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## Laser generation in polycrystalline Cr<sup>2+</sup>: ZnSe with undoped faces

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*Abstract.* An original method has been suggested for producing polycrystalline  $Cr^{2+}$ : ZnSe samples with undoped faces. Generation characteristics of a  $Cr^{2+}$ : ZnSe laser are studied under pulse-periodic pumping by a  $Tm^{3+}$ : YLF-laser. The efficiency of converting the pump radiation into laser generation at a wavelength of 2350 nm is 20%.  $Cr^{2+}$ : ZnSe samples exhibit high resistance to surface breakdown.

*Keywords:* diode pumping,  $Tm^{3+}$ : YLF laser,  $Cr^{2+}$ : ZnSe laser, undoped faces.

Among numerous materials used as active media for femtosecond and tunable mid-IR lasers, most promising are zinc chalcogenides doped with ions of transition metals [1, 2]. In recent years, research activity has been concentrated on enhancing the efficiency and output power of laser radiation needed for constructing compact sources of tunable coherent radiation in the range of  $2-3 \mu m$  [3-5]. As shown in [6] the distribution profile of the dopant determines the profile of absorbed energy, which, in turn, substantially affects the efficiency and absolute values of parameters of laser generation. At high pump power densities there is a high probability of laser breakdown on surfaces of a doped optical element due to a high concentration of the dopant. This problem can be solved by providing a minimal (or zero) concentration of the dopant material on the surface, through which laser radiation is coupled in/out, and a maximal concentration in the sample bulk.

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Received 12 November 2014; revision received 26 November 2014 Kvantovaya Elektronika **45** (1) 8–10 (2015) Translated by N.A. Raspopov In the present work we report results of investigations of generation characteristics of polycrystalline  $Cr^{2+}$ : ZnSe samples obtained by the original method which provides zero concentration of the doping material on the surface of the sample and a maximal concentration inside it.

Polycrystalline ZnSe samples with the size of  $10 \times 15 \times 3$  mm and high optical quality obtained preliminarily by the CVDmethod were polished by diamond powder with the grain size of 1 µm, washed in an ultrasonic bath and placed into a reactor conventionally used for synthesising ZnSe. The CVDreactor comprised the unit for feeding chromium precursor vapours, equipped with a system of independent heating, and a high-precision unit for controlling evaporator temperature. The chromium precursor vapour was introduced into the reactor by a flow of a gas carrier (argon). Chemical deposition of a metal chromium film on the surface of polished ZnSe substrates was performed by reducing chromium trichloride in zinc vapours.

As soon as the chromium film of desired thickness was deposited on the ZnSe surface, the flux of the precursor stopped and hydrogen selenide diluted by argon passed to the reaction zone for depositing ZnSe. Synthesis of zinc selenide was performed by the method thoroughly described in [7]. The layers of ZnSe were grown for 48–72 h (depending on the required deposition thickness). In the result of experiment, three-layer ZnSe-Cr-ZnSe structures with a thickness up to  $6-8 \,\mu\text{m}$  were obtained. The samples grown were extracted from the CVD-reactor and polished to obtain a required geometrical shape. Then, the samples were annealed in evacuated quartz ampoules at a temperature of 1050 °C in argon atmosphere at a pressure of approximately 1 atm for 5-7 days. The process of obtaining the required chromium concentration profile was made noticeably faster under barothermic treatment of synthesised structures. For this purpose, the annealing was performed in a gas-static box at a pressure of 1000 atm and temperature of 1100-1250 °C for 24-36 h.

The concentration of chromium in samples determined by the method of IR Fourier spectroscopy was about  $10^{18}$ –  $10^{19}$  cm<sup>-3</sup> and depended on experimental conditions. The distribution of chromium in samples was found by the optical method using radiation of a Tm : YLF laser at a wavelength of 1908 nm [8]. The concentration profile of a Cr<sup>2+</sup>:ZnSe sample is presented in Fig. 1. One can see that the maximal chromium concentration is observed in the sample bulk, whereas near surfaces it is below a detection limit.

