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ZnO Random Laser Spectra under Nanosecond Pumping

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Abstract—Spectra of ZnO random lasers were obtained using a Peltier-cooled CCD camera Videoscan-285 at a single shot of nanosecond pumping. It was demonstrated that these spectra differ essentially from lasing spectra under picosecond pumping: as a rule, the line widths are significantly larger and the spectra often change essentially from shot to shot in a random manner on the same pumping spot. We suggest that large line widths can be the result of many lasing acts appearing during a single pumping pulse and of the lasing frequency changing in every lasing act. The random variations of spectra from shot to shot can be called forth by spontaneous emission fluctuations.

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1. INTRODUCTION

The possibility of lasing in randomly inhomogeneous media was first predicted by Letokhov in 1967 [1], and experimentally obtained with the dielectric powders doped with neodymium initially in 1986 [2]. After that, lasing was observed in many different random media and, in particular, in the powdered zinc oxide and its disordered films pumped by picosecond pulses [3].

ZnO is a wide band-gap semiconductor ($Eg \approx 3.3$ eV at room temperature), in which the binding energy of the excitons amounts to ~60 meV. The room temperature recombination of excitons in zinc oxide gives UV radiation in the region 385–395 nm with an intrinsic lifetime of less than 200 ps. The same is true for electron-hole recombination in electron-hole plasma (EHP). It could be expected that such a short lifetime may stipulate some peculiarities of ZnO random lasers under nanosecond pumping. The possibility of the existence such peculiarities was confirmed by our previous investigations [4]. In particular, we found that the spectra of such lasers appeared as a manifold of very narrow spikes that, as a rule, was not repeatable. An example of such a spectrum is in Fig. 1. The chaotic character of lasing (irregular appearance and disappearance of intense radiation from shot to shot at the same wavelength) we observed for all samples. The same effect was described in [5, 6].

The main goal of our present investigation is in the study of the spectra of lasing ZnO powders and disordered films. In particular, we hoped to clarify the origin of chaotic lasing. In order to reach such a goal, we used a Peltier-cooled charge-coupled device (CCD) camera (Videoscan-285) that allowed us to register lasing spectra in a single shot of pumping.

2. EXPERIMENTAL

All measurements were completed at room temperature. The powdered samples were placed in thin quartz test tubes and pumped by third harmonics of the two-stage Q-switched Nd:YAG laser (355 nm, ~5 ns, 10 Hz). The maximum pumping energy density was ~70 mJ/cm^2. The pumping spot area was approximately 7×10^{-4} cm^2. It should be mentioned that the intensity distribution inside the pumping spot was not uniform and this nonuniformity was stable from shot to shot, although the total intensity of the shots was not constant.

The image of the pumping spot was focused on the entrance slit of the monochromator with a dispersion of 1.3 nm/mm. One of the output slits was removed and, in its place, the CCD camera was placed. In this situation, the CCD matrix turned out to be slightly behind the position of the output slit. As a result, the CCD matrix (sizes: 8.8×6.6 mm) provided the possibility to register the interval of wavelengths 11.8 nm with a dispersion of ~0.0085 nm/pixel. Our CCD camera could treat approximately three pictures per second; so, under a repetition rate of 10 Hz, it could not register all generation acts.

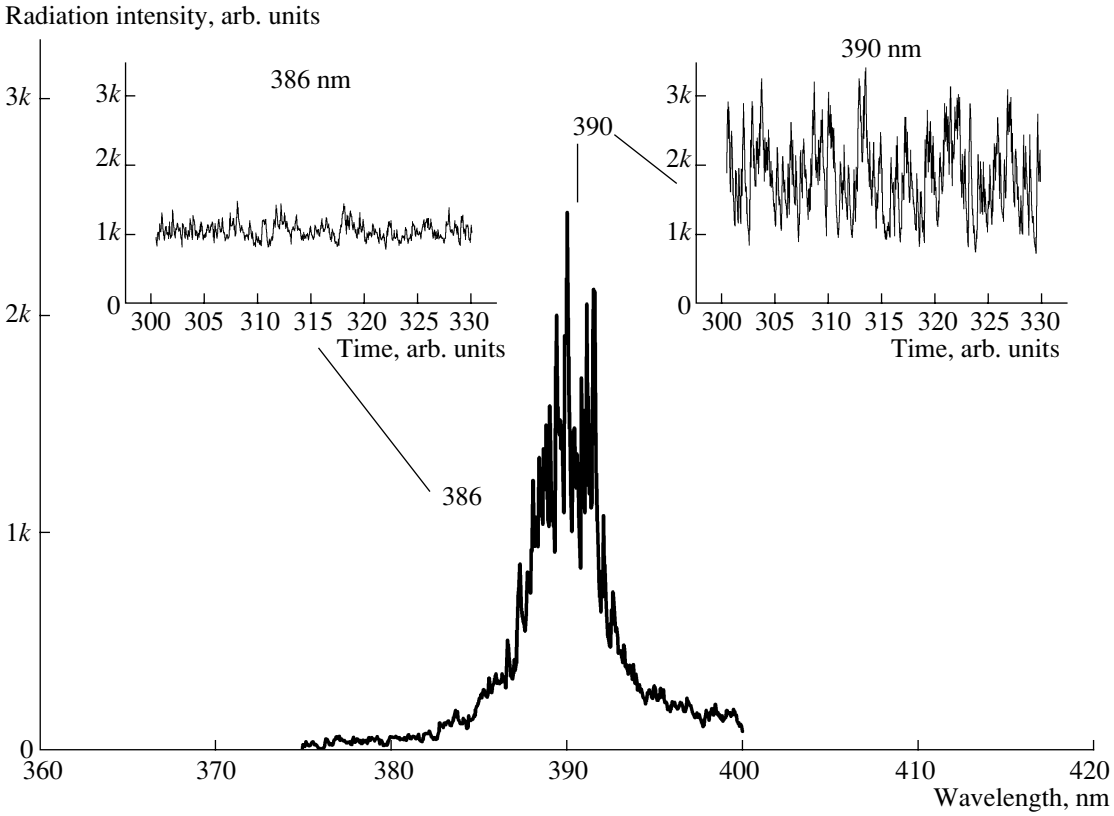

Fig. 1. Lasing spectrum registered with a photomultiplier; insets: time behavior of the signal at a fixed wavelength.

