

## ANALYSIS OF THE ELECTRET EFFECT IN $\text{Zn}_{0.7}\text{Cd}_{0.3}\text{S}$ COMPOSITES

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The characteristics of electret charge creation as well as the electret voltage behaviour and its dependencies on poling electric field, polarisation time and temperature have been investigated in  $\text{Zn}_{0.7}\text{Cd}_{0.3}\text{S}$  solid solution layers in the present paper. The model of space charge formation based on the strong secondary capture and monomolecular recombination is proposed and substantiated by numerical simulation. The parameters, such as effective density of states in the conductivity zone and the recombination time, have been evaluated.

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### 1. Introduction

$\text{A}^{\text{II}}\text{-B}^{\text{VI}}$  semiconductors thin films and their composites, particularly the hetero-structures of  $\text{ZnCdS}$ , have a constantly rising interest from the scientific researches and engineers due to the widespread applications in dynamically tuneable multicolour (white) monolithic nano-lasers [1, 2], solar cells [3], detectors in the range as wide as from the IR (e.g. night vision appliances) [4, 5] to UV [6, 7] and other optoelectronic [8, 9] and nano [10-13] devices. Despite zinc sulphide ( $\text{ZnS}$ ) and cadmium sulphide ( $\text{CdS}$ ) are the most typical materials in the  $\text{A}^{\text{II}}\text{-B}^{\text{VI}}$  compound group, especially attractive are the  $\text{Zn}_x\text{Cd}_{1-x}\text{S}$  solid solutions. Their structure enables to vary the direct energy gap  $E_g$  in extremely wide region from 2.42 eV to 3.66 eV by means of changing Zn/Cd ratio in the compounds [14, 15]. Furthermore, proper doping with shallow impurities (e.g. I [16, 17], Cu [18]) and/or post preparation annealing [19, 20] can be used to change optical characteristics and other physical parameters of compounds additionally.

It has been shown that photoconductive polycrystalline solid solutions layers of  $\text{Zn}_x\text{Cd}_{1-x}\text{S}$  retains well-defined space-charge polarisation [21], the origin of which remains unclear up to now, despite that the effect, named as the electret effect, has been obtained also in the very broad variety of semiconductors as well as of dielectrics. The electret effect can be originated by frozen space-charge or oriented permanent dipole [22]. This polarisation origins the long-time memory, which is interesting as physical phenomenon, and can be used in practice: e.g. in the space-time modulators of light (composing  $\text{Zn}_{0.7}\text{Cd}_{0.3}\text{S}$  layers with segnetoelectric liquid crystals) [23], possible non-volatile memory elements [13], etc.

In this contribution, the properties of electret voltage and their dependencies on the temperature and layer thickness in  $\text{Zn}_{0.7}\text{Cd}_{0.3}\text{S}$  solid solutions composites are studied; the behaviour of electret voltage decay, initiated by depolarisation, and its dependencies on temperature are examined experimentally and simulated numerically. The validity of the proposed model of space charge formation based on the strong secondary capture and monomolecular recombination is confirmed by the adequacy of fundamental parameters used in numerical simulation with known experimental values.

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## 2. Experimental

The  $\text{Zn}_{0.7}\text{Cd}_{0.3}\text{S}$  layers have been fabricated using the thermal evaporation technique under the vacuum,  $\sim 5 \cdot 10^{-5}$  Pa, at the condensation temperature  $T=450$  K onto the glass substrate, which previously has been coated by conductive  $\text{SnO}_2$  layer. The desirable structure of the ternary  $\text{Zn}_x\text{Cd}_{1-x}\text{S}$  composite has been obtained by changing ratio of precursors. The thickness of composite film ( $L = 0.3 - 10 \mu\text{m}$ ) was varied by changing the deposition time, when the velocity of the flow was held to be constant. Layer thickness was controlled by micro-interferometer. The Zn/Cd ratio 0.7/0.3 is chosen here with the aim to obtain high energy band-gap  $E_g \sim 3.2$  eV structure and to fit the optimal inter-layer hetero-junction conditions: high base resistivity and appropriate spectral characteristics, appropriate for e.g. photocell windows. Adding ZnS ( $E_g = 3.66$  eV) to CdS leads to increasing the energy gap from 2.42 to 3.66 eV dependent on the Zn/Cd ratio [14]. The same component ratio of solid solution,  $\text{Zn}_{0.7}\text{Cd}_{0.3}\text{S}$ , was reported by [24] as possessing maximum photocurrent, photo voltage and photo conversion efficiency (the results was found when investigating influence of Zn content to optical and electrical properties).

