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Research Article

Determination of stoichiometry deviation in wide-band II–VI semiconductors on the basis of equilibrium vapor phase composition

Svetlana P. Kobeleva[1]

1 National University of Science and Technology MISiS, 4-1 Leninsky Ave., Moscow 119049, Russia

Corresponding author: Svetlana P. Kobeleva (kob@misis.ru)

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Abstract

A method has been suggested for determining stoichiometry deviation in cadmium and zinc chalcogenides based on the temperature dependence of the ratio of components partial pressures during evaporation of solid compounds in a limited volume. The new method differs from methods implying the collection of excessive component during evaporation in large volumes. The method includes measuring the partial pressures of vapor phase components during material heating to above 800 K, solving a set of material balance equations and the electric neutrality equation, and calculating the stoichiometry deviation in the initial compound at room temperature. Intrinsic point defect concentrations are calculated using the method of quasichemical reactions. The independent variables in the set of material balance equations are the sought stoichiometry deviation, the partial pressure of the metal and the concentration of free electrons. We show that the parameter of the material balance equation which determines the method's sensitivity to stoichiometry deviation, i.e., the volume ratio of vapor and solid phases, can be considered constant during heating and evaporation if this parameter does not exceed 50. If the partial pressure is measured based on the optical density of the vapors, then the sensitivity of the method can be increased to not worse than 10^{-6} at.%.

Keywords

stoichiometry deviation, wide-band semiconductors, cadmium and zinc chalcogenides, partial pressur

1. Introduction

II–VI group semiconductors, including cadmium and zinc chalcogenides, are used for visible and IR range receivers and emitters [1, 2], ionizing radiation detectors [2–5], solar cells [6–8] and for a number of other optoelectronic applications [9].

Intrinsic point defects in II–VI compounds are electrically active and critically affect the electrical conductivity and the optical properties of the compounds [2, 10, 11]. For this reason, determination of stoichiometry deviation δ which is caused, primarily, by intrinsic point defects is important for understanding the intrinsic point defect formation mechanisms and the assessment of materials synthesis process quality. There are currently no standard methods to determine δ [12, 13]. Since the homogeneity region limits are within 10^{-4} at.%, methods of analytical chemistry are not applicable. Nor is secondary ion mass spectroscopy **(SIMS)**, because the problem in question is to determine the content of the main element with an

accuracy of not worse than 10^{-4} at.%. Therefore all the methods of determining δ are based on the specific features of the evaporation of these compounds.

II–VI compounds decompose completely in the vapor phase into metal atoms and diatomic (tetra- or hexa-atomic) chalcogen molecules [10–16]. A description of the evaporation kinetics of II–VI compounds is based on the account of diatomic chalcogen molecules, and the concentration of diatomic and tetra-atomic sulfur and selenium molecules can be calculated on the basis of well-known thermodynamical data [15]. The component partial pressures P_A and P_{B_2} are correlated by the evaporation constant K_{AB} [10]:

$$A_{B_S} = A_V + \frac{1}{2} B_{2V}; \quad K_{AB} = P_A P_{B_2}^{1/2}, \tag{1}$$

where the indices S and V denote the solid and the vapor phases, respectively, A denotes cadmium or zinc atoms and B denotes chalcogen atoms (Te, S, Se).

Despite the relatively small component excess in the solid state, the thermodynamically equilibrium vapor phase consists mainly of metal atoms during material evaporation with an excess of the metal or diatomic chalcogen molecules if there is an excess of the chalcogen. This is illustrated in Fig. 1 showing the ratio of cadmium (P_{Cd}) and tellurium (P_{Te_2}) partial pressures $\gamma = P_{Cd}/P_{Te_2}$ in CdTe at 900 K. In a wide temperature range the equilibrium partial pressures of the components are similar to the equilibrium saturated vapor pressures at each specific temperature and are set by the respective equations [17, 18]:

$$P_{Cd} = 137025 \exp\left(-\frac{1.056}{kT}\right); \tag{2}$$

$$P_{Zn} = 197380 \exp\left(-\frac{1.239}{kT}\right); \tag{3}$$

$$P_{Te_2} = 52372 \exp\left(-\frac{1.183}{kT}\right). \tag{4}$$

The partial pressure of the second component can be calculated based on the evaporation constant (Eq. (1)).

