Semiconductor Physics, Quantum Electronics & Optoelectronics. 2002. V. 5, N 1. P. 58-62.

PACS: 71.55.Gs, 78.60.Fi, 78.66.Hf

On origin of rapid portion of luminance-voltage dependence of ZnS:Mn TFEL devices and its aging behavior

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Abstract. Some peculiarities in the rapid portion of the voltage dependences of luminance and transferred charge as well as in its aging behavior in ZnS:Mn thin film electroluminescent devices made by different deposition techniques have been revealed. The devices with nearly the same Mn concentration (~1 at. %) were deposited by electron-beam evaporation and two atomic-layer epitaxy processes based on chlorine ($ZnCl_2$, $MnCl_2$) or organic (diethyl Zn and $Mn(thd)_3$) precursors. It has been studied interrelation between these peculiarities and the differences observed in the photodepolarization spectra of the devices, which give data about defects in the ZnS:Mn films and the energy of corresponding local states in them. The obtained results are discussed as to physical processes responsible for the rapid portion of the above voltage dependences and for the causes of its change after short-time accelerated aging.

Keywords: electroluminescence, thin-films, ZnS:Mn, aging.

Paper received 26.11.01; revised manuscript received 22.01.02; accepted for publication 05.03.02.

1. Introduction

An important feature of ZnS:Mn AC thin-film electroluminescent (TFEL) devices is the very rapid luminance-voltage (L-V) dependence. A section with a small slope often preceds to the rapid dependence. The share of the former and the slope of the latter are affected by deposition techniques, the Mn concentration, and driving conditions. In addition, they change after aging, which results also in the essential change of the threshold voltage (V_{th}) of the rapid portion of the dependence [1–3]. The character of the L-V dependence corresponds to that of the voltage dependence of the transferred charge (Q). The high steepness of these dependences is due to the positive feedback between three main physical processes: the tunnel generation of free electrons, the multiplication of them, and the generation of a positive space charge (PSC) enhancing the field in the cathodic part of the EL film. Two latter processes result from the impact ionization of the lattice or some centers. It is supposed in most published papers that the lattice ionization and subsequent deep trapping of holes are responsible for the multiplication of electrons and building-up of PSC (see, e.g. [4] and ref. [3,9-12] in it). However, in some papers the important role of the direct impact ionization of some deep centers is pointed out. So, in [5] it is concluded that the impact ionization of zinc vacancies (V_{Zn}), which is a part of donor-acceptor (D – A) complexes, causes the generation of PSC in ZnS:Mn, Cl devices made by the atomic layer epitaxy (ALE) technique. In [1] the ionization of Mn isovalent traps ($\left[Mn_{Zn}^{2+}\right]^0$) was supposed to be the predominant process when the Mn concentration is rather high. The presence of such centers has been confirmed by the study of the photodepolarization (PDP) spectra [2,3]. There is no special consideration in published papers of the physical causes of the effect neither deposition technique nor aging on the rapid portion of the L - V dependence. In this paper, this problem is considered for ZnS:Mn AC TFEL devices made by the electron-beam evaporation (EBE) and two ALE processes using the use of chlorine or organic precursors [3]. Different impurities and intrinsic defects, whose local energy levels have been revealed in the PDP spectra of these devices, are taken into account under the consideration. The impact ionization coefficient

