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Laser oscillation in Cr^{2+}:ZnS waveguide thin-film structures under electrical pumping with impact excitation mechanism

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Abstract. The laser oscillation at room temperature in Cr^{2+}:ZnS waveguide thin-film structures under electrical pumping with the impact excitation mechanism was first discovered after improvement of some waveguide optical properties. However, lasing turned out to be unstable and ceases soon, which is accompanied by strong weakening the emission recorded from the waveguide edge whereas the emission from the structure face remains intensive. It is shown that the above changes stem from increasing optical losses caused by appearance of light scattering in the structure by inhomogeneities formed during lasing as a consequence the most probably of recrystallization processes in the Cr:ZnS film. Some ways are proposed to improve the lasing stability.

Keywords: laser optics, infrared laser, electrical pumping, Cr^{2+}:ZnS, thin films, planar waveguide.

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1. Introduction

A new class of compact broadly tunable mid–infrared (Mid–IR) lasers operating over the $2-5\,\mu m$ range under optical pumping has been intensively investigated in recent 15 years [1-11]. These lasers are based on transitions in divalent transition metal (TM) ions (Cr^{2+}, Fe^{2+}) located in cation sites of chalcogenide semiconductors with a large band gap (ZnS, ZnSe, $Cd_{1-x}Mn_xTe$, CdSe). The major attention of researchers was focused on Cr^{2+}:ZnSe crystals and powders as laser media (see reviews [6, 7] and references therein). Recently, the laser oscillation under optical pumping have been demonstrated in Cr^{2+}:ZnSe planar waveguide structures fabricated by pulsed laser deposition of the thin film on a sapphire substrate [8]. Cr^{2+}:ZnS is also considered as promising laser material [7]. Efficient continuous–wave lasing of Cr^{2+}:ZnS crystals under optical pumping has been reported in [10, 11].

It is of great interest to develop electrically pumped lasers based on the above mentioned materials. Some attempts to pump electrically bulk Cr^{2+}:ZnSe samples met with failure [7]. The electrical pumping with the injection mechanism of the excitation that is generally used in semiconductor lasers is inefficient in the case of intraionic transitions. Excitation of TM ions at such a mechanism is realized not directly, but by resonant transfer of energy from some suitable recombination centers. It is known [12] that TM ions are efficiently excited by hot electron impact at sufficiently high electric fields (≥1 MV/cm). Intense electroluminescence (EL) of TM ions by impact excitation is observed in thin–film electroluminescent (TFEL) structures [12]. In particular, Mid–IR EL of Cr^{2+} ions that is due to the $^5E \rightarrow {}^5T_2$ transition takes place in Cr:ZnS and Cr:ZnSe TFEL structures [13, 14]. At first, this EL was studied by recording the emission through a transparent In_2O_3:Sn (ITO) electrode. However, it is impossible to obtain high gain in this case because of a small EL film thickness (≤1 μm). Therefore, Cr^{2+}:ZnS waveguide TFEL structures and recording the emission from their edge were used later with the purpose to obtain lasing. It is known [12] that a TFEL structure of the MISIM type, where S is the EL film, I is an insulator layer and M is an electrode (ITO and Al), is an optical planar waveguide, if the index of refraction of I layers is lower than that of the EL film. The intense stimulated emission of Cr^{2+} ions excited by hot–electron impact in the above Cr^{2+}:ZnS waveguide TFEL structures with the Cr concentration (C_{Cr}) of $(5-7)\times10^{19}\,cm^{-3}$ was demonstrated [15]. The stimulated character of the

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observed emission was confirmed by the following changes in the EL spectrum recorded from the structure edge at increasing voltage. Extremes inherent to the waveguide modes disappear, but the intensity of the Cr^{2+} band increases significantly. The band narrows from ~450 up to 80 nm. In addition, the voltage dependence of the band peak intensity was much stronger in comparison with the same dependence for the emission recorded through the ITO electrode. In this letter, it is reported on our further effort to obtain for the first time laser oscillation in Cr^{2+}:ZnS waveguide TFEL structures with improved some properties specific to a laser media. The laser oscillation was indeed discovered in these structures. However, they turned out to be unstable. The cause of this instability and possible ways to obtain stable lasing are considered.

