On the Nature of Stimulated Emission in ZnO in a Wide Temperature Range

I. Kh. Akopyan[a], M. E. Labzovskaya[a], *, B. V. Novikov[a], and A. Yu. Serov[a]

[a]*St. Petersburg State University, St. Petersburg, 194034 Russia*

*e-mail: xrul@mail.ru

Abstract—We studied the near-edge emission of MBE ZnO films in wide ranges of excitation intensity (up to 1000 kW/cm^2) and temperatures (5–300 K). The manifestations of exciton–phonon, exciton–exciton, and exciton–electron interactions in stimulated emission spectra are discussed. A change in the mechanisms of stimulated emission in different temperature ranges was found.

INTRODUCTION

ZnO is a conventional object for studying exciton states. Free, bound, and surface excitons in ZnO and their interaction with phonons have been studied in detail. This compound also has many practical applications, for example, in solar cells, medical markers, photocatalysts of many chemical reactions, gas analyzers, sources of intense UV radiation, etc. [1]. The high binding energy in ZnO (60 meV) enables the exciton to take part in some processes at room temperature.

The processes of exciton–exciton interaction are actively studied at high levels of excitation: the emission of free and bound biexcitons and the emission of interacting excitons, in which part of the energy of one exciton is transferred to another with the transfer of the latter to an excited state or causing its ionization (P process). Part of the exciton energy can also be transferred to the electron (exciton–electron interaction). Stimulated emission (SE) and laser generation are observed in the corresponding emission bands under specific conditions. The laser generation thresholds for these processes are expected to be lower than for electron–hole plasma [2]. Laser generation in ZnO microcrystals was observed for the first time in 1989 [3].

This work studies the nature of stimulated emission in a ZnO film in a wide temperature range. The mechanisms of stimulated emission are discussed. It is assumed that stimulated emission takes place at temperatures from 5 to 120 K due to exciton–phonon and exciton–exciton interactions and at 120–300 K due to exciton–exciton and exciton–electron interactions.

EXPERIMENTAL

We studied photoluminescence (PL) at T = 5–300 K in a closed-cycle helium cryostat (Janis Research, United States). Photoluminescence was excited by an LGI-505 nitrogen laser in direct geometry (λ = 337 nm, W_{av} = 105 mW at a frequency of 1 kHz, pulse duration ~7 ns). The excitation density varied from 4 to 1000 kW/cm^2.

We studied a ZnO film with a thickness of d = 420 nm, grown by molecular-beam epitaxy (MBE) on sapphire without subsequent annealing. The films were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The sample was a film of a hexagonal structure with the optical axis c oriented normal to its surface. The low-temperature photoluminescence spectrum measured under weak excitation testified to the high quality of the sample.

