UV radiation of powdered ZnO pumped by nanosecond pulses

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ABSTRACT

Since the intrinsic lifetime of spontaneous recombination UV radiation in zinc oxide is shorter than ~200 ps, it is of interest to obtain stimulated UV radiation of powdered ZnO with pumping pulses of nanosecond duration. This will clarify the possibility of quasi-continuous laser radiation in disordered media. At the same time, this effect can open the way for the developing of a cathodoluminescent screen with narrow spectrum and short persistence time.

Investigations of UV radiation spectra of powdered zinc oxide and some disordered films were conducted. The samples were pumped by the 3-rd harmonics of the two-stage Nd:YAG-laser (λ=355 nm) with the pulse duration ~10 ns. Maximum energy density of the pumping pulses was about 160 mJ/cm^2. Spectra of spontaneous emission were recordered at 300K and 77K. In some of our powdered samples we achieved lasing at 300K. The threshold values of pumping energy density appeared to be approximately two orders of magnitude higher than those under picosecond pumping. Peculiarities of lasing in different samples are demonstrated and discussed.

In the spectra of ZnO films investigated at 300K, the UV band maximum is situated at ~382 nm, while in powders of ZnO this maximum is located at ~389 nm. Besides, in the films the long-wavelength part of the UV band broadens with increase of pumping power.

Keywords: random laser, powdered zinc oxide, stimulated UV radiation.

1. INTRODUCTION

Stimulated radiation in randomly inhomogeneous media was predicted by Letokhov[1] and firstly experimentally demonstrated in the dielectric powders doped with neodymium[2]. Then laser effect was obtained and investigated in the powdered zinc oxide excited by picosecond pulses[3]. ZnO is the wide band-gap semiconductor (~3.3 eV at room temperature) where the binding energy of the exciton amounts approximately 60 meV. The recombination of excitons in zinc oxide gives UV radiation in the range 380-390 nm, with the lifetime of spontaneous emission less than 200 ps. In such situation it is relatively easy to excite zinc oxide by picosecond pumping because during the pumping pulse the spontaneous emission decay practically does not happen.

A quite different situation takes place in the case of nanosecond excitation, which we use in our research. Here the pumping must leave behind spontaneous decay. In other words, initial part of pumping pulse, shorter than spontaneous lifetime, must provide an excitation energy that is enough for lasing. Below, we give simplified estimation of the rise of the threshold at the transition from picosecond to nanosecond pumping. Under nanosecond pumping we may expect quasi-continuous lasing, the effect that was not investigated in the powders up to now. At the same time, this effect can open the way for the developing of a cathodoluminescent screens with narrow spectrum and short persistence time. There has been only a paper[4] where pressed powder of ZnO was pumped by 5 ns pulses.

Thus, we conducted the investigations of UV radiation spectra of powders and disordered films of zinc oxide manufactured by different techniques. In some of the powdered samples studied a narrowing of the UV band was

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observed with the increase of the pumping energy density. At the same time, a number of irregular narrow spikes appeared on the top of this band. These two experimental effects serve as an evidence of lasing in powdered ZnO excited by nanosecond pumping.

2.EXPERIMENT

In our experiments, the samples were pumped with the 3-rd harmonics (λ=355nm) of the two-stage Q-switched Nd: YAG-laser with the 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 ~0.5mW and ~2.9mW with it. The area of pumped spot on the samples was approximately equal to $9 \cdot 10^{-4}$ cm^2. So, available densities of energy were up to 160 mJ/cm^2.

The detection system consisted of the monochromator MDR-23, the photomultiplier (PET-79), and boxcar integrator BCI-280. The data were acquired by a PC. The stepper motor, operated by the same PC, rotated the diffraction grating of the monochromator. The system could accumulate a specified number of data point at every fixed wavelength.

In the experiment, powdered samples were placed in thin quartz test tubes. The majority of the measurements were conducted at room temperature (300K) and few measurements were made at the temperature of liquid nitrogen (77K). Spontaneous emission was averaged over 4-8 pulses; stimulate emission was normally collected without any averaging.

3. SIMPLIFIED ESTIMATION OF THE THRESHOLD INCREASE

Let us estimate how many times the thresholds of lasing under nanosecond pumping will be greater than under picosecond one. The simplest way is to suggest that the pumping pulses are rectangular. Then the energy of pumping that falls on the sample during the lifetime of spontaneous emission (τ) under a long pump must be equal to the energy of a short pump E_{ps}. Since τ is less than 200 ps and the duration of nanosecond pulses is ~10 ns the energy of a long pump E_{ns} must be more than 10/0.2=50 times greater than E_{ps}.