2. Experimental details

The schematic view of the Cr^{2+}:ZnS waveguide TFEL structures under study is shown in Fig. 1. The structures were deposited on a glass substrate and consisted of a Cr:ZnS ~600 nm thick film, SiO_2/Al_2O_3 I layers (~270 nm), an ITO and Al electrodes. The I layers and ZnS film were deposited by electron–beam evaporation. Doping the film with Cr was performed by thermal co–evaporation of chromium. To provide a higher gain, C_{Cr} was increased up to $\sim 4\times10^{20}\,cm^{-3}$. The samples were annealed at 550 °C in vacuum after deposition of the Cr:ZnS film. The Al electrode was made in the form of a strip 5 mm long and 1.5 mm wide. As distinguished from the TFEL waveguide structures studied earlier [15], the edge on both waveguide ends was made by cutting the structure normally to the Al strip. This resulted in lowering the lasing threshold due to increasing emission reflection from the ends. EL was excited by sinusoidal voltage of 15 kHz frequency. The emission spectrum was measured by a grating monochromator and a cooled PbS photoresistor. The spectrum was corrected with account of the spectral sensitivity of the spectrometer and air absorption.

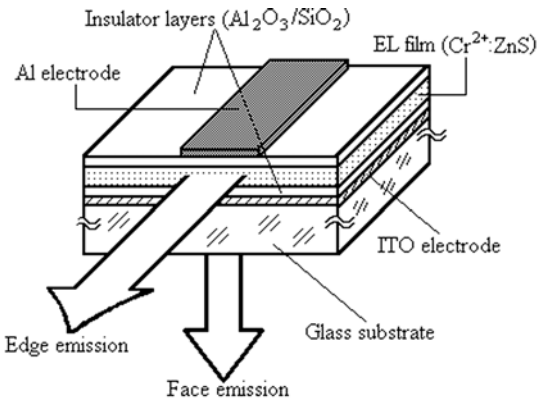

Fig. 1. Schematic view of Cr^{2+}:ZnS waveguide TFEL structures.

3. Results and discussion

The EL spectrum of the Cr^{2+}:ZnS TFEL waveguide structures is shown in Fig. 2 for the emission recorded from the face of an operating cell (i.e. through the ITO electrode) and its edge. From now on the former and the latter will be called "face emission" and "edge emission". The spectrum of the face emission is independent of the applied voltage and consists of an asymmetrical band with the peak shifted to the long–wavelength site, as compared to that in the spectrum of Cr^{2+}:ZnS TFEL structures with a lower C_{Cr} (~2.6 and ~1.8 μm, respectively) [15]. The change of the spectral location of the Cr^{2+} emission band is due to a difference in the local crystal field symmetry of the ions. The lower symmetry results in a long–wavelength shift of the band. Cr^{2+} ions with the lowest local symmetry are predominant obviously in highly doped Cr:ZnS films because of increasing the number of charged defects, in particular of $[Cr_{Zn}^{+}]^{-}$ acceptors [16]. These defects located near Cr^{2+} ions result in local axial symmetry instead of T_d symmetry inherent to cubic ZnS. The spectrum of the edge emission changes with increasing the voltage (Fig. 2, curves $2-4$). Extremes specific to waveguide modes are observed at first when the applied voltage becomes higher than the threshold voltage (~150 V). One from these maxima is close to the peak in the face emission spectrum. The relative intensity in this maximum increases significantly with the applied voltage. The only band with the peak at ~2.6 μm remains at some voltage (~170 V) and narrows by a factor of 2.5 in comparison with the face emission band under the following voltage increase. The changes in the emission spectrum are accompanied by stronger growth of the band intensity with the applied voltage than that of the face emission intensity (Fig. 3). In addition, the dependence of the intensity on the charge (Q) transferred through the structure is also sharper in the case of the edge emission (Fig. 4). These peculiarities indicate that there is optical amplification of the emission propagating along the waveguide and that the edge emission is stimulated at the applied voltage ≥ 170 V.

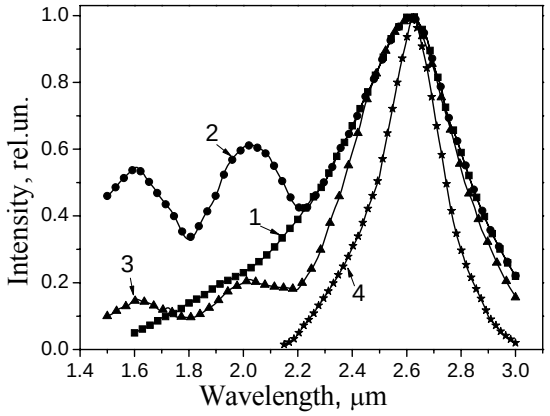

Fig. 2. Normalized spectrum of face (*1*) and edge (*2–4*) emission. Applied voltage, V: 160-175 (*1*); 160 (*2*); 168 (3); 175 (*4*).