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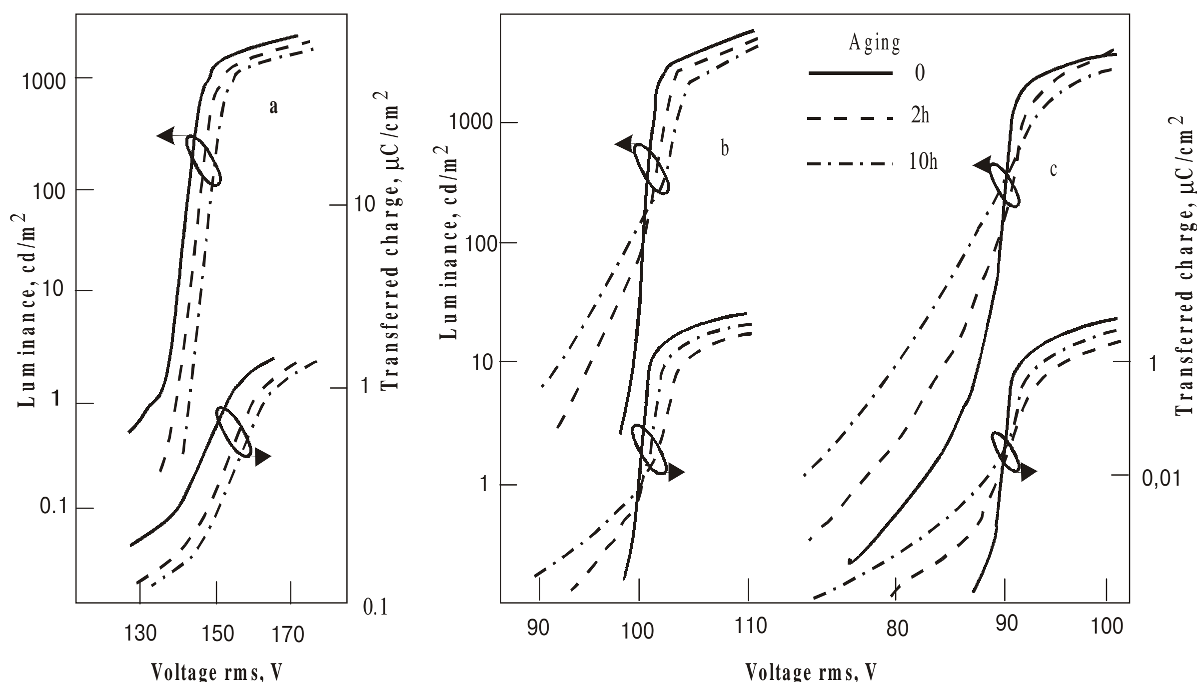

Fig. 1. Voltage dependences of luminance and transferred charge of ZnS:Mn TFEL devices made by EBE (a), ALE "chlorine" (b) and ALE "organic" (c) deposition techniques before and after short-time (2h) aging f=5 kHz.

of these deep centers is estimated relatively to that of the lattice. The part of the revealed defects in the impact formation of PSC as well as their role in an atomic rearrangement during aging are discussed as concerning the observed features of the rapid portion of the L-V dependence and its aging behavior in the above devices.

2. Experimental procedures

The devices under the study had the configuration typical for AC TFEL devices with a ZnS:Mn film sandwiched between two insulator (I) layers. The devices were made by EBE and ALE deposition techniques. In the case of the former, the ZnS:Mn film (~ 650 nm) and I layers (SiO_2 / Al_2O_3, ~ 270 nm) were deposited at 150^0C. Coevaporation of ZnS and Mn were used for doping. Annealing was performed in vacuum at ~ 350 ^{0}C for 1h. The ALE devices had $Al_xTi_yO_z$ insulator layers with the thickness of ~ 300 nm and the ~ 550 nm thick ZnS:Mn film grown by two different processes based on chlorine precursors ($ZnCl_2$, $MnCl_2$) and organic precursors (diethyl zinc and $Mn(thd)_3$) [3]. Below the former and the latter will be denoted ALE "Cl" and ALE "O", respectively. The Mn concentration was about 1 at. % in all above devices.

The voltage dependence of the luminance and transferred charge of the devices as prepared and aged has been measured by common methods [6]. Short-time (up to 10 h) accelerated aging has been performed at 5 kHz sine wave voltage.

The PDP spectrum of the devices has been measured in the region from 1500 to 320 nm as it was described in detail in [3, 7]. This spectrum represents the spectral dependence of the photocurrent (I_{ph}) arising in a precharged devices in the residual polarization field under action of the monochromatic probing light. The devices were charged by low dc voltage ($\cong V_{th}/2$) of the "-Al" polarity. Illumination of them by probing light was from the ITO side. The PDP spectra were normalized on the maximum photocurrent, but were not corrected on the equal number of probing photons. Interference extrema in the spectra were averaged.

3. Results and discussion

The voltage dependences of the luminance and transferred charge of the devices before and after aging are shown in Fig.1. The differences in the initial "soften" section of the characteristics in the EBE, ALE "Cl", and ALE "O" devices as well as its changes after aging of these devices and physical causes of different aging behavior have been considered in detail in [2, 3]. As to the rapid section of the L – V and Q - V dependencies the following peculiarities should be noted.