Somewhat more accurate estimation of the threshold increase with the using of balance equation gives practically the same result. So, simplified estimations show that the threshold density of nanosecond pumping must be approximately 50 times larger than that of picosecond one. Actually it turned out that it is several times larger.

4. RESULTS

We investigated UV emission of powdered samples manufactured by different groups and using different techniques. With the powders, we investigated a series of disordered films of zinc oxide manufactured by thermal or magnetron along sputtering of ZnO on glass, quartz or sapphire substrate. Beforehand, the substrates were coated with a thin (~20-30 nm) layer of metal (In, Ar or Cu). Under the heating of a substrate, the metallic layer forms an assembly of fine droplets. On these droplets columns of zinc oxide grow. The film surface is presented in the micrograph that was made by scanning electron microscope (SEM) in the Institute of crystallography of RAS (Fig.1). In the Fig.2, where a chip of the film is depicted one can see columnar structure of the film.

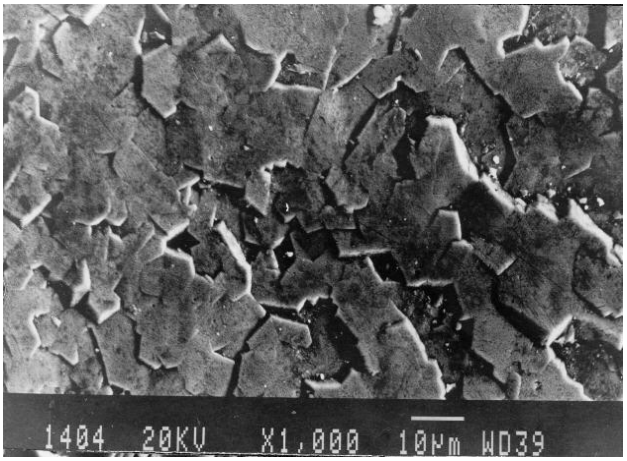

Fig.1. The surface of the film.

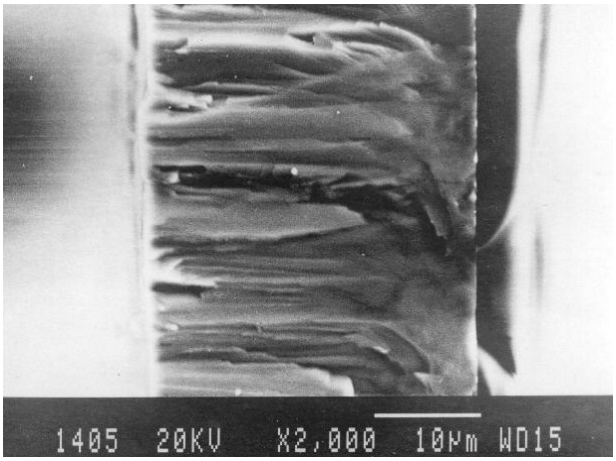

Fig.2. A chip of the film.

4.1 SPONTANEOUS EMISSION

At room temperature, the spectra of spontaneous UV emission of powdered zinc oxide have the maximum at 388-390 nm and the bandwidth of the order of 12 – 16 nm. An example of such spectrum is depicted in Fig.3(a).

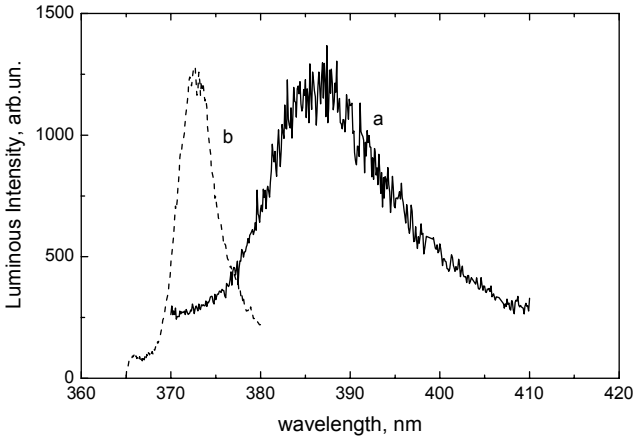

Fig.3. UV-emission spectra of sample #1 at different temperatures: a - 300K; b – 77K

