POINT DEFECTS AND MECHANISMS OF DOPING IN PbSe⟨Se⟩:Bi FILMS

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Quasichemical equations describing the formation of point defects in Bi-doped films of plumbum selenide, grown at various deposition temperatures from the vapor phase saturated with selenium, have been proposed. Experimental results are explained by the amphoteric properties of the dopant.

1. Plumbum selenide attracts attention owing to its employment in instrument structures operating in the infra-red range of optical spectrum [1]. It crystallizes into a structure of the NaCl type with a bilateral region of homogeneity. In so doing, a deviation from the stoichiometric composition towards the prevalence of lead results in vacancies in the anion sublattice and the n-type of conductivity, while the prevalence of selenium induces lead vacancies and the p-type of conductivity [2].

The electric activity of bismuth in plumbum selenide films depends substantially on technological procedures of film growing [3–5] and has not been elucidated in detail. This work aims at studying the role of dominating point defects in PbSe films induced by bismuth.

2. The PbSe⟨Se⟩:Bi films were grown in vacuum from a vapor phase. Two independent evaporators were in use: with the synthesized PbSe:Bi compound and with pure selenium [3]. The as-prepared (111) chips of BaF_2-crystals served as substrates; their temperature was maintained within the interval T_s=500÷650 K. The partial pressure of selenium vapors P_{Se_2} in a deposition region was monitored by varying the temperature of an additional source of selenium T_{Se} =300÷600 K. The electrical parameters of the films were measured by the compensation method in constant electric and magnetic fields.

The experimental dependences of the current carrier concentration in PbSe⟨Se⟩:Bi films on the temperature of the additional source of selenium T_{Se} at various substrate temperatures T_s are presented in Fig. 1. One can see that the higher the content of selenium in vapors, the higher is the concentration of electrons in the film. We notice that such a result is characteristic of the films possessing either the initial n- (curve *1*) or p-type (curve *2*) of conductivity. At first sight, it seems strange, because the excess of Se in pure PbSe behaves as an acceptor [2].

3. The whole spectrum of point defects in doped PbSe⟨Se⟩:Bi films can be described by the system of quasichemical reactions, which are listed in the table. Here, reaction I describes the transition of selenium from vapors (Se_2^v) with the formation of neutral lead vacancies (V_{Pb}^0). Reactions II to IV are responsible for the balance

Quasichemical equations of the formation of point defects in PbSe⟨Se⟩:Bi films, their reaction constants $K = K_0 \exp(-\Delta H/kT)$, and enthalpies ΔH

N	Equation	Reaction constant	K_0	ΔH, eV
I	$\frac{1}{2}Se_2 = Se_{Se} + V_{Pb}^0$	$K_{Se} = \frac{[V_{Pb}^0]}{P_{Se_2}^{1/2}}$	$1.57\cdot10^{58}$, $cm^{-3}Pa^{-1/2}$	0.49
II	"0" $= V_{Se}^0 + V_{Pb}^0$	$K_{Sh} = [V_{Se}^0][V_{Pb}^0]$	$6.71\cdot10^{39}$, cm^{-6}	2.11
III	$V_{Pb}^0 = V_{Pb}^{2-} + 2h^+$	$K_b' = \frac{[V_{Pb}^{2-}]p^2}{[V_{Pb}^0]}$	$4.5\cdot10^{40}$, Pa^2	0.28
IV	$V_{Se}^0 = V_{Se}^{2+} + 2e^-$	$K_a' = \frac{[V_{Se}^{2+}]n^2}{[V_{Se}^0]}$	$4.5\cdot10^{40}$, cm^{-6}	0.28
V	"0"$= e^- + h^+$	$K_i = np$	$1.13\cdot10^{40}$, cm^{-6}	0.59
VI	$Bi_{Pb}^+ + V_{Se}^0 + e^- = Bi_{Se}^- + V_{Pb}^0 + h^+$	$K_{Bi} = \frac{[V_{Pb}^0]\cdot[Bi_{Se}^-]\cdot p}{[V_{Se}^0][Bi_{Pb}^+]n}$	$8.56\cdot10^{85}$ *	9.18*
VII	$Pb^v = Pb_i^+ + e^-$	$K_{Pb} = \frac{[Pb_i^+]\cdot n}{P_{Pb}}$	$1.73\cdot10^{27}$, cm^{-3}	–1.82
VIII	$Se_2^v + Bi_{Se}^- = Bi_{Pb}^+ + 2e^-$	$K_+ = \frac{[Bi_{Pb}^+]\cdot n^2}{[Bi_{Se}^-]P_{Se_2}}$	$5.01\cdot10^{43}$, cm^{-6} Pa^{-1}*	0.01