RESULTS

Figure 1 shows the evolution of the luminescence spectrum of a ZnO film with increasing excitation power at T = 5 K. Curve *1* is recorded at the minimum excitation (the luminescence spectrum coincides with the spectra upon excitation by a He–Cd laser); curves *2–7* describe the photoluminescence spectra upon excitation by a nitrogen laser with increasing power from 3 to 1000 kW/cm^2. Spectrum *1* exhibits the main structure known from previous studies [4], which is characteristic of ZnO luminescence spectra under weak excitations. It consists of emission bands of a free exciton FX (367.7 nm) coupled to donor D(X) and acceptor A(X) exciton centers and bands of the first
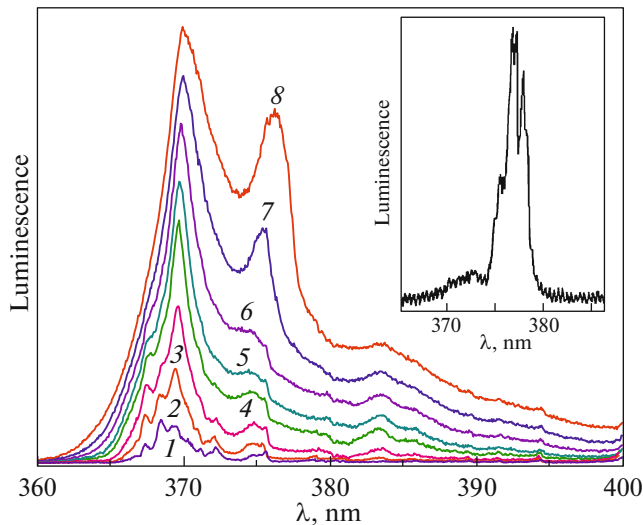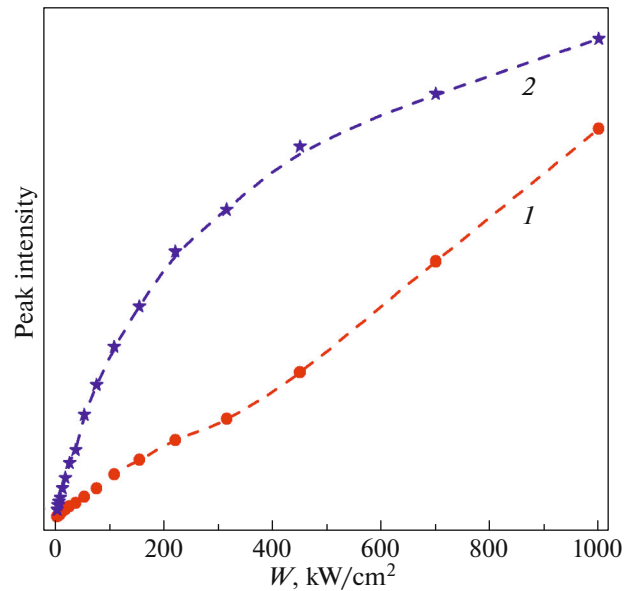
Fig. 1. Photoluminescence spectra of the ZnO film as a function of the excitation intensity at $T = 5$ K; the excitation intensity increases from (*1*) 20 to (*7*) 1000 kW/cm^2. Inset: lasing spectrum in the region of the first phonon repetition of a free exciton at $T = 5$ K.

Fig. 2. Dependences of the intensities of (*1*) band B and (*2*) band A on the excitation power.

and second phonon repetitions (PT) of a free exciton (376 and 383.5 nm, respectively), which are usually weak at 5 K in pure samples.

In the region of 375 nm, a band is observed, the maximum of which is associated in the literature with the exciton−acceptor transition, and radiation from the exciton−exciton interaction (P band, 374.4 nm) is also located here. With an increase in excitation, the shape of the spectrum changes; that is, the lines of bound excitons grow, their intensity is redistributed, and the exciton bound to the acceptor (369.1 nm) grows fastest of all. The free exciton band (curve *6*) broadens and grows, and starting from 400 kW/cm^2, it is observed as a kink in the short-wavelength wing of the intense band with a maximum at 369 nm. The radiation at this wavelength continues to grow even when no bound excitons are observed. It is natural to assume that, as the excitation increases, biexcitons begin to make a significant contribution to the radiation. In [5], biexciton emission was observed in ZnO nanofilms at $\lambda = 369.1$ nm and $W = 200$ kW/cm^2. With a further increase in excitation, the band continues to grow and broaden, acquiring a long-wavelength tail. The position of the band maximum (hereafter referred to as band A) at the maximum excitation is 370 nm (curve *8*).

With an increase in the excitation intensity, the band of stimulated emission in the region of the first phonon repetition rapidly grows with a maximum at $\lambda = 376.5$ nm (hereinafter referred to as band B). A relatively weak band of the second phonon repetition is seen at longer wavelengths. With a further increase in

excitation in the spectral region of the first phase transition, lasing can be observed (Fig. 1, inset).

The behavior of the intensities of the A and B bands differs with increasing excitation power (Fig. 2). Band A (curve *2*) demonstrates intensity saturation at high excitation levels, while band B (curve *1*) begins to increase sharply at $W > 300$ kW/cm^2.

The photoluminescence spectra of the film at maximum excitation in the temperature range of 5−300 K show the difference in the evolution of these bands (Fig. 3). As the temperature increases, band A monotonically shifts to longer wavelengths, decreasing in intensity and broadening; at $T = 300$ K, it becomes a broad band with a maximum at 382 nm [4]. The evolution of the second emission band (band B) is more complex. Band B shifts with temperature to the long-wavelength side; however, its half-width remains practically unchanged over the entire temperature range, and the intensity fluctuates slightly with increasing temperature; namely, it grows up to 120 K and then drops at 160−300 K. Figure 4 shows the decomposition of the bands presented in Fig. 3, demonstrating the dynamics of the temperature change in luminescence in more detail.