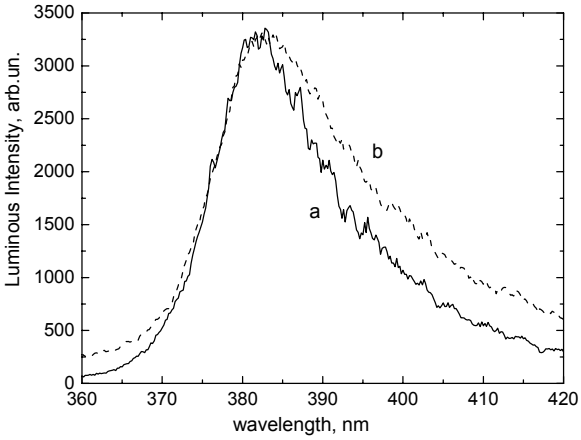

Fig.4. UV-emission spectra of ZnO film at different levels of excitation: a – low level (without amplifier), b – high level (with amplifier)

It was observed that intensity in the maximum of UV band of different samples has a tendency to increase with the increasing of the particle size (in the range between ~150 nm and ~2-3μm).

When the pumping energy increases, the emission bandwidth decreases. (This will be considered in detail in the next subsection). At the temperature of liquid nitrogen, the maximum of UV spectrum is located at 372 nm and the bandwidth is approximately 5 times narrower than that at room temperature, this is demonstrated in Fig.3 (b).

The films investigated were manufactured of the powder (sample #1) but their spectra have maximum at 382 nm and, when the pumping energy increases, their bandwidth does not decrease but widens toward long-wave side (Fig.4). Unfortunately at present we have no idea about the origin of this effect and will study it in future.

4.2 LASING

When the density of pumping energy increases, the stimulated emission arises. It appears in the band narrowing and then lasing arises. Different samples switch from spontaneous emission to lasing in different intervals of pumping energies. The samples investigated significantly differ one from another both by the threshold, by the variation of this interval and by the character of the lasing spectra. Below we present the lasing spectra of samples investigated. It is necessary to point out that it is impossible to compare the intensities corresponding to different curves in the figures since each curve has its own scale. For some of the samples, micrographs made by SEM are presented and approximate sizes of the powders grains are indicated.

The lowest threshold (~2.7 mJ/cm^2) was obtained for the samples #1 (Fig.5) and #5 (Fig.7). As one can see in Fig.6 and Fig.8 the spectra of these samples are rather narrow already at 2.7 mJ/cm^2 and when the pumping increases further they become even narrower and the spikes appear. At the same time, the maximum of the spectra shift to longer wavelengths. As it can be seen in the figures for other samples, this shift takes place for all of our samples, and the value of the shift amounts up to ~3 nm.

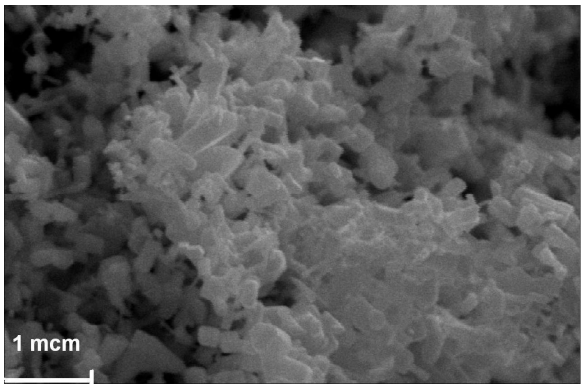

Fig.5. Sample # 1 (0.2 - 0.5 μm)

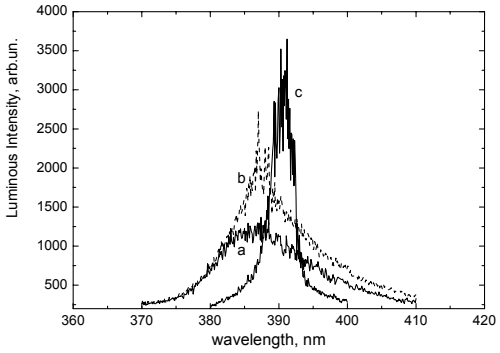

Fig.6. UV-emission spectra of sample # 1 at different levels of excitation: a – 1.7 mJ/cm^2, b – 2.7 mJ/cm^2, c – 27.7 mJ/cm^2 T=300K.

