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Photostimulation of thin-film electroluminescent zinc sulphide structures

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Photostimulated luminescence from thin-film ZnS:Mn structures was studied. Thin-film electroluminescent structures based on ZnS:Mn as a phosphor and aluminium oxide as an insulator were produced using ALD method. Due to high structure quality it was possible to investigate an effect of light stimulated electroluminescence form such structures using 405 nm m blue laser diode as a light source. Two kinds of light-stimulated luminescence were found: short-term luminance growth, explained by additional charge carriers excited by laser beam; long-term luminance growth, which is to be explained in further works.

Keywords: zinc sulphide, ALD, luminescence, photostimulation, TFEL.

Introduction

Thin-film electroluminescent structures (Eng. — TFEL — thin film electroluminescence) based on semiconductors $A^{II}B^{VI}$ are used as electroluminescent displays. Currently, TFEL displays are less common than LCD and OLED devices, but they remain competitive due to high reliability and a wide range of operating temperatures. A detailed description of TFEL displays can be found in the monograph [1] and in a later review [2]. There is a considerable set of studies (and relevant publications) devoted to the study of similar processes in single crystals. The papers [3,4] can be provided as examples.

An optimized version of the structure of such devices has been developed to date (Fig. 1): the main light-emitting layer is a thin film of a wide-band semiconductor doped with luminescent centers. In our case, as well as in the studies of many other authors, it is a layer of zinc sulfide doped with manganese ions. This active layer is covered on both sides with layers of insulator, on top of which electrodes are applied. In order to provide light output, one electrode is made transparent (most often — ITO), the second, background electrode is usually metallic.

The yellow-orange glow of the display is provided by the luminescence of Mn^{2+} ions [5]. The band in the spectrum corresponds to the intraionic transition $^4T_1 \rightarrow {}^6A_1$ in the $3d^5$ manganese ion shell [6,7]. The excitation of electroluminescence of such structures is carried out by the application of an external alternating voltage. According to existing concepts, the main mechanism of excitation is as follows: luminescent centers are excited by collisions with hot electrons. The wide-band semiconductor layer initially does not have free electrons required for such

a process. Electrons are released in this structure from the interface levels at the semiconductor/insulator interface by an external alternating electric field applied to the active layer through the insulating layers [1,2]. Thus, the external field plays a dual role as it ensures both the appearance of free carriers and their acceleration to achieve the necessary energy. The electrons, with sufficient energy, excite the luminescence of ions Mn^{2+} by collision drifting under the action of the field through the ZnS layer, then they drift to the opposite semiconductor/insulator boundary and accumulate on it. During the next half-cycle of external alternating voltage, the process is repeated in the opposite direction [1]. Thus, the structure emits light in both half-cycles of the applied alternating voltage. Such an architecture of the device with insulator layers and alternating current excitation prevents current instabilities and subsequent electrical breakdown of the structure.
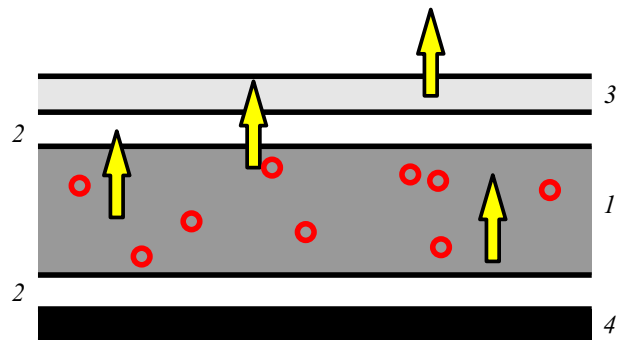

Figure 1. Structure of thin-film electroluminescent indicator (not on scale): *1* — active layer (typically — ZnS:Mn), *2* — insulator layers (typically — Al₂O₃), *3* — transparent electrode (ITO), *4* — metalelectrode.

1. Measuring equipment and examined samples

The luminescence signal was recorded by a photomultiplier and isolated by a selective voltmeter at twice the frequency of the applied voltage (250 Hz).

In this paper, the functioning of TFEL structures produced by atomic layer deposition (ALD) [8–10] was investigated. The application of the atomic layering method made it possible to obtain more detailed and reproducible data by obtaining reliably controlled structures.