3. RESULTS

At the very beginning of the experiments with the CCD camera, it became clear that the cause of the irregular appearance and disappearance of intense radiation at a fixed wavelength consists of the variations of lasing spectra from shot to shot. Analogous lasing spectra variations were obtained in the ZnO pellet prepared from ZnO powder containing grains with sizes 20–180 nm [7]. In our investigation, it was found that the general character and the variations of lasing spectra from shot to shot are significantly different for different ZnO powders and disordered films. Below, we will divide our results into three parts: (i) monodisperse powder; (ii) polydisperse powder; and (iii) disordered film.

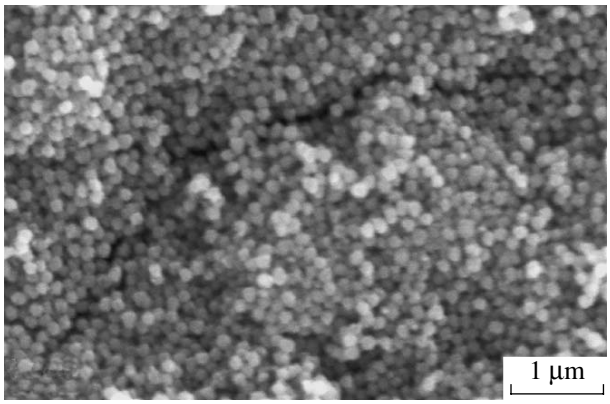

Fig. 2. SEM of the sample USA3.

3.1. Monodisperse Powder

A monodisperse sample (USA3) was prepared at Northwestern University (the United States) [3]. Its scanning electron micrograph (SEM) is presented in Fig. 2. It can be seen that this powder consists of nearly spherical particles with a diameter of approximately 150 nm. This sample gives the most regular and structured spectra, but even these spectra demonstrate shape changes in a random manner. Examples of these spectra for two different positions of pumping spot are provided in Fig. 3.

One can see that the widths of the lines in these spectra are ~1 nm, which is much wider than ~0.2 nm as was obtained under picosecond pumping [8]. In some cases, the picture is even smoothed.

In order to analyze our unstable spectra, we tried to use the following approach:

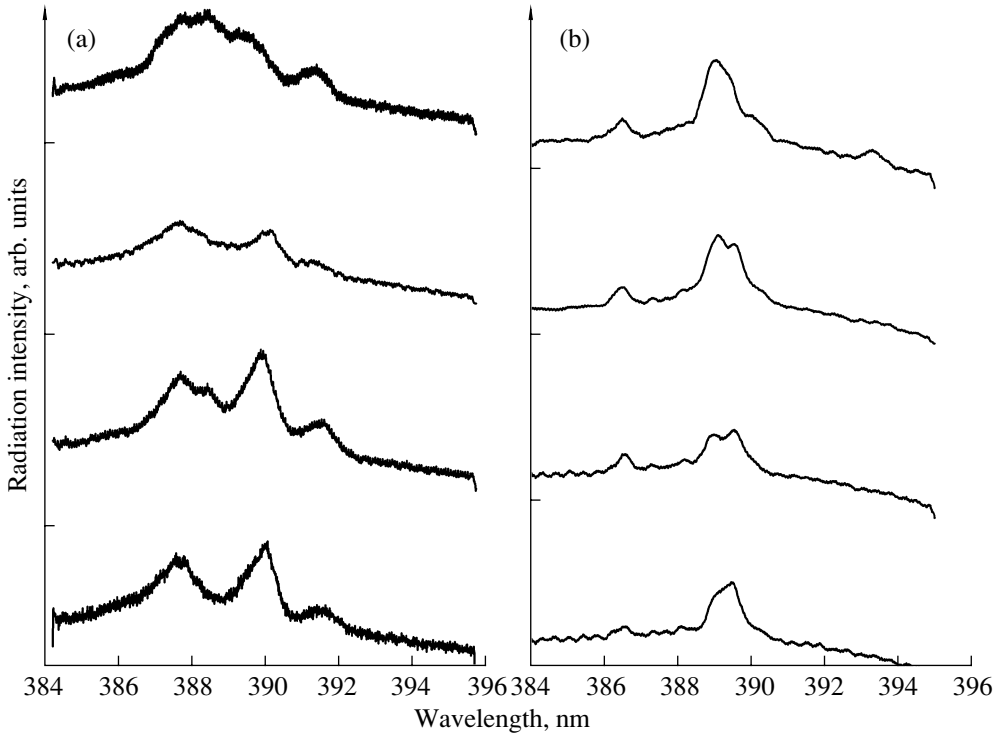

Fig. 3. Examples of USA3 lasing spectra: (a) at the first position, (b) at the second position.