The films of  $\text{Zn}_{0.7}\text{Cd}_{0.3}\text{S}$  have been investigated in the ion contact mode:  $\text{SnO}_2$  layer has been grounded and the free surface of composite layer has been charged by the corona discharge in the air ambience. Afterwards, the surface potential has been measured by dynamical electrometer. The electret voltage has been determined by cooling the layer after its partial free dark discharge, the subsequent discharging by force down to zero surface electrical potential, heating the discharged layer and simultaneously measuring the revealed surface electrical potential of the same polarity, as the initial charge was [25]. When, during the depolarisation, the specimen under investigation has been discharged recurrently, with the aim to maintain zero voltage between  $\text{SnO}_2$  contact and free surface of  $\text{Zn}_{0.7}\text{Cd}_{0.3}\text{S}$  layer, the rate of the surface electrical potential change, caused by the thermo stimulated depolarisation, can be supposed to be strictly proportional to the electrical current of shortened electret. The technics was described in more details elsewhere [25]. Such sequence can be treated as the electrode shortening while depolarising the layer and permits to determine electret voltage more accurate and practical, better than the conventional TSD technics. Also, it is very important that such technics allows minimising near contacts effects arising when using traditional thermo stimulated methods.

Additionally, measurements of thermo stimulated depolarization currents (TSD) have been provided using conventional TSD technics.

## 3. Results and discussion

The dependencies of the electret voltage on the polarisation temperature in  $\text{Zn}_{0.7}\text{Cd}_{0.3}\text{S}$  layer is shown in Fig. 1. It has been established, that the electret voltage  $U_e$  at adequate poling duration grows-up monotonically super linearly with the increasing temperature and reaches saturation at the proximity of 320 K. On the other hand, the saturation bend point shifts to lower temperatures when poling duration  $t_p$  is increased. The electret voltage  $U_e$  shows linear dependency on the poling electric field. It is necessary to note, that the ratio of electret voltage to polarisation one shows well expressed dependency on the sign of poling field (Fig. 2). If the film was polarised by positive electric voltage, the revealed electret potential was found by 20-30% larger than in the case of negative poling, when the other polarisation conditions (the temperature, duration of polarisation as well as poling electrical field) to maintain the same and the layer thickness does not exceed  $2 \mu\text{m}$ . The dependencies of ratio just noted on the sample thickness are more pronounced in the positive surface charge case, also: the ratio decreases by 4 times ( $\sim 2$  times in the case of negative charge), when layer thickness has been increased from  $0.5$  to  $7.8 \mu\text{m}$  (Fig. 2).

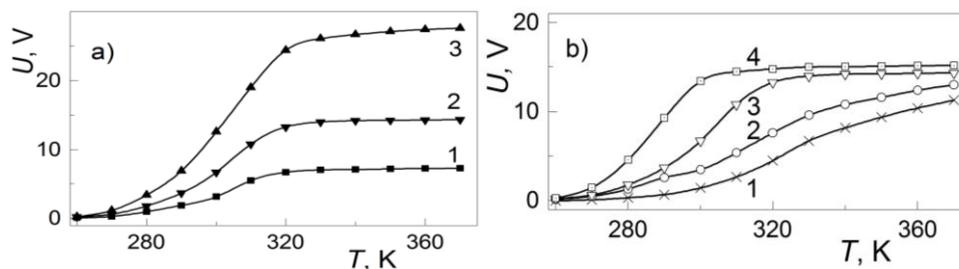


Fig. 1 Dependences of electret potential of  $Zn_{0.7}Cd_{0.3}S$  layers on the poling temperature at different poling electrical field (a) and poling duration (b). a) curve 1 -  $E = 17$ , 2 -  $E = 34$ , 3 -  $E = 68$   $V/\mu m$ ,  $t_p = 15$ , Layer thickness  $L = 3.0$   $\mu m$ . b) curve 1 -  $t_p = 2$ , 2 -  $t_p = 10$ , 3 -  $t_p = 15$  and 4 -  $t_p = 60$  min,  $E = 34$   $V/\mu m$ .  $L = 3.0$   $\mu m$ .