The samples were square films with dimensions 60×60 mm, grown on glass substrates. The lower (opaque) electrode with a thickness of 150 nm was sprayed from a molybdenum target on the IZOVAC Astra-S installation. The upper electrode of ITO $(10\,\Omega/\text{sq}\ 200\,\text{nm}$ thick) was sprayed through a mask with square „windows" and 18×18 mm with separate current leads, so that four independent samples were created on the substrate. The insulator layers and the active layer were applied by atomic layering on the PICOSUM P300B ADV installation.

The aluminum oxide was deposited by alternating admissions of reagents (TMA (trimethylaluminium) + H_2O). The admission time was 0.1 s, the purge time was 3 s for TMA and 5 s for water. The specially-purified nitrogen was used a gas carrier. The temperature in the chamber was $300°C$, pressure — 10^5 GPa. The thickness of each insulator layer was 300 nm. This layer thickness was a compromise between the requirements of the absence of breakdown of these layers and the fact that the largest possible proportion of external alternating voltage was applied to the active layer.

The active layer (ZnS : Mn) with a thickness of 300 nm was applied by successive cycles of substrate treatment with DEZ (diethyl zinc) vapors (discharge time is 0.1 s, pump-down time is 3 s) and hydrogen sulfide (0.1 and 5 s, respectively). The temperature and pressure are the same as for the aluminum oxide deposition process. Doping was carried out by periodic cycles of admission of bis(ethylcyclopentadienyl)manganese (II) ([EtCp]$_2$Mn) (the highest luminescence brightness was achieved with the ratio of cycles DEZ and ([EtCp]$_2$Mn 120/l) Also, after applying the ZnS layer, an additional annealing of 1 h was applied at $500°C$ to increase the brightness.

The quality of the produced layers was controlled by various methods. The presence of the ZnS crystal phase in the light-emitting layer was shown by inelastic (Raman) light scattering. A modular HORIBA-JOBIN-YVON spectrometer with an excitation laser with a wavelength of 632.81 nm was used for Raman measurements. In our case, the main difficulty of the measurements was the small thickness of the ZnS layer and also in the additional amorphous layers of the insulator (Fig. 1). The line of the cubic modification of ZnS $(344.8\,\text{cm}^{-1}$ [11,12]) is clearly distinguishable on the obtained spectra. The width of the line (FWHM) was about $10\,\text{cm}^{-1}$, which indicates the high quality of the crystalline phase. A significant structureless background was present in the spectra of scattered light,

which may also be attributable to the presence of an amorphous phase in the active layer or to scattering in other layers of the structure.

2. Results obtained

The general form of the dependence of the electroluminescence intensity on the applied voltage for such structures is known [1,2]. When studying this dependence, we noted features that had not been previously published by other authors.

As already noted, the excitation of the luminescence of manganese ions is caused by the collision of ions with hot electrons injected by the field from the interface states at the boundary of the semiconductor and insulator layers. Accordingly, the active layer does not emit below a certain voltage value $(80–150\,\text{V}$ — depending on the thickness and type of active material). After the voltage exceeds the threshold value, the field releases the charge carriers and accelerates them to reach an energy sufficient to excite the ions Mn^{2+}. Visual identification of individual processes is hampered by the inevitable heterogeneity of the material at the micro level, blurring possible features on the measured characteristics.

In our case, it was possible to separate the two mentioned processes owing to the use of ALD technology, high quality of the samples obtained.

Fig. 2 demonstrates the intensity-voltage dependences for the studied TFEL structure in the stress region corresponding to the appearance and increase of luminescence $(80–125\,\text{V})$. The appearance of saturation above $120–125\,\text{V}$ is a well-known phenomenon of a different nature [13], which is not considered in this paper
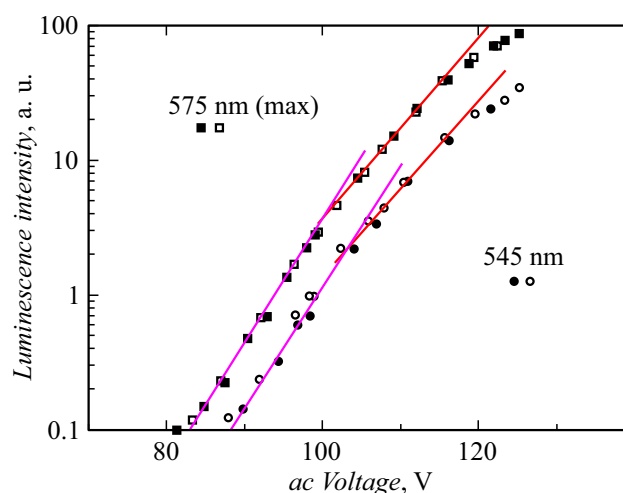

Figure 2. Dependence of the electroluminescence intensity on the applied voltage (effective values). Upper curves — registration at the maximum of the band (575 nm), lower — at wavelength 545 nm. Light icons correspond to an increase of voltage, the results with a decrease of voltage are shown by dark icons.

