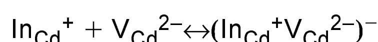


Fig. 3. Formation energies of In_{Cd}–V_{Cd} complex in CdTe as functions of the Fermi level in Cd- and Te-rich conditions.

complex, as well as the cadmium vacancy, shows an ability to capture electrons by acquiring a negative charge, that indicates the acceptor properties of the defect (Fig. 3). The neutral $(In_{Cd}V_{Cd})^0$ and the single charged $(In_{Cd}V_{Cd})^-$ states of the complex are stable. The calculated energy of the transition level $E(0/-) = E_v + 0.17$ eV is close to the experimental values for the ionization energy of the complex [1, 3].

The complex binding energy is the energy difference between the complex formation energy and the sum of the formation energies of its isolated constituents. For the complex $(In_{Cd}V_{Cd})^-$ the binding energy E_b can be found from the reaction



$$In_{Cd}^{+} + V_{Cd}^{2-} \leftrightarrow (In_{Cd}^{+}V_{Cd}^{2-})^{-}$$

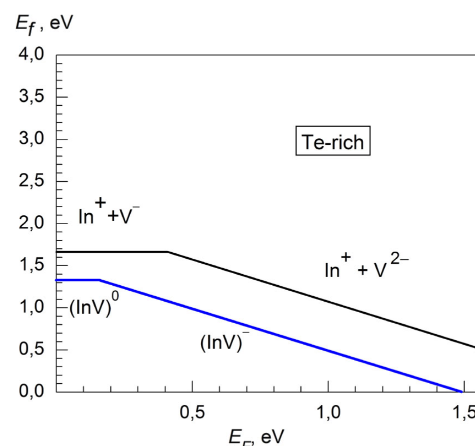


Fig. 4. Formation energies of In_{Cd}–V_{Cd} complex and the sum of formation energies of In impurity and cadmium vacancy in CdTe as functions of the Fermi level (Te-rich conditions).

and it is given as

$$E_b = E_f(In^{+}_{Cd}) + E_f(V^{2-}_{Cd}) - E_f(In^{+}_{Cd}V^{2-}_{Cd})^{-}. \quad (2)$$

The calculated binding energy of the single charged complex is $E_b = 0.59$ eV, and for the neutral complex — $E_b = 0.34$ eV. Consider the graphical interpretation of the calculations. In the case when the indium impurity and cadmium vacancy do not interact, the formation energy of such isolated defects is the sum of their formation energies. Fig. 4 presents the formation energy of the indium impurity-cadmium vacancy complex and the sum of formation energies of indium impurity and cadmium vacancy as a function of the Fermi level. As follows, formation of the complex is more favorable, which means that the complex is stable, and the difference between two dependencies determines the binding energy of the complex.

Consider a model that explains semi-insulating properties of the cadmium telluride doped with indium. We proceed from the assumption that in Te-rich conditions predominant native defects is cadmium vacancies, and formation of interstitial cadmium atoms and tellurium vacancies are unlikely [2]. The formation energies of cadmium vacancy, indium impurity and their complex in Te-rich conditions as functions of the Fermi level are presented in Fig. 5. Bold lines indicate the defects with the lowest formation energies. These defects have the highest concentration under equilibrium conditions, since concentration depends exponentially on the formation energy [5]

$$[X^q] = N_s N_{conf} e^{-\frac{E_f(X^q)}{kT}}, \quad (3)$$

where N_s is the number of lattice sites, N_{conf} is the number of internal degrees of freedom of the point defect (N_{conf} = 12 in the case of impurity-cadmium vacancy complex).

Shape of the broken line formed by the formation energies of the double negatively charged cadmium vacancy, the single positively charged indium impurity and the single negatively charged complex indicates that the position of the Fermi level in the band gap of CdTe is within the range from 0.5 eV to 1.2 eV. Therefore, alloying of cadmium telluride by indium in the equilibrium conditions locates the Fermi level near the middle of the band gap (the Fermi level pinning). This is due to formation of the complex of the indium impurity with cadmium vacancy and their self-compensation. For the Fermi level position in the band gap near 1.0 eV the concentration of all defects is almost the same. Taking into account that the cadmium telluride crystals usually annealed at temperatures close to 1000 K, the concentration of the defects at room temperatures is about $5 \cdot 10^{19}$ cm^{-3}. For the lower concentrations of indium impurity, one should expect the smaller concentrations of the complex and an increase of the double charged cadmium vacancies concentration.

4. Conclusions

It is found that the formation energy of the cadmium vacancy-indium impurity complex is less than the sum of the formation energies of its isolated constituents which means that the complex is stable. The cadmium vacancy-indium impurity complex can be in neutral and single negatively charged states and shows the acceptor properties. Calculated transition energy level E(0/−) = E_v + 0.17 eV is consistent with the experimental data for the ionization energy of the complex. The studies of the formation energies of cadmium vacancy, indium impurity and their complex as a functions of the Fermi level indicate that the position of the Fermi level in CdTe band gap is within the range from 0.5 eV to 1.2 eV. Therefore, alloying of cadmium telluride by indium in the equilibrium conditions locates the Fermi level near the middle of the band gap (the Fermi level pinning), that is the result of self-compensation.

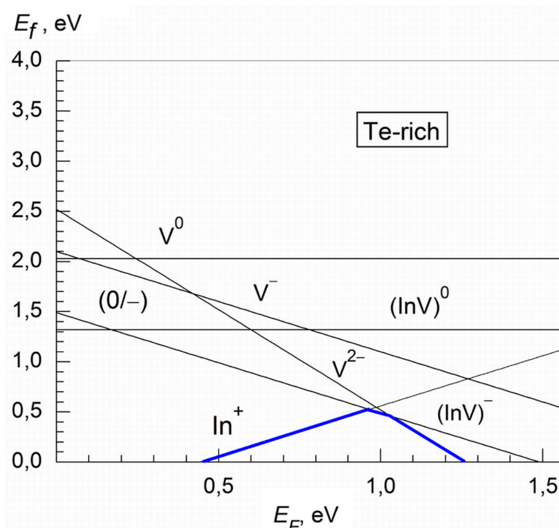


Fig. 5. Formation energies of the defects in CdTe as functions of the Fermi level (Te-rich conditions).

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