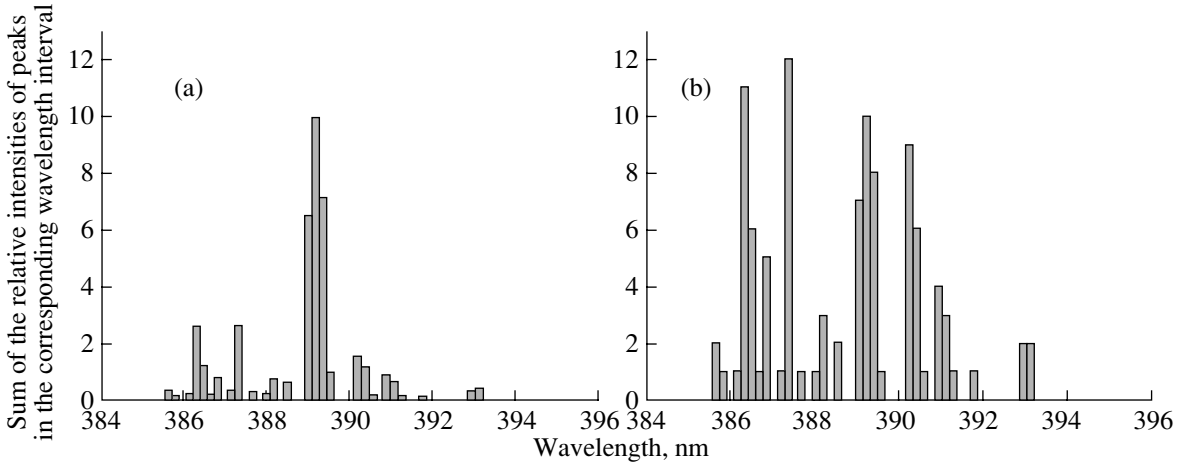

Fig. 4. (a) Spectrum of the sum of the relative intensities of peaks of the sample USA3 at the second position of the pumping spot. (b) Corresponding histogram of the peaks.

• In the series of spectra, we determined the wavelengths of each peak (line) and its intensity related to the highest peak in this spectrum (RI).

• Then, we divided the whole interval of wavelengths, where some lines are in parts (P) with the extension ~0.17 nm, and calculated the sum of RI of all lines that fell into each P.

• We considered the wavelength dependence of these sums as an integral characteristic of the lasing spectra of a given sample at a fixed position of the pumping spot.

In Fig. 4, we show such a spectrum (sum of the relative intensities of peaks) for the monodisperse sample that corresponds to the above-mentioned second position of the pumping spot. For comparison, a normal histogram was also adduced. It is clear that, in our sample, there are several nonoverlapping modes with significantly different qualities. The most frequent appears to

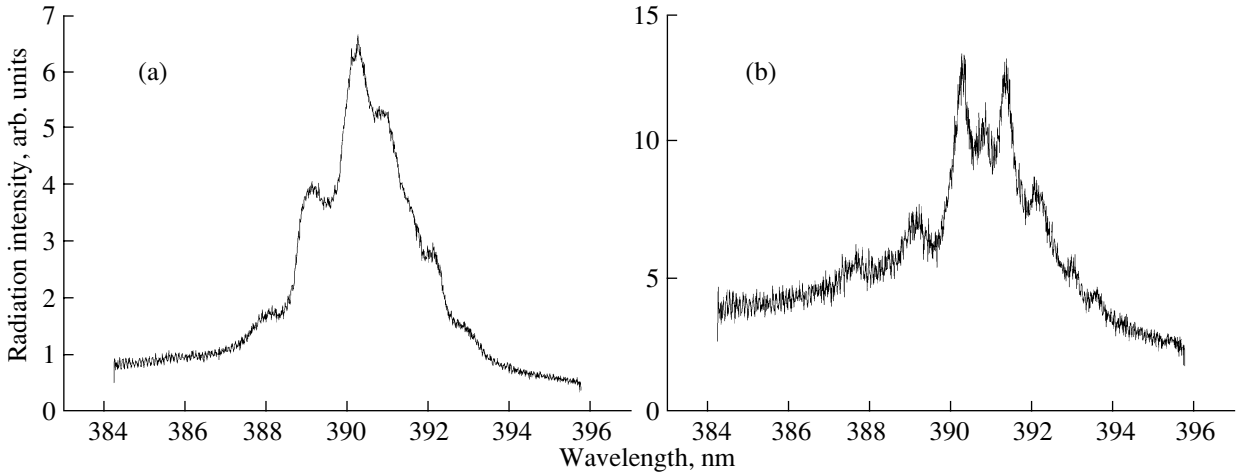

Fig. 5. Examples of polydisperse sample lasing spectra: (a) without structure and (b) structured.

be the most intense mode at ~389.2 nm. Some other modes appear frequently as well, but their intensities are significantly smaller. In part, this could be the result of a smaller gain at the edge of the luminescence band, but the drop in intensity is noticeably stronger than the decrease in the luminescence band. Therefore, we can suggest that these modes have a lower quality factor than the mode at ~389.2 nm.

3.2. Polydisperse Powder

We investigated several polydisperse samples. In some of them (the sizes of powder grains 0.2–2.0 μm), spectra that consiste of one band with a width up to 2–3 nm often appeared (Fig. 5a). The positions of the maximum and the width of these bands randomly varied from shot to shot. Occasionally, structured spectra appeared in certain samples, but there, the widths and positions of the lines seldom repeated themselves (Fig. 5b).

Among the polydisperse samples, we detected some interesting versions of lasing spectra. Thus, in the sample SZ1 (commercial extra-pure powder, Fig. 6), we observed a high-quality mode (line) near 391.5 nm, which appeared very often (see Fig. 7). The width of the large peak was near 0.5 nm.

