QUASICHEMICAL MODELLING OF DEFECT SUBSYSTEM OF TIN TELLURIDE CRYSTALS

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By the method of modelling with quasichemical reactions, formation of native atomic defects in tin telluride crystals has been described. Based on the analysis of electroneutrality condition, concentration dependences of charge carriers and point defects on the temperature and partial vapour pressure of tellurium have been found. The constants of corresponding reactions have been specified.

1. Introduction

Tin telluride is the special material of IV-VI compounds due to sufficiently wide range of homogeneity, which lies completely on the side of chalcogen. Therefore, SnTe is characterized by only p-type of conductivity and high concentration of holes, which is growing with the increasing of tellurium content [1].

Performance specifications of device structures are largely determined by defect subsystem of researched crystals, which depends on the homogeneity region of compounds, the chemical composition of solid solutions based on them, and technological factors of their synthesis and subsequent material treatment. Analysing the current state of the problem, it should be noted that the ambiguity of the experimental data and theoretical interpretation of the nature and type of point defects and their charge states and energy parameters in tin telluride crystals greatly complicates the interpretation of their physical and chemical properties. Therefore, further development of theoretical approaches to the study of the defect subsystem and explanation of existing experimental data remains an urgent problem.

Numerical calculations of the energy spectrum of metal and chalcogen vacancies made in [2] has shown that for IV-VI compounds metal vacancies are double-charged acceptors and chalcogen vacancies are double-charged donors. But based on experiments to study the dependence of concentration of charge carriers on the partial pressure of tellurium atoms, it has been found that the defect formation in the cation sublattice is more probable than in chalcogen sublattice [3]. Therefore, we have considered that the predominant native atomic defects in SnTe are singly and doubly ionized tin vacancies.

The purpose of present work is determination of the nature and charge state of atomic defects in SnTe crystals.

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2. Quasichemical Modelling

For the analysis of defect subsystem of SnTe crystals at two-temperature annealing, modelling method via quasichemical reactions has been used. This method has been successfully used to describe the point defects in SnTe films [4] and in other tellurides, including cadmium [5] and lead tellurides [6, 7].

Stoichiometric composition of tin telluride can be changed by setting the partial pressure of the components (tin, tellurium) on the solid phase or the temperature in the method of two-temperature annealing [8].

Equilibrium of "crystal-vapour" in this case can be described by the system of equations of quasichemical reactions listed in Table 1.

Table 1. Quasichemical reactions of point defect formation at two-temperature annealing

No	Equation of reaction	Equilibrium constant	K^0, (cm^{-3}, Pa)	ΔH, eV
1	$\frac{1}{2}Te_2^V = V_{Sn}^0 + Te_{Te}^0$	$K_{Te_2,V} = \left[V_{Sn}^0\right] \cdot P_{Te_2}^{-1/2}$	$2.7 \cdot 10^{17}*$	$-0.55*$
2	$V_{Sn}^0 = V_{Sn}^- + h^+$	$K_a = \left[V_{Sn}^-\right] \cdot p / \left[V_{Sn}^0\right]$	$1.21 \cdot 10^{16} \cdot T^{3/2}$	0.01[9]
3	$V_{Sn}^0 = V_{Sn}^{2-} + 2h^+$	$K_a' = \left[V_{Sn}^{2-}\right] \cdot p^2 / \left[V_{Sn}^0\right]$	$1.46 \cdot 10^{32} \cdot T^3$	0.14 [9]
4	$"0" = e^- + h^+$	$K_i = n \cdot p$	$3.66 \cdot 10^{31} \cdot T^3$	0.18
5	$2\left[V_{Sn}^{2-}\right] + \left[V_{Sn}^-\right] + n = p$			

Here $K = K_0 \exp(-\Delta H / kT)$ is the equilibrium constant; K_0 and ΔH are values that do not depend on the temperature; P_{Te_2} is the partial vapour pressure of tellurium; e^- is an electron; h^+ is a hole; n and p are concentrations of electrons and holes, respectively; "v" indicates the vapour.

Reaction (1) describes the formation of neutral tin vacancies in the interaction with the vapour of tellurium, (2)-(3) are reactions of ionization of formed defects, (4) is the reaction of excitation of intrinsic conductivity. Equation (5) is overall condition of electroneutrality of the crystal.