Figure 5 shows the temperature dependence of the maxima of the A and B emission bands (curves *5* and *6*) at maximum excitation and the temperature dependences of the main channels of ZnO photoluminescence exciton emission known from the literature [4, 6] (curves *1−4*).

The curve of the temperature change for band A (curve *6*) is practically synchronous with the temperature dependence of FX. The dynamics of band B
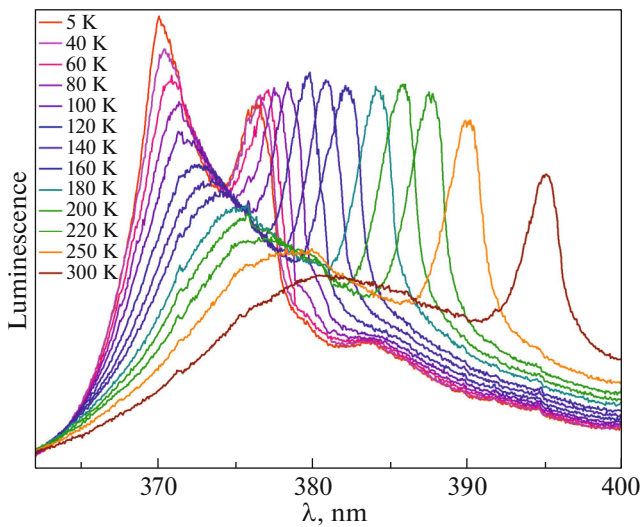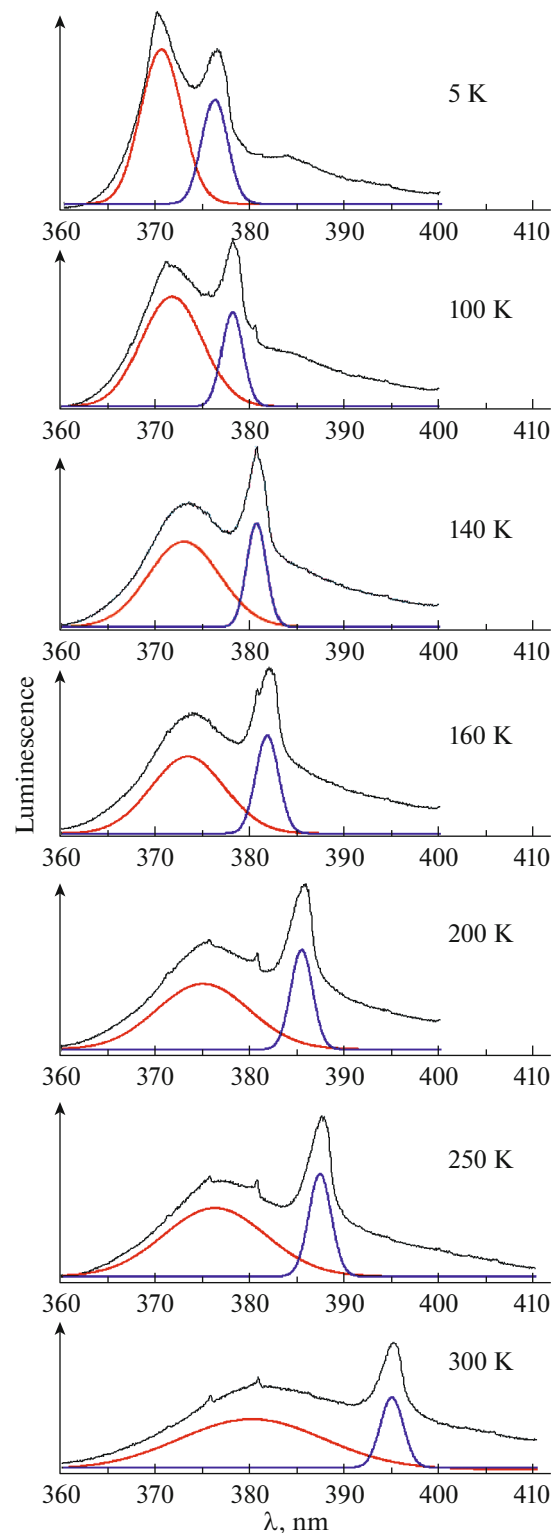
Fig. 3. Photoluminescence spectra of the ZnO film in the temperature range of 5−300 K at excitation power $W = 1000$ kW/cm^2.