It must be noticed that the spectral positions and intensities of spikes are different from one pumping pulse to another. Chaotic character of lasing that is evidenced itself by irregular appearance and disappearance of intensive radiation from shot to shot was recorded for all samples investigated. The same effect was described in Ref.[5]. Its origin is yet unknown and requires a more detailed study.

Analogous results were obtained in several other samples. One of the characteristic sets of spectra is presented in Fig. 9, where the pumping level increases from Fig. 9a to 9d.

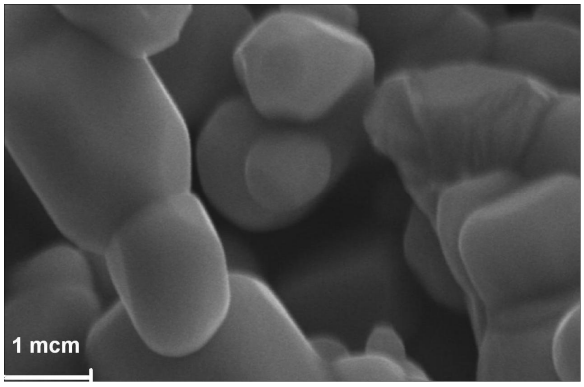

Fig.7. Sample # 5 (1 - 3 μm)

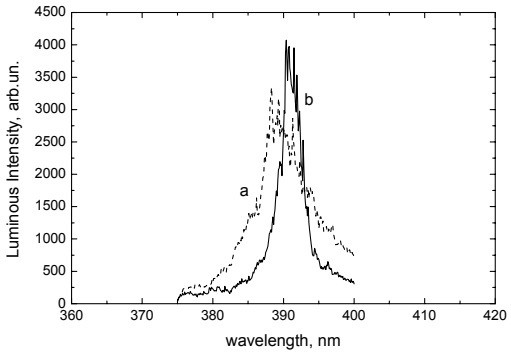

Fig.8. UV-emission spectra of the sample # 5 at different levels of excitation: a – 2.7 mJ/cm^2, b – 8 mJ/cm^2. T=300K.

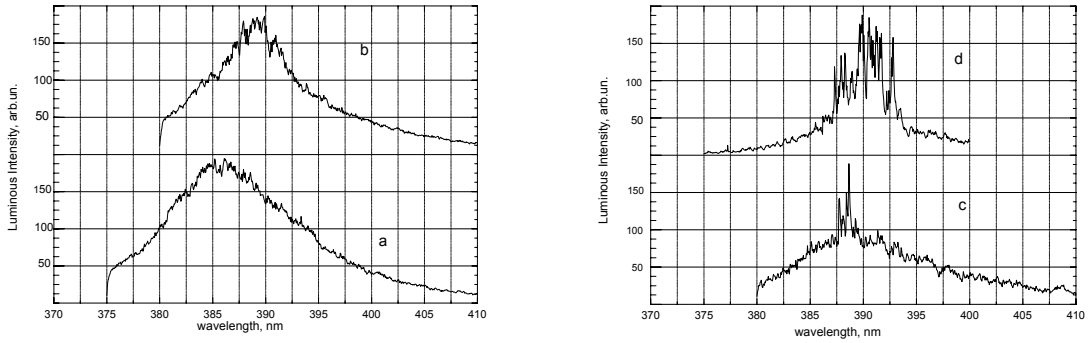

Fig.9. UV-emission spectra of the sample # 7: from *a* to *d* the level of excitation increases. T=300K.

The highest threshold (~27 mJ/cm^2) was found for the sample #3 (Fig.10 and Fig.11). The main peculiarity of this sample is practical lack of spikes even at high level of pumping. It seems that only an amplified spontaneous emission takes place in this case.

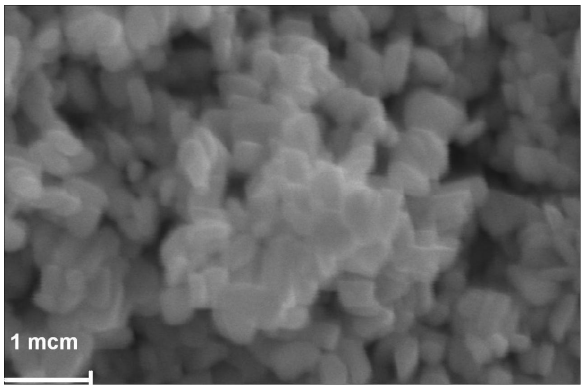

Fig.10. Sample # 3 (0.3 - 0.6 μm)

