Formation and activation of defects in films of $A^{IV}B^{VI}$ compounds in the process of growing from vapor phase

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Abstract. The work has suggested an adequate model describing formation of defects in films of $A^{IV}B^{VI}$ compounds in vapor-phase growth. Being based on this model, it has given an analytical description of dependences for film electrophysical parameters (concentrations n, p and mobilities μ_n, μ_p of free charge carriers) on technological factors of film growth. We have calculated concentrations of activated and inactivated defects as subject to temperature of film deposition. The developed model enables determination of entropy and enthalpy of defect formation processes.

Keywords: defects, thin film, $A^{IV}B^{VI}$ compounds, film growth.

1. Introduction

Semiconductor films of $A^{IV}B^{VI}$ components contain various structural defects affecting considerably their electrophysical behavior. The principal technological parameters determining the structural perfection, level of deviation from stoichiometry of films grown using different methods from the vapor phase are temperatures of deposition and evaporation, partial pressures of vapors of chalcogen and metal in the condensation zone and also during immediate deposition [1].

Ascertaining the nature and behavior of various structural defects is a necessary condition for scientific management of structurally sensitive properties and processes.

2. Experiment and calculations

Most of defects formed in the course of film growth by deposition are thermodynamically unstable, and a system in this case comes into imbalance. Equilibrium can be obtained by various means and, as a rule, is realized by a range of meta-steady states. The defects of one type while interacting can annihilate or create defects of other types.

Often quasi-chemical reactions with predetermined enthalpies are used for supporting technological dependences. Thus, a balance of point atomic defects of a compound *MN* and molecules of vaporized metal *M* or chalcogen *N* at a temperature of film deposition T_S is described, for instance, using the following quasi-chemical reactions and correlations for concentrations and pressures:

$$M^V \rightarrow M_i, \ K_1(T_S) = [M_i] / P_M, \tag{1}$$

$$1/2 N_2^V \rightarrow N_N + V_M, \ K_2(T_S) = [V_M] / P_{N_i}^{1/2}, \tag{2}$$

$$K_i = K_i^0 \exp\left(-\Delta H_i / kT_S\right)$$

is an equilibrium constant, and ΔH_i is enthalpy of the i-th quasi-chemical reaction.

An evaporation of the material *MN* at the evaporator's temperature T_E occurs with dissociation:

$$MN^S \rightarrow M^V + 1/2 N_2^V, \ K_3(T_E) = P_M / P_{N_i}^{1/2}. \tag{3}$$

Solution of the equation set (1)–(3) produces dependences of defect concentration on temperature of deposition and evaporation:

$$[M_i] = [M_i]_\infty \exp\left(-\Delta H_1 / kT_S\right), \tag{4}$$

$$[V_M] = [V_M]_\infty \exp\left(-\Delta H_2 / kT_S\right), \tag{5}$$

$$[M_i]_\infty = K_1^0 P_M(T_E), \ [V_M]_\infty = K_2^0 P_{N_i}^{1/2}(T_E).$$

These dependences are linearized in coordinates of logarithm of concentration inversely proportional to temperature, i.e. depending on the enthalpy sign they must have areas of swift rise at decreasing or increasing temperatures.

It should be mentioned that if a concentration of one type of defects outnumbers and exceeds the intrinsic concentration of charge carriers n_i, a concentration of free charge carriers n equals a concentration of outnumbering defects.

Let us examine experimental dependences of concentration and mobility of free charge carriers upon the temperature of films deposition for lead and tin chalcogenides (Figure) [1]. The films are categorized into two groups: Group 1 contains lead salts and Group 2 contains solid solutions of lead and tin salts. On experimental dependences 1 and 2 of Group 1 both at low ($T_S < 530$ K) and at high ($T_S > 580$ K) deposition temperatures, the changes of concentration of free charge carriers to the temperature are slight, whereas in the inversion area they are great. It should be noted that after the inversion a dependence of the hole concentration is sharper than the electron concentration before inversion. On other dependences, we also note slow changes.

A decreasing concentration of electrons in films of lead chalcogenides can be explained by a decreasing concentration of donors, for example vacancies of chalcogen or interstitial atoms of lead, an increasing concentration of holes can be attributed to an increase of vacancies of chalcogen. We attribute a change in the hole concentration in solid solutions to a change in the concentration of acceptors which are vacancies of tin as well as chalcogen [2].

Thus, on experimental dependences both at low and high temperatures of deposition we observe areas of weak dependence of the concentration and mobility of free charge carriers upon temperature. To describe these dependences, we work out a function for a concentration of defects that is similar to a previous one but has areas of slight change or saturation:

$$[M_i] = [M_i]_0 / (1 + \exp(-\Delta S_1 + \Delta H_1 / kT_S)), \qquad (6)$$

$$[V_M] = [V_M]_0 / (1 + \exp(-\Delta S_2 + \Delta H_2 / kT_S)). \qquad (7)$$

Let us present a model that grounds such tendencies. During the growth an unstable system of defects is formed. It can be an indigested solution of point defects which are activated or deactivated during relaxation of crystal structure. To activated states (centers), we shall attribute defects that can be revealed by electrophysical methods. Thus, an excessive component can generate crystal point defects of different types, saturation or new phases on surface or volume (precipitates), *etc.*