Most of δ measurement methods imply analysis of the material condensing at the cold end of the measuring system [11–14]. In fact, these methods implement evaporation in a large volume during which the excessive component is evaporated, and the composition of the solid compound tends to the so-called congruently evaporating composition, i.e., the only composition at a specific temperature for which the number of metal atoms and the number of chalcogen atoms in the vapor phase are equal, and the ratio of the partial pressures of the metal and the diatomic chalcogen molecule is $\gamma = 2$. This composition gives the minimum Gibbs energy of the crystal and the minimum total pressure of the vapor phase. Thus the methods employing analysis of the excessive component in the vapor phase during evaporation in an unlimited volume allow one to determine δ at the homogeneity region limits. However, as can be seen from Fig. 1, the composition of the equilibrium vapor phase is extremely sensitive to δ during evaporation of a compound in a vapor phase volume that is relatively small in comparison with the solid phase volume. The data shown in Fig. 1 were obtained in the assumption that the volume of the solid phase did not change during evaporation, i.e., evaporation occurred in a small volume.

The aim of this work is to derive a material balance equation describing the composition of equilibrium vapor and solid phases at the evaporation temperature T and to assess the limits of δ that can be determined using this method.

2. Theoretical description of evaporation of II–VI compounds in closed volume

During evaporation of II–VI compounds in a reactor having the volume $V = V_{0s} + V_{0g}$, the number of atoms in the reactor does not change, i.e.:

$$\frac{C_{A_s} V_s + C_{A_g} V_g}{C_{B_s} V_s + C_{B_g} V_g} = \frac{C_{A_{s0}}}{C_{B_{s0}}} = \text{const}, \tag{5}$$

where $C_{A,B}$ is the concentration of the components A and B in the solid ("s") and vapor ("g") phases in the reactor, respectively, and "0" denotes the system status at room temperature.

The stoichiometry deviation is $\delta = CA_s - CB_s < 10^{-4}$ at.fractions.

Therefore

$$\frac{C_{A_{s0}}}{C_{B_{s0}}} = 1 + \frac{\delta_0}{C_{B_{s0}}}. \tag{6}$$

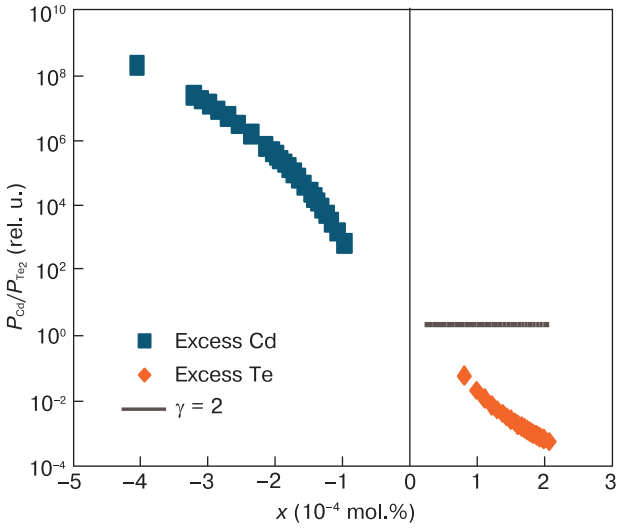

Figure 1. Ratio of partial pressures as a function of δ for CdTe at 900 K.

At a vapor pressure of less than 1 atm, gas can be considered ideal, and therefore

$$C_{A_g} = \frac{P_A}{k_B T}; \quad C_{B_g} = \frac{2P_{B_2}^{1/2}}{k_B T}. \tag{7}$$

where k_B is the Boltzmann constant and T is the temperature, K.

