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Aging of ZnS:Mn thin – film electroluminescent devices grown by two different atomic-layer epitaxy processes

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Abstract. Electroluminescent characteristics and the photodepolarization spectra of ZnS:Mn thin-film electroluminescent devices made with two different atomic-layer epitaxy processes based on chlorine and metalorganic precursors have been studied during initial stage of accelerated aging. Essential differences have been revealed. They are explained in assumption that different impurity centers exist in the ZnS:Mn films grown by using chlorine and metalorganic precursors, namely, $MnCl_2$, Cl_i^-, Cl_S^+ and isovalent oxygen traps, respectively. The mechanism of aging in both types of devices is discussed.

Keywords: electroluminescence, thin films, ZnS:Mn, atomic-layer epitaxy, aging.

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1. Introduction

Various techniques are used to fabricate ZnS:Mn thin-film electroluminescent (TFEL) devices [1]. Atomic layer epitaxy (ALE) is one of the film deposition processes that widely used to produce commercial ZnS:Mn flat panel displays. Easy process control, good reproducibility, low-cost equipment together with high quality of the films are the significant advantages of this technique. At first ZnS:Mn ALE films were grown using a process based on halides ($ZnCl_2$,$MnCl_2$) and H_2S [2]. Although excellent results have been achieved, there are still some aging phenomena, which are believed to be related to the influence of chlorine in the ZnS:Mn films [3, 4]. As an alternative, a new ALE process based on metalorganic precursors, namely on diethyl zinc and tris(2,2,6,6-tetramethyl-3,5-heptanedione) manganese (III) ($Mn(thd)_3$), has been developed [5]. The purpose of this paper is to compare various characteristics of ZnS:Mn devices made with these two different ALE processes and their initial aging behavior in particular.

2. Experimental procedures

The devices had the stack configuration typical for TFEL devices with a 550 nm thick ZnS:Mn film sandwiched between two Al_xTi_yO insulating layers. The ZnS:Mn films were deposited by the two ALE processes mentioned above, which will be denoted below as «Cl» (chlorine) and «O» (organic). The Mn concentration was 0.05 and 0.5 wt.%.

Common electro-optical characteristics such as dependences of the luminance (L), transferred charge (Q), and efficiency (η) on voltage (U), the luminance waveforms and the decay of electroluminescence (EL), transmission spectra, emission spectra of EL and photoluminescence (PL) were measured as described in [1, 4]. Additionally, some variants of the photodepolarization (PDP) spectroscopy proposed recently as a promising method for TFEL devices characterization [4, 6, 7] were used.

The PDP spectrum is the spectral dependence of the photocurrent (I_{ph}) arising in a precharged devices in a polarization field under action of a monochromatic prob-

ing light. Therefore, this spectrum is very informative concerning not only the energy depth of electronic levels responsible for I_{ph} but also the spatial distribution of the polarization field in an electroluminescent film. Since the penetration depth (d_p) of the probing light depends on the absorption factor (k), the photocurrent in the region of the fundamental absorption ($k > 10^5$ cm^{-1}) depends only on the field nearby the lit interface. But an impurity photocurrent is generated in the whole bulk or some its part depending on the impurity concentration. If the field distribution is monotonic, the $I_{ph}(\lambda)$ dependence reflects the contribution of different electron transitions into the photoconductivity. However, if there is at least one potential well or a potential hill in the bulk, i.e. a positive space charge (PSC) or a negative space charge (NSC), respectively, an impurity photocurrent can decrease or even be reverse as compared with I_{ph} resulting from the band-to-band transitions due to existence of regions with the opposite directed field. Varying charging and depolarization of a sample and comparing observed changes in the PDP spectrum with the spectra simulated for different spatial potential distributions [7], one can obtain the information about the space charge (SC) and the energy depth of corresponding traps.

The PDP spectra were studied in the range from 1000 to 320 nm as follows. Charging of the devices previously depolarized by light with λ = 330–340 nm was performed by two ways: 1) using a dc voltage lower than the threshold voltage (U_{th}); 2) using a train of voltage pulses (10^3 pulses of 30 ms width and 100 Hz frequency) with a certain polarity of the last pulse and the amplitude higher than U_{th}. The former results predominantly in the capture of transferred free electrons by the anodic interface states and bulk traps, i.e. in building-up of a negative interface charge (NIC) and a NSC. When the charging voltage (U_{ch}) is higher than U_{th} a PSC is also built-up due to the impact ionization of some deep centers or the lattice. After charging, the sample was short-circuited for 5–10 min until the dark current becomes stable. Then the sample was lit by monochromatic light, beginning from long wavelengthes (λ). The intensity of the probing light was chosen to be small enough in order to prevent significant changes of field distribution during the experiment. The photocurrent was monitored with an electrometer (in the range of 10^{-14}–10^{-8} A) connected with a computer. The interference extrema in the $I_{ph}(\lambda)$ dependence were averaged [6]. The PDP spectra were not corrected on equal number of probing photons. To study the asymmetry of devices the charging voltage of –Al and +Al polarity was used, and the sample was lit from each side (through the ITO or semitransparent Al). To estimate the energy depth of traps, the effect of various depolarization of precharged devices on their PDP spectra was studied. After identical charging of the sample and monitoring of the spectrum, the device was held some time in darkness or under light with chosen photon energy. After each depolarization, the spectrum was monitored again. In addition, the spectral dependence of I_{ph} in uncharged (virgin or depolarized) devices were measured in the inherent field resulting from an equilibrium spatial distribution of charges in the film.

