

Calculation of the Point Defect Ensemble in Zinc Sulfide Single Crystals and Films

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(Received 30 August 2012; published online 29 October 2012)

In the present work, calculation of the concentration of neutral and charged point defects, positions of the Fermi level and free charge carriers in zinc sulfide single crystals and films depending on their condensation conditions was carried out. Experimentally found energy levels of defects in ZnS band gap were used for the calculations.

Keywords: Point defects, Zinc sulfide, Quasi-chemical formalism, Single crystals, Films, Defect concentration.

PACS numbers: 61.72.J, 73.61.Ga

1. INTRODUCTION

It is known that real solids, such as semiconductor crystals and films, have in their composition structural defects of different dimensions. Zero dimensional defects are called point defects (PD). Since intrinsic PD considerably influence the optical and electrophysical properties of A_2B_6 compounds [1, 2], then in order to obtain semiconductor materials with controllable service properties, it is necessary to grow monocrystals and films with programmable PD ensemble. Control of the equilibrium of intrinsic defects in chalcogenides is possible by the change in the conditions of the production and thermal treatment of the samples [3, 4].

From the point of view of the theory, formation of the following neutral defects is possible in zinc sulfide [1, 2]: vacancies in zinc V_{Zn}^0 and sulfur sublattices, interstitial atoms of metals Zn_i^0 and chalcogen S_i^0 and antisite defects Zn_S^0 (S_{Zn}^0). Charged PD, which play role of the electrically active centers, can exist in the crystal lattice of material besides neutral ones. Vacancies V_{Zn}^- , V_{Zn}^{2-} (V_S^+ , V_S^{2+}); interstitial atoms Zn_i^+ , Zn_i^{2+} (S_i^- , S_i^{2-}) and antisite defects Zn_S^- , Zn_S^{2-} (S_{Zn}^+ , S_{Zn}^{2+}) are among them. However, for ZnS crystals, in which PD are generated in the conditions of equilibrium by thermal treatment in the vapor of compound components, antisite defects are not typical and they appear, mainly, under the action of ionizing radiation [2]. Each charged PD generates in the band gap (BG) of semiconductor a localized state (LS) with energy ΔE , which can be situated both near the conduction band (valence band) and then defect is a donor (acceptor) and in the volume and then defect is a trap for charge carriers or recombination center [5].

Up till now there is no clear understanding which types of PD prevail in zinc sulfide depending on the conditions of its production. Quantitative relations between different types of defects, which could allow to establish dependence of the optical and electrophysical properties of material on the concentration and type of defects, are not revealed.

2. EXISTING MODELS OF THE POINT DEFECT ENSEMBLE IN ZnS

Attempts to define the PD ensemble in ZnS monocrystals versus the conditions of their production were performed repeatedly [2, 6, 7]. For the first time, such calculations for the case of complete equilibrium of defects with the use of the Brouwer method were done by the authors of [1, 3]. It was assumed in the modeling that singly and doubly charged vacancies in zinc and sulfur sublattices (V_S^+ , V_S^{2+} , V_{Zn}^- , V_{Zn}^{2-}) are dominant PD in material. A simpler model of the defect formation was used by the author of [7], which in calculations took into account only doubly charged vacancies in zinc and sulfur sublattices V_{Zn}^{2-} , V_S^{2+} . Later on, Morozova developed new ideas about defect structure of material which provided the existence of interstitial atoms in zinc sublattice [2, 6]. As a result, the following types of intrinsic defects were taken into account in the calculations: V_S^0 , V_S^+ , V_S^{2+} , V_{Zn}^0 , V_{Zn}^- , V_{Zn}^{2-} , Zn_i^0 , Zn_i^+ , Zn_i^{2+} . The authors of the work [2] performed modeling for four different variants of energy diagrams for PD levels in the BG of material. Calculations were carried out for both the case of complete equilibrium of defects and the case of defect hardening.