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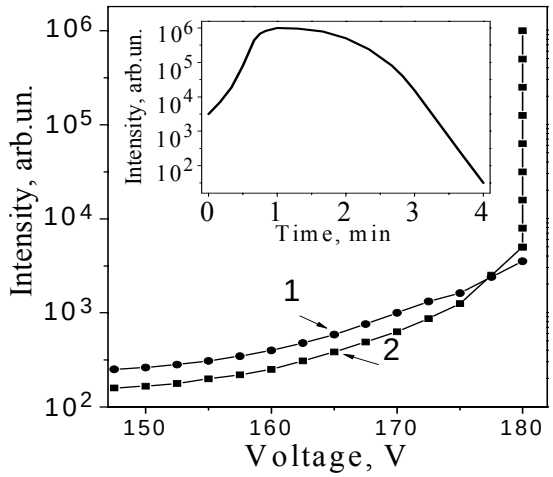

Fig. 3. Dependence of intensity of face (*1*) and edge (*2*) emission on applied voltage. Inset graph shows change of edge emission intensity in time after applying voltage of 180 V.

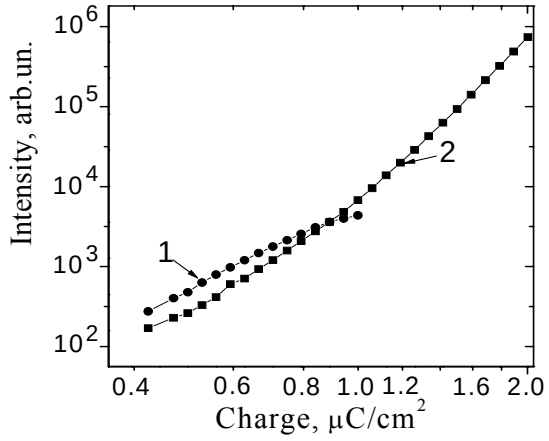

Fig. 4. Dependence of the maximum intensity of face (*1*) and edge (*2*) emission on the transferred charge.

The voltage increase up to ~180 V, which produces electric field in the Cr:ZnS film above 2 MV/cm, results in the fast (for a minute) and very strong (in ~100 times) growth of the edge emission intensity at the fixed applied voltage and only two-fold increase of the charge (Fig. 3). The efficiency of this emission becomes almost two orders higher in its magnitude than that of the face emission, which is equal to $(2-3)\times10^{-3}$. Such a low efficiency is typical for spontaneous EL with the impact excitation mechanism [12] in contrast to the high–efficient injection EL. The strong growth of the edge emission intensity and efficiency indicates that the laser oscillation originated. Unfortunately, the lasing spectrum could not be recorded because the laser generation turns out to be unstable. It ceases soon (see inset in Fig. 3). Moreover, the edge emission becomes very weak in this cell and remains just the same from now on. This means that irreversible changes take place in the waveguide cell during lasing. However, they do not affect Cr^{2+} ion excitation because rather intense face emission persists in the cell. The visual examination of the operating cell after laser generation shows that the Al electrode mirror initially turned mat. The structure also remains mat after etching of the Al electrode. Therefore, large inhomogeneities appeared in the structure. They resulted in light scattering and consequently in significant optical losses in the waveguide. This is the main cause of the lasing cessation and edge emission weakening.

This conclusion is confirmed by the topographical investigation of the structure surface by means of atomic–force microscopy (AFM). Mapping of the relief was performed in tapping mode using the silicon tips of 10 nm nominal apex radii. The topography maps for the initial structure and the operated cell where lasing was observed are shown in Fig. 5. The Al electrode was etched in both cases. One can see the following topology changes after lasing. The relief amplitude becomes larger (see insets in Fig. 5). The root–mean–square value of the surface roughness is 6.5 times increased (from 1.4