In the EBE devices, this section begins before aging at rather low luminance. After aging, it shifts to somewhat higher voltages and lower L. This is accompanied by an increase of its slope. Such a behavior suggests that the energy depth of the filled electronic states, which take part in the tunnel generation of free electrons, increase after aging. This results from a decrease of the number of native defects in the ZnS:Mn films, which follows from changes observed in the PDP spectrum of these devices after aging (Fig. 2a). So, it is seen the significant decrease of I_{ph} in the region from ~3.4 eV to 2.2 eV. The photocurrent in this region is due, as it has been shown earlier [2, 3, 8], to the

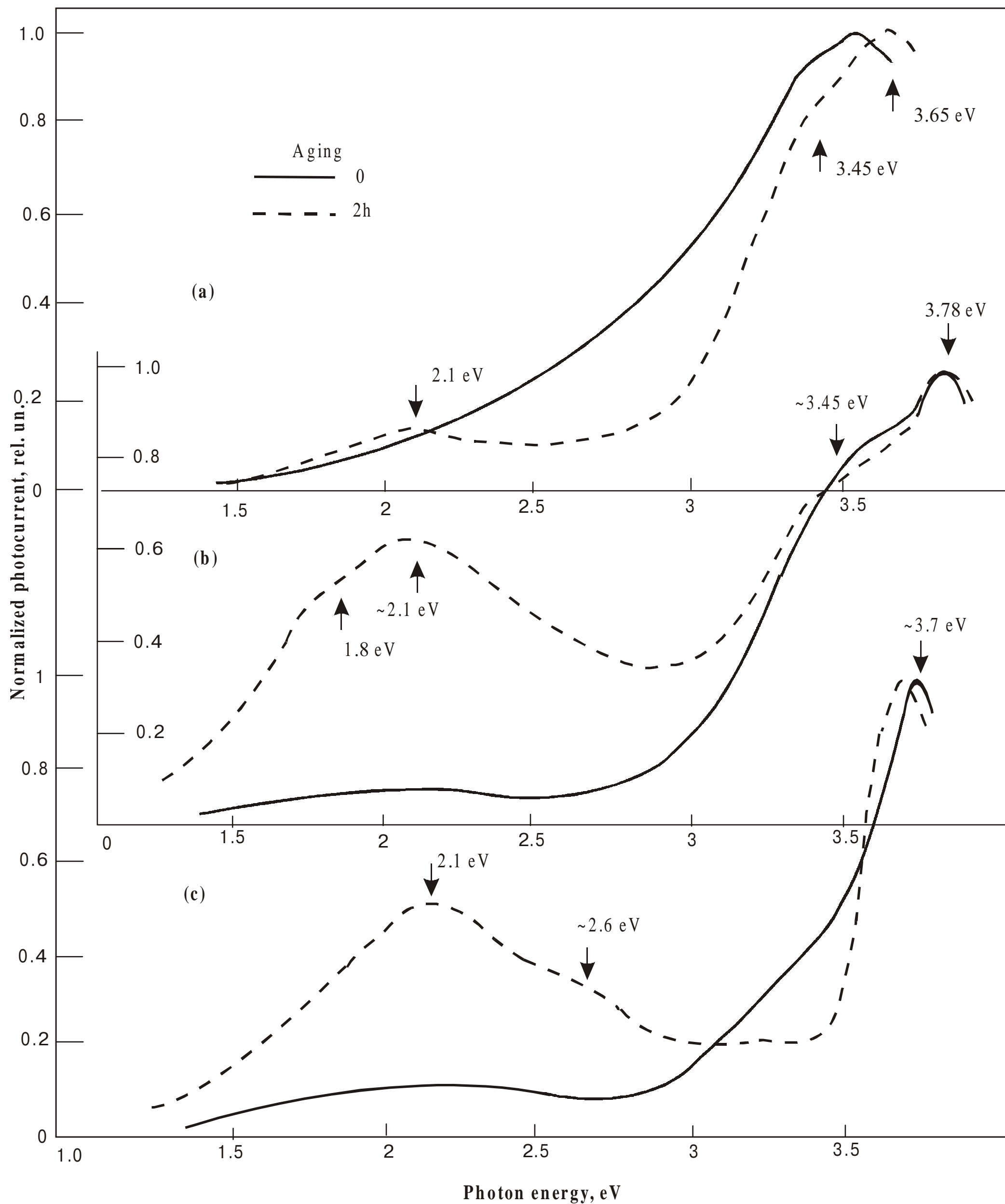

Fig. 2. PDP spectra of ZnS:Mn TFEL devices made by EBE (a), ALE "chlorine" (b), and ALE "organic" (c) deposition techniques unaged and after aging for 2 h.

Table. Ratio of impact ionization coefficients of different centers and lattice at various F_0 and F_s .

