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## POINT-DEFECT CONCENTRATION PROFILES IN THIN PbS FILMS SUBJECTED TO ISOTHERMAL ANNEALING

Y.A.P. SALIY

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Precarpathian National University  
(57, Shevchenko Str., Ivano-Frankivsk 76000, Ukraine)

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It has been shown that a nonuniform distribution of point-defect concentration across thin PbS films of the *p*-type isothermally annealed in vacuum and the formation of a *p-n*-structure in them can be explained by fast diffusion of electrically neutral sulfur interstitial atoms, slow diffusion of electrically charged sulfur and lead vacancies, and reactions occurring between those defects. The evolution of defects has been described by a system of nonhomogeneous diffusion equations, and the corresponding numerical solution has been presented graphically. By fitting the theoretical dependence to experimental data, the values of key kinetic parameters of the process of point-defect isothermal annealing in vacuum have been obtained.

1. Isothermal annealing of  $\text{A}^{\text{IV}}\text{B}^{\text{VI}}$  films in vacuum underlies some simple and effective techniques for fabricating *p-n* film structures for infrared optoelectronic devices [1]. For instance, in work [2], isothermal annealing of sulfur-rich lead sulfide films of the *p*-type grown on  $\text{BaF}_2$  substrates by the molecular beam method at the temperature  $T = 370$  °C in vacuum was demonstrated to invert the conductivity type of the films. Layer-by-layer etching showed that, in the course of annealing, a region with *n*-conductivity expands from the free surface of the film into its depth. The experimental results obtained were qualitatively explained by a prevailing formation of donor vacancies in the chalcogene sublattice owing to the evaporation of superstoichiometric sulfur atoms into vacuum. An attempt to describe theoretically the experimental concentration profile of free current carriers was made in work [3], where the hypothesis of ambipolar diffusion of vacancy defects and free current carriers was applied. However, the calculated analytical dependences, the parameters of which were obtained by analyzing three characteristic experimental points rather than the whole curve, unfortunately,

were not presented to make a comparison with experiment.

2. In order to provide qualitative and quantitative agreement between theoretical dependences and available experimental data, we proposed a simple model which considers the interaction between defects associated with superstoichiometric sulfur (these include acceptor lead vacancies  $V_{\text{Pb}}$  and practically neutral interstitial sulfur atoms  $S_i^0$ ) and their diffusion towards the free surface, as well as the diffusion of stoichiometric sulfur towards this surface, which is equivalent to the back diffusion of donor sulfur vacancies  $V_{\text{S}}^+$  into the film depth. We also obtained the space-time distribution of point defects across a thin monoblock lead sulfide film at its isothermal annealing in vacuum.

Point defects in lead chalcogenides are known to be mainly responsible for their electrophysical properties. We suppose that, according to the film manufacturing technique under conditions of a sulfur excess, point defects of two types prevail in films of the *p*-type before their annealing, namely, acceptor lead vacancies  $V_{\text{Pb}}^-$  and electroneutral interstitial sulfur atoms  $S_i^0$ ; we also suppose that donor sulfur vacancies  $V_{\text{S}}^+$  emerge in the course of annealing. Inhomogeneity arises as a result of evaporation of a volatile component – both superstoichiometric and stoichiometric sulfur – into vacuum.

3. The condition of local electroneutrality allows one to unambiguously determine the difference between free current carrier concentrations in terms of the difference between the concentrations of electrically active defects:

$$n - p = [V_{\text{S}}^+] - [V_{\text{Pb}}^-].$$

Defect-inducing sulfur atoms comprise three fractions: two superstoichiometric,  $S_{ni}$  and  $S_{nv}$ , associated with sulfur interstitial atoms  $S_i^0$  and lead vacancies  $V_{Pb}^-$ , respectively, and one stoichiometric,  $S_{sv}$ , associated with sulfur vacancies  $V_S^+$ . The concentrations of those sulfur fractions ( $n_{ni}$ ,  $n_{nv}$ , and  $n_{sv}$ , respectively) are coupled with the concentrations of defects as follows:

$$[V_S^+] = n_{sv,0} - n_{sv}, \quad [V_{Pb}^-] = n_{nv}, \quad [S_i^0] = n_{ni}.$$

Let us express the equations, which describe the variations of sulfur fraction concentrations, in terms of the diffusion coefficients of the corresponding components and the reaction constants of atomic transitions from a site position into an interstitial one and backwards:

$$\partial n_{sv}/\partial t = D_{sv}\partial^2 n_{sv}/\partial z^2 - \alpha_{sv}n_{sv}(n_{ni,0} - n_{ni}),$$

$$\partial n_{nv}/\partial t = D_{nv}\partial^2 n_{nv}/\partial z^2 - \alpha_{nv}n_{nv}(n_{ni,0} - n_{ni}),$$

$$\partial n_{ni}/\partial t = D_{ni}\partial^2 n_{ni}/\partial z^2 +$$

$$+(\alpha_{sv}n_{sv} + \alpha_{nv}n_{nv})(n_{ni,0} - n_{ni}),$$

where  $D_{sv}$ ,  $D_{nv}$ , and  $D_{ni}$  are the coefficients of sulfur atom diffusion in the migration processes associated with sulfur vacancies, lead vacancies, and interstitial sulfur, respectively; and  $\alpha_{sv}$  and  $\alpha_{nv}$  are the reaction constants of the direct transition of a stoichiometric sulfur atom and the reverse transition of a superstoichiometric sulfur atom into an interstitial position.