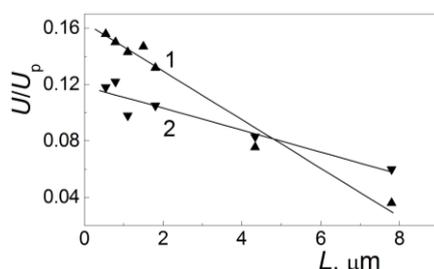


Fig. 2 Dependences of relative electret potential ( $U/U_p$  is the ratio of electret to poling voltage) on the  $Zn_{0.7}Cd_{0.3}S$  layer thickness. Positive (curve 1) and negative (2) charging potential was applied.  $T_p = 320$  K,  $t_p = 15$  min.

These dependencies indicate that the polarisation effects zones are concentrated in the near-electrode regions of  $Zn_{0.7}Cd_{0.3}S$  layer. The occurrence and the significance of these near-electrodes regions has been also confirmed by analysis of peculiarities of longitudinal kinetics of photoconductivity [26], by combined experiment on photo capacitance and photoconductivity [27], alike as by the results of our investigations by means of TSD.

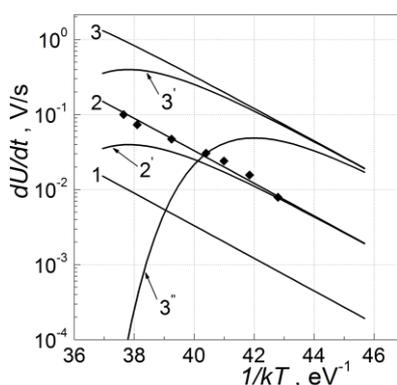


Fig. 3. The dependency of thermo depolarisation rate of  $Zn_{0.7}Cd_{0.3}S$  layers on reciprocal temperature ( $\blacklozenge$ ), as well as the results of computer simulation. It has been supposed in the model, that the effective density of states in the conductivity zone  $N_c$  is equal to  $2 \cdot 10^{23}$  (curve 1),  $2 \cdot 10^{24}$  (2) and  $2 \cdot 10^{25}$   $m^{-3}$  (3); recombination times  $t_r - 10^{-3}$  (curves 1-3),  $10^{-4}$  ( $3'$ ) and  $10^{-6}$  s ( $2'$ ); poling electrical field -  $E = 5$   $V/\mu m$ ; activation energy -  $W_t = 0.5$  eV.

The dependency of the rates of thermo-depolarisation on the temperature in the  $Zn_{0.7}Cd_{0.3}S$  layers has been presented in Fig. 3. It shows linear run. Dots represent the experimental results of

the initial decrease rate of the electret voltage, measured when specimens have been depolarised by linear heating and subsequent periodical discharging of the layer by force to reach zero potential. These results show Arrhenius-like behaviour, but the activation energy calculated from thermo depolarisation rate on the reciprocal temperature depends on the poling field and declines from 0.5 to 0.36 eV when poling field strength has been varied from 5 to 50 V/ $\mu\text{m}$  [21].

Trying to validate the assumptions on the recombination' mechanism, TSD measurement was provided, using different (Al and Cu) upper layer electrodes (underneath one was  $\text{SnO}_2$ , as was used in other experiments). Dependencies of thermo stimulated depolarisation current on the temperature in  $\text{Zn}_{0.7}\text{Cd}_{0.3}\text{S}$  layers with Al and Cu upper electrodes are presented in Fig. 4. The different poling field – 2 and 0.5 V/ $\mu\text{m}$  was applied to specimens with Al and Cu upper electrodes, respectively, to preserve layers from breakage. The well expressed differences between TSD current behaviour was detected when poling field sign was changed using different electrodes. The change in the TSD current sign and zero line crossing was observed when positive (+U on the upper electrode) polarization was used. In the case of negative polarisation, no TSD current direction change was found, but TSD exhibits double inversion. The thermo stimulated current's behaviour possessing pronounced inversion was observed not only in the  $\text{Zn}_x\text{Cd}_{1-x}\text{S}$  layers but in many other composite semiconductors [26].