(curve *5*) do not coincide with any previously studied and interpreted photoluminescence band, confirming its complex nature. Several temperature ranges can be distinguished, in which its changes with temperature coincide with different radiation channels. In the range of 5−50 K, the behavior of the temperature dependence is close to that of the first phonon repetition of a free exciton. Up to $T = 120$ K, band B shifts almost identically to band A; however, with a further increase in temperature, the slope of the curve strongly increases, and already at $T = 230$ K, the curve coincides with the course of the dependence of the second phonon repetition of a free exciton. Such a shape of the temperature dependence of band B suggests a different nature of stimulated emission in a wide temperature range.

DISCUSSION OF RESULTS

The results suggest that with increasing excitation power, the lines of bound excitons increase in intensity and broaden; however, they do not noticeably shift to the long-wavelength side. The line at 369.1 nm (3.36 eV) increases most intensively. According to our data, it belongs to the formation of a biexciton [5]. Subsequently, this band, together with the lines of free and bound excitons, forms a broad band with a long-wavelength tail and a maximum at ~370 nm; the band half-width is 48 meV. We assume that under strong excitations, the band consists of partially ionized and screened exciton states and an electron−hole plasma. Theoretical calculations at the excitation powers suggest that an electron−hole plasma can form in ZnO [2, 7].

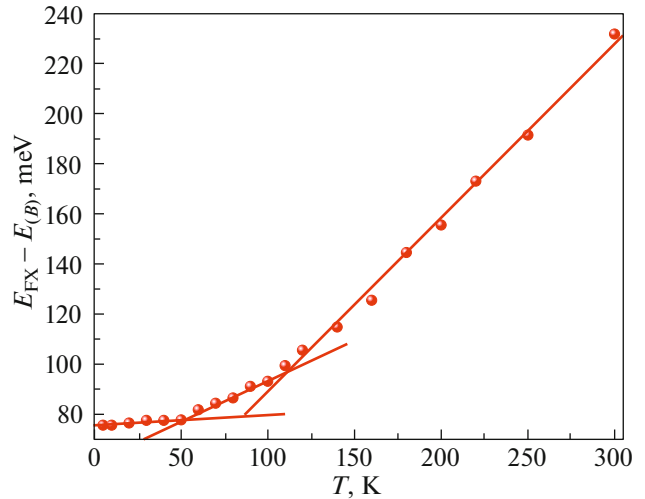**Fig. 4.** Decomposition of the photoluminescence spectra at different temperatures.

As the excitation intensity increases, a narrow stimulated emission peak appears at the long-wavelength decay of the maximum (band B). Stimulated emission
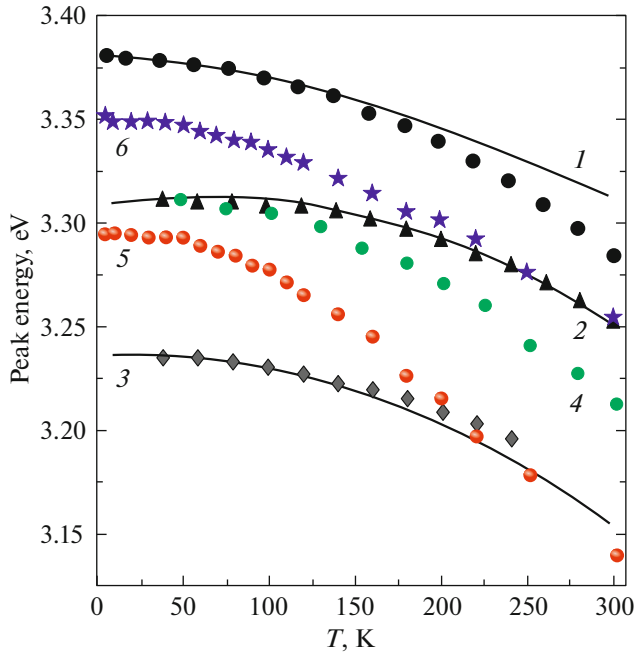
Fig. 5. Temperature dependence of the luminescence band maxima of the ZnO film: (*1−4*) data [6] for (*1*) FX, (*2*) 1LO(FX), (*3*) 2LO(FX), and (*4*) exciton−exciton interaction by data [4]; (*5*, *6*) experimental results at $W = 1000$ kW/cm^2 for (*5*) band B and (*6*) band A.