Recently, we received samples where a narrow line was sometimes observed together with broad ones. One of these samples (SZ5) (Fig. 8) was prepared at Moscow State University from the sample SZ1 by milling followed by annealing. An example of this sample spectrum is in Fig. 9. Here, the width of the narrow line

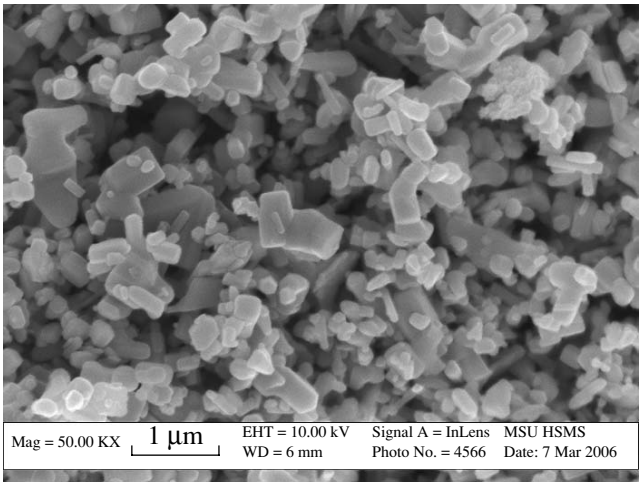

Fig. 6. SEM of the sample SZ1.

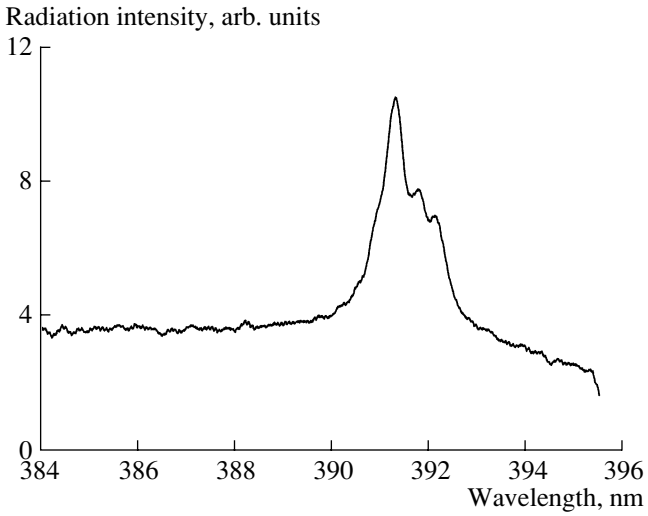

Fig. 7. Lasing spectrum of the sample SZ1.

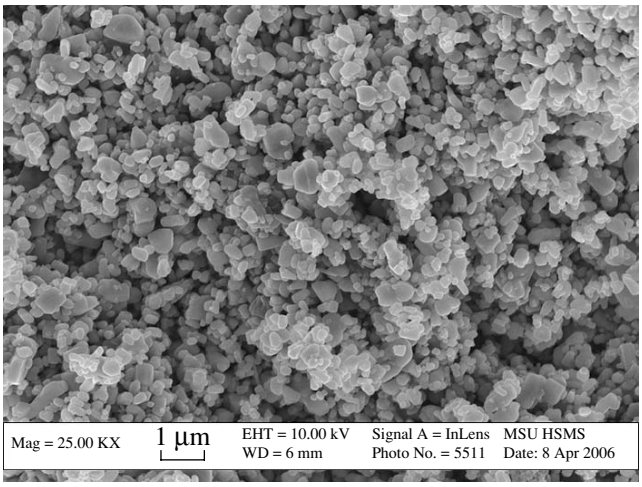

Fig. 8. SEM of the sample SZ5.

is ~0.2 nm. It is near the line widths observed under picosecond pumping.

Below, we present spectrum of the sum of the relative intensities of peaks of the samples SZ1 and SZ5 (Figs. 10 and 11).

From Figs. 10 and 11, it is clear that, in these polydisperse samples, there are practically continuous sets of modes. At the same time, in these spectra, there are intervals of wavelengths where lasing appears more frequently and with a higher intensity. These results mean that the frequency positions of modes (resonances) in ZnO powders are strictly bound to their morphology. However, the essence of this connection is not yet clear.

Some interesting results were obtained with the samples made at Shanghai Institute of Technical Physics of the Chinese Academy of Sciences. These samples were synthesized using the chemical precipitation method. Stoichiometric $ZnCl_2$ was added into the solution of NH_4HCO_3 mixed with lauryl sodium sulfate ($C_{12}H_{25}NaO_4S$). The solution was filtered and the resulting solids were washed several times with alcohol. The precursors were then dried at 50–60°C for 3–4 h, and, finally, the precursors were annealed at 250, 400, 500, 600, and 700°C for 1 h in ambient air or Ar.

It was found that the samples annealed at 250 and 400°C did not laze even under maximal available pumping. The same is true for the sample annealed in Ar at 500°C. All other samples lased. The most interesting are the spectra of the sample annealed in air at 700°C (sample Ch-air700). The SEM of this sample is in Fig. 12 and an example of its lasing spectrum is provided in Fig. 13.

In the spectra of this sample, very narrow lines appeared rather frequently. In Fig. 13, the width of the line 391.8 nm does not exceed 0.1 nm. It is even narrower than the lines that were observed in different ZnO powders in the experiments with picosecond pumping.

The remainder of the samples from this series which demonstrated lasing had higher lasing thresholds and line widths of ~0.5–0.8 nm. The sample that was annealed at 700°C in argon (Ch-Ar700) is substantially similar to the previous sample. Its SEM is in Fig. 14 and an example of the spectrum is provided in Fig. 15. But, such narrow lines appear in the spectra of this sample rather seldomly.