Dependences of the concentration of different types of PD in ZnS monocrystals on the vapor pressure of compound components obtained by different authors are represented in Fig. 1. In the conditions of complete equilibrium of defects, interstitial zinc Zn_i^+ , Zn_i^{2+} (Fig. 1a) was the prevalent type of defects in ZnS at high pressures of zinc vapor together with doubly charged vacancies of metal V_{Zn}^{2-} .

In this case, concentrations of Zn_i^{2+} and V_{Zn}^{2-} in a wide pressure range coincide, and as a result, electrical properties of material are determined here by the singly charged interstitial zinc Zn_i^+ . Concentration of charged sulfur vacancies in material was found to be much lower than of defects in zinc sublattice.

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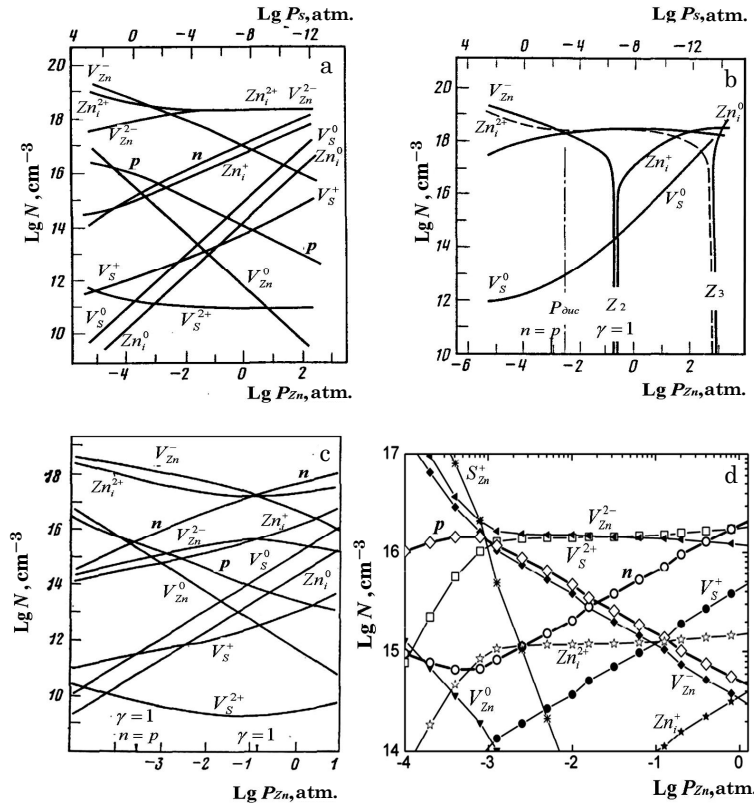


Fig. 1 – Calculation dependences of the defect concentration in ZnS monocrystals on the pressure of zinc vapor: complete equilibrium of defects at 1423 K [2] (a); defect hardening from 1423 K to 0 K [2] (b); complete equilibrium of defects at 1423 K [6] (c); equilibrium of defects at 1343 K [8] (d)

At high pressures of sulfur electrical properties of material are determined by the singly charged vacancies of zinc V_{Zn}^- , which lead to the p -type conduction. Concentration of neutral intrinsic defects was significantly lower than of the charged ones. Transition from the n -type conduction to the p -type one occurred at pressures $P_{Zn} = 10^2 \cdot 10^3$ Pa.

Hardening of crystals did not lead to the essential change in the ensemble of PD of chalcogenide (Fig. 1b). The same defects, as well as in the conditions of their equilibrium, were dominant in different pressure ranges of zinc vapor; and only in the region of high pressures of metal vapor concentration of doubly charged interstitial zinc atoms Zn_i^{2+} considerably decreased and concentration of neutral atoms increased. Concentration of charged PD after hardening remains high and was equal to $14^8 \cdot 10^{20} \text{ cm}^{-3}$.