Accepting that the solid phase is homogeneous, the component concentration in the solid phase can be expressed via the concentration of intrinsic point defects:

$$C_{A_S} = C_{A_A} + C_{A_B} + C_{A_i},$$

$$C_{B_S} = C_{B_B} + C_{B_A} + C_{B_i}, \tag{8}$$

where A_A and B_B are lattice site atoms, A_B and B_A are antistructural defects and A_i and B_i are interstitial atoms. All these defect types can be neutral, single- or double-charged.

Taking into account Eqs. (6)–(8) one can rewrite Eq. (5) as follows:

$$\delta - \delta_0 + \frac{\alpha}{k_B T}\left(P_A - 2P_{B_2}\right) = 0, \tag{9}$$

where $\alpha = V_g/V_s$.

Here we take into account that

$$\frac{C_{B_s}}{C_{B_{s0}}} \cong 1; \quad \delta_0 \ll 1.$$

This is the sought material balance equation which correlates, via the partial pressures of the components, the vapor phase composition, having current thermodynamically equilibrium composition of the evaporating compound δ for the volume ratio of the vapor and solid phases α, with the sought stoichiometry deviation at room temperature δ_0. The concentration of intrinsic point defects will be expressed via the constants of the quasichemical reactions of their formation [10]:

$$CX_j^i = P_A^j n^i K_{X_j^i}, \tag{10}$$

where X is the type of intrinsic point defects, $i = 0, +1, +2, –1, –2$ for neutral, single- and double-charged acceptors and single- and double-charged donors, respectively; $j = +1$ for chalcogen vacancies and interstitial metal atoms (donor centers); $j = +2$ for metal atoms at chalcogen sites (antistructural defects in the chalcogen lattice which are acceptor centers); $j = –1$ for interstitial chalcogen atoms and metal vacancies (acceptor centers); $j = –2$ for antistructural defects in the metal lattice (donor centers). The quasichemical reaction constants have Arrhenius' form:

$$K_X = K_{X0} \exp\left(-\frac{E_a}{k_B T}\right). \tag{11}$$

Taking into account earlier results [1], Eq. (9) contains three independent variables: P_A, n and δ_0. One more equation which contains the independent variables P_A and n is the electrical neutrality equation:

$$n + V_A^- + 2V_A^{--} + A_B^- + 2A_B^{--} + B_i^- + 2B_i^{--} =$$
$$= p + A_i^+ + 2A_i^{++} + V_B^- + 2V_B^{++} + B_A^+ + 2B_A^{++}, \tag{12}$$

$n \times p = n_i^2$, n_i being the intrinsic concentration of the semiconductor [19].

If the volume of the vapor phase is sufficiently large, the parameter α depends on the evaporation temperature and the parameter δ_0. Let us determine the conditions under which α can be considered constant.

If the change in the volumes of the solid and vapor phases is $\Delta V = \Delta V_s = -\Delta V_g$, then

$$\frac{V_g}{V_s} = \frac{\frac{V_{g0}}{\Delta V} + 1}{\frac{V_{s0}}{\Delta V} - 1}. \tag{13}$$

The sought condition is satisfied if

$$\frac{V_{s0}}{\Delta V} \gg 1, \tag{14}$$

and

$$\frac{V_{g0}}{\Delta V} \gg 1. \tag{15}$$

Let us determine the limits of $V_{g0}/\Delta V$.

At the metal excess side:

$$\frac{V_g}{\Delta V} = \frac{k_B T C_{A_s}}{P_A}, \tag{16}$$

and at the chalcogen excess side:

$$\frac{V_g}{\Delta V} = \frac{k_B T C_{B_s}}{2P_{B_2} A}. \tag{17}$$

Based on the P–T diagram of cadmium and zinc chalcogenides [10, 14], the maximum P_{Cd} for CdTe is about 5 atm at 1250 K, the concentration of Cd and Te atoms is about 10^{22} cm^{-3} and $V_{g0}/\Delta V \cong 500$. The maximum pressure is even lower, i.e., ~0.2 atm, and $V_{g0}/\Delta V \cong 10000$. With a decrease in temperature, the $V_{g0}/\Delta V$ ratio grows exponentially and hence over the entire solid phase existence temperature range the condition of Eq. (15) is satisfied.

