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V.M. MARKUSHEV
M.V. RYZHKOV
C.M. BRISKINA✉

Characteristic properties of ZnO random laser pumped by nanosecond pulses

Institute of Radio Engineering and Electronics of RAS, 11, Mokhovaya St., Moscow, 125009, Russia

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ABSTRACT Investigations of UV radiation spectra of powdered zinc oxide and its unordered film were conducted. The samples were pumped by 3-rd harmonics of the two-stage Nd:YAG-laser ($\lambda = 355$ nm) with pulse duration ~ 10 ns. Maximum density of energy of pumping pulses was about 150 mJ/cm^2. With some of our samples, we achieved lasing. The threshold values of the pumping energy density occurred higher than those under picosecond pumping approximately for one-two orders of magnitude. It was shown that the threshold of lasing and the character of lasing spectra depend on the morphology of particles forming a powder. The long-wavelength shift of the maximum of lasing spectra with a rise of the pumping was observed. It was interpreted as a result of participation of electron–hole plasma recombination in the process of lasing. A chaotic character of lasing spectra was observed and partially analyzed.

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1 Introduction

Investigations of light behavior in optically inhomogeneous media represent a significant part of modern physical optics. These investigations include photon crystals, light localization in randomly inhomogeneous media and random lasers. The possibility of laser effect existence in randomly inhomogeneous media was predicted by Letokhov [1] and firstly experimentally demonstrated on the dielectric powders doped with neodymium [2]. Then lasing was obtained and investigated in different random media and, in particular, in the powdered zinc oxide and its unordered films pumped by picosecond pulses [3].

ZnO is the wide band-gap (~ 3.3 eV at room temperature) semiconductor in which the binding energy of the exciton amounts approximately 60 meV. The recombination of excitons in the zinc oxide gives UV radiation in the region 380–390 nm with the intrinsic lifetime shorter than 200 ps. In such situations, it is relatively easy to excite a powder of zinc oxide by picosecond pulses because during the pump pulse spontaneous decay practically does not happen. Quite another situation takes place in the case of nanosecond excitation, which we use in our research. Here the pumping must "surpass" spontaneous decay. In other words initial part of pumping pulse, considerably shorter than intrinsic lifetime, must provide an excitation energy that is enough for lasing. As a result the lasing threshold will rise roughly speaking 50 times, that is approximately equal to the ratio of pulses duration (~ 10 ns) to intrinsic lifetime (< 200 ps).

It is of interest to find out what are the characteristic properties of lasing under nanosecond pumping. In particular, we may expect quasi-continuous lasing, the effect that as yet was not investigated in the powders. At the same time the lasing of powdered ZnO under nanosecond pumping may open the way for working out cathodoluminescent screens with very short persistence time that are necessary for high speed photo registers. Up to now there were no investigations of ZnO random laser with nanosecond pumping except for the paper [4]. However in. [4] where 5 ns pulses pumped pressed powder of ZnO although certain effect was obtained, it was not seriously investigated. As will be shown below, the character of lasing spectra obtained by us is not similar to ones obtained in [4] at all.

So in this communication we will report on lasing in ZnO submicrometer powders and unordered film under nanosecond pumping. We performed the analysis of the threshold and lasing spectra dependence on the morphology of powder grains, reveal chaotic character of lasing spectra and the electron-hole plasma plausible participation in the lasing.

2 Experiment

In our experiments the samples were pumped by 3-rd harmonics ($\lambda = 355$ nm) of the two-stage Q-switched Nd:YAG-laser with pulse duration of approximately 10 ns and repetition rate 20 Hz. For variation of the pumping power with the second stage (amplifier) or without it, we used the set of filters with different transmission at 355 nm. The average pumping power without amplifier was ~ 0.5 mW and ~ 2.9 mW with it. The minimum area of pumping spot was approximately 10^{-3} cm^2. So, available densities of energy were up to 150 mJ/cm^2. In the experiment powdered samples were placed in thin quartz test tubes. All measurements were conducted at room temperature.

The sample emission was directed to the monochromator MDR-23 being in series with photo multiplier (PET-79) or with CCD camera. Accordingly, two technique of registration

✉ Fax: 7-495-203-8414, E-mail: chara@mail.cplire.ru

were used. In the first technique, a photo multiplier connected to boxcar integrator BCI-280 was utilized. A PC registered the resulting signal. The stepper motor operated by the same PC rotated the diffraction grating. The system could accumulate a given number of signals at every fixed wavelength. In the second technique, a CCD camera (Videoscan-285) was utilized in order to register spectra of lasing during a single pumping pulse.