		F_0, MV/cm	4			5			6		
		F_s, MV/cm	1.3	1.6	2.0	1.3	1.6	2.0	1.3	1.6	2.0
Centers	e_c, eV	C, at.%									
$[Mn^{2+}_{Zn}]^0$	3.4	1	0.6	0.18	0.07	4.6	0.65	0.18	55	3.5	0.50
V^{2-}_{Zn}	2.7	10^{-2}	0.025			0.4	0.03		10	0.26	0.02
$(V^{2-}_{Zn}-V^{+}_{S})$	2.1	10^{-2}	0.10			2.8	0.10		136	1.6	0.08
$(V^{2-}_{Zn}-Cl^{+}_{S})$	1.8	10^{-2}	0.18			6.5	0.22		510	4.0	0.12
O-center	2.6	0.5	1.6	0.03		26	1.8	0.03	790	17	1.1

photoionization of single and double charged zinc vacancies (V_{Zn}^{-} , V_{Zn}^{2-}), the ionization energy of which is equal to 0.55 –0.6 eV and ~ 2.7 eV, respectively. The decrease of the concentration of V_{Zn}^{-} and V_{Zn}^{2-} acceptors after aging causes lowering of the concentration of native donors, too (according to the principle of charge compensation). As a consequence, the Fermi level drops in the bulk and at the interfaces, i.e. the energy depth of the source of free electrons, which tunnel from filled interface states, increases after aging. In the PDP spectrum of the aged EBE devices, there are, besides of the main peak of the intrinsic photocurrent at ~ 3.65 eV, only a weak peak at ~ 2.1 eV and the very intensive peak at 3.4 - 3.45 eV. The former has been attributed to complexes of native defects (V_{Zn}^{2-} - V_S^{+}) [2]. The latter, which increases with the Mn concentration, is related to the isovalent traps $\left[Mn_{Zn}^{2+}\right]^0$ [2,3]. Therefore only these centers can contribute markedly to the impact processes mentioned above in the EBE aged devices.

In the ALE "Cl" devices, the rapid portion of the L – V dependences begins before aging right at low luminance. During the short-time aging its beginning shifts to higher L and V (Fig.1b). In addition, the slope of this section decreases somewhat. These changes are accompanied by the significant increase of the " soften " section of the characteristics at V< V_{th}, which is explained by appearance of a shallow electron source in the EL film [3]. The increase of the charge transferred at low voltages is just the main cause of the above changes in the rapid portion. The transferred charge trapped at the anodic interface results in arising of a polarization field opposite to the external one. Therefore, the field F_s in the S layers is reduced at given voltage and, as a consequence, the V_{th} increases. The formation of the polarization field leads also to a slower increase of F_s with V which can be a cause of the decrease of the slope of the rapid portion after aging. The decrease of the slope may result also from appearance of new centers with the lower ionization energy, which take part in the formation of PSC in addition to $\left[Mn_{Zn}^{2+}\right]^0$ traps. Indeed, it is seen in the PDP spectra of the ALE "Cl" device (Fig. 2b) that the very intensive band with the maximum at 1.8 - 2.1 eV appears after aging. It has been related to donor-acceptor (D–A) complexes, namely Cl_s and native donors associated with V_{Zn}^{2-} [3].

In the ALE "O" devices, the rapid portion of the L – V and of the Q – V dependences is preceded by the marked "soften" section not only after aging, but also before it (Fig.1c). The beginning of the rapid portion shifts after aging to lower voltages and remains at about the same luminance level (~ 8 – 10 cd/m^2), on the contrary to its aging behavior in the EBE and the ALE "Cl" devices. The slope of this portion decreases significantly during initial stage of aging (5 – 7 h). Taking into account the consideration given above for the ALE "Cl" devices, one can suggest that centers shallower significantly than $[Mn^{2+}]^0$ traps arise in the ALE "O" devices during aging and these centers are just responsible mainly for the impact formation of PSC. This suggestion is confirmed by peculiarities in the PDP spectra of these devices as compared with those of the EBE and the ALE "Cl" devices (Fig. 2c). It is as follows: (1) the weaker photocurrent related to the Mn traps before aging; (2) its significant decrease after aging, which is accompanied by the appearance of new rather intensive peaks at ~ 2.6 eV and ~ 2.1 eV. It has been suggested in [3] that these peculiarities in the PDP spectra of the ALE "O" devices result from the presence in the ZnS:Mn film some oxygen centers which are originated from non-dissociated fragments of used organic precursor molecules. Dissociation of the fragments during aging leads to the increase of the concentration of oxygen centers. It is known that oxygen incorporates into the lattice of II-VI compounds as isovalent traps $[O_s^{2-}]^0$ [9]. In addition, O^{2-} ions can form complexes with other defects, e.g. V_{Zn}^{2-} and Mn^{2+} ions. The formation of (O^{2-} - Mn^{2+}) complexes can result in the lowering of the concentration of $\left[Mn_{Zn}^{2+}\right]^0$ traps and, consequently, of the decrease of their peak in the PDP spectrum. At the same time, new centers with the lower ionization energy, such as $[O_s^{2-}]^0$, (O^{2-} - V_{Zn}), (O^{2-} - Mn^{2+}), might arise and take part in impact building-up of PSC. This may be just responsible for the new peaks in the PDP spectrum and the decrease of both the slope and the threshold voltage of the rapid portion of the L – V dependence. There is no experimental evidence of existence of oxygen residues in the ALE "O" ZnS: Mn film. However the above suggestion is confirmed by the following. Firstly, the rather high oxygen concentration (0.2 – 0.9 at. %) has been revealed in ALE SrS: Ce films grown from thd-precursors [10]. Secondly, the special dopping of ALE "Cl" ZnS: Mn films with oxygen results in changes in the PDP spectrum analogous to the above mentioned peculiarities in the PDP spectrum of the ALE "O" devices [11].