Development of the ideas about defect structure of chalcogenides occurs by the calculation of PD ensemble in material and comparison of the obtained results with the experimental data concerning the dependence of the concentration of free charge carriers or conduction on the pressure P of compound components at annealing. High-temperature conduction of zinc sulfide at different vapor pressures of compound components was studied by Lott in the works [9, 11]. It was established that in the region of high pressures of zinc ($P_{Zn} > 10^4$ Pa) dependence of the conduction of intrinsic monocrystals on the pressure of zinc vapor is described by the expression $\sigma \sim P^\alpha$, where $\alpha = 0,5$ at 1373 K and $\alpha = 0,4$ at 1343 K.

This implies that electrical properties of material in this region are determined by singly charged PD. The authors explain features of the behavior of equilibrium diagram of defects in the region of sulfur excess by the possibility of appearance of antisite defects which being the donors compensate the influence of zinc vacancies which are the acceptors. The corresponding calculations are given in [8]. To our opinion, such explanation is not relevant, since formation of antisite defects in wide band gap compounds is low-probable [2, 6]. Calculation of the PD equilibrium in ZnS films is not performed till now.

3. CALCULATION TECHNIQUE OF THE POINT DEFECT ENSEMBLE

Calculation of the PD ensemble in monocrystals and films of zinc sulfide was carried out using the quasi-chemical formalism [3] in software environment Maple. This technique is based on the analysis of thermodynamic equilibrium of all defects, as well as electrons and holes in the crystal volume (complete equilibrium of PD). Calculation procedure is reduced to the solution of the system of equations which describe introduction of neutral defects from gaseous phase into solid, and their ionization jointly with complete equation of electrical neutrality of material and equation describing its intrinsic conduction. Then concentration of neutral defects can be calculated using quasi-chemical equations given in [2]. Concentration of charged PD was calculated by the Fermi-Dirac statistics and equation of electrical neutrality [11].

It is necessary to note that investigations of the properties of semiconductors are most often performed at temperatures close to the room one. In this case, PD spectrum in material can be described by the model of partial equilibrium or hardening [3, 5]. Then, at sufficiently fast cooling of the samples freezing of PD, which appeared in semiconductor at high temperature, takes place. However, cooling does not influence the equilibrium balance of electrons and holes. As a result, at rather low temperature all electrons and holes recombine, and excess of free carriers is trapped by intrinsic defects which pass to the neutral state. The corresponding processes can be taken into consideration if write the correlations characterizing constancy of the total concentration of charged and neutral PD in material during hardening [3].

4. CALCULATION OF THE POINT DEFECT ENSEMBLE IN ZINC SULFIDE

4.1 Calculation of the point defect ensemble in ZnS monocrystals

We have used the quasi-chemical formalism for the investigation of the PD ensemble state in ZnS crystals and films [3]. The model of defect formation proposed by Morozova [2, 6] was applied in the modeling. Formation of neutral and charged defects by both the Schottky and Frenkel mechanisms are provided in this model: V_S^0 , V_S^+ , V_S^{2+} , V_{Zn}^0 , V_{Zn}^- , V_{Zn}^{2-} , Zn_i^0 , Zn_i^+ , Zn_i^{2+} .

On the first stage, for the purpose of the choice of the most adequate constants of quasi-chemical equations by the comparison of the calculation results with the data of experimental works, we have performed the calculation of PD ensemble in ZnS monocrystalline samples. In the case of complete equilibrium, concentration of neutral defects can be determined by the use of the following relations:

$$n \cdot p = K_i = f(T), \quad (4.1)$$

$$[V_{Zn}^0] = P_{Zn}^{-1} K_{V_{Zn}} = P_{Zn}^{-1} K_{01} \exp\left(-\frac{H_1}{kT_S}\right), \quad (4.2)$$

$$[Zn_i^0] = [V_{Zn}^0]^{-1} K_F = [V_{Zn}^0]^{-1} K_{02} \exp\left(-\frac{H_2}{kT_S}\right), \quad (4.3)$$

$$[V_S^0] = P_{Zn} K_{V_S} = P_{Zn} K_{03} \exp\left(-\frac{H_3}{kT_S}\right), \quad (4.4)$$

where P_{Zn} is the partial pressure of zinc at annealing of monocrystals; k is the Boltzmann constant; H_1 , H_2 , H_3 are the formation enthalpies of the corresponding defects; K_{01} , K_{02} , K_{03} are the constants of quasi-chemical equations [3].