We will now assess the validity range of the condition expressed by Eq. (14).

If metal is in excess in the vapor phase, then

$$\frac{V_s}{\Delta V} = \frac{V_s k_B T C_{A_s}}{V_g P_A} = \frac{k_B T C_{A_s}}{\alpha P_A}. \tag{18}$$

If chalcogen is in excess in the vapor phase, then

$$\frac{V_s}{\Delta V} = \frac{V_s k_B T C_{B_s}}{V_g 2P_{B_2}} = \frac{k_B T C_{B_s}}{2\alpha P_{B_2}}. \quad (19)$$

The condition of Eq. (14) is satisfied if:

– for metal excess

$$\alpha < \alpha_{cr.} = \frac{0.1 k_B C_{A_s}}{P_A}; \quad (20)$$

– for chalcogen excess

$$\alpha < \alpha_{cr.} = \frac{0.1 k_B C_{B_s}}{2P_{B_2}}. \quad (21)$$

Figure 2 shows the critical values of the parameter α for the homogeneity range limits at the Cd excess side, at the Te excess side and for the congruently melting composition P_{min}.

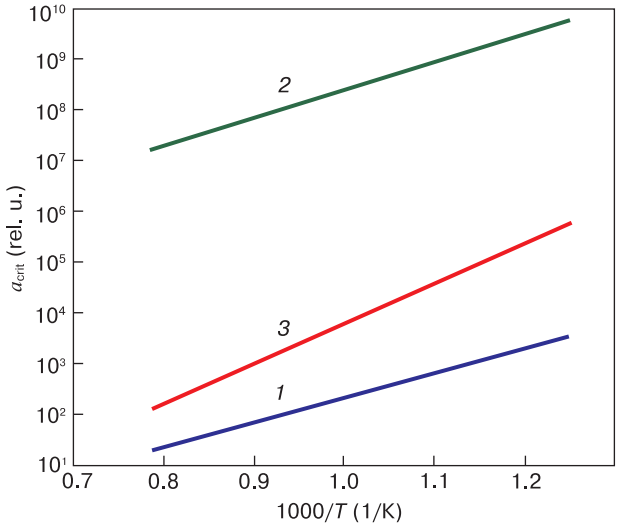

Figure 2. Temperature dependence of critical ratio of vapor and solid phase volumes for CdTe: (*1*) at the Cd excess side, (*2*) at the Te excess side and (*3*) for the congruently evaporating composition P_{min}.

It can be seen from Fig. 2 that the volume ratio of the vapor and solid phases required for the parameter α to be considered independent on evaporation conditions in Eq. (9) is sufficient for the parameter α to not exceed 50–100 depending on the evaporation temperature. The smaller the parameter α, the more sensitive the partial pressure measurement results to the parameter δ_0.

This is illustrated by Fig. 3 showing the trend of change in the temperature dependence of γ with a change in the parameter α for the case when the composition P_{min} contains an excess of chalcogen (example is the CdTe compound) for three initial δ_0 (*1* for the greatest chalcogenide excess, *3* for the composition P_{min} and *2* for a composition with metal excess).

The solid lines in Fig. 3 for the composition P_{min} are the temperature dependences for the case when charged defects are predominant, and the dotted lines show the dependence of vapor composition at above T_{Pmin} for the case of predominantly electrically neutral defects. The vapor composition for $\gamma = 2$ corresponds to congruent evaporation of the compound.

Thus, the sets of Eqs. (9) and (12) contain three independent variables. If during heating of the reactor with the material to the temperature *T* one can measure the partial pressure of at least one of the components, then, given the evaporation constant and the constants of intrinsic point defect formation reactions, one can calculate *n* and δ_0.

However there is currently no authentic information on the composition and formation parameters of intrinsic point defects in II–VI compounds. Even for the best studied material CdTe there are at least 6 defect formation models suggesting different compositions and formation reaction parameters [20–25]. Therefore measurements of the temperature dependence of vapor composition during evaporation in a limited volume are useful for refining the model of defect formation in the material.

