 © 2007 — Institute for Single Crystals

# Defect formation in diffusive layers of ZnSe:Sn and ZnSe:Mg

***V.I.Gryvul, V.P.Makhniy, I.V.Tkachenko***

Yu.Fed'kovich Chernivtsi National University,
2 Kotsyubinsky St., 58012 Chernivtsi, Ukraine

*Received March 19, 2007*

Equilibrium concentrations of point defects in ZnSe layers obtained by Sn and Mg diffusion from vapor phase at 1150 K have been calculated using the quasi-chemical reaction method. The calculated results are compared to data obtained from thermo-e.m.f., conductivity and luminescence spectra measurements.

Методом квазихимических реакций рассчитаны концентрации равновесных точечных дефектов в слоях ZnSe, полученных диффузией Sn и Mg из паровой фазы при 1150 К. Результаты расчетов сопоставлялись с данными термоэдс, проводимости и спектров люминесценции.

Zinc selenide is among the most prospective semiconductors for short-wavelength optical devices (blue LEDs and UV radiation detectors) [1, 2]. The crystal properties are defined by the set of intrinsic and extrinsic point defects that is as a rule a complex ensemble and depends on numerous technological factors. In this connection, a combination of experimental study methods with computerized calculations is desirable to provide information required to establish the defect formation mechanisms. In this work, that problem is solved for zinc selenide doped with magnesium and tin, since the previous studies have shown that those impurities contribute considerably to the enhancement of the edge emission efficiency [3, 4].

The undoped ZnSe crystals grown from a stoichiometric melt under inert gas pressure were taken as the initial samples. That choice was dictated by several reasons. First, the technology mentioned is the most widespread one in preparation of large-size, high-quality crystals [5]. Second, it is just such samples for which both qualitative and quantitative composition of intrinsic point defects (IPD) has been established reliably to date. According to [6], the disordering in the undoped ZnSe crystals grown from melt occurs according to the Schottky scheme and the concentrations of predominant cationic vacancies $[V''_{Zn}]$ and anionic $[V^{\bullet}_{Se}]$ ones amount about $5 \cdot 10^{21}$ cm$^{-3}$ at 300 K. The validity of the adopted defect formation model is confirmed also by the fact that the calculated free electron concentration at 300 K amounts $10^6$ cm$^{-3}$ (Table) is not in contradiction with experimental values of that parameter being within limits of $10^5$ to $10^7$ cm$^{-3}$ in the initial samples [6].

The layers were formed by isothermal annealing the 4×4×1 mm$^3$ substrates in saturated Sn or Mg vapor inside of an evacuated ($10^{-4}$ Torr) quartz ampoule at $T_a$ = 1150 K for several hours. The thickness of diffusion layers with Sn and Mg additives depends at $T_a$ = const on the additive type and the annealing duration and varies within 3 to 5 μm in our case. This is quite sufficient to measure correctly the electrical and optical characteristics, taking into account that the mean absorption depth of the exciting quanta does not exceed 0.1 μm. It is to note also the constant energy positions of singularities in the λ-modulated optical transmission and reflection spectra

Table. Point defects concentrations in the studied objects

| IPD type | ITD concentration at 300 K, $cm^{-3}$ | | |
|---|---|---|---|
| | ZnSe | ZnSe:Sn | ZnSe:Mg |
| $n$ | $10^6$ | $10^{17}$ | $3{\cdot}10^{-24}$ |
| $p$ | $10^{-14}$ | $10^{-25}$ | $3{\cdot}10^{15}$ |
| $V_{Zn}$ | $2{\cdot}10^{-21}$ | $4{\cdot}10^{-43}$ | $2{\cdot}10^{21}$ |
| $V_{Se}$ | $4{\cdot}10^{10}$ | $2{\cdot}10^{21}$ | $10^{-26}$ |
| $V_{Zn}^{'}$ | $6{\cdot}10^{8}$ | $10^{-2}$ | $3{\cdot}10^{21}$ |
| $V_{Zn}^{''}$ | $6{\cdot}10^{21}$ | $5{\cdot}10^{21}$ | $10^{5}$ |
| $V_{Se}^{\bullet}$ | $7{\cdot}10^{21}$ | 5·1021 | 7·1015 |
| $V_{Se}^{\bullet\bullet}$ | $4{\cdot}10^{-2}$ | $5{\cdot}10^{-13}$ | $3{\cdot}10^{4}$ |
| $Se_i$ | – | – | $10^{16}$ |
| $Se_i^{'}$ | – | – | $10^{19}$ |
| $Sn_{Zn}^{\bullet}$ | – | $10^{19}$ | – |
| $Sn_{Se}^{'}$ | – | $10^{19}$ | – |
| $(V_{Zn}^{''}V_{Se}^{\bullet})$ | $3{\cdot}10^{16}$ | $3{\cdot}10^{14}$ | $10^{-2}$ |

near the intrinsic absorption edge of zinc selenide. This fact evidences that no any new chemical compound of the ZnSe crystal lattice atoms with the diffused dopant is formed. The conductivity type of the diffusion layers was determined by the thermo-e.m.f. sign while the ionization energy of the electrically active centers, basing on the temperature dependences of the resistance $R_0$ between two ohmic contacts (this is rightful because $R_0$ is inversely proportional to conductivity). The contacts were prepared by vacuum thermal deposition of spatially separated In and Ni strips onto the surface of ZnSe:Sn and ZnSe:Mg samples, respectively. The emission spectra were measured using an universal setup including a MDR-23 diffraction monochromator and a standard synchronic detection system [7]. The photoluminescence (PL) was excited by a nitrogen laser at $\lambda_m \approx 0.337$ µm and the emission spectra $N_\omega$ were constructed taking into account the nonlinearity of the optical path elements.

