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The manifestation of ordered generation in a disordered environment of ZnO whiskers

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Laser generation in disordered systems based on arrays of ZnO nanocrystals of various morphologies obtained by the original hydrothermal method is studied. It was found that in a visually disordered system of nanocrystallites, a limited number of agglomerates playing the role of optical resonators may exist. Resonators can be considered as a closed structure generating radiation with certain repetitive parameters. The parameters and morphology of such resonators, as well as the nature of the laser radiation generated by them, are discussed.

Keywords: zinc oxide, hydrothermal synthesis, nano crystals, ordered and disordered generation, resonators.

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1. Introduction

Zinc oxide due to its unique electronic and optical properties (band gap in UV-range and large bond energy of excitons) draws researches interest for long time. Different nanostructures based on ZnO (nanowhiskers, nanorods, thin films etc.) can be assumed as promising candidates to create laser devices of micrometer size. Especially actual the studies of optical resonators are, in particular, formed by self-organizing micro- and nanostructures (arrays of nanocrystals, nanocrystallites, nanowhiskers, nanotubes, etc.). In such resonators simultaneously benefits are implemented of both radiative recombination in material as internal light source, and resonator, formed by the structure itself. Studies of laser generation (LG) in such structures arise the issue whether the stimulated radiation of such ensemble is only sum of contributions of single nanorods or it is cooperative in the sense of random generation [1].

The literature describes studies of accidental (spontaneous) LG observed in different, mainly, disordered systems ZnO, such as, nanorods, powders, nanotubes etc. [2–8].

In all described cases the resonator, obviously, is accidental group of single whiskers or nanocrystallites, acting as scattering centers, which results in generation of optical radiation on arbitrary tracks. In major of described cases the occurrence of arbitrary LG means observation in samples radiation of narrow overshoots corresponding to laser modes formed in occasional medium. Radiation in major cases has no specified direction. The spatial pattern of radiation varies from frame to frame at nominally equal conditions, due to this uncertainty occurs in calculation of accurate parameters of the resonator.

On other hand, we actively study the generation observed most frequently on single nanorods, nanowires or whiskers ZnO [9–12]. I this case the whisker having definite geometry can act as resonator. Photons in such system are limited by total internal reflection at ZnO-air interface, which significantly increases the generator Q factor. The radiation of such system demonstrates the presence of a well-developed mode structure.

In this paper, we study laser generation in disordered systems based on ZnO nanocrystallite (whisker) arrays obtained by an original hydrothermal method [13]. The parameters and nature of both the laser radiation itself and of the optical resonators that cause it are discussed.

2. Samples and experimental technique

Photoluminescence (PL) studies were carried out in a closed-cycle helium cryostat manufactured by Janis Research Company in the temperature range 5−300 K. MDR-204-2 (LOMO-Photonics, St. Petersburg) double monochromator with a dispersion of 25 A/mm was

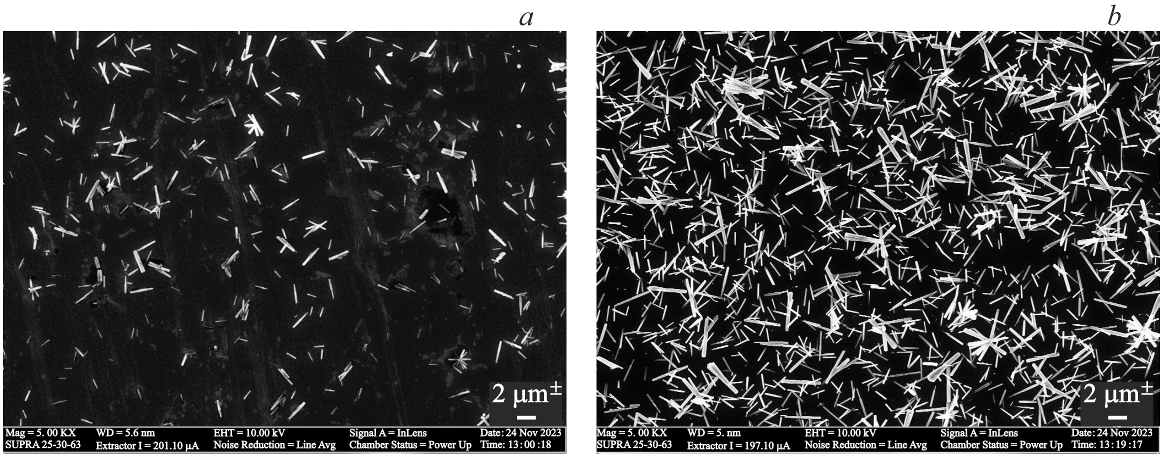

Figure 1. SEM-image of two points of surface of studied object ZnO.

used. PL spectra were excited by UV solid-state laser LCM-DTL-374QT ($\lambda = 355$ nm). Emission power, W, varied in the range from 1 to 600 kW/cm^2. Direct-geometry studies were conducted.

