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Stimulated emission of Cr^{2+} ions in ZnS:Cr thin-film electroluminescent structures

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Abstract. First observation of stimulated Cr^{2+} emission in ZnS:Cr electroluminescent (EL) impact-excited thin-film waveguide structures is reported. The structures consist of the following thin films deposited on a glass substrate: a transparent In_2O_3:Sn electrode, an insulator SiO_2/Al_2O_3 layer (~270 nm), an EL ZnS:Cr film (~600 nm), the same insulator layer, and an Al electrode. The stimulated character of the emission recorded through the edge of the structure is evidenced by the following. With increasing the applied voltage, a broad band with three waveguide mode maxima in the edge emission spectrum changes into an intensifying and narrowing band. The maximum of this band is the same as that of the Cr^{2+} emission band recorded through the face, i.e. through the In_2O_3:Sn electrode (1.75 and ~2.6 μm at the Cr concentrations $(5\text{-}7)\times10^{19}$ and $(2\text{-}3)\times10^{20}$ cm^{-3}, respectively). The five-fold narrowing is observed when increasing the voltage by ~4% in the case of the lower Cr concentration. The voltage and frequency dependences of the edge emission are stronger than those for the face emission. A small manifestation of the gain occurrence in the ZnS:Cr TFELS is also observed in the face emission. The possibility to create a new type of electrically pumped lasers with the impact excitation mechanism is discussed.

Keywords: stimulated emission, ZnS:Cr, impact electroluminescence, thin-film, optical waveguide.

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1. Introduction

There are two main mechanisms of the excitation of electroluminescence (EL) in solids: 1) injection of minority charged carriers and recombination with majority ones; 2) impact excitation of luminescent centers by hot electrons accelerated in a high electric field (≥ 1 MV/cm). The former was realized in a wide variety of light emitting diodes and semiconductor lasers. However, the employment of this mechanism is very complicated in the case of wide-gap semiconductors and materials doped with transition metals (TM) or rare earths (RE). First, it is difficult to form a *p-n* junction. Second, some indirect process is necessary to excite TM and RE ions with intraion radiative transitions. This process includes the resonant transfer of the excitation energy from some recombination centres to TM and RE ions. At the same time, intensive EL with the impact excitation mechanism occurs in wide-gap semiconductors (ZnS, ZnSe, SrS, etc.) doped with TM or RE [1]. In spite of this fact, there is no any solid-state laser with the impact mechanism of the EL excitation. Moreover, reliable publications on the stimulated emission in the case of this EL mechanism are absent. The reason of this is the difficulty to obtain a sufficiently high electric field in bulk materials because of the avalanche breakdown. That is why intensive impact EL is only observed in thin-film structures of a MISIM type (here M denotes an electrode, S is an EL film, and I is an insulator layer) [1]. I layers in such thin-film electroluminescent structures (TFELS) serve as a ballast capacitance resistor preventing from the breakdown. However, attainable optical gain is low in TFELS for the onset of the marked stimulated emission even at a high excitation level, if light is emitted from the structure face, i.e. through a transparent In_2O_3:Sn (ITO) electrode. This is related with a very small thickness of EL film (≤ 1 μm).

The possibility to obtain the high gain, when light is laterally transferred in the EL film and emitted from the structure edge, has been theoretically considered in [2]. It is known [1] that TFELS with I layers that has the refractive index lower than that of the EL film represent a planar optical waveguide. Therefore, the main part of

emission in such TFELS is transferred along the EL film due to the total internal reflection on the S-I interfaces and extracted through the edge. Edge TFEL structures have been extensively investigated and developed in 1980-1990 for the creation of visible-light emitters with very high luminance [1, 3]. However, stimulated emission in such TFELS was not observed because of the use non-laser EL materials (e.g., ZnS:Mn) as well as of the high optical losses resulting from the scattering of light on grain boundaries in EL polycrystalline films and from the absorption of light by various lattice defects. One can expect that these losses should be significantly diminished in the near-infrared (NIR) and mean-infrared (MIR) regions. The scattering decreases as λ^n when the wavelength (λ) increases ($n = 1 - 4$ depending on the size of scattering particles). The absorption by lattice defects also decreases at $\lambda > 1$ μm significantly. This has been shown by studying the photodepolarization spectra of TFELS [4,5].