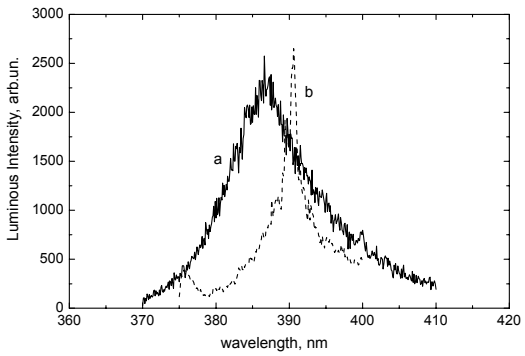

Fig.11. UV-emission spectra of the sample #3 at different levels of excitation: a – 27.7 mJ/cm^2, b – 156.7 mJ/cm^2. T=300K.

Samples #4 (Fig.12) and #6 (Fig.13) did not lase at all up to maximum available energy density ~160 mJ/cm^2.

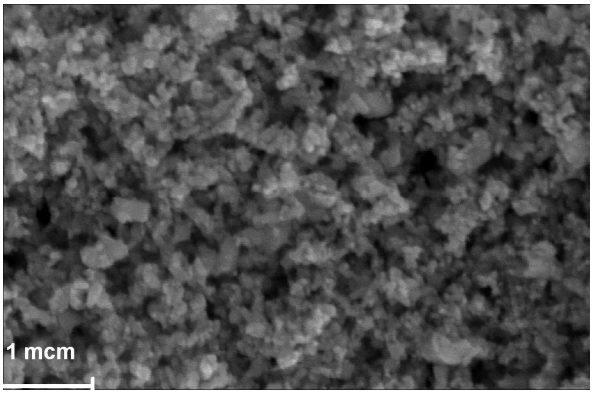

Fig.12. Sample # 4 (0.2 - 0.4 μm)

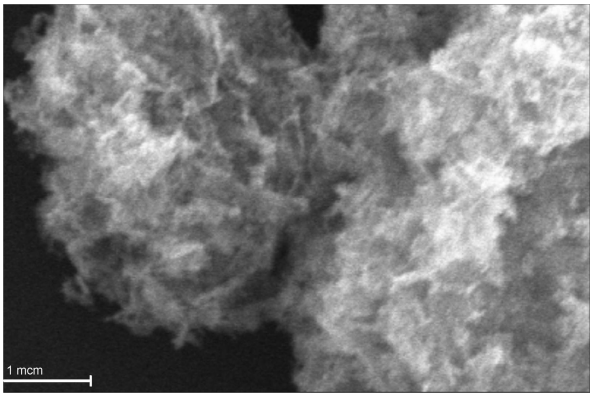

Fig.13. Sample #6 (<0.2 μm)

One should note that the powder particles in samples #4 and #6 have not visible sharp borders similar to those seen in the SEM images of the other samples. Apparently, these powders consist of small particles that are stuck together forming the lumps.

The most interesting results were obtained in sample # 2 (Fig.15). It is practically monodisperse and its particles represent spheres with diameter ~0.15 μm (Fig.14). This sample demonstrates very weak spontaneous emission but when pumping energy increases emission intensity sharply increases and the width of the band diminishes. As the result, only few narrow lines with the width 0.5-1 nm exist in the spectra. These lines differ from the spikes in the Fig.6, 8 and 9 significantly. They have almost no pedestal, which is rather large in the case of samples # 1, #5 and # 7. It is very likely that this pedestal is conditioned by amplified spontaneous emission. It seems that the resonant feedback in sample #2 is considerably stronger than in other samples, due to sample's monodispersivity.

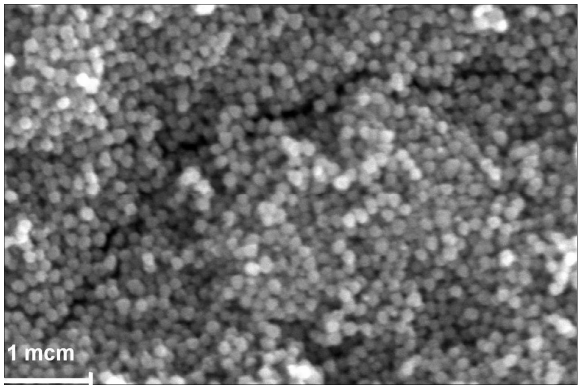

Fig.14. Sample # 2 (0.15 μm)