Note. * — our calculations

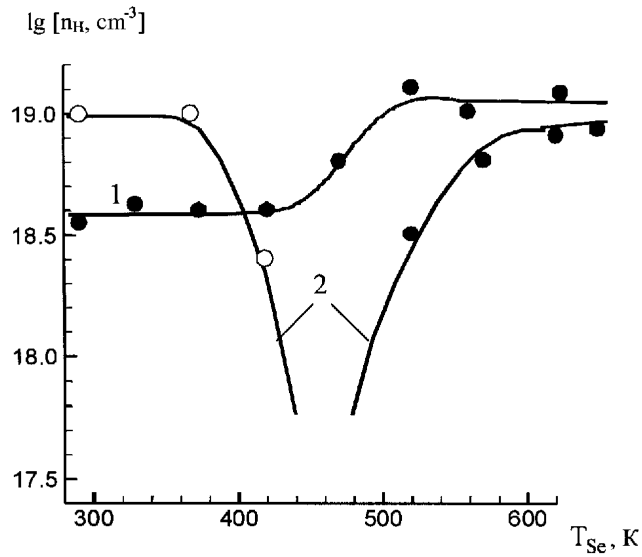

Fig. 1. Dependences of the Hall concentration of current carriers $n_{\rm H}$ in PbSe⟨Se⟩:Bi films on the temperature of the additional source of selenium $T_{\rm Se}$ at various temperatures of the substrate $T_{\rm s} = 520$ (*1*) and 620 K (*2*). Symbols ∘ and symbol • correspond, respectively, to the n- and p-types of conductivity [3]

of Schottky defects and their ionization. Equation V determines the intrinsic conductivity. Equation VI is responsible for the amphoteric action of the bismuth impurity. Here, bismuth is distributed in both the cation and anion sublattices by forming the $V^0_{\rm Se}$ and $V^0_{\rm Pb}$ vacancies, respectively, at the deposition temperature $T_{\rm s}$. Equation VII governs the transition of lead from the vapor, equation VIII the distribution of bismuth between the sublattices of the main matrix under the influence of excess selenium.

The equation of electroneutrality for the considered mechanisms of formation of point defects reads

$$n + 2[V^{2-}_{\rm Pb}] + [{\rm Bi}^-_{\rm Se}] = p + 2\,[V^{2+}_{\rm Se}] + [{\rm Bi}^+_{\rm Pb}] + [{\rm Pb}^+_i]. \quad (1)$$

The system of equations I—VIII in the table and Eq. (1), provided that $N_{\rm Bi} = [{\rm Bi}^-_{\rm Se}] + [{\rm Bi}^+_{\rm Pb}]$, enable one to determine the concentration of each defect:

$$[{\rm Pb}^+_i] = \frac{P_{\rm Pb}\,K_{\rm Pb}}{n}, \quad [V^{2-}_{\rm Pb}] = \frac{K_{\rm Se}\,P^{1/2}_{\rm Se_2}\,K'_{\rm b}}{K_i^2}n^2,$$

$$[V^{2+}_{\rm Se}] = \frac{K_{\rm Sh}\,K'_a}{K_{\rm Se}\,P^{1/2}_{\rm Se_2}\,n^2},$$

$$[V^0_{\rm Pb}] = K_{\rm Se}\,P^{1/2}_{\rm Se_2}; \quad [V^0_{\rm Se}] = \frac{K_{Sh}}{K_{\rm Se}\,P^{1/2}_{\rm Se_2}},$$