The recent study [6] of ZnS:Er TFELS, which emit in both the visible and NIR regions, has shown some essential differences in characteristics of the emission recorded through the face and the edge (hereafter the former and the latter will be called "the face emission" and "the edge emission"). The intensity of the NIR bands in the EL spectrum (λ_{max} = 0.985 and 1.535 μm) is higher relatively to the intensity of the green band (λ_{max} = 0.535 μm) in the edge emission than in the face emission. This confirms that optical losses in the NIR region are lower in comparison with those in the visible region. In addition, the main 1.535 μm band, which results from the $I_{13/2} \rightarrow I_{15/2}$ transition in Er^{3+} ion, narrows with increasing applied voltage (V) in the edge emission, but its halfwidth in the face emission does not change. This observation has been explained as a manifestation of the occurrence of an optical amplification of the emission propagating in the waveguide. Observed narrowing of the 1.535 μm band is small (~1.7 times). Therefore, the gain is rather low in the edge ZnS:Er TFELS studied. It is necessary to enhance the gain for the irrefutable confirmation of the possibility to obtain the stimulated emission in TFELS with the impact excitation mechanism. There are two ways for the gain enhancement. The first consists in increasing the excitation level and decreasing the optical losses in the edge ZnS:Er TFELS. The second more feasible way is the use of laser materials with a lower pumping threshold for EL films. Recently a low-threshold optically pumped lasers have been created using ZnS:Cr and ZnSe:Cr crystals [7, 8]. Attempts to create lasers with electrical pumping in these crystals were not successful, whereas the spontaneous NIR EL emitted through the ITO electrode has been obtained [5].

In the present paper, we report on the first results of studying edge ZnS:Cr TFELS. Characteristics of the Cr^{2+} emission recorded from the edge and face of these structures are compared. In the edge emission, some peculiarities specific only to the stimulated emission have been observed for the first time. The possibility to create a new type of electrically pumped lasers has been discussed.

2. Experimental details

The schematical view of the TFELS under study is shown in Fig. 1. The waveguide TFELS of the MISIM type consists of a glass substrate, ITO and Al electrodes, SiO_2/Al_2O_3 I layers and a ZnS:Cr film. The Al electrode was in the form of a strip. The edge was made by cutting the TFELS normally to the electrode strip. The waveguide was 4 - 6 mm long, 1 - 2 mm wide and 0.6 - 0.65 μm thick. The I layers and ZnS film were deposited by electron-beam evaporation. Doping with Cr of the ZnS film was performed by thermal co-evaporation of chromium. The samples with the Cr concentration (C_{Cr}) of (5-7)×10^{19} and (2-3)×10^{20} cm^{-3} were studied. EL was excited by sinusoidal voltage of 5-20 kHz frequency (f). The emission spectrum of Cr^{2+} ions was measured by a MDR-12 monochromator with a cooled PbS photoresistor.

3. Results and discussion

The EL spectrum of the ZnS:Cr TFELS with C_{Cr} of (5-7)×10^{19} cm^{-3} at increasing voltage of 20 kHz is shown in Fig. 2 when the emission was recorded from the face and edge. The photoluminescence (PL) spectrum of ZnS:Cr crystals is also shown [7]. It is seen that the Cr^{2+} emission in the crystals and films occurs within the same spectral region, but has some different spectral distribution. The emission of the ZnS:Cr TFELS consists of two bands. The maximum of the main band (at 1.75 μm) is not far from the maximum of the PL spectrum. The second band is located in the longwave tail of the EL spectrum. This band becomes dominant when the Cr concentration in the films increases (Fig. 3) as well as when the ZnS:Cr crystals have some degree of hexagonality [8]. Therefore, the longwave band of ZnS:Cr is attributed to the emission of Cr^{2+} ions in a low-symmetry crystal field [8, 9].

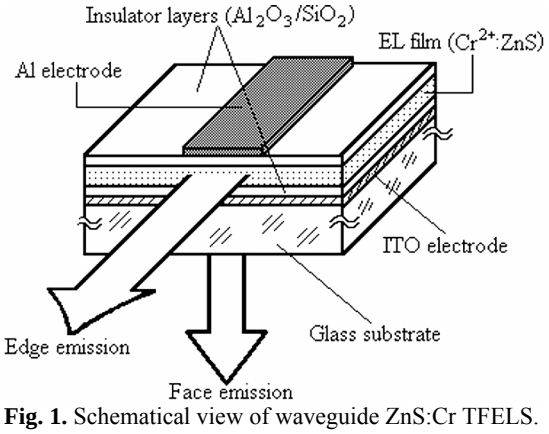

Fig. 1. Schematical view of waveguide ZnS:Cr TFELS.