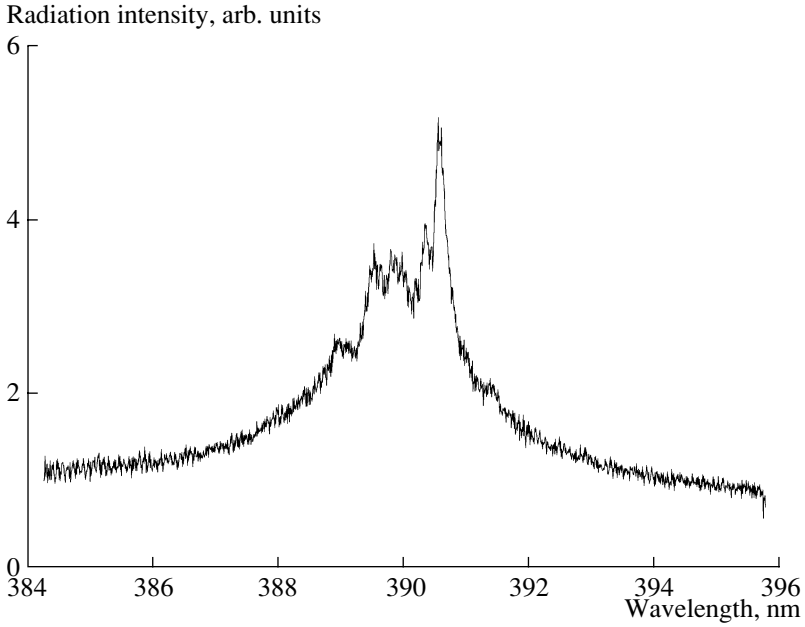

Fig. 9. Example of SZ5 lasing spectrum.

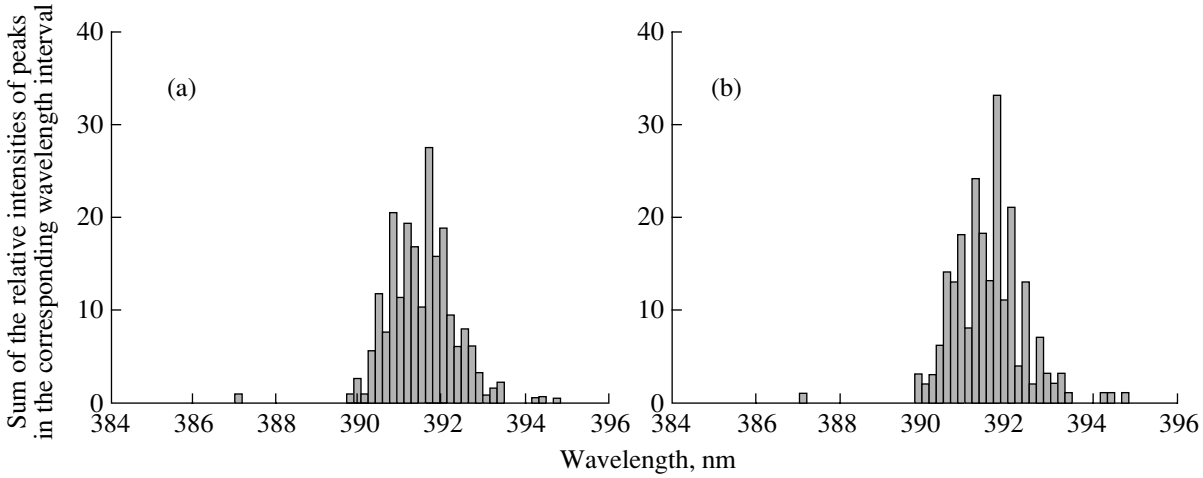

Fig. 10. (a) Spectrum of the sum of the relative intensities of peaks of the sample SZ1. (b) Corresponding histogram of the peaks.

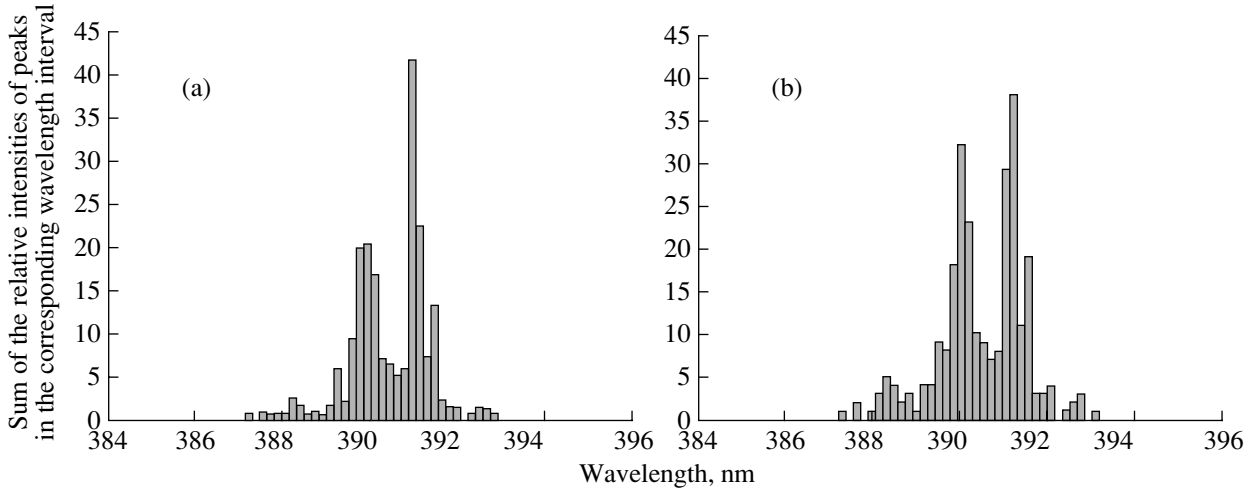

Fig. 11. (a) Spectrum of the sum of the relative intensities of peaks of the sample SZ5. (b) Corresponding histogram of the peaks.

To analyze the lasing spectra of these samples, we examined the spectra of the sum of the relative intensities of peaks obtained according to the procedures described above and the corresponding histograms of the peaks (Figs. 16 and 17).

From Figs. 16 and 17, it is clear that, together with the continuous collection of modes in these samples as in samples SZ1 and SZ5, certain preferred modes exist. Here, again, one can see the relation between the collection of lasing modes and the morphology of the powders.