All characteristics were measured before and after accelerated aging performed under 5 kHz sine voltage at a fixed transferred charge (Q = 1 μC/cm^2) for 0.5–10 h. The device will be termed «virgin», if no voltage has been applied to it, «unaged» if a voltage has been applied only during measurements of the initial characteristics, and «aged» if accelerated aging has been performed. For some qualitative trends on long-term aging of the devices, see Ref. [5].

3. Results and discussion

Dependences of luminance and transferred charge on applied voltage at 5 kHz for the unaged and aged devices of both types are shown in Fig. 1. The magnitudes of luminance and luminous efficiency are approximately the same in the «O» and «Cl» devices [5]. For both types of the devices, the short-time aging results in a decrease of the threshold voltage and in some softening of the low-voltage portion of the characteristics. However, the $L(U)$ dependence of the unaged «Cl» devices is very sharp, whereas there is a low-voltage portion with a smaller slope in the unaged «O» devices. The slope of the softened portion of the $L(U)$ and $Q(U)$ curves decreases significantly during aging in the «Cl» devices, but it remains practically constant for the «O» devices. Hence in the «Cl» devices some shallower source of free electrons appears during aging, and its energy depth becomes smaller and smaller with aging, whereas in the «O» devices only the number of the shallow electron states increases with aging time.

The EL spectrum of both types of the devices consists of one Mn^{2+} band that does not change during aging. The same band is observed in the PL spectra too (Fig. 2), but the position of its maximum is somewhat different for the «Cl» and «O» devices: 585 and 590 nm, respectively. This results from the different crystal field symmetry around Mn^{2+} ions in the ZnS:Mn films with the hexagonal and cubic crystal structure. There are blue and red

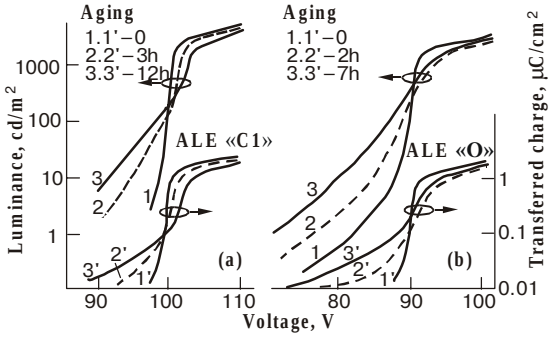

Fig. 1. Voltage dependences of luminance and transferred charge of «Cl» (a) and «O» (b) devices unaged and aged for different time. C_{Mn} = 0.5 wt.%, f = 5 kHz

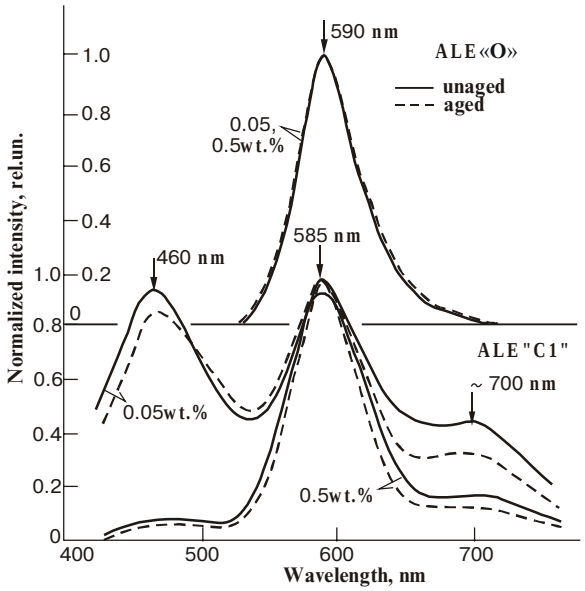

Fig. 2. PL spectra of «O» and «Cl» devices with different Mn concentration before and after aging for 2 hours.

bands in addition to the Mn^{2+} band in the PL spectrum of the «Cl» devices (Fig. 2b). In Ref. 4, these bands were attributed to the A center (complex of V_{Zn} with $\left[Cl_S^-\right]^+$) and a quasi-molecular center ($MnCl_2$), respectively. Some changes are observed in these bands during aging; in particular, the intensity of the red band is reduced significantly. The PL spectrum of the «O» devices is the same as the EL spectrum and is independent of the aging history (Fig. 2a). This further supports the view that both the blue and red bands are related to the presence of chlorine in the ZnS:Mn films.