The concentrations of equilibrium point defects were calculated using the quasi-chemical reaction method under account for the assumptions that follow. The first assumption relates to the maximum concentration of dopants $C_d$ that should not exceed $10^{19}$ $cm^{-3}$. This excludes the formation possibility of solid solutions $Zn_xMg_{1-x}Se$ or $Zn_xSn_{1-x}Se$ and $ZnSn_{1-x}Se_x$ types. Second, since $C_d <<[V_{Zn}^{''}]$, $[V_{Se}^{\bullet}]$, the vacancy mechanism should be assumed for the dopant atom entering into the matrix crystal lattice. In this case, the isovalent magnesium dopant occupies the zinc vacancies, while tin (due to its amphoteric character) both cationic and anionic vacancies. Moreover, magnesium generates the additional interstitial selenium atoms $Se_i$ in a concentration commensurable with that of the magnesium introduced, that is, $[Se_i] \approx C_{Mg}$ [8].

The above conditions make it possible to write the corresponding electric neutrality equations for magnesium-doped crystals as

$$p + [V_{Se}^{\bullet}] + 2[V_{Se}^{\bullet\bullet}] + [V_{Zn}^{'}V_{Se}^{\bullet\bullet}] - n - [V_{Zn}^{'}] - 2[V_{Zn}^{''}] - [Se_i^{'}] - [V_{Zn}^{''}V_{Se}^{\bullet}] = 0 \quad (1)$$

and for tin-doped ones, as

$$p + [V_{Se}^{\bullet}] + 2[V_{Se}^{\bullet\bullet}] + [V_{Zn}^{'}V_{Se}^{\bullet\bullet}] + [Sn_{Zn}^{\bullet}] + [V_{Se}^{\bullet\bullet}Sn_{Se}^{'}] - n - [V_{Zn}^{'}] - 2[V_{Zn}^{'}] - [Se_i^{'}] - [V_{Zn}^{''}V_{Se}^{\bullet}] - [V_{Zn}^{''}Sn_{Zn}^{\bullet}] - [Sn_{Se}^{'}] = 0. \quad (2)$$

Here the symbols $Sn_{Zn}$ and $Sn_{Se}$ denote tin atoms within the cationic and anionic sublattices, respectively; "•" and "’", the positive (donor) and negative (acceptor) charges of point defects, respectively. The complex defects of $([V_{Zn}^{''}V_{Se}^{\bullet}])$, $([V_{Zn}^{'}V_{Se}^{\bullet}])$ and other types are formed predominantly due to

Coulombian interaction [9]. The estimations show [6] that the concentration of charged associates exceeds by more than three orders that of neutral ones, thus, the latter can be neglected. Moreover, as $[V_{Se}^{\bullet\bullet}] << C_{Sn} << [V_{Zn}'']$, the amount of complexes including the tin impurity can be neglected as a first approximation. Taking into account the above considerations, the associates of the $(Sn_{Zn}^{\bullet}Sn_{Se}')$ can be neglected, too. The absence of charged $Mg^{\bullet}$ defects in the Eq.(1) is associated with the fact that the isovalent magnesium impurity does not form local levels within the ZnSe band gap [9]. Finally, it is worth to note the extremely low formation probability of $(V_{Zn}'V_{Se}^{\bullet\bullet})$ associates, since the both types of intrinsic point defects exhibit accepting properties [1].

The calculation procedure of equilibrium point defect concentration at the doping temperature ($T_a$ = 1150 K) and the experiment one (300 K) is presented in detail elsewhere [6, 9]. The dopant concentration was selected to be maximum ($C_d = 10^{19}$ cm$^{-3}$) and the calculation results for the undoped and doped ZnSe crystals are presented in Table. The data on the IPD concentration in the initial samples are taken from [6]. The consideration of Table allows us to conclude that: (1) while tin introduction causes a considerable increase in the electron conductivity of the substrate surface layers, the magnesium doping results in its inversion. In contrast, the concentration product of the free charge carriers is the same for the all three sample types and amounts about $10^8$ cm$^{-3}$. Thus, the validity of the mass action law testifies to correctness of the selected assumptions and calculations. (2) Introduction of Sn and Mg decreases also sharply the concentrations of $(V_{Zn}'V_{Se}^{\bullet})$ associates that, according to [6], are responsible for the low-energy emission. At the same time, the concentration of shallow centers ($V_{Se}^{\bullet}$ and $Sn_{Zn}^{\bullet}$ in ZnSe:Sn layers and $V_{Zn}'$ and $Se'_i$ in ZnSe:Mg samples) is rather high. In this connection, a considerably increased fraction of the edge emission as compared to the low-energy one could be expected for the doped samples.