Let us assume that N_0 is the concentration of defects formed during a period of evaporation with deposition material, for instance, a superstoichometric concentration of one of the components, where a part of defects is activated by the concentration N_a and another part remains inactivated by the concentration $N_{\bar{a}}$, thus

$$N_0 = N_a + N_{\bar{a}}. \qquad (8)$$

Transmission from one state to another in this system occurs with a change of entropy and enthalpy. A necessity of an evident accounting for change of entropy ΔS in calculations of equilibrium concentrations of defects is suggested in [3] and used, for example, in [4, 5].

$$N_a = N_{\bar{a}} \exp(\Delta S - \Delta H / kT), \qquad (9)$$

then

$$N_a = N_0 / (1 + \exp(-\Delta S + \Delta H / kT)). \qquad (10)$$

Let us use similar correlations to explain dependence of mobility on the deposition temperature. According to Matissen's rule, we add together reciprocals to mobility μ_i, related to different scattering processes

$$\frac{1}{\mu} = \sum_i \frac{1}{\mu_i}. \qquad (11)$$

Let us examine scattering processes on ionized defects and phonons μ_{ph}. The mobility is connected with scattering on ionized defects in the inverse ratio to their concentration $\mu \sim \dfrac{1}{N}$. Thus,

Table 1. Parameters of approximation of technological dependences of concentration N_{i0}, ΔS_i, ΔH_i and mobility $\Delta \mu_{i0}$, ΔS_i, ΔH_i, μ_{ph} of free charge carriers in *MN*.

No.	Compound	N_{10}, 10^{18} cm^{-3}; $1/\mu_{10}$, (V·s)/m^2	ΔS_1	ΔH_1, eV	N_{20}, 10^{18} cm^{-3}; $1/\mu_{20}$, (V·s)/m^2	ΔS_2	ΔH_2, eV	$1/\mu_{ph}$, (V·s)/m^2
1	PbSe	1.9 ± 0.1	-18 ± 2	-0.81 ± 0.09	0.97 ± 0.07	43 ± 3	2.1 ± 0.1	
		1.9 ± 0.1	-17 ± 1	-0.72 ± 0.03	0.74 ± 0.02	34 ± 2	1.9 ± 0.1	0.30 ± 0.02
2	PbSe$_{0.8}$Te$_{0.2}$	2.0 ± 0.1	-25 ± 2	-1.20 ± 0.09	0.54 ± 0.07	37 ± 1	1.9 ± 0.1	
		14.0 ± 0.8	-29 ± 1	-1.15 ± 0.06	100 ± 2	35 ± 8	2.0 ± 0.5	0.70 ± 0.04
3	PbTe	0.20 ± 0.02	-15 ± 1	-0.77 ± 0.04				
		2.1 ± 0.1	-33 ± 1	-1.31 ± 0.05	0.17 ± 0.02	38 ± 6	2.0 ± 0.3	0.28 ± 0.02
4	(SnTe)$_{0.2}$(PbSe)$_{0.8}$	5.0 ± 0.2	-19 ± 3	-0.9 ± 0.1				
		8.6 ± 0.2	-23 ± 1	-0.97 ± 0.06				
5	Pb$_{0.8}$Sn$_{0.2}$Te	1.52 ± 0.02	-18 ± 1	-0.89 ± 0.06				
		4.1 ± 0.1	-20 ± 3	-0.8 ± 0.1	43 ± 1	15 ± 3	1.0 ± 0.1	0.23 ± 0.02
6	SnTe	130 ± 5	-40 ± 6	-2.1 ± 0.2	180 ± 10	20 ± 2	0.9 ± 0.1	
		8.8 ± 0.1	-40 ± 10	-2.0 ± 0.5	5.5 ± 0.5	12 ± 2	0.5 ± 0.1	0.018 ± 0.002

Table 2. Constants of equilibrium of reactions of exceeding atomic defects formation in *MN*. Pressure is measured in mm Hg, concentrations in cm^{-3}, enthalpies in eV.

	PbSe	PbTe	SnTe
K_1^0 (ΔH_1)	$7.03\cdot10^9$ (-1.98)	$4.03\cdot10^{12}$ (-1.45)	$1.7\cdot10^{18}$ (-1.61)
K_2^0 (ΔH_2)	$4.05\cdot10^{18}$ (0.21)	$2.12\cdot10^{18}$ (0.11)	$4.6\cdot10^{18}$ (0.38)
K_3^0 (ΔH_3)	$1.05\cdot10^{16}$ (3.86)	$9.15\cdot10^{14}$ (3.51)	$1.9\cdot10^{14}$ (3.80)

$$\mu_i = \mu_{i0} / \left(1 + \exp\left(-\Delta S_i + \Delta H_i / kT_S\right)\right). \qquad (12)$$

It is considered that a phonon constituent of scattering does not depend on the concentration of defects.