We should note that traditionally for the calculation of charged defects and free charge carriers in ZnS monocrystals the authors [2, 6] have used constants of quasi-chemical reactions that does not allow to take into account the change of the Fermi level in material. To our opinion, in this case usage of the Fermi-Dirac statistics jointly with the equation of electrical neutrality represented in the form of (4.5)-(4.9) is more reasonable:

$$n = \frac{N_c}{\exp\left[\frac{(E_g - \mu_F)/kT}{1}\right] + 1}, \quad (4.5)$$

$$p = \frac{N_v}{\exp\left[\frac{(\mu_F)/kT}{1}\right] + 1}, \quad (4.6)$$

$$[X_{di}^{z+}] = \frac{[X_{di}^0]}{g_d \exp\left[-\frac{(E_g - E_{di} - \mu_F)/kT}{1}\right] + 1}, \quad (4.7)$$

$$[X_{ai}^{z-}] = \frac{[X_{ai}^0]}{g_d \exp\left[-\frac{(E_g - E_{ai} - \mu_F)/kT}{1}\right] + 1}, \quad (4.8)$$

$$\begin{aligned} n + [V_{Zn}^-] + 2[V_{Zn}^{2-}] = \\ = p + [V_S^+] + 2[V_S^{2+}] + [Zn_i^+] + 2[Zn_i^{2+}] \end{aligned} \quad (4.9)$$

where μ_F is the Fermi energy in semiconductor; z is the degree of ionization of defects; $[X^0]$ is the concentration of neutral defects; $[X_{di}^{z+}]$ and $[X_{ai}^{z-}]$ are the donor and acceptor concentrations, respectively.

Temperature dependence of the ZnS BG width was also taken into account in the modeling in the form of [2]

$$E_g(T) = E_g(0) - 5,263 \cdot 10^{-4} \cdot T \quad (4.10)$$

In further calculations we will count ionization energy of all charged defects as well as the Fermi energy from the bottom of the conduction band. We will take the factors of spin degeneration of levels to be equal to $g = 2$ for singly charged donor defects and $g = 1/2$ for acceptor doubly charged centers according to [12].

We have used the data of the 4-th Morozova model [2] as the ionization energy of charged PD in modeling.

In the calculations of the concentration of intrinsic defects in the case of hardening of semiconductor, additional equations of the following form were added to the system of equations which describe the equilibrium state of defects:

$$[Zn_i^0] + [Zn_i^+] + [Zn_i^{2+}] = [Zn_i]_{tot} = f(T), \quad (4.11)$$

$$[V_S^0] + [V_S^+] + [V_S^{2+}] = [V_S]_{tot} = f(T), \quad (4.12)$$

$$[V_{Zn}^0] + [V_{Zn}^-] + [V_{Zn}^{2-}] = [V_{Zn}]_{tot} = f(T), \quad (4.13)$$

where $[Zn_i]_{tot}$, $[V_S]_{tot}$, $[V_{Zn}]_{tot}$ are the total concentrations of PD in the samples in the case of complete equilibrium.

Results of the numerical calculation of the concentration of PD, charge carriers, and Fermi level in ZnS monocrystals versus the P_{Zn} for the cases of complete equilibrium of defects and their hardening are shown in Fig. 2.

Analysis of the obtained data implies a sufficiently good agreement of our results and the calculation results of Morozova [2, 6]. Moreover, these results agree with the experimental data of the determination of the free charge carrier concentration in material. This confirms realism of the chosen model of defect formation, constants of quasi-chemical reactions, and ionization energies of defects as well.