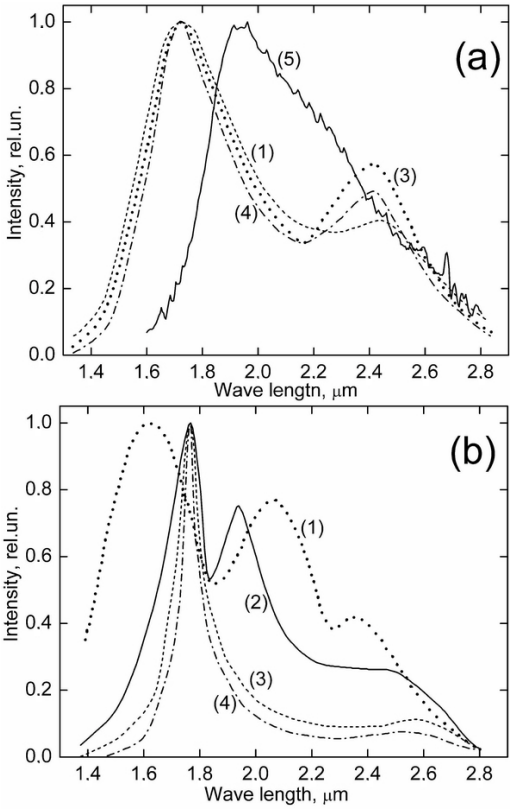

Fig. 2. EL spectrum of face (a) and edge (b) Cr^{2+} emissions at various voltages, *V*: *1* – 150, *2* – 151, *3* – 154, *4* – 157. f = 20 kHz. C_{Cr} = (5-7)×10^{19} cm^{-3}. Curve *5* in (*a*) is PL spectrum of ZnS:Cr crystals [1].

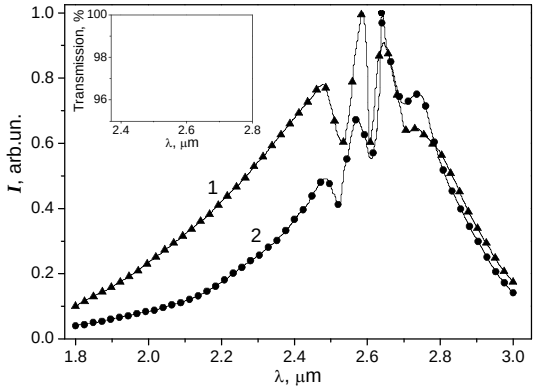

Fig. 3. EL spectrum of face (*1*) and edge (*2*) emission for ZnS:Cr TFELS with C_{Cr} of (2-3)×10^{20} cm^{-3}. V = 180 V. Curve in insertion shows transmission of atmosphere on the length between the sample and photodetector.

The EL spectrum of the face emission somewhat changes with increasing *V*. The main band slightly narrows and the relative intensity of the second band first increases, but then decreases. On the contrary, the behavior of the edge emission spectrum is essentially different. At the threshold voltage of EL, there are three maxima in the spectrum; the main maximum is not far from that of the Cr^{2+} emission. These maxima are due to the waveguide modes propagating at different angles (all of them were condensed by a lens during measurements of the spectrum). Spectral redistribution of this emission takes place with increasing *V*. The waveguide-mode maxima first decrease and then disappear. The most intensive emission appears in the region that coincides with the central part of the main Cr^{2+} emission band. The emission in this region intensifies stronger than in other regions of the spectrum with further increasing voltage. In addition, the significant narrowing of the main Cr^{2+} emission band occurs. The voltage dependences of the main band halfwidth for the face and edge emissions at f = 20 kHz are compared in Fig. 4a. The halfwidth for the former decreases only by ~20% when the voltage increases by 6 V (i.e. by ~4%), whereas the halfwidth of the edge emission decreases more than by a factor of five. The halfwidth of the narrowest band obtained is larger than the oscillation line width of the ZnS:Cr laser only less than two-fold (80 and 50 nm, respectively). The significant narrowing of the Cr^{2+} band in the edge emission is also observed in the case of the higher Cr concentration (Fig. 3). The most significant narrowing takes place within the steep section of the voltage dependence for the emission intensity (I) that is shown in Fig. 4b. The narrowing of the band decreases on the saturation section of the $I(V)$ dependence. The saturation is typical for TFELS of the MISIM type [1] and is due to the voltage redistribution between the I layers and the EL film, when the Ohmic resistance (R) of the latter decreases and becomes commensurable with the capacitive resistance of the I layers (the capacitive resistance of the EL film and the I layers is almost the same). The decrease of R is related with a significant increase of the active current caused by the avalanche multiplication of electrons.

It is seen from Fig. 4b that the voltage dependence of the edge emission intensity is steeper than that of the face emission. This is one essential peculiarity of the edge emission more. The frequency dependence of the intensity of the edge emission at a fixed voltage is also steeper as compared with the $I(f)$ dependence for the face emission (Fig. 5). It should be noted that the sublinear character of the $I(f)$ dependence and a decrease of I at f > 15 kHz are caused by growth of the voltage drop at the transparent ITO electrode with increasing the capacitive current passing through TFELS. The resistance of the ITO electrode was rather high (~300 Ohm/□) to diminish the optical absorption of the Cr^{2+} emission by free electrons. The main band halfwidth of the edge emission at a fixed voltage diminishes when f becomes higher (Fig. 5), while the face emission band does not change markedly.