3 Results

In some of the investigated powdered samples, a narrowing of the UV band was observed with a rise of the pumping energy density. At the same time a number of irregular narrow spikes appear on this band. Both these facts we consider as a visualization of lasing in powdered ZnO excited by nanosecond pumping. The same picture was observed for unordered columnar film.

Different samples switch from the amplified spontaneous emission to the lasing (appearance of narrow lines of lasing) in the different intervals of pumping values. The samples investigated significantly differ one from another both by the threshold, by this interval and by the character of the lasing spectra.

At first we investigated lasing spectra using photo multiplier.

3.1 *Results obtained with photo multiplier*

At the beginning we will point out that in our figures that demonstrate the spectra, it is impossible to compare the intensities corresponding to different curves as each curve has its own scale. Micrographs of the samples made by scanning electron microscope (SEM) are represented below in the figures where approximate grain sizes of these powders are indicated.

The lowest threshold ($\sim 2.7\ \mathrm{mJ/cm^2}$) was obtained for the samples #1 (Fig. 1) and #5 (Fig. 3). As it is demonstrated in the Figs. 2 and 4 the spectra of these samples are rather narrow already at $2.7\ \mathrm{mJ/cm^2}$ and when the pumping increases farther they become still narrower and the spikes appear. In the same time the maximum of the spectra shifts to the long-wavelength side. As it can be seen in the figures for other samples this shift takes place for all of our samples; the value of the shift amounts up to ~ 3 nm. From Figs. 2 and 4 it is clear that the lasing spectra of ZnO powders under nanosecond pumping are quite different than ones obtained in [4], where spectra consist of almost equidistant lines in the region from 360 nm till 430 nm.

For all samples investigated chaotic character of lasing was recorded. It demonstrates itself by irregular appearance and disappearance of intensive radiation from shot to shot (The same event was described in [5]). So, the fine structure of the spikes in our spectra can not exactly reflect their real shape since in our method of registration, at different wavelengths the sample emission registered is due to different pumping pulses.

The highest threshold ($\sim 27\ \mathrm{mJ/cm^2}$) was found for the sample #3 (Figs. 5 and 6). For this sample it is characteristic that the switching from spontaneous emission to lasing occurs in wide interval of pumping energy. The other peculiarity

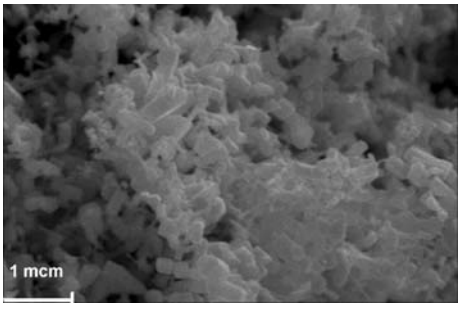

FIGURE 1 Sample #1 (200–500 nm)

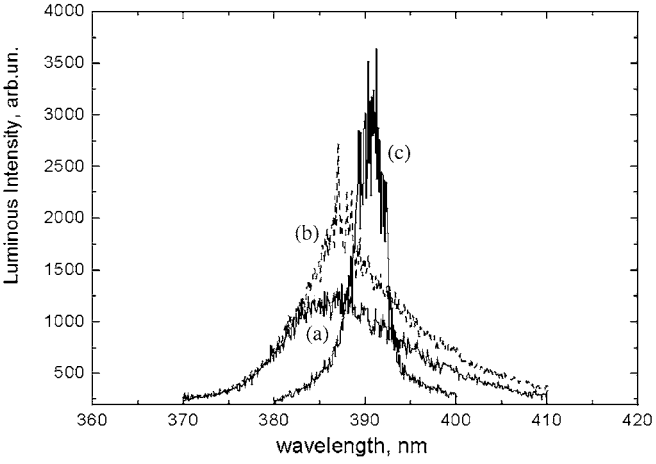

FIGURE 2 UV-emission spectra of sample #1 at different levels of excitation: (**a**) $1.7\ \mathrm{mJ/cm^2}$; (**b**) $2.7\ \mathrm{mJ/cm^2}$; (**c**) $26.7\ \mathrm{mJ/cm^2}$