Here, it is important to mention specifically that, in this section, we observed an interesting effect—the appearance of single narrow lines in the lasing spectra of certain samples that are thoroughly annealed. As is known, annealing provides a good crystallization and lack of defects, and, as a result, enhances the quality of the powder grains. On these grounds, it is possible to suggest that the narrow lines observed correspond to the modes concentrated mainly within the grains of the powder.

3.3. Disordered Film

For disordered films, we used films with a columnar structure that were prepared at the Institute of Crystallography of the Russian Academy of Sciences. The technology for the growth of such films was as follows: ZnO powder was precipitated from the gas phase at 600–700°C on an amorphous substrate with a previously made microrelief of a seeding material. The columns are placed at a right angle to the substrate; their diameter and the film thickness are determined by the duration of crystallization. The lasing spectra of such films are even more smooth than the spectra of polydisperse powders (Fig. 18).

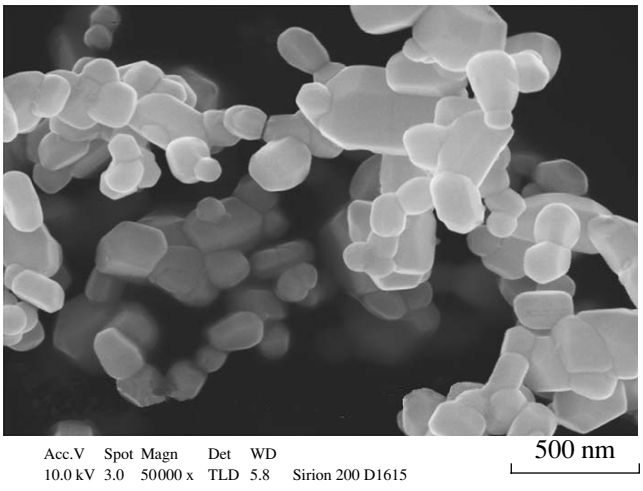

Fig. 12. SEM of the sample Ch-air700.

It may be mentioned that, although the form of bands in Fig. 18 is similar to the band of ASE, the position of the band maximum changes from shot to shot. Therefore, these bands seemingly are a result of many overlapping lazing modes.

4. DISCUSSION

In our experiments with the nanosecond pumping on a relatively large pumping spot, we found that the lasing spectra of ZnO powders and disordered films have the following peculiarities:

(1) As a rule, the line widths are significantly larger than under picosecond pumping.

(2) Often, the spectra essentially change from shot to shot in a random manner on the same pumping spot.

The simultaneous presence of wide and narrow lines in certain lasing spectra shows that heating can hardly be the cause of line broadening under nanosecond pumping. We suppose that large line widths are due to the existence of several lasing acts during every pumping shot, since the intrinsic lifetime of exciton recombination and recombination of electron-hole plasma in ZnO (<200 ps) is significantly shorter than the pumping pulse duration, which amounts to several nanosecond. It is also very plausible that, during each lasing act, the frequencies of some modes (lines) slightly change as was observed under picosecond pumping in [9]. To verify these suppositions, we are preparing experiments with the time resolution of spectra.

Preliminary result is represented in Fig. 19, where a strongly enlarged image of the CCD matrix is given. Here, the lasing pulse of the sample Ch-air700 is registered. In this figure, in the horizontal direction, the parameters are 0.085 nm per 10 pixels, while in the vertical direction, these are 100 ps per 6 pixels.

In Fig. 19, it can be seen that some bright traces are inclined. This means that the wave length of some lasing modes changes in the course of generation as we supposed. It should be mentioned that the relatively large size of the pumping spot also provides the existence of many modes there.

The problem of the origin of lasing spectra randomness (from shot to shot) is complex enough. The smooth

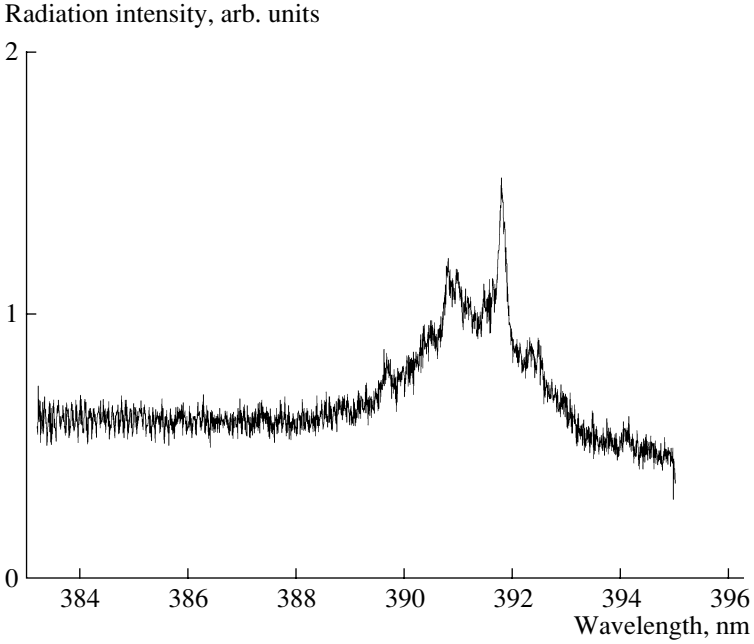

Fig. 13. Example of lasing spectrum of the sample Ch-air700.