The laser element cut from the  $Cr^{2+}$ : ZnSe crystal had no antireflection coatings. Plates of  $Cr^{2+}$ : ZnSe were placed at the Brewster angle to the optical axis of the cavity (Fig. 2) and pressed to a copper heatsink through indium gasket without



Figure 1. Normalised profile of chromium distribution over thickness of the ZnSe sample with a total thickness of 5 mm.

active cooling. The crystal was excited at a wavelength  $\lambda_{\rm p}$  = 1908 nm by radiation of a repetitively pulsed diode-pumped Tm:YLF-laser. The duration of Tm:YLF-laser pulses was 500-1000 ns (depending on the power) at a pulse repetition rate f = 10 kHz. Radiation of the pump laser (1) was focused by the lens system (2) through a dichroic mirror (3) inside the  $Cr^{2+}$ : ZnSe sample (4) into a spot of diameter ~600 µm. The cavity of length 60 mm was formed by the dichroic mirror (3)and a flat-concave outcoupling mirror (5) (the reflection coefficient was ~80% in the range 2.3–2.4  $\mu$ m) with the radius of curvature R = -300 mm. The laser radiation power was measured with a calibrated power meter Gentec with the spectral sensitivity range of 0.5-10 µm. Time parameters of generation were measured with a photodetector based on a MCT-structure with the response time of  $\sim 5 \times 10^{-9}$  s. Output radiation was spectrally analysed by a Solar M833 diffraction monochromator with the resolution of 0.5 nm.



**Figure 2.** Schematic diagram of the  $Cr^{2+}$ :ZnSe laser: (1) Tm:YLF laser; (2) lens system; (3) dichroic mirror; (4) active element made of  $Cr^{2+}$ :ZnSe; (5) outcoupling mirror.

Generation characteristics of polycrystalline  $Cr^{2+}$ : ZnSe samples with a minimal chromium concentration on the surface obtained by the method described above were compared to those of polycrystalline samples with a maximal concentration of chromium on the surface obtained by the conventional method [9]. The effective chromium concentrations in the samples were close and equal to  $\sim 2 \times 10^{19}$  cm<sup>-3</sup>. The active elements had no antireflection coatings. At the pump radiation power of ~2.5 W, close values of the average generation power (~0.5 W) were obtained (Fig. 3). The greater threshold power of samples with undoped faces is, probably, related to nonoptimal doping conditions and, hence, to higher losses due to scattering. The maximal power and efficiency of laser generation were limited by the pump power and high pulse repetition rate.



Figure 3. Output power of the  $Cr^{2+}$ : ZnSe laser vs. pump power in the case of an active elements with (1) 'minimal' and (2) 'maximal' surface chromium concentrations.

Generation spectra of both samples did not substantially differ, at a higher pump power they shifted to a longer-wavelength range approaching the maximum of the active medium gain at 2350 nm at the generation linewidth of 50-70 nm.

Estimates of the power density corresponding to surface breakdown in undoped ZnSe samples and in the samples with maximal and minimal surface concentrations of chromium made for the case of tight focusing of the pump radiation at a wavelength of 1908 nm (at a pulse duration of ~100 ns) show a noticeable difference between the samples of undoped ZnSe and samples with a maximal surface chromium concentration (~5.6 and ~2.5 J cm<sup>-2</sup>, respectively). Nevertheless, the power density for the samples with a minimal chromium concentration on the surface actually did not differ from that for undoped ZnSe samples.

Further optimisation of the method of producing ZnSe-Cr + ZnSe-ZnSe structures may, seemingly, substantially enhance the laser resistance of optical elements and efficiency of generation especially in the range of high radiation powers.

Thus, we have fabricated polycrystalline  $Cr^{2+}$ : ZnSe samples with a maximal chromium concentration in the sample bulk and zero concentration on the surfaces through which the laser radiation is coupled in/out. Comparison of the efficiencies of generation in the  $Cr^{2+}$ : ZnSe samples with undoped faces and in samples produced by the conventional method shows close results. An enhanced resistance of the obtained  $Cr^{2+}$ : ZnSe samples to surface laser breakdown has been demonstrated.

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