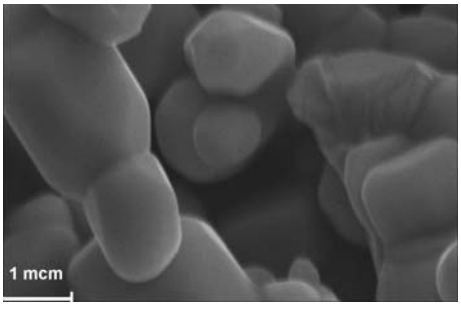

FIGURE 3 Sample #5 (1–3 μm)

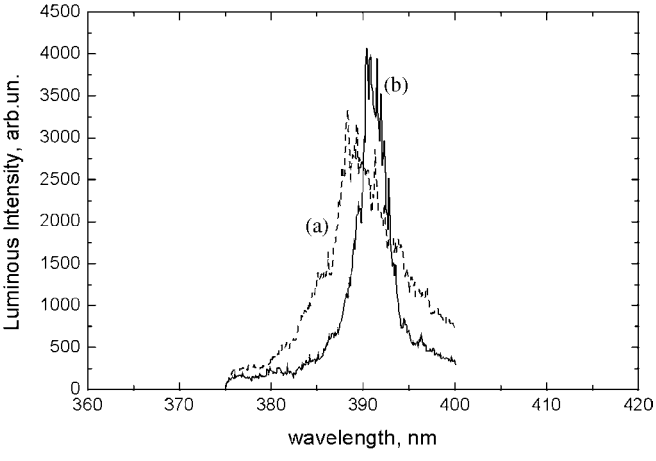

FIGURE 4 UV-emission spectra of the sample #5 at different levels of excitation: (**a**) $2.7\ \mathrm{mJ/cm^2}$; (**b**) $8\ \mathrm{mJ/cm^2}$

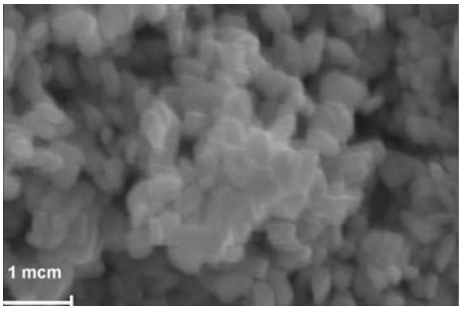

FIGURE 5 Sample #3 (300–600 nm)

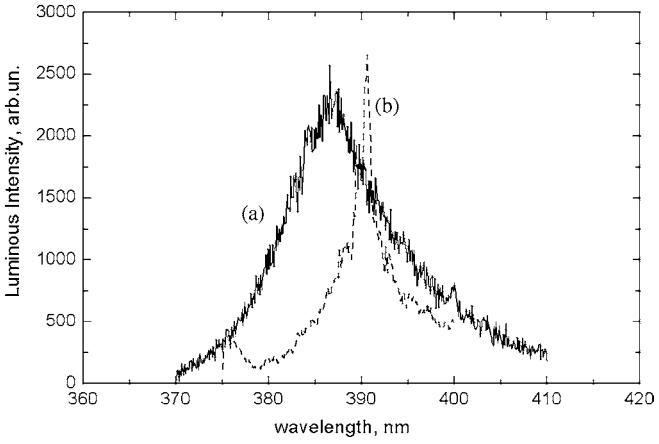

FIGURE 6 UV-emission spectra of the sample #3 at different levels of excitation: (**a**) 27.7 mJ/cm^2; (**b**) 150 mJ/cm^2

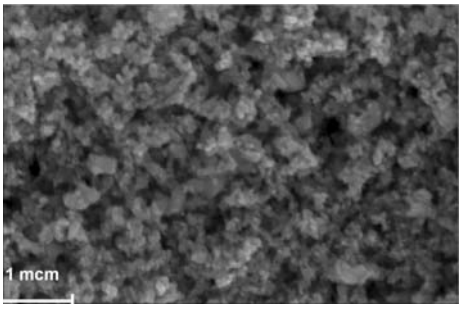

FIGURE 7 Sample #4 (200–400 nm)

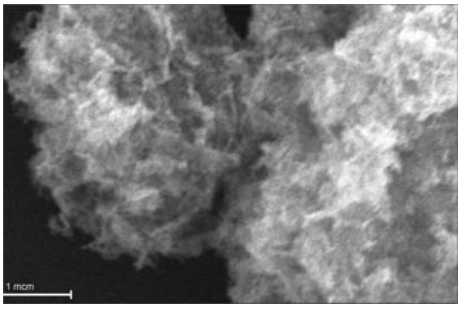

FIGURE 8 Sample #6 (< 200 nm)