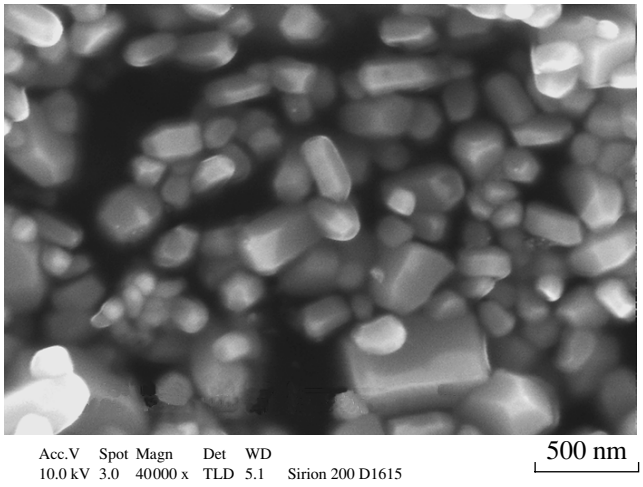

Fig. 14. SEM of the sample Ch-Ar700.

and random character of the lasing spectra of the films shows that the smoothing and randomness of lasing spectra of the powders are not a result of powder grain movement during the pumping shot.

An interesting idea about the origin of lasing spectra randomness is given in [10], where random changes of the lasing spectra from shot to shot were experimentally observed in a dye solution with scatterers. Modeling light transport through a random amplifying system by a random walk (using the Monte Carlo method), the authors obtained spectra that are similar to the experimental ones. As a result, they consider lasing as the process of spontaneous photon amplification on very long paths in a random media with a gain. "In this phenomenon, shot to shot spectra are intrinsically different due to the inherent randomness in the spontaneous emission process," write the authors. Of course, the validity of this idea for ZnO powders, where, as it follows from experimental results, resonance effects are definitely present requires detailed follow-up analyses.

From our point of view, lasing spectra randomness must be connected with certain fluctuations that are significant for this process. In particular, the number of spontaneous photons participating in the build-up of laser emission of any mode may fluctuate from shot to shot and lead to variations in lasing spectra. In order to verify such a supposition, simplified modeling of the lasing process through the use of the Liouville quantum equation for the density matrix and reduced Maxwell equations for the electromagnetic field was performed. Preliminary calculations show that, if modes don't overlap with each other, spontaneous emission fluctuations are really significant when the pumping power is near the threshold value. Under a high-pumping power, spontaneous emission fluctuations don't play an important role in this case. But, when overlapping takes place and different modes are working, even if partially, at the cost of the same radiation sources, spontaneous emission fluctuations become very considerable. Details of the modeling and its results will be described and discussed elsewhere.

A comparison of spectra of the sum of the relative intensities of peaks for mono- and polydisperse samples allows us to say that the number of lazing modes in polydisperse samples is considerably higher than in the monodisperse samples. From this fact, we can conclude

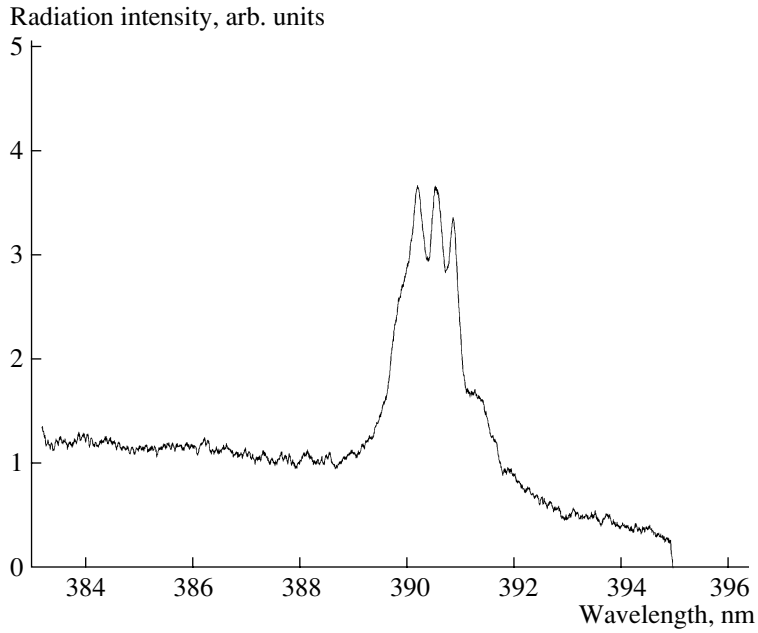

Fig. 15. Example of lasing spectrum of the sample Ch-Ar700.

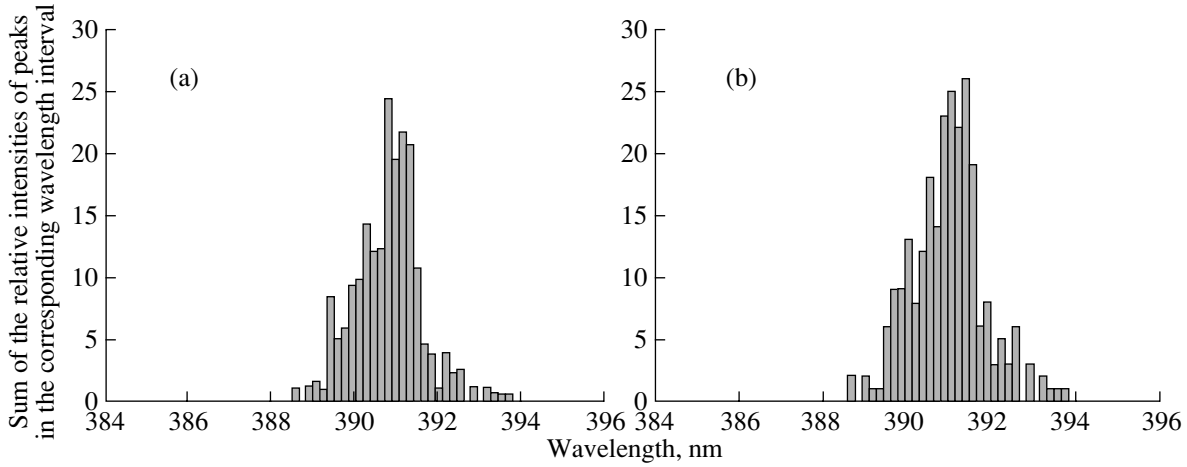

Fig. 16. (a) Spectrum of the sum of the relative intensities of peaks of the sample Ch-air700. (b) Corresponding histogram of the peaks.