A new experimental fact is the opportunity to distinguish two areas close to linear dependencies based on the dependence of the intensity of the glow on the applied voltage. The transition from one dependence to another occurs around $100-110$ V (the value also depends on the thickness of the sample). It can be noticed that the linear sections for two wavelengths in the luminescence spectrum of the structure are almost parallel both for the section $90-110$ V, and for the section $110-120$ V. In our opinion, such parallelism indicates that the influence of the voltage value relates to the excitation of luminescence, and the actual band in the spectrum remains unchanged. The activation voltage calculated from experimental data for the section $80-110$ V is 5.2 V, for the section $110-120$ V — 6.4 V. It should be remembered that this voltage value is calculated for the integral intensity and is not the actual microscopic energy of the activation process. Since the dependence of the luminescence intensity on voltage is attributable to the activation process of Mn^{2+} ions, it is natural to assume that at the site of voltages $80-110$ V the field predominantly releases carriers, and at $110-120$ V site they are accelerated to the necessary energies.

The intensity-voltage dependencies were recorded with additional external illumination to check the extended position. It was assumed that the additional generation of carriers due to external illumination would increase the luminescence intensity and change the characteristics of the area responsible for the activation of carriers.

A laser with a wavelength of 405 nm (3.06 eV) was used for additional illumination, which could not lead to interband absorption in zinc sulfide ($E_g = 3.7$ eV at 300 K [14]), or to absorption in ions Mn^{2+} [15] and directly cause luminescence, but could experience absorption and ensure the release of carriers from defective levels in the band gap
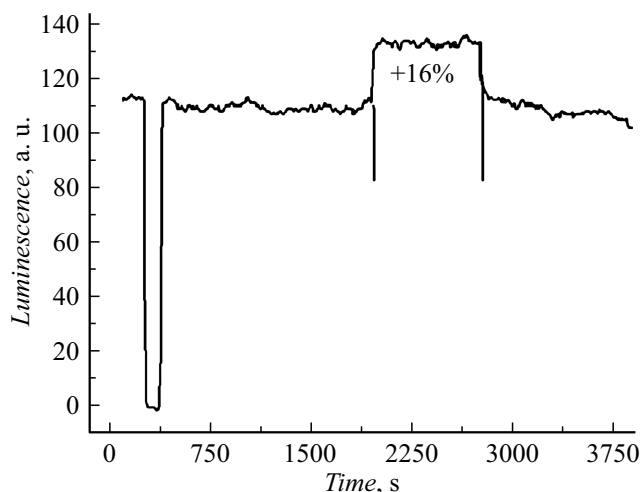
Figure 4. Electroluminescence spectra: *1* — without additional illumination; *2* — with additional illumination; *3* — difference of the curves *1* and *2*. The curve *4* — spectral dependence of the relative increase of intensity.

of the active layer of the studied structure. In addition, the additional illumination was constant for isolating only the electroluminescence signal, and the electroluminescence signal was recorded at the second harmonic of the applied field — as in the other experiments on electroluminescence.

As expected, the additional illumination noticeably increased the luminescence intensity (Fig. 3).

The spectral distribution of the additional intensity along the contour of the band is shown in Fig. 4. The figure shows the spectrum of the electroluminescence band and similar spectra in the backlit mode. Curve *3* — difference of spectra *1* and *2* — i.e. additional intensity. The relative magnitude of the additional luminescence relative to the intensity of the baseband is shown by the curve *4* (with scale on right axis).

Both the electroluminescence spectrum dependence and combined luminescence dependence are approximately similar, the band maxima fall on the same wavelength for both dependences. It should be noted that the calculated relative increase of the intensity of the glow is η (curve *4* in Fig. 4) $\eta = (L_{ph-el} - L_{el})/L_{el}$ has a clearly defined minimum in the band maximum area. This fact will be discussed later.