The original hydrothermal method for obtaining ZnO samples on a silicon substrate is described in detail in [13]. Images were obtained using Supra 25 Zeiss scanning-electron microscope (SEM).

In the present paper one of such samples is studied. The surface of the sample is made of nanorods (nanocrystallites) with different orientations on the surface of the silicon substrate and with average sizes of $l \sim 1-2$ mkm and $d \sim 100$ nm (Figure 1). Nanocrystallites are scattered over the sample in a heterogeneous manner. Not only the density of filling the surface with nanorods varies from point to point, but also the sizes and type of structured formations. In some cases they form visually random or structured clusters.

3. Results and discussion

A series of measurements of PL spectra was made for different points on surface of described above sample ZnO at low temperature ($T = 5$ K) and high (up to ~ 600 kW/cm^2) excitation power of laser. It was identified that on major part of surface PL spectra are rather similar and correspond to common radiation of ZnO under strong pumping. In radiation wide smooth band with maximum $\lambda \sim 371$ nm is observed [14]. But in some selected points of sample the pattern of radiation abruptly changes. On long-wave edge of the band 371 nm in region starting from 374 nm, in some points from 372 nm, and further, narrow (1.6−1.9 meV), practically equidistant peaks occur (Figures 2, 3). At different points of the sample the number, intensity and spectral composition of the peaks differ, but the spectral region of the radiation and the general nature of the spectra remain practically unchanged. Distance between peaks on average is 0.3−0.5 nm.

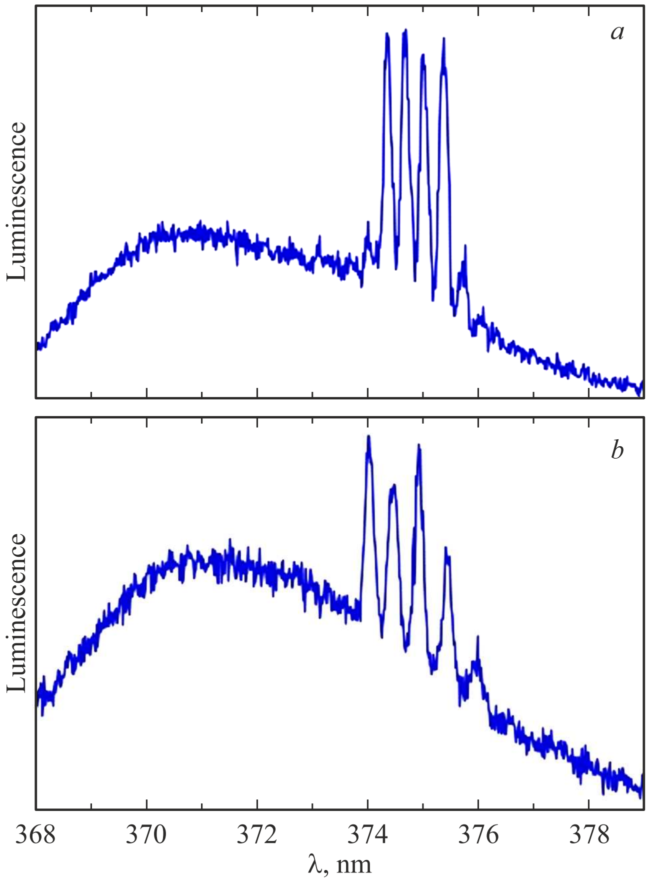

Figure 2. PL spectra of two different selected points on surface of sample ZnO.

Well developed mode structure of spectra confirms occurrence in specific selected points of sample stimulated by laser generation with rather low (~ 55 kW/cm^2) (Figure 3) excitation threshold. Figure 3 shows radiation of one of such points below (curve *1*) and above (curves *2−5*) of generation threshold.

