Low-threshold lasing in ZnO microtetrapods

A P Tarasov¹²⁴, Ch M Briskina¹, V M Markushev¹, A M Opolchentsev³ and A S Lavrikov³

¹ Kotel'nikov Institute of Radio-Engineering and Electronics of Russian Academy of Sciences, 11-7 Mokhovaya, Moscow, Russia, 125009
² Moscow Institute of Physics and Technology (State University), 9 Institutskiy per., Dolgoprudny, Moscow Region, Russia, 141701
³ Federal Scientific Research Centre “Crystallography and Photonics” of Russian Academy of Sciences, 59 Leninskiy pr., Moscow, Russia, 119333

Abstract. Lasing of ZnO microtetrapods in the spectral range of exciton recombination was studied at room temperature. Samples were produced by a method of pyrolytic carbothermal synthesis. With nanosecond pumping in Al-doped ZnO sample the record low value of the lasing threshold was observed. The threshold pumping energy was 0.13 µJ/cm². The dependences of the integrated intensity on the pumping level were obtained. As expected, they appeared to be linear in the lasing region. It was shown that with pumping level increase the intensities of laser lines is red shifted, i.e. long wavelength lines become more intensive. This is suggested to be related to the band-gap renormalisation as a result of possible heating or electron-hole plasma formation. The possible nature of the laser resonator in the tetrapod was discussed. Most likely that the resonator is formed at the bottom of the tetrapod leg where its cross-section is hexagonal. The appearance of the whispering gallery modes is possible in such resonator.

Zinc oxide (ZnO) is a direct semiconductor with a band-gap energy of about 3.3 eV. High exciton binding energy (59 meV) allows registration of the exciton recombination radiation in near-UV up to temperature 500°C. ZnO is known to be able to crystallize in many different forms, from which tetrapod-shape morphology is one of the most attractive. Among all possible properties of such structure, lasing appearance (particularly, in the spectral range of the exciton radiation) due to existence of local resonators is of our great interest. A number of studies devoted to tetrapod-based microlasers are presented in the literature [1, 2] but many problems remain to be solved. Namely, one can single out the achievement of the low lasing threshold and clear understanding what resonator participates in lasing and where it is located.

In this work we studied the lasing in ZnO microtetrapods at room temperature. The samples were produced by a method of pyrolytic carbothermal synthesis which consists in the following. The decalcified paper filter that served as a porous cellulose currier was impregnated with Zn acetate water solution (40 g/l). Then, thermal treatment at high temperature (maximum temperature was 1050°C, rate was 4.2 deg/min) was conducted. The holding at constant temperature was 15 - 50 min. The synthesis was perfomed in high purity alundum crucibles in air flow with a rate of 0.5 - 9 l/min. The subsequent cooling up to a room temperature was provided during ~ 20 h. Some samples were doped with Al by pouring the metal powder on the paper filters before the synthesis. Doping level was 5
at.%). The examples of the photograph of the crucible with ZnO tetrapods after the synthesis and the SEM image of ZnO tetrapod are presented in figure 1.

\[ \text{Figure 1. a) The photograph of the crucible with ZnO tetrapods; b) The microphotograph (SEM) of the ZnO microtetrapod.} \]

The excitation of the samples radiation was performed by the 3rd harmonic of a Nd:YAG laser (355 nm). Pulse duration and repetition rate were \( \sim 10 \) ns and 15 Hz, respectively. The pumping energy was varied from 30 nJ to several \( \mu \)J. The laser beam was focused into a spot on the sample using a short-focus lens. Radiation of the samples was registered with the use of the monochromator MDR-206 in couple with the Peltier-cooled CCD camera Videoscan-285. The registered spectral range was 35 nm (from 373 to 408 nm). In order to register stable good-quality signal, the accumulation was used (50-200 pulses).