The effect of external illumination is shown in Fig. 5. It can be seen that the external illumination changes the initial part of the dependence with low intensity and shifts the threshold voltage to lower values (transition from curves *1* to curves *2* and *3*). This is especially noticeable on the curve *3*. The recorded luminescence level starts significantly lower (up to 30 V) at voltages, and there are no signs of a fracture in the dependence of the electroluminescence intensity on the voltage in this case. Such an experiment confirms the initial assumption about the nature of the observed characteristic fracture.

In the course of experiments with external illumination, it was found that the effect of additional illumination of the luminescent structure is not limited to the generation of

Figure 3. An increase of the intensity of electroluminescence of the ZnS : Mn display with additional illumination by light with a wavelength of 405 nm (in the interval $2000-3000$ s). The dip in the left part of the graph shows the signal level when the radiation of the sample is completely blocked, this allows estimating the relative increase of electroluminescence during photostimulation.
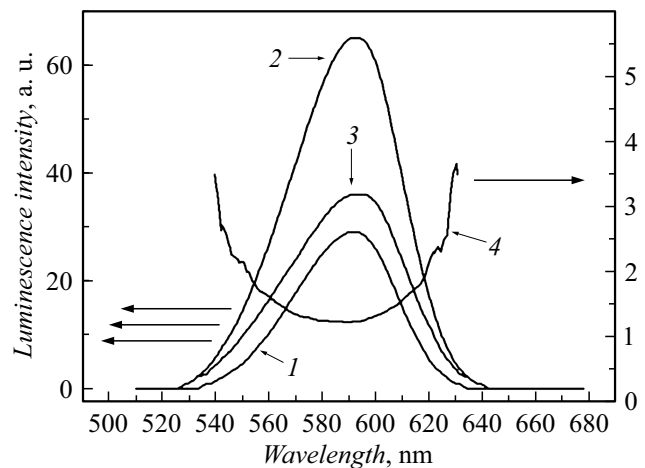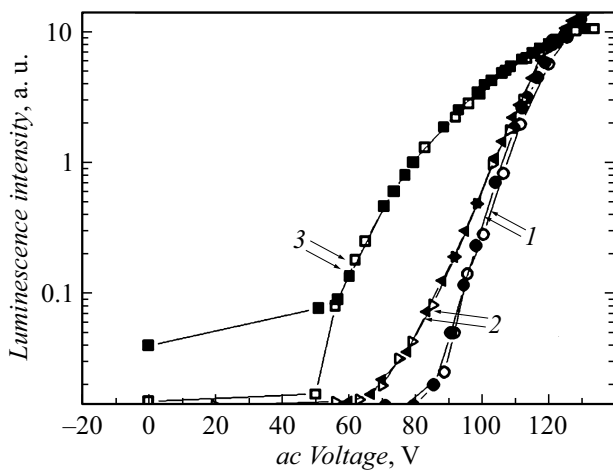
Figure 5. The dependence of the intensity of electroluminescence on the voltage at different levels of illumination. Light icons — when the voltage increases, dark — when the voltage decreases. Curves *1* — without backlight, curves *3* — backlight at 50 W/cm², curves *2* — intermediate backlight level 10 W/cm².

additional carriers and the resulting change in the intensity dependence on the amplitude of the applied alternating voltage. The effect of a long-term increase of luminescence intensity was found in areas that experienced additional external illumination.

The intensity of the additional electroluminescence depended on the operating mode of the luminescent structure. At the highest brightness of the latter (the highest applied voltages), the additional brightness was barely discernible, and at low and medium voltages, the additional intensity reached 100% and more. The chart on Figure 6 also shows that the difference in the intensity of the glow from the previously illuminated area and the area that was not exposed to illumination almost did not change during the experiment (90 min). Such spots with added intensity were observed for several days after additional illumination in some experiments.

3. Discussion of findings

The combined effect of the electric field and illumination on luminescence is known, see, for example [16,17]. Single crystals with a low concentration of impurity were studied in [16]. The main attention was paid to the processes of competition between the main band of luminescence of ions Mn^{2+} and bands with a shorter wavelength of light. This is different from the content of this work.

First of all, it should be pointed out that in this work the existence of two mechanisms of increasing electroluminescence due to external illumination was highlighted: relatively fast (Fig. 3) and relatively slow (Fig. 6).