The PDP spectra of the «Cl» and «O» devices are different. This is illustrated by the spectra measured after identical charging of the devices by a dc (–Al) voltage of about $U_{th}/2$ (Fig. 3). The main maximum is due to band-to-band transitions and lies at 3.78 eV in the spectrum of the «Cl» devices and at 3.68 eV in that of the «O» devices. This difference is due to the different band gap of hexagonal and cubic ZnS. After aging of the «O» devices this maximum is somewhat shifted to the lower photon energy (on 20–30 meV for 10 h). In these devices, unaged and aged, the photocurrent decreases rapidly with the photon energy ($h\nu$). But in the «Cl» devices there is a rather strong impurity photocurrent with nonmonotonic spectral dependence near the main maximum. After aging the I_{ph} decreases, mostly at ~3.6 eV, and a maximum at 3.45 eV becomes well distinguished if the Mn concentration (C_{Mn}) is low. The photocurrent in this region increases with C_{Mn} and becomes invariable during aging. Thus, there are two impurity bands with maxima at ~3.6 eV and 3.45 eV. They are visible distinctly in the $I_{ph}(\lambda)$ dependence of the uncharged devices (Fig. 4). The band at ~3.6 eV has been related earlier to shallow chlorine acceptors (Cl_i) [4]. Absence of this band in the PDP spectra of the «O» devices supports its connection with Cl centers. The band at 3.45 eV has been assigned to the isovalent traps $[Mn_{Zn}^{2+}]^0$. This interpretation is based on the following: 1) the band does not observed in the PDP spectra of ALE undoped ZnS devices (our unpublished data) and its intensity increases with C_{Mn}; 2) the identical band is also observed in the PDP spectra of evaporated ZnS:Mn films and becomes major at $C_{Mn} > 1$ wt. % [6]; 3) the maximum in the excitation spectrum of PL of ZnS:Mn films coincides with this band [8]; 4) there are theoretical and experimental evidences, that the Mn substitutional defects forms in the band gap a local level splitted off from the valence band ([9] and ref. [5] in it). In the PDP of the «O» devices this band is only observed as a knee at 3.5–3.1 eV before aging when C_{Mn} is high. After aging even for 0.5 h the photocurrent in this region drastically falls and a small other maximum at ~3.2 eV appears, which is accompanied by some decrease of the optical transmission in the corresponding spectral range.

At $h\nu < 3$ eV a broad nonelemental band is observed in the PDP spectra of both types of the devices. Its intensity relatively to the main maximum increases after aging especially for the «Cl» devices. The increase is slowed down with the aging time in the both types, but it takes place earlier in the «O» devices (after 7–10 h as compared to ~30 h in the «Cl» devices). In the spectrum of the «Cl» devices two components in this band can be revealed: the main at ~2.1 eV and the second, which appears after aging, at ~1.7 eV. In the spectra of the «O» devices, the position of the main maximum of this band is somewhat

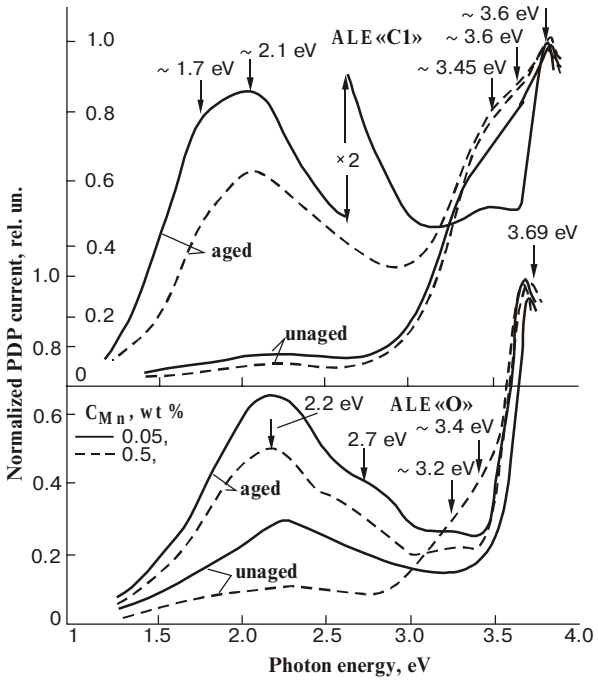

Fig. 3. PDP spectra of «Cl» and «O» devices with different Mn concentration unaged and aged. Charging by dc voltage of 70 V, –Al. Illumination from the ITO side.

different (~2.2 eV). The more complicated structure is observed after aging, namely a knee at ~2.7 eV becomes noticeable. Moreover, after charging by $U_{ch}>U_{th}$, the maximum is shifted to ~2.4 eV. For the «Cl» devices this band has been related earlier [4] to complexes of zinc vacancies (V_{Zn}^{2-}) with native donors (V_s) and Cl_S^- donors (~2.1 and ~1.7 eV, respectively). Such a suggestion was based on comparison of the PDP spectra of these devices with those of evaporated ZnS:Mn devices [6] as well as with the photocapacitance data for ZnS and ZnS:J crystalls [10]. Differences of this band observed in the case of the «O» devices can be attributed to the creation of new complexes of V_{Zn} with some impurity defects and to new impurity centers, which are present only in these ZnS:Mn films.