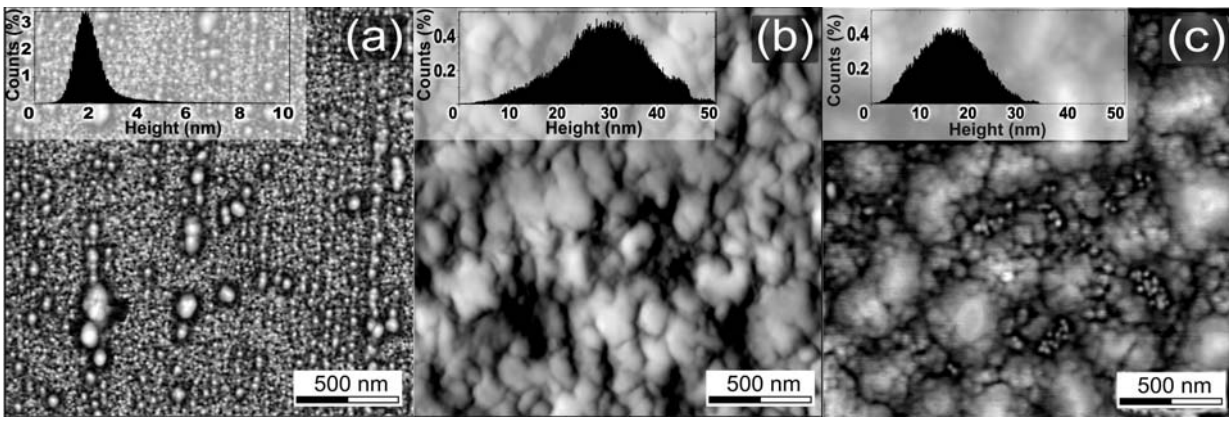

Fig. 5. AFM image of the initial structure (a), operating cell after lasing (b) and the structure near of this cell (c). Al electrode was etched. On insets: corresponding height histograms.

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up to 9.1 nm). The size of inhomogeneities (grains) is also increased significantly. With the conserved log–normal type of the grain size distribution, their most probable diameter enlarges from 23 up to 170 nm, and its maximum value increases from 90 up to 400 nm. The above changes in the surface topology after lasing obviously stem from recrystallization processes taking place in the Cr:ZnS film under action of the high–intense laser radiation, but not the field. This is confirmed by the following. The analogical topology changes are also observed outside the operated cell not far from it (~0.5 mm), where there is no electric field, but the laser emission propagates into this region because the studied waveguide is planar. The laser emission propagates in the waveguide mainly within this film and cannot result in any change in the large band gap amorphous insulator layer Al_2O_3/SiO_2. Hence, the inhomogeneities on the surface of the upper I layer display an enlargement of crystal grains in the Cr:ZnS film.

The origin of recrystallization in the Cr:ZnS film during lasing is probably caused by local heating owing to absorption of the laser radiation with the wavelength close to 2.6 μm. Noticeable heating the whole operating cell was not detected. There is no absorption band of ZnS in this spectral region. The weak Cr^{2+} absorption band is at the shorter wavelengths than the emission band. Therefore, it is likely that the laser radiation is absorbed by Cr clusters which form in high–doped Cr:ZnS films due to chromium segregation. Degradation processes related to Cr segregation were observed in ruby rods with high C_{Cr} at early stages of ruby laser development.

It follows from the results mentioned above that using a high Cr concentration is not a satisfactory choice to obtain the stable laser oscillation in Cr^{2+}:ZnS TFEL waveguide structures. In addition, the high C_{Cr} can result in the fluorescence quenching. Any noticeable concentration quenching was not observed in Cr^{2+}:ZnS crystals up to $C_{Cr} = 10^{20}\,cm^{-3}$ [9]. To lower the lasing threshold and to increase gain in the structures with fairly low C_{Cr} ($< 10^{20}\,cm^{-3}$), the improvement of optical properties of the waveguide is necessary.

4. Conclusion

For the first time the laser oscillation in the Cr^{2+}:ZnS:Cr waveguide thin–film structures under electrical pumping with the impact excitation mechanism is demonstrated. However, discovered lasing turns out to be unstable and ceases soon. This is accompanied by strong weakening the edge emission. It is shown that the above changes stem from increasing optical losses due to appearance of light scattering by inhomogeneities formed very likely in consequence of recrystallization processes in the Cr:ZnS film during lasing. These processes result more probably from local heating owing to absorption of laser radiation by metal clusters existing in high–doped Cr:ZnS films because of chromium segregation. Therefore, Cr^{2+}:ZnS TFEL structures with the fairly low C_{Cr} and improved some waveguide optical properties should be used to obtain stable lasing. In particular, it is necessary to reduce the outflow of emission through the waveguide walls and from lateral sides of the operating cell. Continuation of studying the Cr^{2+}:ZnS waveguide TFEL structures as a laser medium is needed to create compact inexpensive electrically pumped Mid–IR laser sources of a new type, which could be attractive for some applications.

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