$$[{\rm Bi}^-_{\rm Se}] = \frac{N_{\rm Bi}}{\frac{K_{\rm Se}\,P^{1/2}_{\rm Se_2}\,K_i^3}{K'_b\,K_{\rm Sh}\,K_{\rm Bi}\,n^4} + \frac{K_+\,P_{\rm Se_2}}{n^2} + 1},$$

$$[{\rm Bi}^+_{\rm Pb}] = \frac{N_{\rm Bi}}{\frac{K'_b\,K_{\rm Sh}\,K_{\rm Bi}\,n^4}{K_{\rm Se}P^{1/2}_{\rm Se_2}\,K_i^3 + K_+\,P_{\rm Se_2}\,K'_b\,K_{,}\,K_{,}\,n^2} + 1}. \quad (2)$$

The concentration of electrons can be found by substituting expressions (2) for the concentrations of defects into the electroneutrality equation (1):

$$n + 2\,\frac{K_{\rm Se}\,P^{1/2}_{\rm Se_2}\,K'_b}{K_i^2}n^2 + \frac{N_{\rm Bi}}{\frac{K_{\rm Se}\,P^{1/2}_{\rm Se_2}\,K_i^3}{K'_b\,K_{\rm Sh}\,K_{\rm Bi}\,n^4} + 1} =$$

$$= \frac{K_i}{n} + 2\,\frac{K_{\rm Sh}\,K'_a}{K_{\rm Se}\,P^{1/2}_{\rm Se_2}\,n^2} +$$

$$+ \frac{N_{\rm Bi}}{\frac{K'_b\,K_{\rm Sh}\,K_{\rm Bi}\,n^4}{K_{\rm Se}\,P^{1/2}_{\rm Se_2}\,K_i^3 + K_+\,P_{\rm Se_2}\,K'_b\,K_{\rm Sh}\,K_{\rm Bi}\,n^2} + 1} + \frac{P_{\rm Pb}\,K_{\rm Pb}}{n}. \quad (3)$$

Taking into account that the Hall concentration $n_{\rm H}$, which is measured experimentally (Fig. 1), is equal to $n_{\rm H} = n - p$ and, according to equation V of the table, $K_i(T_s) = np$, we obtain the following expression:

$$n_{\rm H} = n[1 - K_i(T_{\rm s})/n^{-2}]. \quad (4)$$

4. The results of calculations of the dependences of the defect concentrations and the Hall concentration of current carriers in PbSe⟨Se⟩:Bi films on the temperature of the additional source with pure selenium $T_{\rm Se}$ at various deposition temperatures $T_{\rm s}$ are shown in Fig. 2. Their analysis testifies to that the enrichment of the vapor with selenium in the deposition region, similarly to rising the temperature of the additional source, causes a reduction of the bismuth concentration in the anion sublattice $[{\rm Bi}^-_{\rm Se}]$ of the basic matrix (curve *3*). The concentration of doping impurity in the cation sublattice $[{\rm Bi}^+_{\rm Pb}]$ grows at that (curve *4*). We notice that the character of the dependence of the amphoteric impurity