The spectral dependences of the photocurrent in the uncharged devices lit from the ITO side are shown in Fig. 4a. Similar to other Figures, the positive I_{ph} corresponds to movement of electrons from the bottom interface to the bulk. The photocurrent in the fundamental band in both types of the devices before aging is just positive. Therefore, interface states at the bottom interface are enriched by electrons, which is inherent to the boundary between *n*-type semiconductor (ZnS:Mn) and a material with a higher electron work function ($Al_xTi_yO_z$). The direction of the impurity photocurrent near the main maximum (up to ~3.1 eV) is the same, however, in the low-energy band it is opposite. From this it follows that the absorption factor for the bands at ~3.6 eV and 3.45 eV is rather high, and this photocurrent is generated mainly in a part of the bulk adjacent to the lit interface (Fig. 4b). But less absorbed light ($h\nu$<3 eV) generates the photocurrent in the whole bulk where there is the oppositely directed field between two «enriched» interfaces. After aging of the «Cl» devices the photocurrent in the main maximum decreases, but its direction does not

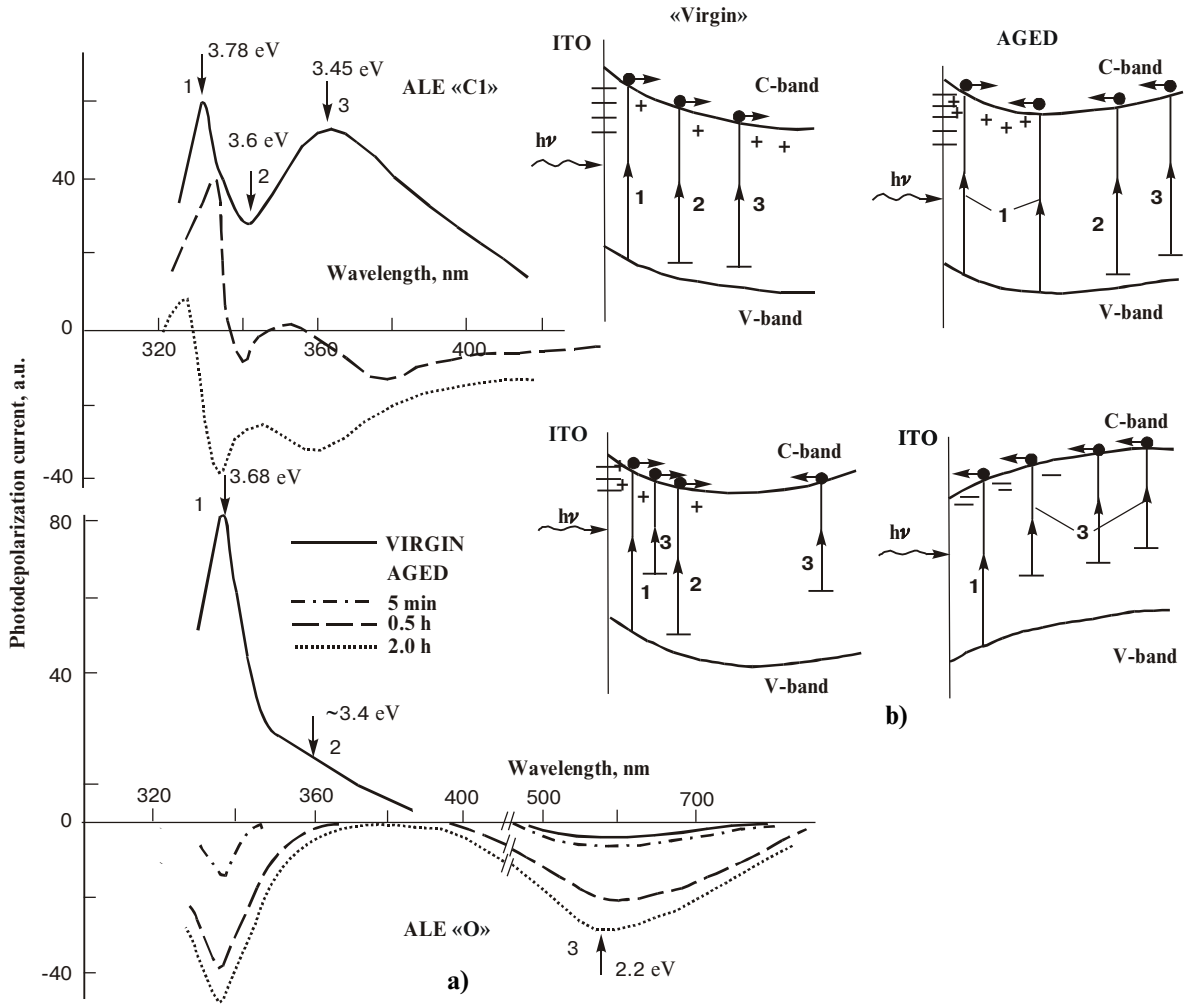

Fig. 4. a) Spectral dependence of photocurrent in the equilibrium state of «Cl» and «O» devices virgin and aged. C_{Mn}=0.5 wt.%. Illumination from the ITO side.