Equations (1)-(5) make it possible to determine the concentration of holes p using quasichemical constants of reactions K and the partial vapour pressure of tellurium P_{Te_2}:

$$Ap^3 - Bp - C = 0, \tag{6}$$

where $A = 1$; $B = K_a K_{Te_2,V} P_{Te_2}^{1/2} + K_i$; $C = 2K_a' K_{Te_2,V} P_{Te_2}^{1/2}$.

Based on relations (1)-(6) we can determine also the concentration of electrons n, Hall concentration p_H and the concentration of tin vacancies $[V_{Sn}^-]$, $[V_{Sn}^{2-}]$:

$$n = K_i / p; \tag{7}$$

$$p_H = p - K_i / p; \tag{8}$$

$$[V_{Sn}^{2-}] = K_a' K_{Te_2,V} P_{Te_2}^{1/2} \cdot p^{-2}; \tag{9}$$

$$[V_{Sn}^-] = K_a K_{Te_2,V} P_{Te_2}^{1/2} \cdot p^{-1}. \tag{10}$$

3. Equilibrium Constants of Quasichemical Reactions

The proposed model of quasichemical reactions can be used for numerical calculations of equilibrium concentration of charge carriers and concentration of atomic defects in tin telluride crystals, if the equilibrium constants of quasichemical reactions and their temperature dependencies are known with sufficient accuracy.

Equilibrium constants K_a and K_i have been calculated using the band theory of non-degenerate semiconductors. Equilibrium constant of the reaction of defect ionization is

$$K_a = N_v \exp(-E_a / kT), \qquad (11)$$

where E_a is the ionization energy of acceptor point defects; N_V is the valence-band density of states

$$N_v = 2(2\pi m_{pd}^* kT/h^2)^{3/2}, \qquad (12)$$

where m_{pd}^* is the effective mass of holes for the density of states $m_{pd}^* = (g_v^2 m_{p1} m_{p2} m_{p3})^{1/3}$, $g_v = 4$; m_{p1}, m_{p2}, m_{p3} are tensor components of effective mass of holes.

It has been taken into account that $K_a' = K_a^2$.

The equilibrium constant of reaction of excitation of intrinsic conductivity is

$$K_i = N_c N_v \cdot \exp(-E_g/kT), \qquad (13)$$

where E_g is a band gap; N_C is density of states in the conduction band.

The numerical values of the parameters required for the calculation are taken from [10].

The equilibrium constant $K_{Te_2,V}$ has been found by approximating the experimental dependence of the logarithm of the partial pressure of tellurium on inverse temperature (Fig. 1).

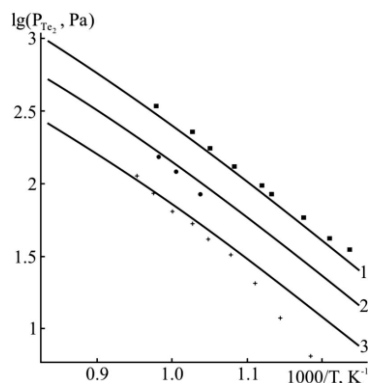Found effective values of K_0 and ΔH for equilibrium constants are shown in Table 1.

Fig. 1. The dependence of the partial vapour pressure of tellurium on the annealing temperature for SnTe crystals of composition p: 1 – 1.00·10²¹ cm⁻³; 2 – 8.82·10²⁰ cm⁻³; 3 – 7.56·10²⁰ cm⁻³. Curves – calculation. Points – experimental data [11].

4. Results and Discussion

The calculation results of dependence of Hall concentration of holes p_H on annealing temperature T at constant partial vapour pressure of tellurium P_{Te_2} for the resulting values of

constants are presented in Fig. 2. Within the boundaries of homogeneity region, with increasing annealing temperature at constant partial vapour pressure of tellurium, Hall concentration of holes decreases (Fig. 2). The theoretical curves satisfactorily describe the experimental data; this indicates the adequacy of accepted model of defect subsystem.
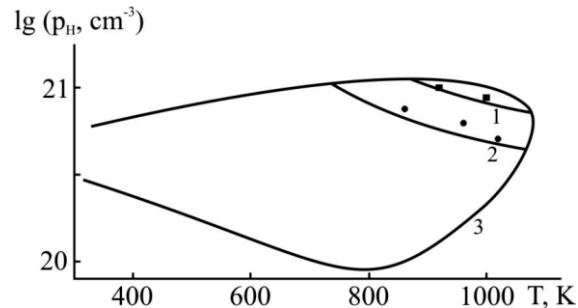

Fig. 2. The dependence of Hall concentration of charge carriers p_H on annealing temperature T at the partial vapour pressure of tellurium P_{Te_2}: 1 – 100 Pa; 2 – 10 Pa; 3 – homogeneity region of SnTe [12]. Curves – calculation. Points – experimental data [11].