We define adjusting parameters N_{10}, ΔS_1, ΔH_1, N_{20}, ΔS_2, ΔH_2 approximating experimental dependences of concentrations of free charge carriers on the temperature of condensation $n(T_S)$, and parameters $\dfrac{1}{\mu_{10}}$, ΔS_1, ΔH_1, $\dfrac{1}{\mu_{20}}$, ΔS_2, ΔH_2, $\dfrac{1}{\mu_{ph}}$ approximating experimental

dependences of mobilities $\mu(T_S)$. Let us consider the hypothesis that the values of the pairs of adjusting parameters ΔS_1, ΔH_1 and ΔS_2, ΔH_2 are close to the concentration as well as to the mobility in groups of lead chalcogenides and solid solutions of lead and tin chalcogenides displayed in Table 1. We see that for most of components the increases in entropy and enthalpy calculated by the concentration and mobility are practically similar. By values, the calculated increases in enthalpies differ approximately twofold from those used in [6] (Table 2). The table shows that at defined pressures of chalcogen and metal in a vapor-phase with a change of the deposition temperature the concentration of vacancies of metal increases slightly, and that of interstitial atoms decreases abruptly, it is shown by minus-plus signs and values of enthalpies changes.

For a part of the processes of activation in Table 1, both entropy and enthalpy decrease (a change of these values is negative), i.e. the atoms turn into a crystal (main position) solid phase from an amorphous (interstitial position) phase, for another part both entropy and enthalpy increase (a change of these values is positive), i.e. the atoms of metal of a crystal phase turn into a vapor phase.
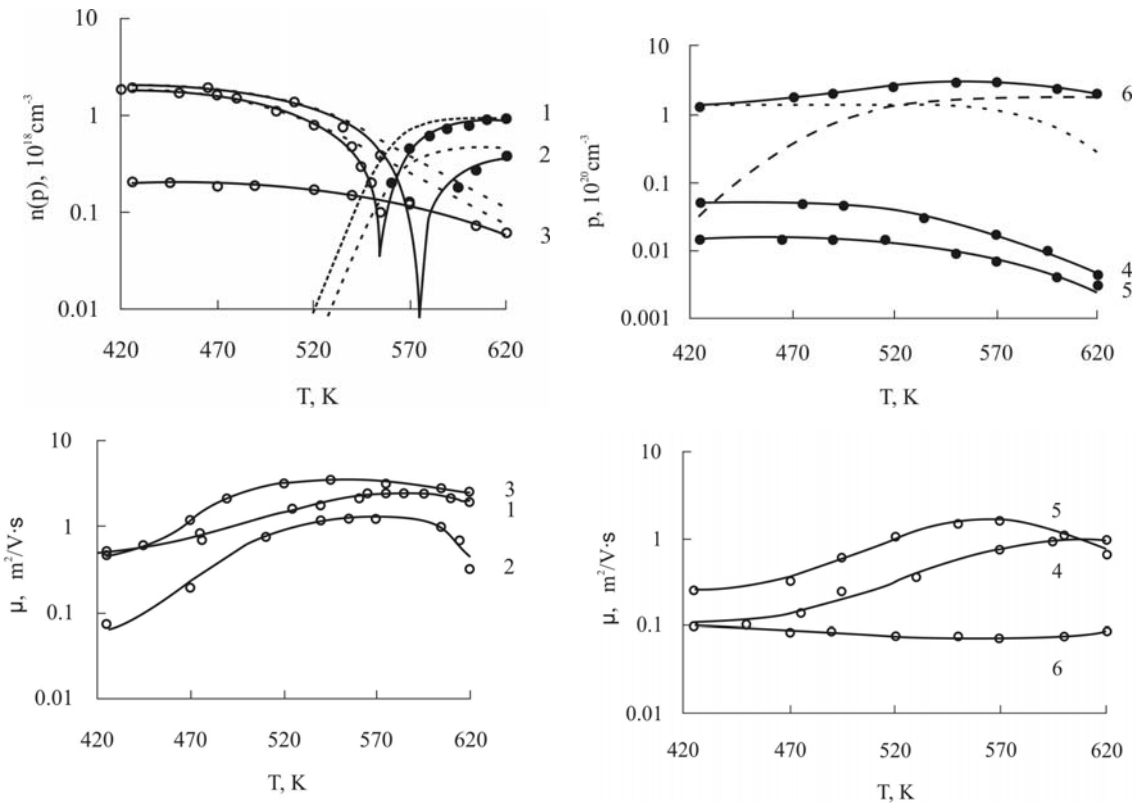
Dependences of the concentration and mobility of charge carriers on temperature at 77 K in A^{IV}B^{VI} films, $T_E = 820$ K, numbers at the curves correspond to numbers of compounds in Table 1. For films 1, 2, a transition from *n*- to *p*-type takes place at the increase of temperature; films 3 – *n*-type; 4, 5 and 6 – *p*-type of conductivity. The dotted lines denote concentrations of defects if films contain both types.

3. Summary

The work has suggested a model of formation and activation of point defects in films of $A^{IV}B^{VI}$ compounds in vapor-phase growth, which sufficiently explains temperature dependences of the concentration and mobility of free charge carriers for six analyzed substances.

Enthalpies for reactions of formation and activation of point defects were found.

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