b) Proposed band bending near-by illuminated interface.

change whereas I_{ph} in the near-by bands is reversed. This suggests that the enriched type of the band bending at the interface takes place as before. However, in the bulk a redistribution of the potential occurs which causes a location of the potential well nearer to the interface (Fig. 4b). Since the thickness of the space-charge region is proportional to $(n_D–n_A)$, where n_D and n_A are the concentration of donors and acceptors, respectively, a narrowing of this region suggests an increase of the concentration of non-compensated donors in the bulk. This is in accordance with the increase of the low-voltage conductivity of the ZnS:Mn(Cl) films (Fig. 1a). Aging of the «O» devices even for a short time (~ several minutes) results in the reverse of the photocurrent within the fundamental band. The direction of I_{ph} in the low-energy band remains the same. This suggests that the band bending becomes similar to that of depleted interface states (Fig. 4b). This becomes possible, if a layer with a lower electron function appears at the interface. The qualitatively similar aging behavior is observed for the upper interfaces in both types of the films when they are lit from the Al side.

The positive direction of the photocurrent takes place in the whole spectrum of both types of the devices charged by $U_{ch}<U_{th}$ of (–Al) polarity. The magnitude of I_{ph} increases with U_{ch} in all the bands almost equally. Therefore, after such a charging a NIS_a at the bottom (anodic) interface is built-up predominantly, and the field is unidirectional in the greater part of the bulk. If U_{ch} is of (+Al) polarity, the opposite direction of the PDP current is expected. Indeed, this is observed in the case of the «Cl» devices. However, in the PDP spectra of the «O» devices unaged and aged an essential peculiarity after such a charging takes place (Fig. 5). When U_{ch}(+Al) is rather low the direction of I_{ph} is abnormal, and only its magnitude is different as compared with that after charging by the same U_{ch}(–Al). It is smaller, especially in the low-energy impurity band, if the sample is lit from ITO side (Fig. 5a). But if lighting takes place from the Al side the photocurrent in the main maximum is even somewhat greater (Fig. 5b). The direction of I_{ph} becomes normal when U_{ch}(+Al) is increased up to a certain value (~ 70 V). This peculiarity suggests that after applying of low (+Al) voltage some NIC_c at the cathodic bottom interface and, in addition, a significant NSC in the bulk are built-up, which cause a spatial distribution of the potential similar to that after charging by (–Al) voltage except of a lower field at the bottom interface and a somewhat higher field at the upper one (Fig. 5c). It is possible if, firstly, the interfaces are asymmetrical with regards to the voltage polarity and, secondly, there are many deep electron traps in the bulk. Only after filling these traps, NIS_a at the anodic upper interface is built-up and the direction of the PDP current becomes normal (Fig. 5d).

The energy depth of the bulk electron traps in the «O» devices has been determined from the study of the effect of the depolarization in darkness or under light on the PDP spectra measured after charging by low dc voltage and lighting from the ITO side. The depolarization in darkness results in a decrease of I_{ph} in the whole spectrum

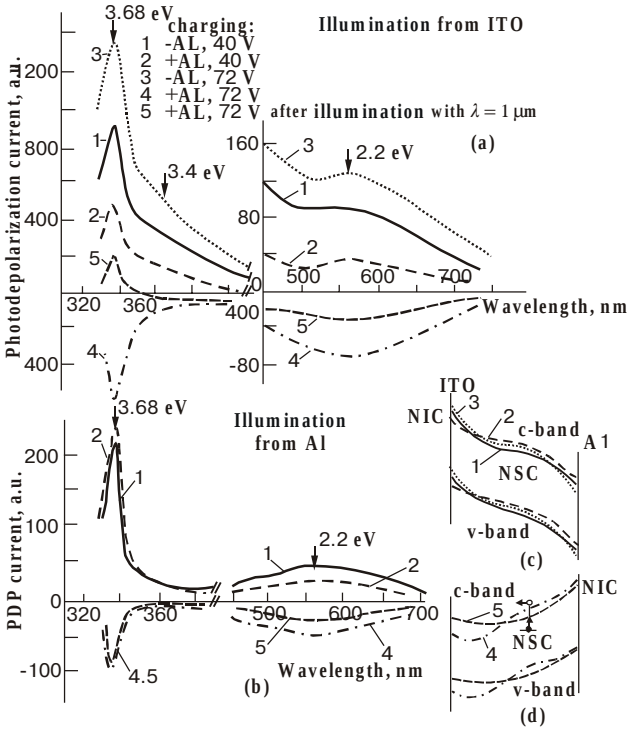

Fig. 5. PDP spectra of «O» device after charging by various dc voltage lower than U_{th} of both polarities. Illumination from the ITO side (a) and Al side (b). C_{Mn} = 0.5 wt.%.
(c, d) Proposed qualitative diagrams of band bending in ZnS:Mn film, corresponding to PDP spectra marked identically.