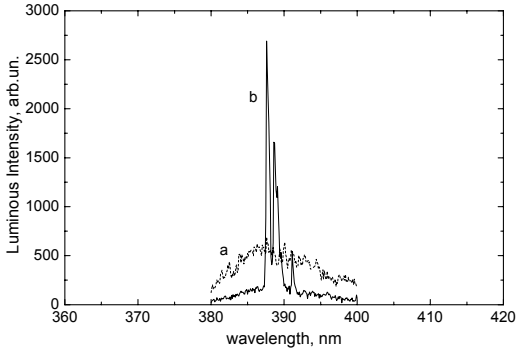

Fig.15. UV-emission spectra of the sample #2 at different levels of excitation: a – 2.7 mJ/cm^2, b – 16 mJ/cm^2. T=300K.

In our method of spectral recording, different spectral points correspond to different laser pulses. The instability of the pumping laser output may lead to the distortion of the spectra. We made all possible efforts to stabilize the pumping power, however a great variation of the emission signal from shot to shot was observed. This variation was significantly greater than the pumping instability could give. We consider these variations as the evidence of the chaotic character of lasing, similarly to that observed in[5]. So we can say that the fine structure of the spikes in our spectra sometimes doesn't exactly reflect their real shape. But some lines recur many times, for example those in the spectra of sample #2, as it is demonstrated in Fig.16. This can be considered as an evidence of real existence of such narrow lines. They may belong to the resonant modes.

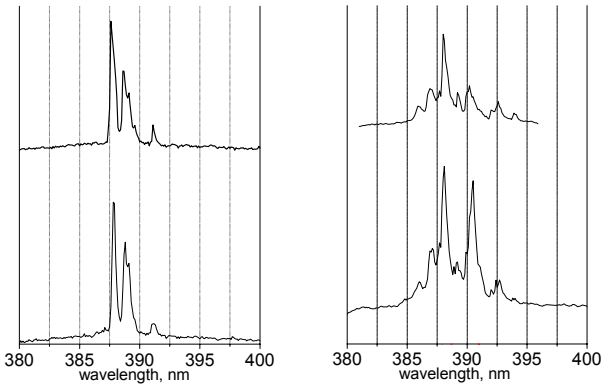

Fig.16. Sample # 2. Comparison of lasing spectra for different shots.
Pumping level 27.7 mJ/cm^2.

5. SHORT DISCUSSION

Now we will briefly shortly 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 occurs in the regime 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 was observed.

The authors of[6] interpret the UV spectra of ZnO thin films as a result of EHP recombination and confirm this interpretation by the comparison of the experimental spectra with the calculations of band-gap energy shift as a function of carrier density. It is most probably that in our case EHP recombination takes place also since the pumping density is seemingly high enough for the EHP formation. Actually, energy density 20 mJ/cm^2 corresponds to approximately $35\cdot10^{15}$ photons/cm^2 for pumping wavelength 355 nm. Assuming that the penetration depth is ~0.1μm we get ~$35\cdot10^{20}$ photons/cm^3. Really to estimate the carriers' concentration it is necessary to take into account the fact that pumping pulse duration is much longer than lifetime of carriers. This means that actual maximum carrier concentration (N_{max}) will be noticeable smaller. To estimate this reduce we can use the approach suggested in Section 3. Since the lifetime of carriers in EHP is shorter than the lifetime of exitons, we'll take for approximate estimation τ=0.1 ns. Than N_{max} is approximately 100 times smaller than the density of falling photons. In other words N_{max} ~$3\cdot10^{19}$ cm^{-3}, that is evidently enough for EHP formation.

6. CONCLUSION

Spectra of UV spontaneous emission and lasing for ZnO powders were investigated under nanosecond pumping. As it should be awaited, 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 we got 2.7-26.7 mJ/cm^2 that is up to hundred times more. It seems that not only a short intrinsic lifetime of exciton recombination plays a role here but also some other factors that yet are of unknown nature. One of such factors may be a role of EHP whose lifetime must be shorter than lifetime of excitons.

The samples investigated differ one from the other significantly by the threshold and by the character of the lasing spectra. It seems to be the result of different morphology of the particles forming different powders.

Chaotic character of lasing that is evidenced by irregular appearance and disappearance of radiation from shot to shot was recorded for all samples investigated. The same effect was described in Ref.[5]. Its origin is yet unknown and requires more detailed study.

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