The initial conditions in our problem correspond to a uniform distribution of all three components of sulfur:

$$n_{sv}(z, 0) = n_{sv,0}, \quad n_{nv}(z, 0) = n_{nv,0},$$

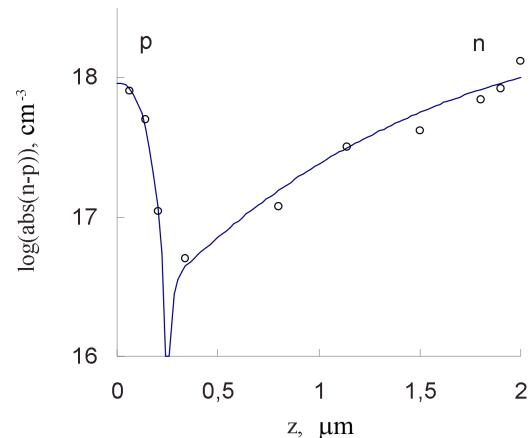
$$n_{ni}(z, 0) = n_{ni,0}, \quad 0 < z < d.$$

The boundary conditions correspond to the absence of the flux of sulfur across the substrate-film interface:

$$\partial n_{sv}(0, t)/\partial z = 0, \quad \partial n_{nv}(0, t)/\partial z = 0,$$

#### Calculated values of the fitting parameters in the theoretical dependences

Initial concentrations		Diffusion coefficients		Reaction constants	
$n_{sv,0}$ , $\text{cm}^{-3}$	$1.0 \times 10^{18}$	$D_{sv}$ , $\text{cm}^2\text{s}^{-1}$	$4.2 \times 10^{-13}$	$\alpha_{sv}$ , $\text{cm}^3\text{s}^{-1}$	$2.5 \times 10^{-15}$
$n_{nv,0}$ , $\text{cm}^{-3}$	$1.2 \times 10^{18}$	$D_{nv}$ , $\text{cm}^2\text{s}^{-1}$	$7.0 \times 10^{-15}$	$\alpha_{nv}$ , $\text{cm}^3\text{s}^{-1}$	$5.0 \times 10^{-12}$
$n_{ni,0}$ , $\text{cm}^{-3}$	$2.6 \times 10^{18}$	$D_{ni}$ , $\text{cm}^2\text{s}^{-1}$	$3.5 \times 10^{-12}$		



Profiles of the experimental distribution of current carriers over the thickness of an epitaxial PbS film with the *p*-type of conductivity annealed in vacuum at a temperature of 370 °C for 1.5 h (circles) and the calculated concentration distribution of electrically active defects (solid curve). The coordinate  $z = 0$  corresponds to the substrate-film interface

$$\partial n_{ni}(0, t)/\partial z = 0, \quad t > 0,$$

and to the sulfur evaporation at the film-vacuum interface:

$$n_{sv}(d, t) = 0, n_{nv}(d, t) = 0, n_{ni}(d, t) = 0, t > 0.$$

4. The equations were integrated numerically. The calculation parameters presented in the Table were determined by fitting the experimental dependences by theoretical ones. The experimental concentration profile for free current carriers and the calculated concentration profile for electrically active defects are depicted in the Figure. The profile of the current carrier concentration distribution over the film thickness was determined by Hall effect measurements combined with layer-by-layer specimen etching according to a technique described in work [4]. The accuracy of thickness measurements was 0.1 μm, and that of concentration did not exceed 5%. The figure clearly demonstrates good agreement between calculated and experimental curves, which evidences for the adequacy of the model.

5. The table makes it evident that the coefficient of sulfur atom diffusion over interstitial sites,  $D_{ni}$ , proved

to be the highest, while that associated with lead vacancies,  $D_{nv}$ , the lowest. The ratio of three orders of magnitude between them is plausible, being valid for the majority of lead chalcogenides [5]. A comparison between the reaction constants also demonstrates that the occupation of an interstitial position by a superstoichiometric sulfur is 2000 times more probable than that by a stoichiometric one, which also seems plausible, because a superstoichiometric sulfur at a lattice site is surrounded by lead vacancies weakening the bonds of this sulfur.

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ПРОФІЛЬ КОНЦЕНТРАЦІЇ  
ТОЧКОВИХ ДЕФЕКТІВ В ТОНКИХ  
ПЛІВКАХ PbS ПРИ ІЗОТЕРМІЧНОМУ ВІДПАЛІ

Я.П. Салій

Р е з ю м е

Показано, що неоднорідність розподілу концентрації точкових дефектів за товщиною і пов'язане з цим утворення  $p-n$ -структур в ізотермічно відпалених у вакуумі тонких плівках PbS  $p$ -типу можна пояснити швидкою дифузією електрично нейтральних міжвузловинних атомів сірки і повільною дифузією електрично активних вакансій свинцю та сірки, а також реакціями між цими дефектами. Еволюцію дефектів описано системою неоднорідних дифузійних рівнянь, чисельний розв'язок яких представлено графічно. З апроксимації експериментальних даних розраховано залежністю одержано параметри процесу еволюції точкових дефектів під час вакуумного відпалу.