Fig. 6. Temperature dependence of energy of the free exciton−SE band distance $\Delta E = E_{FX} - E_{(B)}$.

was also observed in ZnO in [2, 8, 9]. The interpretation of the results is complicated because in this spectral region, there are lines of different nature: P band, 1LO phonon repetition of a free exciton, and a conduction band−acceptor transition.

Studies of the temperature dependence show that at $T = 5$ K, the stimulated emission in our samples is close in spectral position to the position of the first phase transition of a free exciton. However, the temperature shifts of these bands differ significantly. In the temperature range of 220−240 K, the temperature behavior of stimulated emission coincides quite precisely with the behavior of the 2LO exciton phonon repetition. If we assume that stimulate emission is associated with the recoil of phonons to the lattice, difficulties arise in describing the process in the temperature range of 5−200 K and in the transition from a one-phonon to a two-phonon process. On the other hand, stimulated emission of the exciton−exciton and exciton−electron interactions arises at a high excitation intensity. In the temperature dependence of the distance energy between a free exciton and stimulated emission (Fig. 6), three temperature regions with different slopes can be distinguished, which testify in favor of different stimulated emission mechanisms in these temperature ranges. The energy of the exciton−SE band distance varies slightly in the temperature range of 5−100 K, and at $T > 100$ K, it sharply increases with temperature. We can assume the pres-

ence of the P process. The temperature course of the stimulated emission band is similar to the course of the band in [2], where the authors assumed the P process.

CONCLUSIONS

We studied the near-edge emission of MBE ZnO films in wide ranges of excitation intensity (up to 1000 kW/cm^2) and temperatures (5−300 K). The effect of the exciton−phonon, exciton−exciton, and exciton−electron interactions on the stimulated emission nature is discussed. At high temperatures ($T > 160$ K), exciton−exciton and exciton−electron interactions are the predominant mechanisms of stimulated emission in ZnO.

FUNDING

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

REFERENCES

1. C. Klingshirn, J. Fallert, H. Zhou, J. Sartor, C. Thiele, F. Maier-Flaig, D. Schneider, and H. Kalt, Phys. Status Solidi B **6**, 1424 (2010).

2. R. Matsuzaki, H. Soma, K. Fukuoka, K. Kodama, A. Asahara, T. Suemoto, Y. Adachi, and T. Uchino, Phys. Rev. B **96**, 125306 (2017).

3. V. A. Gaisin, B. S. Kulinkin, and B. V. Novikov, JETP Lett. **49**, 686 (1989).

4. I. Kh. Akopyan, M. E. Labzovskaya, B. V. Novikov, A. Yu. Serov, N. G. Filosofov, and N. R. Grigor'eva, Phys. Solid State **62**, 2138 (2020).

5. I. Kh. Akopyan, M. E. Labzovskaya, B. V. Novikov, V. G. Talalaev, J. W. Tomm, and J. Schilling, Phys. Solid State **61**, 402 (2019).

6. U. Ozgur, Ya. I. Alivov, C. Liu, A. Teke, M. A. Reshchikov, S. Dogan, V. Avrutin, S.-J. Cho, and H. Morkos, J. Appl. Phys. **98**, 041301 (2005).

7. N. N. Vasilyev, E. N. Borisov, and B. V. Novikov, Phys. Solid State **62**, 1774 (2020).

8. C. Cachoncinlle, C. Hebert, J. Perrière, M. Nistor, A. Petit, and E. Millon, Appl. Surf. Sci. **336**, 103 (2015).

9. J. Fallert, R. J. B. Dietz, M. Hauser, F. Stelzl, C. Klingshirn, and H. Kalt, J. Lumin. **129**, 1685 (2009).

Translated by O. Zhukova