The theoretical calculation results correlate rather well with the experimental data. First of all, it is to note that the PL spectra of diffusion layers at 300 K include only one blue band, in contrast to the initial substrates (Fig.). The experiment has shown also that the specific thermo-e.m.f. α of the

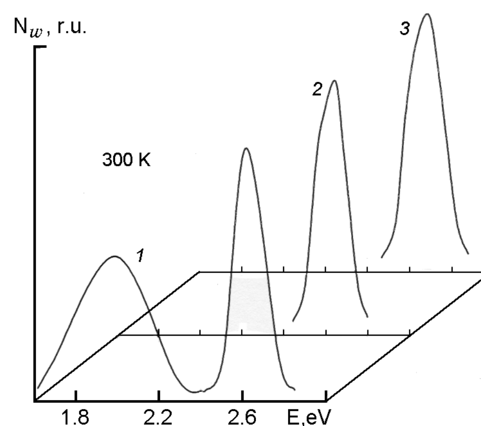


Fig. Luminescence spectra of initial ZnSe crystals (*1*) and those doped with tin (*2*) and magnesium (*3*).

ZnSe:Sn layers is negative and amounts about 5 μV/K near room temperature. In contrast, the ZnSe:Mg samples show a positive thermo-e.m.f. that evidences the hole conductivity thereof. Moreover, the α value is about 60 μV/K, thus exceeding that of ZnSe:Sn layers by one order. Since the specific thermo-e.m.f. is as a first approximation in inverse proportion to the concentrations of major charge carriers [10], the revealed differences in α of the diffusion layers do not contradict to the data from Table. The temperature dependences of the layer resistance confirm additionally the correctness of the calculations performed. So the energy slope of the $\ln R_0 - 10^3/T$ straight lines in the room temperature region is 30 meV and 200 meV for ZnSe:Sn and ZnSe:Mg samples, respectively. Those values agree well with the ionization energy of levels corresponding to the donor ($V_{Se}^{\bullet}$ and $Sn_{Zn}^{\bullet}$) and acceptor ($V_{Zn}'$) centrs in ZnSe [11, 1]. The role of acceptor centers $Sn_{Se}'$ in the formation of electric and luminescence properties of ZnSe:Zn layers remains unclear to date due to lack of information on their energy position within the band gap of zinc selenide.

Thus, the results obtained evidence convincingly the possibility to prepare the diffusion layers with sufficiently high electron and hole conductivity and predominant edge emission. In contrast, the elucidation of luminescence mechanisms and the recombination center nature require an additional study.

### References


1. A.N.Georgobiani, B.M.Kotlarevsky, *Izv.AN SSSR.Ser.Fiz.*, **49**, 1916 (1985).
2. T.V.Blank, Yu.A.Goldberg, *Fiz.Tekhn.Poluprov.*, **37**, 1025 (2003).
3. S.V.Zubritsky, Yu.F.Vaksman, V.V.Serdyuk, *Zh.Prikl.Spektr.*, **45**, 857 (1986).
4. V.P.Makhniy, N.D.Raransky, M.M.Sletov, I.V.Tkachenko, *Neorg.Mater.*, **40**, 1 (2004).
5. N.K.Morozova, V.A.Kuznetsov, V.D.Ryzhikov. Zinc Selenide: Preparation and Optical Properties, Nauka, Moscow (1992) [in Russian].
6. I.V.Tkachenko, Ph.D.Thesis (Phys.-Math.) Chernivtsi Univ. (2005) [in Ukrainian].
7. V.P.Makhniy, Principles and Methods of Modulation Spectroscopy, Ruta, Chernivtsi (2001) [in Ukrainian].
8. Yu.N.Dmitriev, V.D.Ryzhikov, L.P.Galchinetsky, Thermodynamics of Isovalent Doping of Crystals of Semiconductor Compounds $A^2B^6$, VNII Monokristallov, Kharkiv (1990) [in Russian].
9. V.P.Makhniy, N.D.Raransky, Physicochemical Principles of Formation and Analysis of Point Defects in Semiconductors, Ruta, Chernivtsi (2003) [in Ukrainian].
10. K.V.Shalimova, Physics of Semiconductors, Energoatomizdat, Moscow (1985) [in Russian].
11. V.V.Serdyuk, Yu.F.Vaksman, S.V.Zubritsky et al., *Fotoelektronika*, No.2, 98 (1988).


## Дефектоутворення у дифузійних шарах ZnSe:Sn і ZnSe:Mg

***В.І.Гривул, В.П.Махній,І.В.Ткаченко***

Методом квазіхімічних реакцій розраховано концентрації рівноважних точкових дефектів у шарах ZnSe, отриманих дифузією Sn і Mg з парової фази при 1150 K. Результати розрахунків зіставляються з даними термоерс, провідності та спектрів люмінесценції.