(somewhat greater in the low-energy band), independent on the polarity of U_{ch} (Table 1). Therefore, the fields at the bottom interface decreases owing to the thermal ionization of filled interface states. In addition, an oppositely directed field near the other interface appear due to recapture of released and transferred electrons. The depolarization by light of certain wavelength (0.8–1.5 μm) for the same time as in darkness results in the reduction of the fundamental band just as after the dark depolarization, but the reduction factor for the low-energy band is significantly greater. Hence, the light acts only on the bulk traps, ionizing them and enhancing thus the field with opposite direction because of created free electrons

Table 1. Reduction factor of photocurrent at various maxima in PDP spectrum of aged «O» devices charged similarly (U_{ch} = = 40 V, –Al) and then depolarized for 10 min differently. Aging time 2 h. C_{Mn}= 0.5 wt. %.

$h\nu_{max}$, eV / Depolarization	3.65	3.2	2.7	2.2
In darkness	1.2	1.3	1.4	1.4
By light, λ =1 μm	1.3	1.3	3.0	3.5

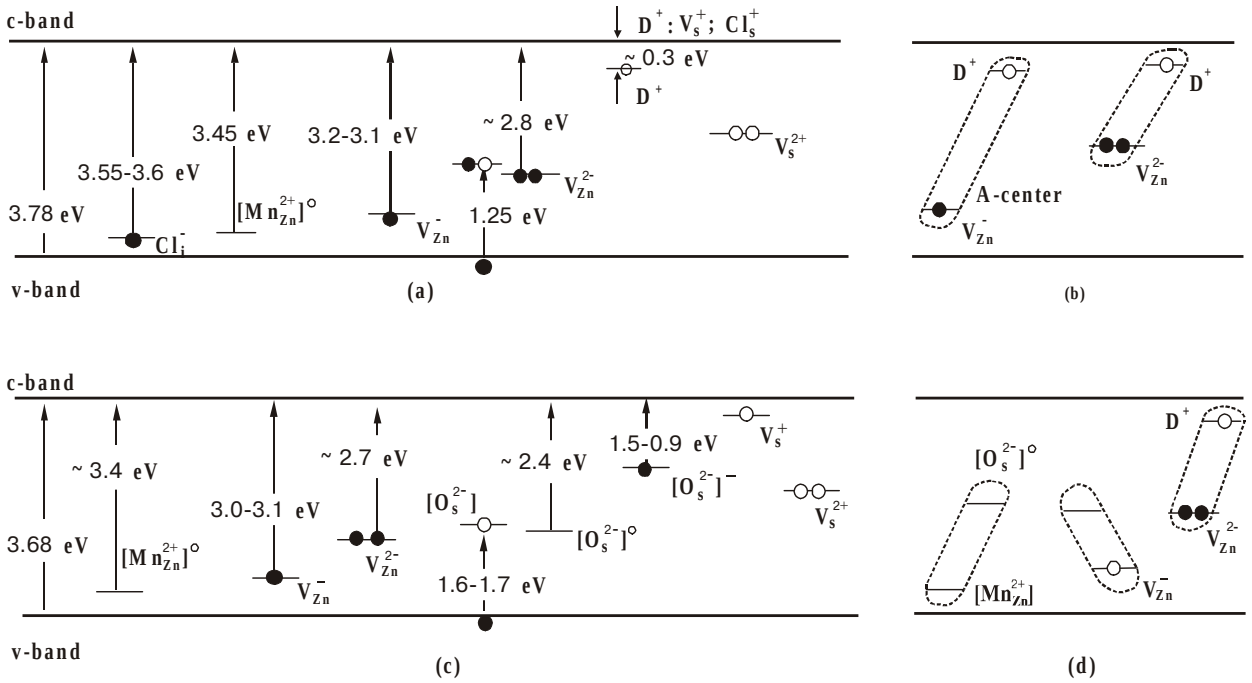

Fig. 6. Suggested energy-level diagram of point (a, c) and complex (b, d) defects in ZnS:Mn film of «Cl» (a,b) and «O» (c,d) devices (for explanation see the text).

are captured at the upper interface. It follows that the energy depth of the bulk electron traps is 0.9–1.5 eV. The most striking effect of this infrared light on the PDP spectrum is observed after charging by the rather high (+Al) voltage (~ 70 V) that causes already the normal direction of I_{ph}. Illumination after such a charging by light with wavelength of 1 mm results in reversing of the photocurrent in the main maximum (see, curves 4,5 in Fig. 5a). This is explained in Fig. 5d. Electrons released by the light from the bulk traps are captured at the bottom interface and create the field with the opposite direction. The effect of both above depolarizations on the weak maximum at ~3.2 eV, which appears in the PDP spectra after aging of the «O» devices, is the same as on the main maximum (Table 1). This suggests that I_{ph} in this maximum is generated near the interface, but not in the bulk.