3. Measurement of component partial pressures

The optimum implementation of the suggested method for determining stoichiometry deviation is the partial pressure measurement approach put forward by R.F. Brebrick, based on the optical density of the vapor phase at the specific wavelength [26] typical of the atoms or molecules being studied. The reactor design contains two interconnected containers. One container is held at

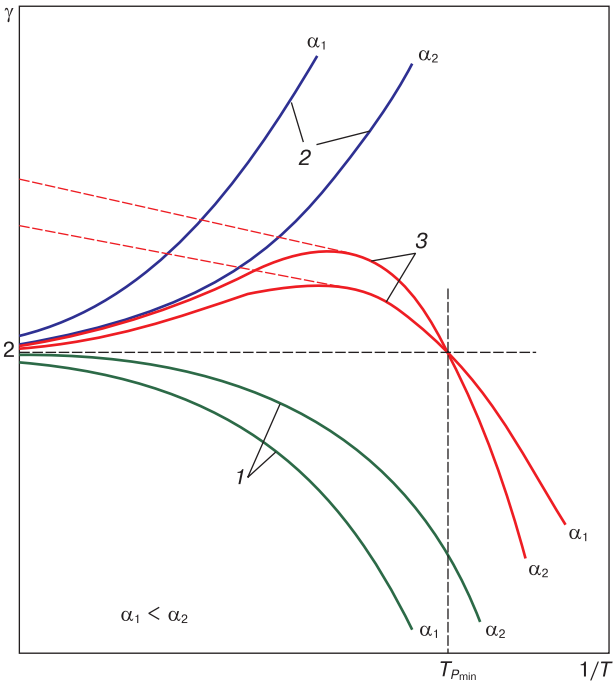

Figure 3. Temperature dependences of $\gamma = P_A/P_{B_2}$: (*1*, *3*) $\delta_0 < 0$; (*2*) $\delta_0 > 0$ (*1* is composition with maximum excess of chalcogen; *3* is the composition P_{min} at the temperature T_{min}; *2* is composition with excess metal).

a relatively low and variable temperature, where the test material is loaded. The other one is an optical section held at a higher temperature than that of the test material container, for preventing deposition of the material onto the optical windows. For the design option described [26], the parameter α does not exceed 50. It is this method that showed that the vapor phase of II–VI compounds at the homogeneity range limits consists mainly of the excessive component, and that over a wide temperature range the component partial pressures are equal to the component saturated vapor pressures. Thus the method was only used for studying the homogeneity range limits. The earlier reported detection limit of 10^{-4} mol.% [13] does not correspond to the solid state stoichiometry deviation sensitivity (no such calculations were carried out [26]), but to the underestimated sensitivity of the method to the vapor phase composition. However, even with this sensitivity to individual components, the variation range of γ is at least eight orders of magnitude.

Another reactor design option was suggested [27] in which the optical section and the evaporated compound container are integrated. This embodiment allows one to use Eq. (9) for δ_0 calculation over a wide range (up to 10^{-6} at.% of excessive component). This reactor design option for measurement of equilibrium partial component pressures of cadmium and zinc chalcogenides allows one to reduce the parameter a and hence to increase the stoichiometry deviation sensitivity of the method.

4. Conclusion

It was suggested to analyze the composition of equilibrium vapor phase using the material balance equation

$$\delta - \delta_0 + \frac{\alpha}{k_B T}\left(P_A - 2P_{B_2}\right) = 0,$$

where the parameter $\alpha = V_g/V_s$ determines the sensitivity of the method to δ_0. Conditions were assessed under which the parameter α can be considered constant for δ_0 calculation simplicity. Coupled with the solution of the electrical neutrality equation, this provides for the completeness of the set of two equations with two variables, i.e., δ_0 and the concentration of conduction electrons. Partial pressure measurements on the basis of the optical density of vapors are the most suitable variant. Taking into account the sensitivity of pressure measurements based on the optical density of vapors, one can calculate δ_0 in the range of up to 10^{-6} at.%.

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