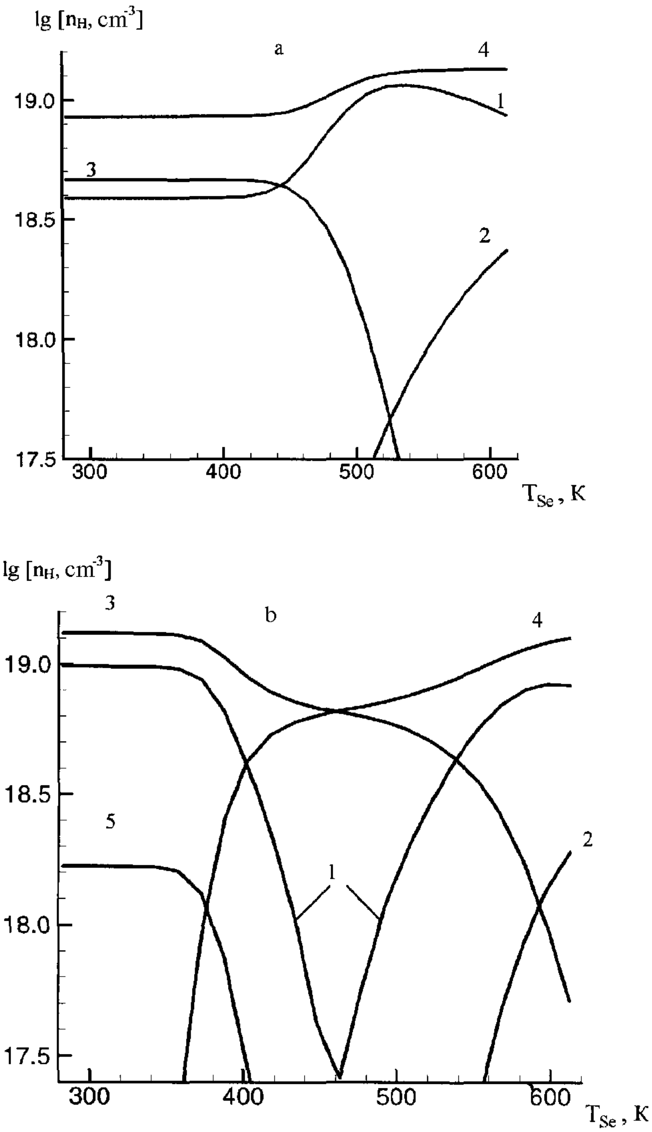

Fig. 2. Calculated dependences of the current carrier and defect concentrations in PbSe⟨Se⟩:Bi films on the temperature of the additional source of selenium $T_{\rm Se}$: $n_{\rm H}$ (*1*), $[V_{\rm Pb}^{2-}]$ (*2*), $[{\rm Bi}_{\rm Se}^{-}]$ (*3*), $[{\rm Bi}_{\rm Pb}^{+}]$ (*4*), and $[V_{\rm Se}^{2+}]$ (*5*). The temperature of the substrate $T_{\rm s} = 520$ (*a*) and 620 K (*b*)

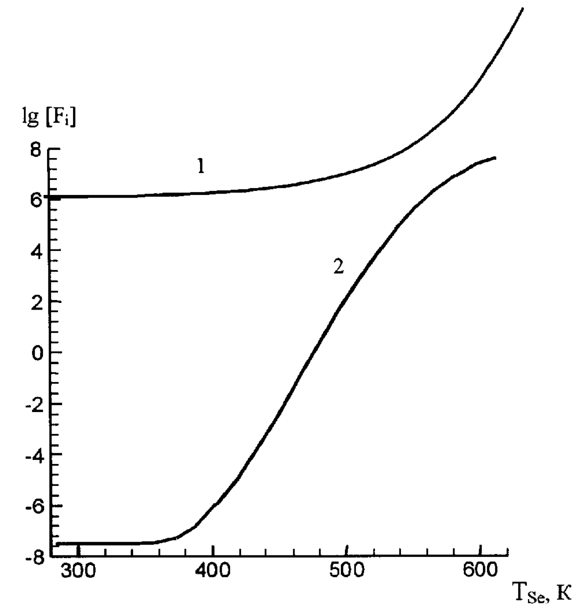

Fig. 3. Dependences of the relative compensation factors $F_i = [{\rm Bi}_{\rm Pb}^{+}]/[{\rm Bi}_{\rm Se}^{-}]$ in PbSe⟨Se⟩:Bi films PbSe ⟨Se⟩:Bi on the temperature of the additional source of selenium $T_{\rm Se}$ at $T_{\rm s} = 520$ (*1*) and 620 K (*2*)