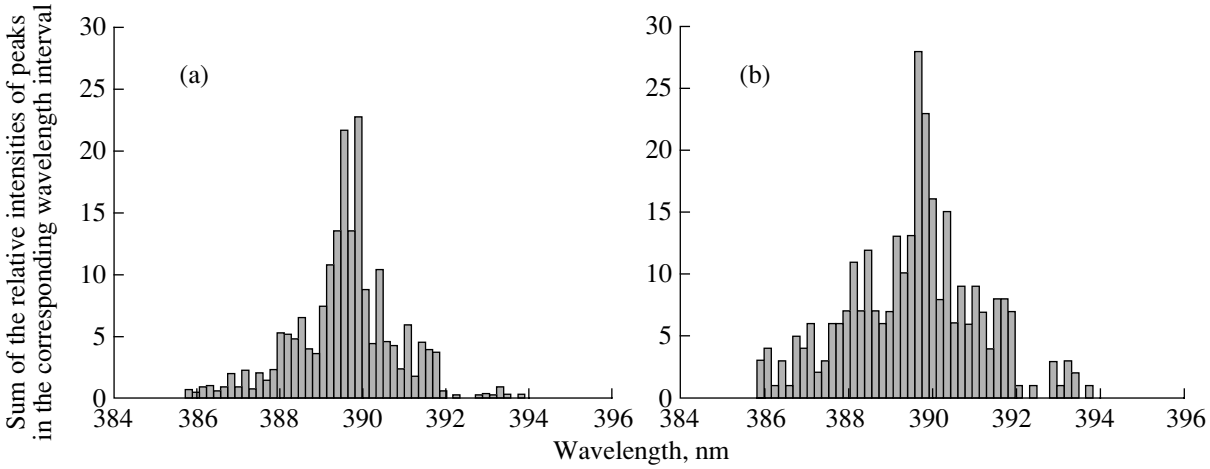

Fig. 17. (a) Spectrum of the sum of the relative intensities of peaks of the sample Ch-AR700. (b) Corresponding histogram of the peaks.

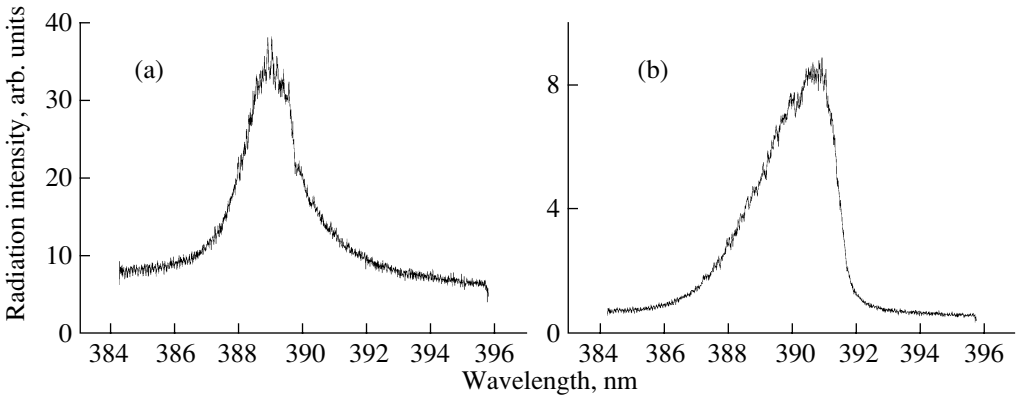

Fig. 18. Examples of the lasing spectra of columnar film.

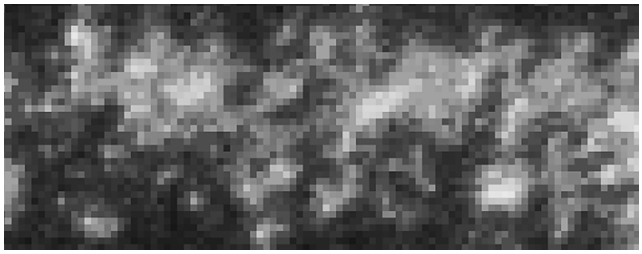

Fig. 19. Spectrum of the sample Ch-air700 lasing pulse with time resolution (preliminary result).

that the probability of modes overlapping in the case of polydisperse samples is much higher. Correspondingly, spectra variations due to spontaneous emission fluctuations may be more expressed in the polydisperse samples. This is in accordance with the experiment.

The other possible cause of the lasing spectra randomness may be the random walk of excitons, electrons, and holes during the time interval between the lasing acts. Such a walk may produce random distributions of the radiation sources that mean random initial conditions of the serial acts and random distribution of the gain.

5. CONCLUSIONS

Investigations of ZnO random laser spectra due to a single shot of nanosecond pumping were performed using a Peltier-cooled CCD camera Videoscan-285. It was found that these lasing spectra of ZnO powders and disordered films noticeably differ from lasing spectra obtained under picosecond pumping: as a rule, the line widths are significantly wider; the spectra essentially change from shot to shot in a random manner on the same pumping spot.

We suppose that large line widths are due to the existence of several lasing acts during every pumping shot and that, during each lasing act, the frequencies of some modes (lines) slightly change. In order to verify these suppositions, we are preparing experiments with a time resolution of the spectra.

We suspect that the randomness of lasing spectra is stipulated by the fluctuations of a spontaneous photon numbers participating in the build-up of laser emission of any mode. This idea is confirmed by simplified modeling of the lasing process.

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