As follows from the above results, there is an optical amplification of the Cr^{2+} emission in the edge ZnS:Cr TFELS. The gain is sufficiently high to generate a rather intensive stimulated emission in these TFELS. The optical amplification affects also the Cr^{2+} face emission, but significantly more weakly because the passage length of this emission is three orders of magnitude lower than that of the edge emission. Some narrowing of the Cr^{2+} band in

the face emission spectrum (Fig. 2) is a manifestation of the amplification effect. In addition the influence of the gain on the face emission is supported by the nonmonotonic change of the intensity of the longwave band relative to the main band intensity with increasing the voltage. An initial increase of the relative intensity results from the lower lifetime (τ) of excited low-symmetrical Cr^{2+} ions than τ of the high-symmetrical ones [8]. The further relative decrease of the intensity of the longwave band stems from a competitive effect of the gain increase for the main band.

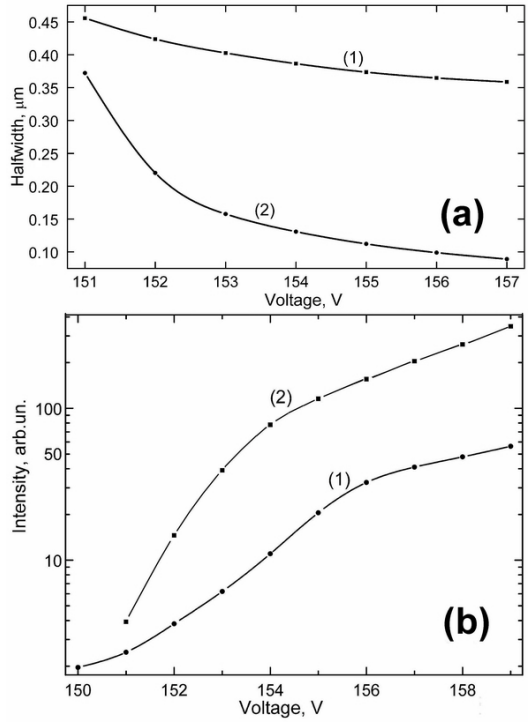

Fig. 4. Voltage dependence of: (a) Cr^{2+} band halfwidth for the face (*1*) and edge (*2*) emissions; (b) maximum intensity of the face (*1*) and edge (*2*) Cr^{2+} emissions. f = 20 kHz. C_{Cr} = (5-7)×10^{19} cm^{-3}.

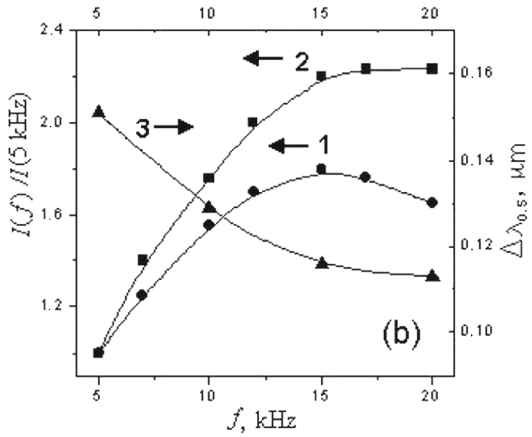

Fig. 5. Frequency dependence of the intensity for the face (*1*) and edge (*2*) Cr^{2+} emissions as well as of the Cr^{2+} band halfwidth for the edge emission (*3*). V = 156 V. C_{Cr} = (5-7)×10^{19} cm^{-3}.

4. Conclusion

Thus, for the first time the stimulated emission is obtained in ZnS:Cr at the electrical impact excitation. To our knowledge, this is the first observation of the impact-excited stimulated emission in solid states apart of our observation of the rather insignificant effects of the stimulated emission in the edge ZnS:Er TFELS [6]. The obtained results show the possibility of the creation of new electrically pumped compact inexpensive lasers based on edge TFELS doped with TM and RE, which are especially actual for the NIR and MIR regions. One can expect that the intensity and efficiency of these lasers will be lower than those of injection lasers and optically pumped ones due to thin active layers and low efficiency of the impact excitation mechanism. However, this will not prevent from a wide variety of applications of new lasers, e.g. in medicine and spectral chemical sensoring. Optimization of the waveguide properties of the TFELS and using distributed feedback optical coupling are needed to realize such lasers. It is also expected that making the ZnS:Cr TFELS with the Fabry-Perot cavity will result in the intensive stimulated face Cr^{2+} emission, possibly, even in lasing.

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