After charging the «Cl» and «O» devices by a train of voltage pulses with amplitude ≥ 150 V (i.e., $U_{ch}>U_{th}$) a decrease of the low-energy band relative to the fundamental band takes place as compared with the ratio of their intensity after charging by $U_{ch}<U_{th}$, provided that the absolute magnitude of I_{ph} in the main maximum is nearly the same after both charging. In the «O» devices, the decrease is accompanied by a shift of the maximum of this band from 2.2 to 2.4 eV and appearance of a knee at the former maximum. Such a modification of the PDP spectra can be explained by building-up of a PSC in addition to NIS and NSC. The PSC arises due to direct impact ionization of some centers and/or as a result of capture of free holes, creating by impact ionization of the lattice, by some traps. Thus, a potential well and two regions with the opposite field direction appears in the bulk. As a consequence, the photocurrent, which is generated in the whole bulk, is reduced. If there are several different centers, PSC should be created mainly at the most deep hole traps or traps with the larger capture cross-section. Therefore, the photocurrent in the corresponding spectral range would be reduced. This enables to explain the observed change of the low-energy nonelemental band in the PDP spectrum of the «O» devices.

The energy depth of hole traps responsible for PSC has been estimated from the study of the depolarization by light of various λ of the devices charged by $U_{th}>U_{ch}$. A considerable depolarization of the «Cl» devices, consisting in almost the tenfold reduction of I_{ph} in the whole spectrum, is observed when λ = 1 μm, whereas such a light does not affect if the devices were charged by $U_{ch}<U_{th}$. For the "O" devices the light with λ = 700–800 nm is the most affecting. Therefore, the energy levels of hole traps are located at ~1.2 eV and 1.6–1.7 eV above the valence band in the «Cl» and «O» devices, respectively. The action of this light is explained as follows. Photons with corresponding energy transfer holes captured during charging by high voltage into the valence band. Free holes drift and are recaptured until they reach the interface where recombine with captured electrons. Thus, a decrease of both the PSC and NIC occurs.

An energy-level diagram of point and complex defects in the ALE ZnS:Mn films is suggested (Fig. 6), taking into account the obtained results, published data (see, e.g. [11] and references [6, 7] in [6]), and the analysis of the most possible impurities specific to the used ALE proc-

esses. In addition to native defects, two point Cl defects (shallow acceptors Cl_i^- and donors Cl_S^-), quasimolecular centers ($MnCl_2$, $ZnCl_2$), and donor-acceptor pairs ($Cl_S^- - V_{Zn}^-$, $Cl_S^- - V_{Zn}^{2-}$) are considered. Choice of oxygen among impurities, which can be incorporated into the films from thd-precursors (O, H, C), is based on the notion that only oxygen can form electrically and optically active centers. We have no experimental evidence of existence of oxygen residues in the «O» ZnS:Mn films. However, the rather high its concentration (0.2–0.9 at. %) has been revealed in ALE SrS:Ce films grown from thd-precursors [12]. Oxygen incorporates in sulfur compounds of two-valence elements (ZnS, CdS, SrS, etc.) as the isovalent traps $[O_S^{2-}]^0$ which can be in three states: neutral, ionized (by light, the impact or the capture of a free hole) and negatively charged after the capture of an electron. The great electron affinity of O^{2-} ion causes a rather large cross-section for the capture of an electron by these traps. In addition, O^{2-} ions can form complexes with other defects (V_{Zn} and Mn^{2+}).

The following mechanisms of aging in both type of the ALE ZnS:Mn devices are suggested. In the virgin «Cl» devices the chlorine resides in a substitutional sites (Cl_S^-, the shallow donors and their complexes with V_{Zn}^-, i.e. A-center), the quasi-molecular centers ($ZnCl_2$, $MnCl_2$), and interstitials (Cl_i^-, shallow acceptors). It is possible, that initially Cl_i^- ions are a consistent of $MnCl_2$ or $ZnCl_2$ centers. During aging the quasimolecules are dissociated, Cl_i^- ions drift and are incorporated into vacant sulfur sites (V_S), converting into shallow donors Cl_S^+. These result in: 1) weakening of the red band in the PL spectrum (Fig. 2) and the PDP current at ~ 3.6 eV (Fig. 3); 2) rising of the Fermi level in the bulk and at the interfaces, which causes a decrease of U_{th} and the slope of the low-voltage portion of $L(U)$ and $Q(U)$ dependences (Fig. 1); 3) the recharge of zinc vacancies from V_{Zn}^- to deeper V_{Zn}^{2-}; 4) the formation of the complexes of V_{Zn}^{2-} with Cl_S^+ and V_S^+, that leads to the intensification of the low-energy band in the PDP spectra (Fig. 3).