At annealing of tin telluride under conditions when the material is saturated with metal or chalcogen, the concentration of holes is determined by boundaries of homogeneity region (Fig. 2, curve 3).

The calculation results of the concentration of defects and charge carriers depending on the annealing temperature T and the partial vapour pressure of tellurium P_{Te_2} for the resulting values of constants are shown in Fig. 3-4.

Singly charged tin vacancies $[V_{Sn}^-]$ give the greatest contribution to the conductivity (Fig. 3-4). Increasing the annealing temperature at constant partial vapour pressure of tellurium causes significant decrease of the concentration of singly charged tin vacancies $[V_{Sn}^-]$ (Fig. 3, curve 2), which leads to decrease of hole concentration p (Fig. 3, curve 1). In this case, concentrations of doubly charged tin vacancies $[V_{Sn}^{2-}]$ and electrons n increase (Fig. 3, curves 3, 4).
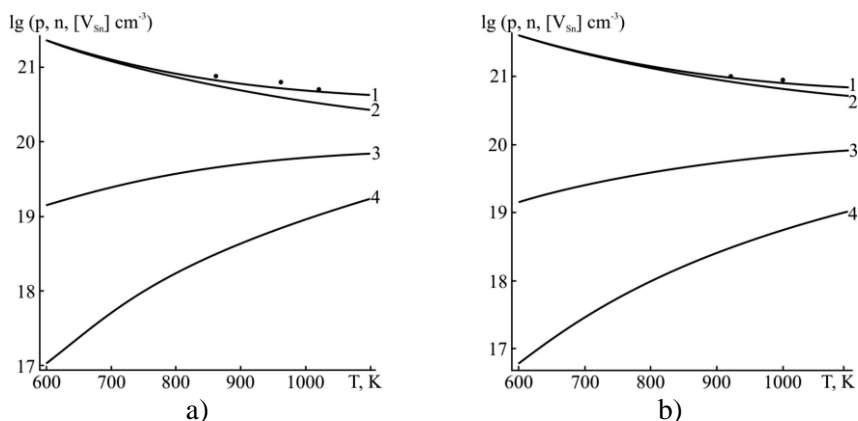

Fig. 3. Dependences of concentration of holes p (1), tin vacancies $[V_{Sn}^-]$ (2), $[V_{Sn}^{2-}]$ (3) and electrons n (4) on the annealing temperature T at the partial vapour pressure of tellurium P_{Te_2}: 10 Pa (a); 100 Pa (b). Points – experimental data [11].

Increasing the partial vapour pressure of tellurium at constant annealing temperature leads to rising the concentration of holes p (Fig. 4, curve 1) due to increase of the concentration of singly ionized tin vacancies $[V_{Sn}^-]$ (Fig. 4, curve 2). In this case the concentration of electrons n decreases (Fig. 4, curve 4), and the concentration of doubly charged tin vacancies $[V_{Sn}^{2-}]$ changes slightly (Fig. 4, curve 3).

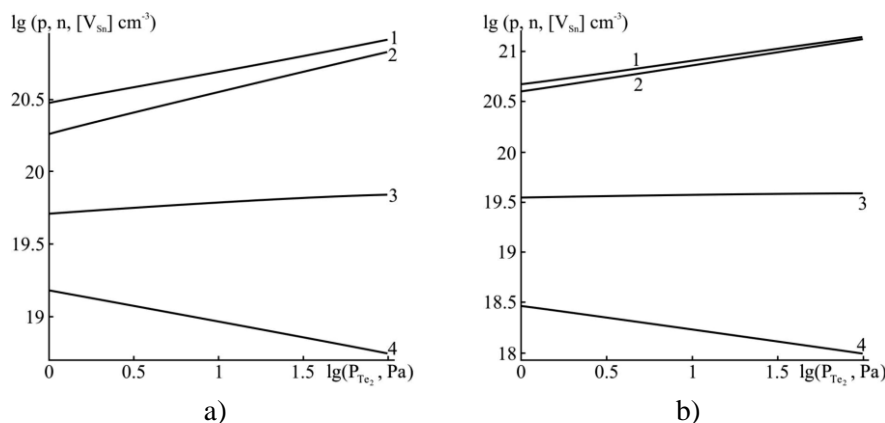a)   b)