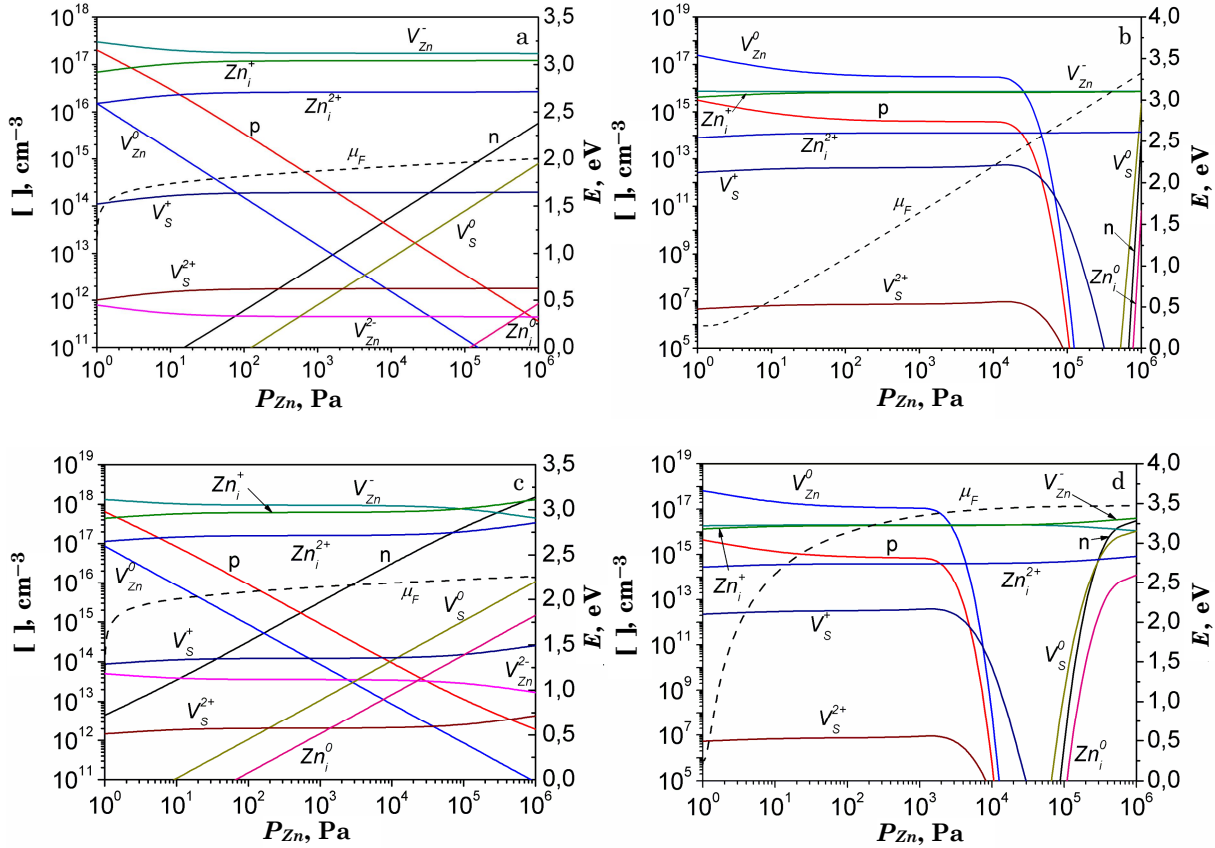


Fig. 2 – Dependences of the concentration of intrinsic PD, charge carriers, and Fermi energy on the partial pressure of zinc vapor at different annealing temperatures ($T = 1173$ K (a, b); $T = 1423$ K (c, d)) of ZnS monocrystal: complete equilibrium (a, c); hardening to $T = 293$ K (b, d)

4.2 Calculation of the point defect ensemble in ZnS films for the cases of complete equilibrium and hardening

It was established in the investigation of the defect formation processes in ZnS monocrystals that the used models of defect formation with the corresponding sets of constants of quasi-chemical equations describe well the experimental data [2, 6]. This allows to apply them for the calculation of the ensemble of PD in zinc sulfide films deposited in quasi-equilibrium conditions. In this case, the calculation technique of the PD concentration, which is used to study annealing of monocrystals at excess vapor pressure of compound components, should be adapted for the case of defect formation in films obtained by the deposition method in quasi-closed volume. This can be carried out due to the connection between evaporation temperature of material (T_e) and pressure of zinc (or sulfur) vapor formed as a result of dissociation of zinc sulfide during its evaporation. In the following, it is necessary to take into account the process of vapor condensation of compound components into solid phase at the substrate temperature (T_s).