The authors believe that the mechanism of the „fast" effect is mostly understandable. External illumination generates additional carriers that are involved in the ac-

tivation of ions Mn^{2+}, and thereby leads to an increase of the intensity of electroluminescence. This corresponds to changes in the lower part of the dependences of the electroluminescence intensity on the applied voltage (Fig. 3). Thus, it allows indicating the voltage region that corresponds to the activation process of carriers. The blurring of the threshold between linear sections and a noticeable decrease of the threshold voltage during illumination seem to be reliable arguments in favor of the proposed mechanism.

An effect similar to „rapid" increase of luminescence efficiency was published earlier in [17]. The observation of an increase of the intensity of the glow band $^4T_1 \rightarrow {}^6A_1$ in $3d^5$ ion shell Mn^{2+} was recorded in the said work. However, the work [17] did not compare the dependences of the intensity of the glow on the voltage under conditions of additional illumination and without it; the separation into fast and slow components was not considered. The general conclusion of the work [17] about the generation of additional charge carriers by light coincides with one of the conclusions of this work.

The effect of a long aftereffect of additional lighting was also reported in this work. The illustrations presented in Fig. 6 seem quite convincing. However, the nature of this effect requires additional studies.

First of all, it should be noted that the effect is not caused directly by additional heating of the active layer. This clearly follows from the long-term (up to several days) manifestation of the effect of enhanced electroluminescence after external illumination. Nevertheless, it cannot be ruled out that the illumination and the heating caused by it could cause structural changes in the active layer (recrystallization or, conversely, amorphization), however, given that the additional brightness in the corresponding places disappears over time, it appears that the reason for the additional brightness is some deep centers that arise with additional illumination. Based on the available data, it is not yet possible to detail the mechanism of impact of these additional centers.
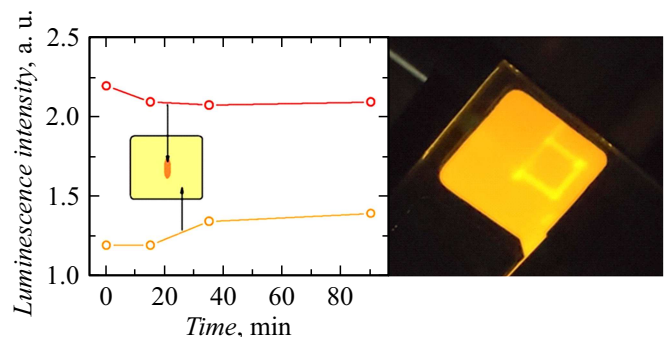

Figure 6. The manifestation of a prolonged increase of the intensity of electroluminescence as a result of additional illumination. The glow of the display is shown on the right, on which a rectangle is „drawn" by the external backlight. Two dependences of the electroluminescence intensity on time are shown on the left: for the peripheral part of the display and for the illumination area.

Comparison of electroluminescence and photostimulated electroluminescence spectra (Fig. 4) also leaves questions. A simple increase of the number of photostimulated free electrons should lead to a proportional increase of intensity over the entire spectral band. The predominant increase of the glow at the edges of the strip also needs an explanation.

Note that additional illumination at a wavelength of 405 nm should, in addition to generating free electrons, create other charged carriers — holes. As can be assumed, laser light (405 nm) can activate carriers not only from interface levels, but also from „tails" of densities of states in the volume of active material. The concentration of ions Mn^{2+} in the sample is high, on the order of $1-2\%$, which corresponds to the substitution of every fifth neighbor-cation in the lattice ZnS. In turn, manganese has other valence states, not only Mn^{2+}, for example, Mn^{3+} [15]. Therefore, even with low mobility of holes, the capture of holes at Mn^{2+} is possible. The ion Mn^{2+} is likely to be in an excited state and is able to luminesce with the subsequent recombination of an electron at such a center. Perhaps such a process will have a different excitation efficiency compared to the main one.

It can also be assumed that the described mechanism of luminescence excitation should not depend on an external field, and thus the corresponding part of the luminescence should not be detected at twice the frequency of the field. However, such a consideration would not take into account the fact that the electrons for the excitation of manganese ions in any case should receive energy from the applied field.

Conclusions

Experiments with photostimulated electroluminescence made provided a better understanding of the processes in the light-emitting structure. It is shown that external illumination by photons with energy less than the band gap width of the active material leads to two effects:

1) a relatively rapid increase of luminescence due to additional carriers, which changes the nature of the dependence;

2) long-term „memory"≃– a long-term increase of the intensity after the illumination stops.

Conflict of interest

The authors declare that they have no conflict of interest.

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