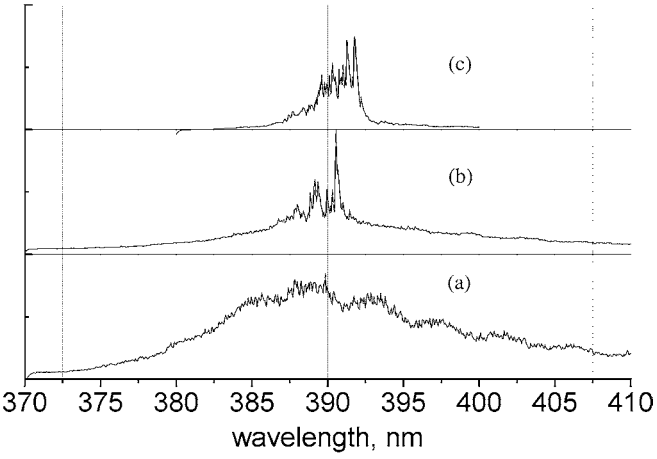

FIGURE 9 UV-emission spectra of the columnar film at different levels of excitation

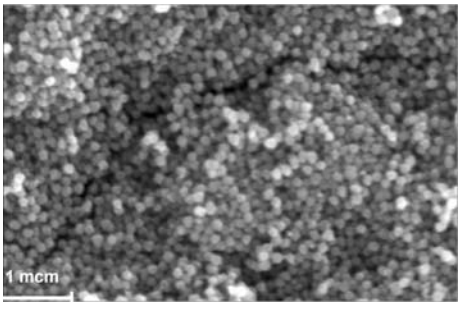

FIGURE 10 Sample #2 (~ 150 nm)

of this sample is practical lack of spikes even at high level of pumping. It seems that here only amplified spontaneous emission takes place.

Samples #4 (Fig. 7) and #6 (Fig. 8) did not lase at all up to maximum available pumping energy density (~ 150 mJ/cm^2).

It is possible to observe that in the sample with high threshold and in samples that did not lase at all there are no well-defined facets of the particles. In the same time such facets can be seen in the samples with low threshold.

UV spectra of unordered columnar film at different levels of excitation are represented in Fig. 9. The character of these spectra does not differ from spectra of the samples #1 and #5.

The most interesting results were obtained with the sample #2 (Fig. 11). This sample is practically monodisperse and its particles represent spheres with diameter ~ 150 nm (Fig. 10). It demonstrates very weak spontaneous emission and a moderate threshold, but when pumping energy increase enough emission intensity sharply increases and the width of the band diminishes. As a result in the spectra only few narrow lines with the width 0.5–1 nm exist. These lines differ from the spikes in the Figs. 2 and 4 significantly. They have almost no pedestal, which is rather large in the case of samples #1 and #5. It is very likely that this pedestal is conditioned by amplified spontaneous emission. It seems that in sample #2 resonant feedback is considerably more effective than in others due to its uniformity and monodispersivity and such powders can be considered as a disordered photonic crystals.

3.2 *Results obtained with CCD-camera*

Attempting to find the cause of lasing spectra chaotic behavior, we have recently used CCD-camera to register lasing spectra during a single pumping pulse. These experiments were performed with the low threshold sample #5. We registered the central part of the spectra – from 384 nm

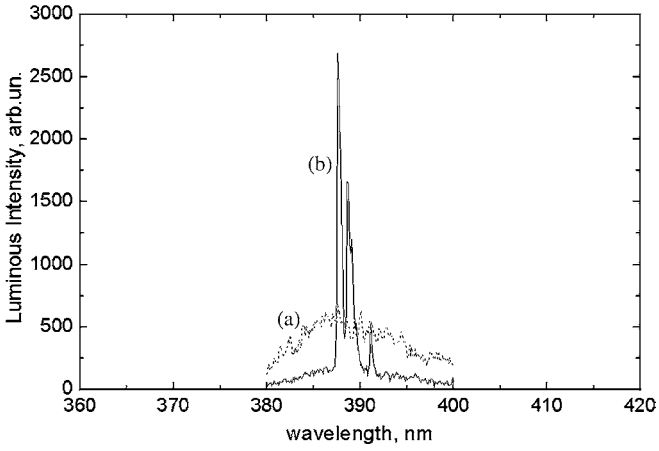

FIGURE 11 UV-emission spectra of the sample #2 at different levels of excitation: (**a**) 2.7 mJ/cm^2; (**b**) 16 mJ/cm^2

up to 396 nm. Some typical spectra obtained are represented in Fig. 12.