To describe the state of complete equilibrium of intrinsic PD in ZnS films, the system of quasi-chemical equations (4.1)-(4.9) can be used; however, it should be supplemented by two additional correlations. The first correlation describes evaporation of compound at evaporator temperature T_e and takes into consideration its

dissociation in the transition from solid phase (S) into vapor (G). The second equation characterizes the “sulfur vapor-condensate” equilibrium with the formation of intrinsic defects in ZnS film at the deposition temperature T_s [2, 14]:

$$ZnS^S \leftrightarrow Zn^G + \frac{1}{2}S_2^G, K_{ZnS} = P_{Zn} \cdot P_{S_2}^{1/2} = f(T_e), (4.14)$$

$$\frac{1}{2}S_2^G \leftrightarrow S_S^0 + V_{Zn}^0, \frac{[V_{Zn}^0]}{P_{S_2}^{1/2}} = K_{S_2} = f(T_s). (4.15)$$

We should note that at modeling of PD ensemble in films, as well as in monocrystals, one should consider two limiting cases: complete equilibrium and hardening of defects. This is connected with the fact that in order to obtain structurally perfect films, we have used high-temperature regimes of layer condensation, $T_s = 573-973$ K, (complete equilibrium of defects) with further fast cooling of the samples to room temperature (hardening).

We have solved the modernized system of quasi-chemical equations by the technique applied in the case of the study of the defect formation processes in monocrystals. However, in calculations of the PD ensemble in films we have used measurements (corrected by the photoluminescent methods) of the VAC CLSC and $\sigma - T$ dependences of the activation energies of defects. We have determined the corresponding values of the energy

level depths of intrinsic defects (ΔE) in the experimental works [14, 15]. The calculation results of the PD ensemble in ZnS films depending on the evaporator temperature T_e at constant substrate temperature T_s are given in Fig. 3. In Fig. 4 we show the calculation results of the concentration of defects on the substrate temperature T_s at constant evaporator temperature T_e . Ranges of the temperatures T_e , T_s used in the modeling corresponded to those realized experimentally.