Bi on $T_{\rm Se}$ is defined by the deposition temperature $T_{\rm s}$ (Fig. 2). For example, only an insignificant growth of $[{\rm Bi}_{\rm Pb}^{+}]$ and an abrupt reduction of $[{\rm Bi}_{\rm Se}^{-}]$ are observed at $T_{\rm s} = 520$ K (Fig. 2*a*, curves *4* and *3*, respectively); but not above than at $T_{\rm s} = 620$ K, $[{\rm Bi}_{\rm Se}^{-}]$ decreases more slowly while $[{\rm Bi}_{\rm Pb}^{+}]$ grows abruptly (Fig. 2,*b*, curves *3* and *4*, respectively). That is, at low deposition temperatures $T_{\rm s}$, the mechanism of the replacement of lead vacancies by bismuth prevails at all studied values of $T_{\rm Se}$ (Fig. 2,*a*, curve *4*), while it dominates at high $T_{\rm s}$ only provided a considerable partial pressure of selenium vapors $P_{{\rm Se}_2}$ in the deposition region (Fig. 2,*b*, curve *4*). If $T_{\rm Se}$ is insignificant, the point defects of the ${\rm Bi}_{\rm Se}^{-}$ type play the key role (Fig. 2,*b*, curve *3*). This conclusion is also confirmed by the dependences of the relative compensation factor for those defects $[{\rm Bi}_{\rm Pb}^{+}]/[{\rm Bi}_{\rm Se}^{-}]$ on $T_{\rm Se}$ (Fig. 3).

We note that the concentrations of neutral vacancies, both lead $V_{\rm Pb}^{0}$ and selenium $V_{\rm Se}^{0}$ ones, are insignificant and amount to $10^{8} - 10^{10}$ cm^{-3} at $T_{\rm s} = 520$ K and $10^{10} - 10^{13}$ cm^{-3} at $T_{\rm s} = 620$ K. The concentration of charged interstitial Pb atoms $[{\rm Pb}_i^{+}]$ varies within the limits 10^{13}–10^{16} cm^{-3} and does not affect essentially the Hall concentration of current carriers. The concentration of lead vacancies $[V_{\rm Pb}^{-}]$ tends to grow only if the temperature of the additional source with selenium is substantial (Figs. 2,*a* and 2,*b*, curves *2*), while the concentration of selenium vacancies $[V_{\rm Se}^{2+}]$ falls down sharply at that (Fig. 2,*b*, curve *5*). These concentrations are also substantially lower than the concentrations of the amphoteric bismuth impurity in the cation, $[{\rm Bi}_{\rm Pb}^{+}]$, and anion, $[{\rm Bi}_{\rm Se}^{-}]$, sublattices (Fig. 2).

Thus, the experimental results can be explained satisfactorily by the amphoteric properties of the bismuth doping impurity in PbSe⟨Se⟩:Bi films. An increase of the partial pressure of selenium vapors P_{Se_2} in the deposition region induces the growth of the Pb-vacancy concentration, which is a reason for the bismuth redistribution between the anion and cation sublattices of the basic matrix.

1. *Abrikosov N.Kh., Shelimova L.E.* Semiconducting Materials Based on $A^{IV}B^{VI}$ Compounds. — Moscow: Nauka, 1975 (in Russian).
2. *Freik D.M., Prokopiv V.V., Galushchak M.O. et al.* Crystal Chemistry and Thermodynamics of Atomic Defects in $A^{IV}B^{VI}$ Compounds. — Ivano-Frankivsk: Plai, 1999 (in Ukrainian).
3. *Zykov V.A., Gavrikova T.A., Nemov S.A.* // Fiz. Tekhn. Polupr. — 1995. — **29**, N 2. — P. 309—315.
4. *Zykov V.A., Gavrikova T.A., Ilyin V.I. et al.* // Ibid. — 2001. — **35**, N 11. — P. 1311—1315.
5. *Freik D.M., Yatsura A.M.* // Fiz. Khim. Tverd. Tila. — 2004. — **5**, N 2. — P. 286—291.

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ТОЧКОВІ ДЕФЕКТИ І МЕХАНІЗМИ ЛЕГУВАННЯ У ПЛІВКАХ PbSe⟨Se⟩:Bi

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Р е з ю м е

Запропоновано квазіхімічні рівняння утворення точкових дефектів у легованих вісмутом плівках селеніду свинцю, вирощених із парової фази при різних температурах осадження за умови насичення пари селеном. Експериментальні результати пояснено, виходячи з амфотерних властивостей легуючої домішки.