It is obvious that these spectra differ significantly from ones obtained with picosecond pumping, see for example [6], where the line width is ~ 0.2 nm. In our case even in the spectrum where individual lines are sharply defined (Fig. 12a) their width is not smaller than 0.5 nm and they overlap each other. Often spectra turned out to be substantially smoothed (Fig. 12b) and sometimes there is wide rectangular-shape band (Fig. 12c). We presuppose that such character of the lasing spectra is the result of wavelength changing in the process of lasing. Since this process is much longer than intrinsic lifetime of working radiation, it can be divided in a several parts with somewhat different wavelengths. These suppositions require special verification in the experiments with the time resolution.

4 Discussion

Let us discuss the origin of UV radiation in our experiments. There are at least two possibilities: exciton recombination and recombination of electron–hole plasma (EHP). The characteristic peculiarity of the spectra obtained by us is the shift of the band maximum to long-wavelength side when the pumping energy increases. It is known that the wavelength of exciton recombination radiation is shifted to the long-wavelength side when the recombination happens in the process of exciton-exciton scattering. (One of two excitons recombines and the other gets over in the excited state). The band corresponding to such recombination (so-called P-line) appearing when the pumping level is high enough does not shift with further pumping rise. But in our experiments continuous shift of the band maximum with the pumping rise was observed. It is similar to the results obtained for ZnO epitaxial thin films in [7].

The authors of [7] interpret their UV spectra as a result of EHP recombination and confirm this interpretation by the comparison with the calculations of the band gap energy shift as a function of carrier density. It is most probably that in our case also EHP recombination takes place since the pumping density is high enough for EHP formation. Actually, energy density 20 mJ/cm^2 corresponds to $\sim 35 \times 10^{15}$ photons/cm^2 for pumping wavelength 355 nm. Suggesting that the penetration depth is ~ 0.1 μ we get $\sim 35 \times 10^{20}$ photons/cm^3. But it is necessary to take into account that pumping pulse duration is much longer than lifetime of carriers. This means that actually maximum carrier concentration will be roughly speaking 50 times smaller. In other words we have as if $\sim 0.7 \times 10^{20}$ photons/cm^3. So, if even only small part of these