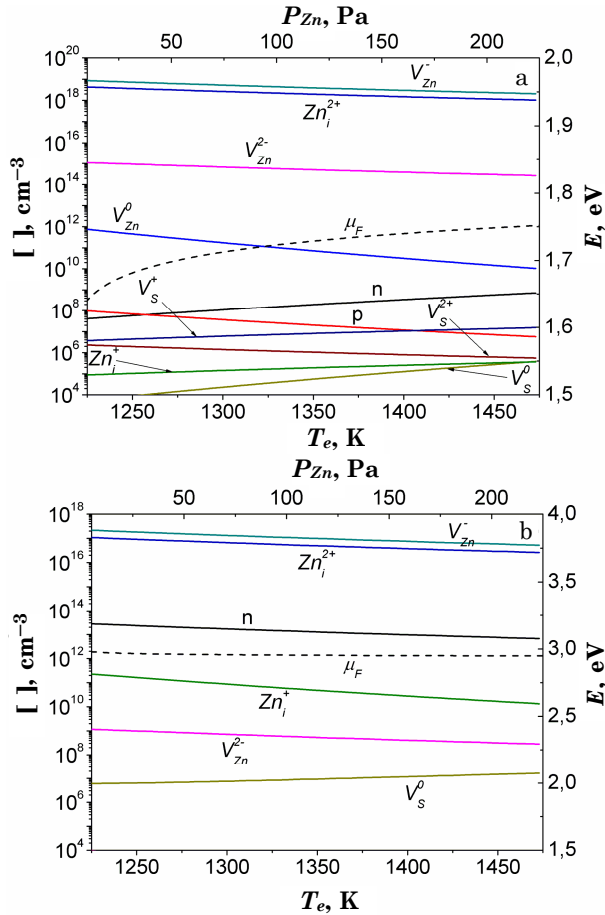


Fig. 3 – Dependences of the concentration of intrinsic PD, charge carriers, and Fermi energy in ZnS films on the evaporator temperature T_e at constant substrate temperature $T_s = 623 \text{ K}$: complete equilibrium (a); hardening to $T = 293 \text{ K}$ (b)

As seen from the figures, concentration of free charge carriers, PD, and Fermi level in films considerably depend on the conditions of film deposition. In the whole investigated range of physical and technological conditions of condensation, V_{Zn}^- and Zn_i^{2+} are dominant PD in both unhardened and hardened layers. Moreover, the doubly charged vacancies of zinc V_{Zn}^{2-} are present in appreciable concentration in slowly cooled films, while interstitial singly charged zinc atoms Zn_i^+ are observed in hardened layers. Concentration of all neutral PD is significantly lower than of the charged ones and we can neglect their presence in compound.

As the calculation results show, ZnS films have n -type conduction almost in the whole range of condensation temperatures. Films with p -type conduction can be obtained only in the narrow range of substrate temper-

atures at $T_s < (600-550) \text{ }^\circ\text{C}$ and during establishment of the equilibrium state of defects. But these physical and technological conditions cannot be realized in reality. Thus, results of the modeling coincide well with the experimental data [14], which implies that monocrystals and films of undoped zinc sulfide always have n -type conduction.

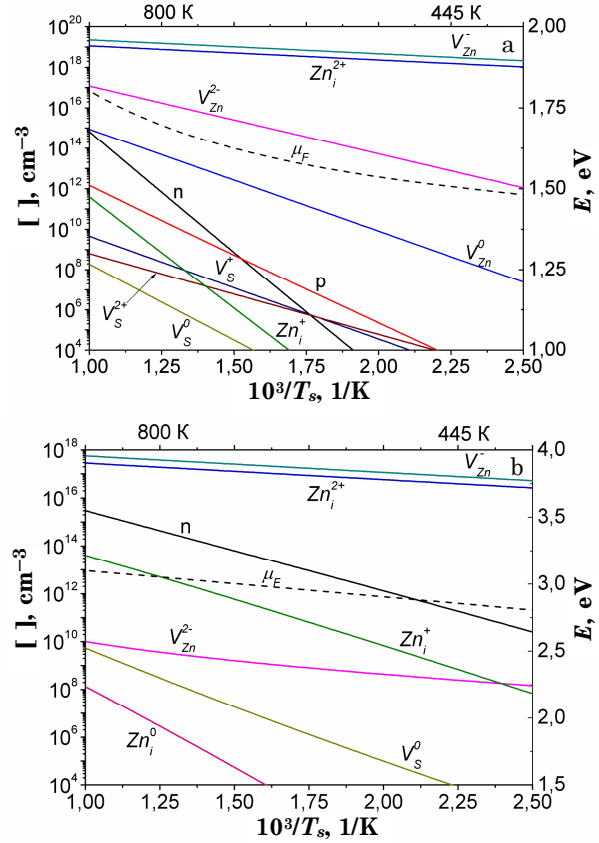


Fig. 4 – Dependence of the PD concentration in ZnS films on the inverse substrate temperature $10^3/T_s$ at constant evaporator temperature $T_e = 1253 \text{ K}$: complete equilibrium (a); hardening to $T = 293 \text{ K}$ (b)

As seen from Fig. 3 and Fig. 4, at the increase in the evaporator and substrate temperatures, conduction of the films increases, however, concentration of intrinsic charge carriers in this case does not exceed 10^5 - 10^6 cm^{-3} , and in the majority of the cases it equals to the value of 10^8 - 10^{10} cm^{-3} . Hardening of the layers leads to a slight increase in the layer conduction in comparison with the samples which are slowly cooled. Thus, results of the modeling indicate that ZnS films in a wide range of the condensation temperatures remain high-resistance. These conclusions also correlate well with the data obtained during measurements of the conduction of ZnS films by us [14] and other authors [16, 17].