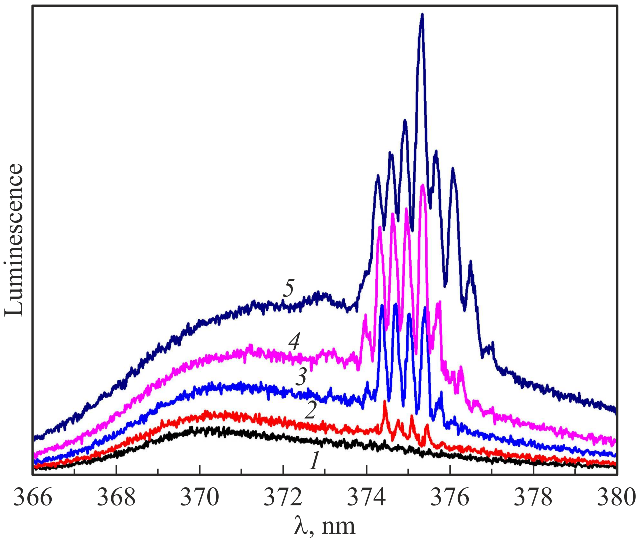

Figure 3. Spectra of photoluminescence of selected point of sample ZnO at different powers of pumping W. *1* — $W = 45.5$; *2* – 68; *3* — 93; *4* — 146; *5* — 311 kW/cm^2 and $T = 5$ K.

As it is known [14], with increase in the excitation intensity in the PL spectrum of ZnO, radiation of exciton molecules, bands of exciton-exciton interaction (P-process) occurs, and at maximum intensity the radiation of electron-hole plasma occurs. PL spectra significantly changes. The exciton radiation disappears due to excitons screening, and in PL spectra of ZnO the band with maximum near 374 nm occurs. Apparently, just with this band in our samples the laser generation is associated.

The appearance of the spectra and the low excitation threshold most likely indicate ordered generation with the formation at given point of the sample of either ordered structure of whiskers (nanocrystallites) forming the closed resonator, or the existence of single whisker as the resonator. On other hand, photos of sample surface demonstrating chaotic location of ZnO whiskers suppose rather disordered resonator, with generation of the optical radiation at tracks similar to occasional.

To clarify structure parameters the additional experiments were executed. It was detected that all selected points of sample surface demonstrating LG presence, similar to those presented in Figures 2 and 3 are stable, and spectra of their PL can be repeated during new independent experiment upon photographic evidence of point position on sample surface during initial study. Comparison of PL spectra showed that spectral composition of radiation obtained at different time from same point practically coincide exactly, this ensures statement of repeatability of the experiment i.e. fixed (nonrandom) position of the resonator on surface and its stable parameters, this is impossible for the random generation.

Thus, there is good reason to speak about the occurrence of stable closed resonator at individual points of the sample,