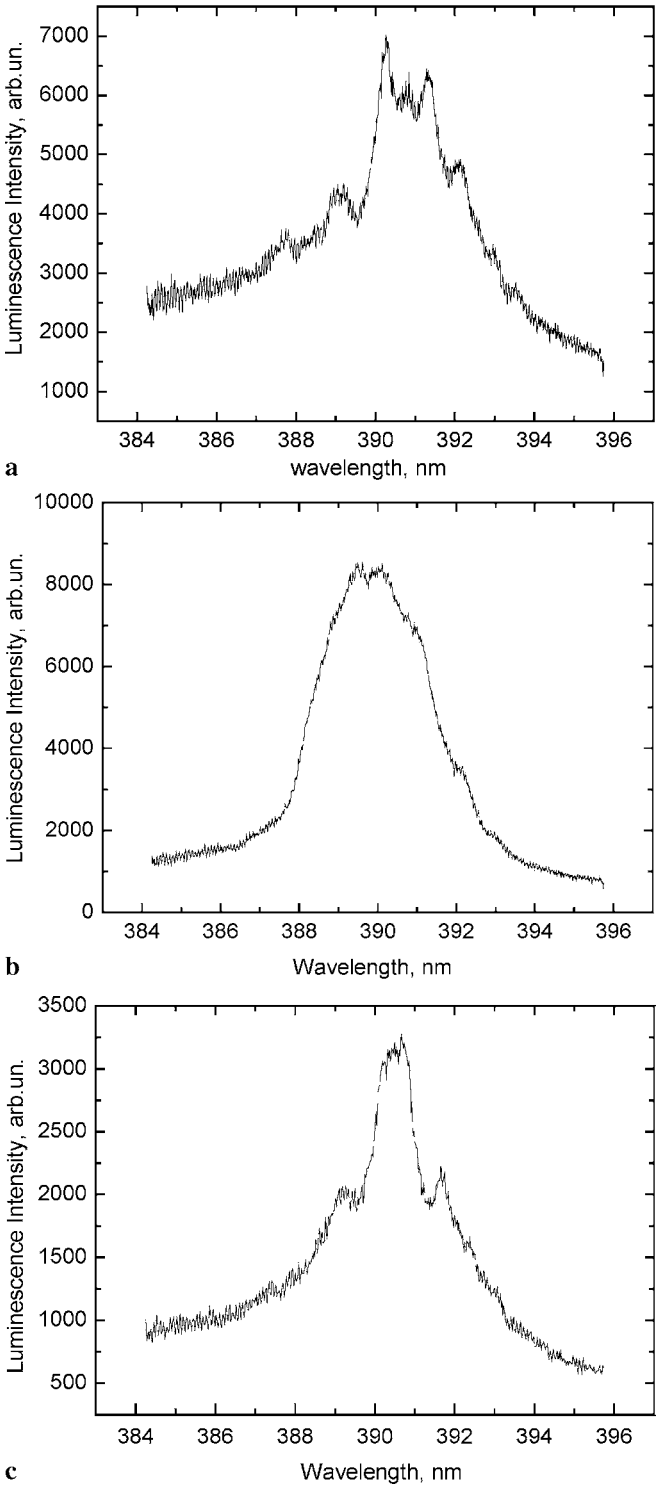

FIGURE 12 Lasing spectra of the sample #5 obtained during single pumping pulse: (**a**) linear; (**b**) smoothed; (**c**) quasi-rectangular band

photons will be absorbed with free carrier generation the concentration of the carriers can be higher than 10^{19} cm^{-3}, that is enough for EHP formation.

5 Conclusion

Spectra of UV lasing for ZnO powders and unordered film were investigated under nanosecond pumping. Some peculiarities of such lasing were revealed.

The threshold energy density of nanosecond pumping turned out to be considerably higher than that of picosecond one. So, under picosecond pumping threshold usually is not larger than 200 μJ/cm^2 while in our experiments at approximately the same area of a pumping spot we got 2.7–26.7 mJ/cm^2. It seems that not only a short intrinsic lifetime of exciton recombination plays a role here but also some other factors. In particular, the long-wavelength shift of the spectra maximum may serve as the evidence of plausible participation of the EHP recombination in the lasing.

The samples investigated differ significantly one from another by the thresholds. Seemingly it is the result of different morphology of the particles forming different powders.

As mentioned above in the sample with high threshold and in samples that did not lase at all, there are no well-defined facets of the particles, but such facets can be seen in the samples with low threshold. The facets' existence can be considered as evidence of relatively good crystallinity of the powder particles. The samples with well-defined facets show relatively lower threshold for the beginning of emission band narrowing, which we consider to be visualization of amplified spontaneous emission (ASE). The same samples also show lined spectra in the region of the band maximum that indicated the existence of the resonant feedback. The samples with poor quality particles demonstrated a high threshold of the band narrowing and no lined spectra, or did not show even any sign of ASE.

At the same time the samples investigated differ by the character of the lasing spectra. This character reflects the proportion of resonance and nonresonance feedback contributions in lasing. From our experimental results it seems that this proportion depends on the particles' form and on their size distribution. Results obtained with the monodisperse sample of spherical particles show that monodisperse powder provide more resonance feedback than polydisperse ones. It manifests itself by practical absence of pedestal in lasing spectra.

The chaotic character of lasing that demonstrates itself by irregular appearance and disappearance of lasing at fixed wavelength from shot to shot was recorded for all samples investigated. Attempting to find out the origin of this effect, we registered the lasing spectra due to single pumping pulse. It was revealed that in these spectra the lines are significantly broader than it was observed under picosecond pumping. This is most probably connected with the changing of lasing wavelength in the process of nanosecond lasing. Since the intrinsic lifetime of radiation provided by the exciton recombination in ZnO (< 200 ps) is much shorter than pumping pulse duration (~ 10 ns) it is plausible that several lasing pulses happen during single pumping pulse. The wavelengths of lasing in these pulses can be different and seemingly random. It is possible that the wavelength changes during single lasing pulse also. To verify such suppositions, it is necessary to do experiments with the time resolution that we plan to perform in future.

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