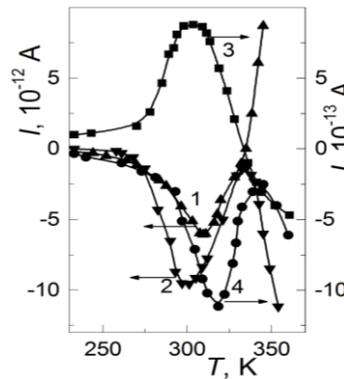


Fig. 4. Dependencies of thermo stimulated depolarisation current on the temperature in  $\text{Zn}_{0.7}\text{Cd}_{0.3}\text{S}$  layers with Al (curves 1, 2) and Cu (3, 4) upper electrodes; positive (+U on the upper electrode) polarization (1, 3) and negative (2, 3) one, was applied, respectively.

The behaviour of TSD and its dependence on the electrode materials and on the polarity of initial charge as well as the recognised facts, stated for the structures, analogous to  $\text{Zn}_{0.7}\text{Cd}_{0.3}\text{S}$ , allows to expect for the possibility of monomolecular recombination type in the films under our examination and prevailing of n-type carriers as also was estimated by investigation on the sign of thermo stimulated current in [27].

Experimentally observed accumulation of space charge in near-electrode regions [21,27] have been encountered in process description. The technics of ion contact mode, applied in our experiments, can be approached as measurements using blocking electrodes [21]. Invoking these assumptions the polarization behaviour in  $\text{Zn}_x\text{Cd}_{1-x}\text{S}$  layers can be described by the model introduced by Gorokhovatsky [22]. The physical basis of this phenomenon can be understood on the assumption, that, when heating the specimen, the structured thermo stimulated depolarisation (the changes of polarisation value and sign) can occur in the intrinsic field of the initial charge, which was created by the master polarization of the layer. The new polarization state is created in this stage. In the present model, the prevailing factors of the depolarisation are the space charge extraction or/and neutralisation of this charge by equilibrium conductivity.

The temperature dependency of surface charge redistribution between the densities of homo-charge  $\sigma_i$  and hetero-charge  $\sigma_n$  can be found solving the following expression [22]:

$$d\sigma_n(T)/dT + (\lambda T / \varepsilon\beta)\sigma_n(T) = (\lambda T / \varepsilon\beta)\sigma_i(T), \quad (1)$$

where  $\sigma_t = (1/2)en_t(T)L$ ,  $\lambda(T) = e\mu n(T)$  – equilibrium conductivity,  $e$  – electron charge,  $L$  – layer thickness,  $\mu$  – mobility,  $\varepsilon$  – dielectric permittivity,  $n_t(T)$  and  $n(T)$  – trapped and free charge carrier concentration, and  $\beta$  – heating rate. It is apparently, that charge carrier concentration  $n$  and  $n_t$  in the TSD processes is related with the trapping and recombination mechanism [27]. Adopting this model, the depolarisation current density  $j(x)$  should be written as:

$$j(x) = d\sigma_n / dt = \lambda[E(x) + E_n(x)], \quad (2)$$

where  $E(x)$  and  $E_n(x) = -\sigma_n(T)/\varepsilon$  are the hetero-charge and the shielding homo-charge electric fields, respectively.

In the case of blocking electrodes (ion contact mode), near-electrode polarisation process and monomolecular recombination type, the general equation for depolarisation current Eq. 2 can be simplified and changing time variables to temperature ones (heating rate was constant) can be written explicitly by the expressions for the displacement current density [22, 28], where:

$$j(T) = e\mu E_0 \tau_t \omega_t n_{t0} \exp\left(-\frac{W_t}{kT} - \int_{T_0}^T \frac{\omega_t}{\beta} \exp\left(-\frac{W_t}{kT'}\right) dT'\right) \quad (3)$$

when the assumption of weak secondary capture ( $\tau_r \ll \tau_t$ ,  $\tau \approx \tau_r$ ) was used, and