In the virgin «O» devices, if there is oxygen, it can reside not only in the lattice sides as the isovalent traps $[O_S^{2-}]^0$, but also as one of ions within some neutral inactive fragments of $Mn(thd)_3$ non-dissociated during growth of the film. A small part of oxygen is also believed to reside at the interfaces in the form of a very thin interlayer significantly enriched by O, which serves as a shallow source of free electrons. Before aging only two indications of the presence of oxygen centers are observed in the PDP spectra: 1) the shift to higher energy (2.2–2.4 eV) and intensification of the low-energy maximum; 2) a significant weakening of the band of the Mn traps (Fig. 3). The former can be explained by the photoionization of the oxygen traps with the energy depth ~2.4 eV below the conduction band. This correlates with the observation of a luminescent band at 550–560 nm in ZnS:O [see, e.g. ref. [6] in [6]). To explain the second indication we could suggest only one hypothesis that O^{2-} ions are located in the bulk mainly near by Mn^{2+} ions (maybe, in accordance with the «volume compensation principle»[11]), creating a new complex defect ($[Mn_{Zn}^{2+}]^0 - [O_S^{2-}]^0$) with the another energy depth than that of the single Mn trap. Replacement of one of four S^{2-} ions nearby to Mn^{2+} ion by O^{2-} ion has no effect on the intraionic transitions in the 3d-shell of the Mn^{2+} ion since the symmetry of the crystalline field does not change markedly. However, it can result in significant change of the energy of the distorbed local state of the lattice.

It was suggested that during aging the fragments are dissociated, and O^{2-} ions migrate through sulfur vacancies, forming complexes with other defects, enlarging the $ZnS_{i-x}O_x$ interlayer and enriching it up to $x \approx 1$. Such a somewhat intuitive suggestion permits to explain the following changes in the PDP spectra after aging: 1) the small shift of the main maximum (Fig. 3) because of the band gap of $ZnS_{i-x}O_x$ becomes smaller when x increases; 2) the appearance of the small maximum at ~3.2 eV of the photocurrent generated near by the interfaces, which is accompanied by an increase of the optical absorption in this spectral region correlative with the band gap of ZnO; 3) the qualitative change of the electronic states at the interfaces (Fig. 4); 4) the further decrease of the Mn trap band in the PDP spectrum and the increase of the low-energy band simultaneously with the change of its structure (Fig. 3). The enhancement of the «softened» portion of $L(U)$ and $Q(U)$ curves without a noticeable change of its slope during aging (Fig. 1) can be also explained by an increase of the thickness of the $ZnS_{1-x}O_x$ interlayer. At last, the peculiarities related to the presence of a significant NSC, affecting the spatial field distribution at low voltage, can be attributed to the oxygen traps which have a large cross-section for the capture of an electron. It should be noted that NSC at deep electron traps have been also revealed in ALE (thd) SrS:Ce films actually containing much oxygen [13].

Explanation of the change during aging of the high-voltage portion of $L(U)$ and $Q(U)$ dependences in both types of the devices will be discussed elsewhere.

Conclusions

Significant differences have been revealed in some initial characteristics and the all characterization of the aging behavior of the ZnS:Mn ALE «Cl» and «O» devices. The main causes of the differences are due to different impurities in the ZnS:Mn films, namely, chlorine centers in the former and, more probably, oxygen centers in the latter. The different crystal structure of the films affects only some characteristics inessential to aging. In both types of the as-grown films, there are some non-dissociated complexes (fragments) from used precursors, and atomic rearrangement proceeds during aging, which results from their dissociation and the drift (migration) of both the impurity ions and the native defects. This rearrangement is different in the «Cl» and «O» devices and causes the following main different consequences:

1) Conversion of the shallow Cl_i^- acceptors to the shallow Cl_S^+ donors during aging results in a rising of the Fermi-level in the bulk. As a consequence the energy depth of filled interface states, which are the source of free elec-

trons, decreases. In the «O» devices, migration of impurity ions creates a thin rather conductive interlayer at the interfaces, from which electrons are injected to the ZnS:Mn film. During aging the interlayer thickness increases, but the potential barrier for electron tunneling does not change.

2) The ionized Cl_s^+ donors can serve as shallow electron traps (~0.3 eV), but NSC on these traps exists only for a short-time at low fields. On the contrary, in the «O» devices a great NSC at deep electron traps (0.9-1.2 eV) is created. Therefore, the impurity centers in these devices, being initially neutral, have a large cross-section for capture of an electron.

Two main recommendations can be drawn from the obtained results concerning the improvement of stability of the devices on the initial stage of aging: 1) to decrease the number of sulfur vacancies, through which the drift of the impurity ions occurs; 2) to decrease the amount of trace elements from the precursors (Cl and O) in the films.

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