In the spectra of all samples studied in this work we observed the permanence of laser lines positions and their relative intensity ratios from shot to shot at the constant pumping level. Also the spectra shape before and after the accumulation did not change. All of this indicates that observed lasing was caused by the optical modes of tetrapods and it was not random lasing.

In figure 2(a) the spectra at two different pumping levels of one of the studied samples are shown. For this sample, the dependence of the integrated intensity (the integral of the spectrum over the wavelength) on the pumping level was obtained (figure 2(b)). Here, one can see that the slope in the range from zero pumping to the threshold (~1000 nJ) is noticeably lower than that at higher pumping levels.

\[ \text{Figure 2. a) The exciton radiation spectra at two different pumping levels: at the threshold (pumping energy } E_p = 999 \text{ nJ), above the threshold (} E_p = 2721 \text{ nJ); b) The dependence of the integrated intensity on the pumping level.} \]
Studying the radiation of Al-doped sample (ZnO:Al) we observed significantly lower lasing threshold than one for the previous-discussed sample. The spectra of this sample at pumping levels near the lasing threshold are shown in figure 3(a). Here, the threshold is just ~ 40 nJ. One can see that the most intensive laser line is located at 386.8 nm.

![Exciton radiation spectra of the ZnO:Al sample](image)

**Figure 3.** a) The exciton radiation spectra of the ZnO:Al sample at pumping levels near the threshold; b) The dependence of the integrated intensity on the pumping level for ZnO:Al sample.

The dependence of the integrated intensity on the pumping level for ZnO:Al sample is shown in figure 3(b). Since the estimated size of a pumping spot on the sample is ~200 µm, for the threshold pumping energy of ~ 40 µJ, we obtain the energy density ~ 0.13 mJ/cm² and the power density ~ 13 kW/cm². As we know, it is the record low value. For example, in Ref.[3] and Ref.[4] where ZnO tetrapods were produced by a similar method the thresholds were 0.55 mJ/cm² and 0.815 mJ/cm², correspondingly. Here, it is important to note that comparing the threshold values in the units of energy density for different samples is correct only in case of equal (or at least close) durations of pumping pulses. In other cases it is more correct to compare them in the units of power density.

![Lasing spectra of the ZnO:Al sample](image)

**Figure 4.** The lasing spectra of the ZnO:Al sample at different pumping levels.

In figure 4 the lasing spectra (in range from 386.3 nm to 390.5 nm) registered in a wide range of pumping levels are presented. It is seen that at low pumping levels the short wavelength laser lines are
the most intensive ones. With the increase of the pumping level the intensity ratio increases towards long wavelength lines. Such relative change of the intensities speaks to the dependence of the gain medium on the pumping level. We suggest that it is related to the band-gap renormalization as a result of possible electron-hole plasma formation, which leads to the redshift of the exciton luminescence. Also such shift can appear due to heating of a sample area under the pumping. We will carefully check this in future work.

The nature of the laser resonator in the tetrapod is a crucial point. To our opinion, two possible resonators can exist in the tetrapod. The first one is formed by the pair of tetrapod legs, which can provide closed trajectories of photons [5]. Since in the present case the cross-section along the tetrapod legs changes its shape and size, most likely that the resonator is formed at the bottom of the leg where the cross-section is hexagonal (see figure 5). The appearance of the whispering gallery modes (WHM) is possible in such resonator. For example, such situation was observed in [6] where lasing in microtowers shaped similar to tetrapod legs in the present case was studied.

![Figure 5. The SEM image of the tetrapod with a hexagonal cross-section in its leg.](image)

To summarize, low-threshold lasing was obtained in Al-doped ZnO tetrapods produced by a method of carbolytic carbothermal synthesis. In further work the effect of Al-doping on the threshold value will be studied in detail.

We also observed the relative change in the intensity of the laser lines with the increase of the pumping level, which is probably related to the band-gap renormalization. It is suggested that a hexagonal part of the tetrapod leg forms a possible resonator with WGM.

References

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