Fig. 4. Dependences of concentration of holes p (1), tin vacancies $[V_{Sn}^-]$ (2), $[V_{Sn}^{2-}]$ (3) and electrons n (4) on the partial vapour pressure of tellurium P_{Te_2} at the annealing temperature T: 1000 K (a); 800 K (b).

Above mentioned specific behaviour of hole concentration depending on the partial vapour pressure of tellurium and annealing temperature is well illustrated in 3d-diagram (Fig. 5).
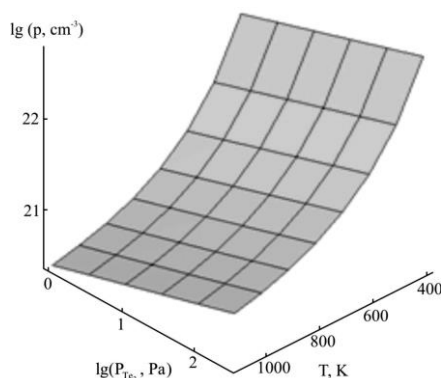

Fig. 5. 3d-Diagram of the dependence of hole concentration on partial vapour pressure of tellurium P_{Te_2} and annealing temperature T.

The ratio of concentration of tin vacancies $q = [V_{Sn}^-]/[V_{Sn}^{2-}]$ decreases with increasing annealing temperature (Fig. 6), and it grows with increasing partial vapour pressure of tellurium (Fig. 7). Such growth is more intensive for the lower annealing temperature (Fig. 7, curve 1).
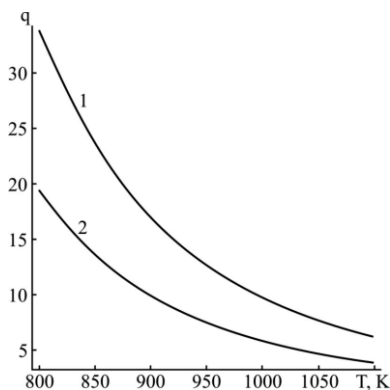
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Fig. 6. The dependence of the ratio of concentration of tin vacancies $q = \left[V_{Sn}^- \right] / \left[V_{Sn}^{2-} \right]$
in SnTe crystals on the annealing temperature T at the partial vapour pressure of
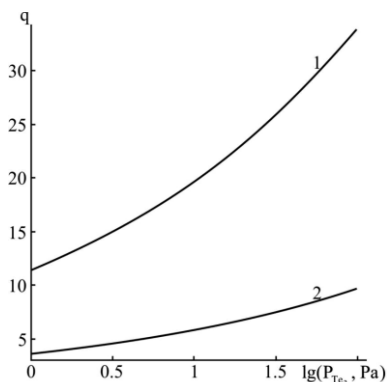*tellurium* P_{Te_2} : *1 – 100 Pa, 2 – 10 Pa.*

Fig. 7. The dependence of the ratio of concentration of tin vacancies $q = \left[V_{Sn}^- \right] / \left[V_{Sn}^{2-} \right]$
in SnTe crystals on the partial vapour pressure of tellurium P_{Te_2} *at the annealing*
temperature T: 1 – 800 K, 2 – 1000 K.

5. Conclusions

Using quasichemical reactions, defect formation in tin telluride crystals at two-temperature annealing has been described.

The constants of quasichemical reactions of defect formation in tin telluride crystals have been specified.

Analytical expressions for Hall concentration, concentrations of holes and electrons, tin vacancies via constants of quasichemical reactions and the partial vapour pressure of tellurium have been obtained.

It has been shown that in SnTe crystals, concentration of charge carriers is determined by singly charged tin vacancies.

Acknowledgements

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