5. CONCLUSIONS

In the work, calculation of the concentration of neutral and charged PD, free charge carriers, and position of the Fermi level in monocrystals and films of zinc sulfide depending on the conditions of film production is performed using the quasi-chemical approach.

It is shown that in the whole investigated range of the physical and technological condensation conditions, V_{Zn}^- and Zn_i^{2+} are the dominant PD in both hardened and unhardened layers.

Doubly charged vacancies of zinc V_{Zn}^{2-} are present in slowly cooled films, while interstitial singly charged zinc atoms Zn_i^+ are observed in hardened layers. Concentration of all neutral PD is considerably lower than of the charged ones, and, therefore, one can neglect their presence in the compound.

It is established that almost in the whole range of the condensation temperatures ZnS films have *n*-type conduction.

REFERENCES

1. A.N. Georgobiani, *Fizika soedineniy A2B6* (M.: Nauka: 1986).
2. N.K. Morozova, V.A. Kuznetsov, *Sul'fid tsinka. Poluchenie i opticheskie svoystva* (M.: Nauka: 1987).
3. F. Kreger, *Khimiya nesovershennykh kristallov* (M.: Mir: 1969).
4. S.A. Medvedev, *Vvedenie v tekhnologiyu poluprovodnikovyykh materialov* (M.: Vysshaya shkola: 1970).
5. M. Atakova, P. Ramazanov, E. Sal'man, *Izv. Vuz. Fiz.* **10**, 95 (1973).
6. N.K. Morozova, O.N. Morozova, *Neorganicheskie materialy* **17**, 1335 (1981).
7. H. Wiedemeier, *Z. Anorg. Allg. Chem.* **632**, 1717 (2006).
8. K. Lott, S. Shinkarenko, *Physica B* **404**, 5006 (2009).
9. K. Lott, L. Torn, O. Volobujeva, *Phys. Status Solidi (b)* **229**, 361 (2002).
10. K. Lott, L. Turna, O. Volobujeva, *Physica B* **308**, 932 (2001).
11. O. Madelung, *Fizika tverdogo tela. Lokalizirovannye sostoyaniya* (M.: Nauka: 1985).
12. V.V. Kosyak, M.M. Kolesnyk, A.S. Opanasyuk, *J. Mater. Sci: Mater. Electron.* **19**, 375 (2008).
13. I.P. Kalinkin, V.B. Aleskovskiy, *Epitaksial'nye plenki soedineniy A2B6* (Leningrad: Izd-vo LGU: 1978).
14. D. Kurbatov, V. Kosyak, A. Opanasyuk, *Physica B* **404**, 5002 (2009).
15. D. Kurbatov, A. Opanasyuk, S. Kshnyakina, *Rom. J. Phys.* **55**, 213 (2010).
16. Y. Venkata Subbaiah, P. Prathap, K. Ramakrishna Reddy, *Appl. Surf. Sci.* **253**, 2409 (2006).
17. Y. Venkata Subbaiah, P. Prathap, K. Ramakrishna Reddy, *J. Phys. D: Appl. Phys.* **40**, 5275 (2007).

ACKNOWLEDGEMENT

The author of the paper expresses his gratitude to Dr. Associate Prof. Opanasyuk A.S. and Ph.D. Kosyak V.V. for the support in the statement of the calculation method of PD ensemble and active participation in the discussion of the results.

The work has been performed under the financial support of the SASII (project No M/209-2012) and the Ministry of Education and Science, Youth and Sport of Ukraine.