An estimation of the ratio of the impact ionization coefficient of the lattice (α_l) and the different deep centers above mentioned (α_c) has been carried out as follows. The most often used expression for α_l in the case of high fields (> 1 MV /cm), at which TFEL devices operate usually, is [12]:

$$\alpha_l = \frac{e\ F_s}{\varepsilon_l} \exp\left(-\frac{F_0^2}{F_s^2}\right) \quad (1)$$

where F_s and F_0 are the field in the film and a characteristic field, respectively; $F_0^2 = A\varepsilon_l$; A is a constant for the given semiconductor, ε_l is the ionization energy of the lattice.

The analogous expression can be used for α_c :

$$\alpha_c = \frac{eF_s}{\varepsilon_c} C \exp\left(-\frac{A\varepsilon_c}{F_s^2}\right) \quad (2)$$

where C is the atomic concentration of the centers and ε_c is their ionization energy.

After division (2) by (1) we obtain:

$$\alpha_c / \alpha_l = \frac{C\,\varepsilon_l}{\varepsilon_c} \exp\left[\frac{F_0^2}{F_s^2}\,(1 - \varepsilon_c / \varepsilon_l)\right] \qquad (3)$$

In semiconductors with parabolic bands $\varepsilon_l \approx 1.5\,\varepsilon_g$ (ε_g is the band gap), that is it is equal to ~ 5.5 eV for ZnS. As to the magnitude of ε_c, it is nearly equal to the energy depth of the center level relatively to the conduction band. This is due to the participation in the impact process of an ion heavy as compared with free carriers, which provides conservation of momentum of particles before and after impact of a hot electron with the center. The possible difference in the magnitude of the impact cross-section for different centers was not taken into account although in the case of the Mn traps and complex centers the cross-section may be larger than for the lattice ions. The results of such estimation carried out with variation of F_s and F_0 is given in Table. As seen, the impact ionization of the Mn traps can be the dominant process if $C_{Mn} \geq 1$ at. %, $F_s \leq 1.6$ MV/cm and $F_0 = (5-6)$ MV/cm. In the ALE "Cl" devices an additional contribution of the impact ionization of V_{Zn}^{2-} in D–A complexes is possible too. In the case of the presence of oxygen centers with $e_c \leq 2.6$ eV and $C_c \geq 0.5$ at.%, their impact ionization should be expected to play the major role.

3. Conclusions

The very rapid dependence of L and Q on applied voltage is due to the positive feedback between three major processes of the high-field electroluminescence: the tunnel generation of free electrons, the impact multiplication of them, and the formation of PSC, which result from impact ionization of the lattice and / or some deep centers directly. The threshold and the slope of the rapid section are affected, on the one hand, by the presence of centers, whose impact ionization coefficient is competitive with that of the lattice. On the other hand, the existence of a shallow electron source effects on them, because of transferring of electrons before the threshold of the impact processes causes a reduction of the field in the EL film owing to field clamping. Aging behavior of the rapid section is different depending upon the nature and energy depth of the defects. In the case of only intrinsic defects and the Mn isovalent traps (e.g., as in EBE ZnS:Mn devices), the number of nature acceptors and donors decreases after aging because of their annihilation and gettering to the interfaces or grain boundaries during drift in the high field [2]. This results in an increase of V_{th} and the slope of the rapid section. The impact ionization of the Mn traps may be predominantly responsible for the generation of the holes, when the Mn concentration is higher than 1 at.%. If there are some impurity defects, as in the ALE devices, their drift causes the formation of the complexes with other impurity or native defects. Their ionization energy is essentially lower than that of the lattice and the Mn traps. Therefore, the slope and V_{th} of the rapid section decreases after aging in such devices.

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