$$j(T) = e\mu E_0 \tau_t \omega_t n_{t0} \exp\left(-\frac{W_t}{kT} - \int_{T_0}^T \frac{\omega_t \tau_t}{\beta \tau_r} \exp\left(-\frac{W_t}{kT'}\right) dT'\right) \quad (4)$$

in the case of strong secondary capture ( $\tau_t \ll \tau_r$ ,  $\tau \approx \tau_t$ ). The last approach can be appreciated when the trap levels are sparsely populated, i.e.  $n_t \ll N_t$ . Here  $\omega_t$  is the frequency factor evaluated as  $\omega_t = N_c S_t v_T$ ,  $S_t$  – cross-section of capture centres,  $v_T$  – thermal velocity of free electron,  $E_0$  is the poling electrical field,  $n_{t0}$  – initial concentration of trapped electrons,  $N_c$  and  $N_t$  – effective density of states in the conductivity zone and in the trap levels,  $W_t$  – activation energy,  $k$  – Boltzmann constant,  $T_0$  – initial temperature (therein, temperature  $T = T_0 + \beta t$ ). The  $\tau_t$ , i.e. the time constant of the capture to the centres, described by energy  $W_t$  and  $\tau_r$  – time constant of recombination can be expressed as follows:

$$\tau_t = 1 / (N_t - n_t) S_t v_T, \quad \tau_r = 1 / p_r S_r v_T, \quad (5)$$

where  $S_r$  and  $p_r$  are the cross-section and concentration of vacancies in the recombination centres, respectively.

Two instances – a weak and strong capture cases – have been studied in this work by fitting experimental results in combination with theoretical models described by Eqs. 3 and 4. The starting parameters and baselines for the simulation have been taken from present and earlier [5, 21] experimental research (e.g. activation energy 0.4 eV, at  $E_0 = 23$  V/ $\mu\text{m}$  and 0.5 eV at  $E_0 = 5$  V/ $\mu\text{m}$  [21]) or have been chosen as acceptable typical known values of the related compounds. The depolarisation current was calculated by means of approximation of experimental results using the least-square technics, applying the aforementioned parameters and changing the effective density of states in the conductivity zone  $N_c$  and the recombination time  $\tau_r$  as fitting variables.

When the model of weak secondary capture has been applied, the simulation results did not succeeded to match the experimental ones. The best coincidence of experimental and calculated results was obtained in the case of strong secondary capture model (Fig. 3, curve 2), when  $\tau_r = 1 \cdot 10^{-3}$  s and  $N_c = 2 \cdot 10^{23}$  m<sup>-3</sup> have been taken. The acceptable results were received with the parameters, effective density of states in the conductivity zone  $N_c = 2 \cdot 10^{23} \div 2 \cdot 10^{24}$  m<sup>-3</sup> and the

recombination time  $\tau_r = 10^{-3} \div 10^{-2}$  s. It must be emphasized, that  $N_c$  acts only as the scaling factor, increasing depolarisation current, evaluated as a rate of the surface electrical potential change in our experiment. On the other hand the diminishing of recombination time  $\tau_r$  leads to the sub-linear deflection from linear temperature dependency of thermo depolarisation rate. The effect becomes more pronounced at elevated temperatures. The value of the effective density of states in the conductivity zone  $N_c$  calculated here is in accordance with the one received by [29] as established by means of Hall effect measurements, as well as with the results reported elsewhere [30,31]. This congruence in addition substantiates the validity of the simulation model.

The processes observed and simulated in present investigation can be generalized to similar structures and the main conclusions drawn in this work should, therefore, be applicable to other amorphous disordered heterogeneous semiconductors, including organic ones.

#### 4. Conclusions

The polarisation phenomena and electret charge concentration take place in the near-electrode region of  $Zn_{0.7}Cd_{0.3}S$  layers.

The thermo depolarisation processes in  $Zn_{0.7}Cd_{0.3}S$  composites can be simulated by the model, based on the strong secondary capture and monomolecular recombination. The validity of the proposed model is confirmed by the adequacy of fundamental parameters used in numerical simulation with the known experimental values. The effective density of states in the conductivity zone  $N_c = 2 \cdot 10^{23} \div 2 \cdot 10^{24} \text{ m}^{-3}$  and the recombination time  $\tau_r = 10^{-3} \div 10^{-2}$  s, has been obtained with before mentioned approach.

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