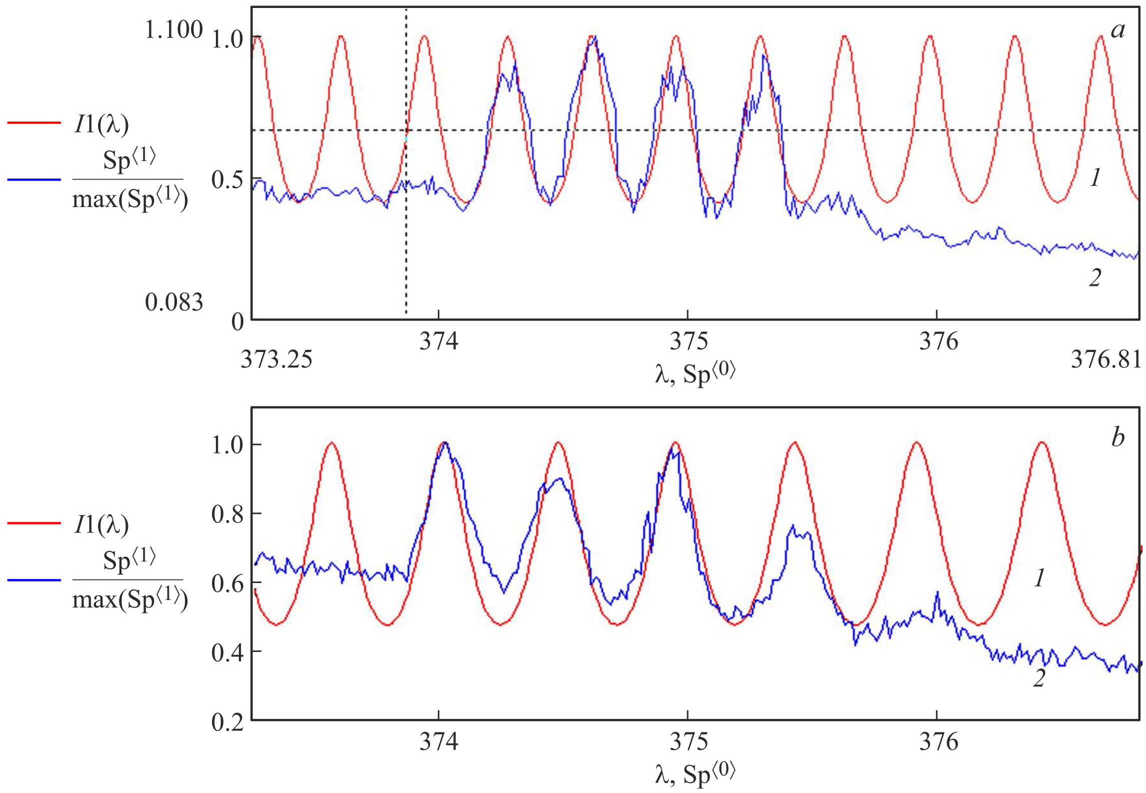

Figure 4. Calculation results of resonator parameters, performed for point **a** (*a*) and point **b** (*b*) from Figure 2; *1* — calculated curve, *2* — experimental PL spectra of selected point.

in the resonator a resonant standing optical wave can be formed, and it can be described by the Fabry-Perot resonator model. Further discussions means making such resonator model based on its parameters, calculated based on experimental results.

So, parameters of mode structure of our spectra are similar to LG on single rods ZnO [9–12]. Calculation of resonator parameters based on Fabry-Perot model at intermode spacing $\Delta\lambda \sim 0.3-0.45$ nm and considering refraction index ZnO in this spectral region ($n \sim 2.59$ for $\lambda = 373.5$ nm and 2.513 for $\lambda = 375.65$ nm) [15], in our case gives resonator size at least $\sim 60-100$ mcm, this is not contrary to the experimental data obtained on single ZnO whiskers earlier [9,10]. However, SEM-images of the surface of our sample (Figure 1) show the absence of such a size of formations, both single and structured. On other hand, small size ($l \sim 2$ mkm and $d \sim 100$ nm) make practically impossible LG on single rods ZnO due to high mirror losses during multiple reflections on interface ZnO/vacuum [12].

We can suppose in our case that existence of some intermediate option of, apparently, external resonator, in which LG source is ensemble of whiskers, most likely, spread in environment. In this case LG limitations for minimum size of whisker shall be removed, as major portion of the resonator length in vacuum, and mirror losses in this part of the resonator are significantly lower due to lower number of interfaces per unit of resonator length. So, for studied by us case we can suggest the Fabry-Perot resonator, in which the active medium occupies only part of total length of the resonator. Base on this model the preliminary calculations were performed, where by parameters adjustment to values of our experimental spectra the possible options of resonators on our sample were obtained [16]. Figure 4 present the calculation results. It is obvious that PL spectra one of the selected points of sample (in particular point **a** in Figure 2, curve *2* in Figure 4, *a*) practically coincide with the calculated values (curve *1*). The resonator corresponding to this calculation has total length $L = 200$ mcm, with active part length ZnO $L_{\mathrm{ZnO}} = 0.8$ mcm.

For another point (point **b** in Figure 2) (Figure 4, *b*) the resonator has total length $L = 190$ mkm, with active part length ZnO $L_{\mathrm{ZnO}} = 5.8$ mkm. Note that values were obtained for polarization $E \perp c$, calculation for polarization $E \parallel c$ gives value of active part length larger by about three times. Such resonators can comprise, for example, some number of whiskers located at significant (tens micrometers) distance from each other.

4. Conclusion

The laser generation in disordered systems based on ZnO nanocrystallite arrays obtained by original hydrothermal method is studied. It is identified that in individual points of the visually disordered system of nanocrystallites occurrence of ordered laser generation is possible. We suppose presence in such points of agglomerates playing role of optical resonators and presenting ordered, most likely closed structure of nanocrystallites, generating radiation with definite repeating parameters. To describe the studied case we used Fabry-Perot resonator model, in which the active medium occupies only part of total length of the resonator. Based on the mode possible options of parameters of the resonators are calculated.

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Conflict of interest

The authors declare that they have no conflict of interest.

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