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Near-band-edge photoluminescence in ZnO powder at room and nitrogen temperatures

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Experimental study of the photoluminescence of zinc oxide powder have been carried in the exciton region of the spectrum at room and nitrogen temperatures. In the ultraviolet region of the spectra, an edge emission band of excitons is detected. The effect of temperature have been observed on the position and intensity of the photoluminescence band.

Keywords: photoluminescence, band emission, powder, zinc oxide, spectrum.

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Zinc oxide (ZnO) is a wide-band semiconductor (II–VI) material which has high potential of use in various applications. In recent years ZnO was widely studied in various forms. The most studied are powders [1], bulk single-crystals [2], thin films [3,4], nanogranules [5], nanowires [6] and nanorods [7]. ZnO has crystal structure of wurtzite with hexagonal lattice cell and ratio of lattice constants c/a between 1.5393 and 1.6035, has large bond energy of exciton (60 meV [4]), which by about 3 times higher then in wide-band semiconductors ZnSe and GaN (25 meV) [8]. Having relatively large exciton bond energy and wide band gap $E_g = 3.37$ eV at room temperature [9], ZnO is assumed as competitor to GaN, which currently is used to manufacture light emitting diodes (LEDs), lasers and detectors in a near ultraviolet (UV) and blue-green regions of the spectrum [10]. The exciton structures in ZnO were extensively studied [11,12], and it is known that due to low dielectric permittivity and large effective masses the excitons have large bond energy. Besides, due to large bond energy of biexcitons (12–20 meV) ZnO is a promising material for use in optical devices associated with excitons [13].

ZnO is a bright UV-emitter/absorber, and in this relation the study of this oxide in UV-region of spectrum is of special interest. UV-radiation, or so called near-band-edge emission, is located near its absorption edge (3.381 eV [13]), and occurs as a result of exciton recombination. During recent years the photoluminescent properties of ZnO in UV-region of spectrum were extensively studied for its different forms and in different conditions [1,14–18]. Paper [18] identified that the near-band-edge emission depends on structure and morphology of ZnO. Besides structural factors there is effect of external conditions, such as temperature and energy of laser radiation [1].

So, studies of effect of external conditions, and, in particular, of the temperature mode on ZnO photoluminescence is of great interest both from fundamental and applied point of view. This study objective is the photoluminescence study in powder of micron particles of ZnO at room (293 K) and nitrogen (77 K) temperatures. At that for UV-radiation excitation the nitrogen laser was used.

The test set-up diagram is shown in Fig. 1. For the photoluminescence excitation of polycrystalline powder ZnO the pulse repetitively pulse nitrogen laser was used. The laser generated pulses 10 ns wide with repetition frequency 100 Hz, and excitation wavelength 337 nm. Average output power of the laser was 10 mW. UV-excitation of the laser source *1* was focused by the quartz lens *2* into the cuvette *3* with the studied sample. The sample was polycrystalline powder ZnO with particles size 3–5 μm. The cuvette was at room temperature or was located into the cryostat with liquid nitrogen *4*. After the cuvette the light beam passed through a system of focusing lens *5*, *6*, optical probe *7* and optical fibre *8* and supplied to spectrometer FSD-8 (*9* in Fig. 1) connected to PC *10*. Using the matrix detector the spectrometer measured the photoluminescence spectra in spectral band 200–850 nm at the exposure time of 100 μs to 20 s. The spectral resolution during measurement was ~ 1 nm.

Fig. 2 shows the photoluminescence spectra of sample of polycrystalline ZnO used as source of UV-radiation excitation with wavelength $\lambda_{ex} = 337$ nm at room and

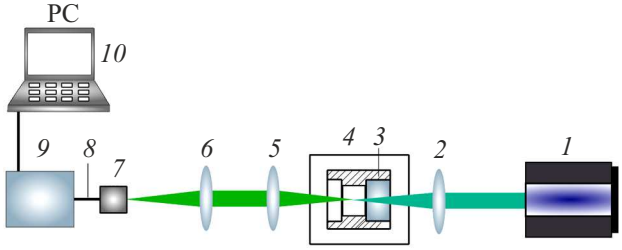

Figure 1. Diagram of test set-up. *1* — laser, *2, 5, 6* — lens, *3* — cuvette with sample, *4* — cryostat, *7* — optical probe, *8* — optical fibre, *9* — spectrometer FSD-8, *10* — PC.

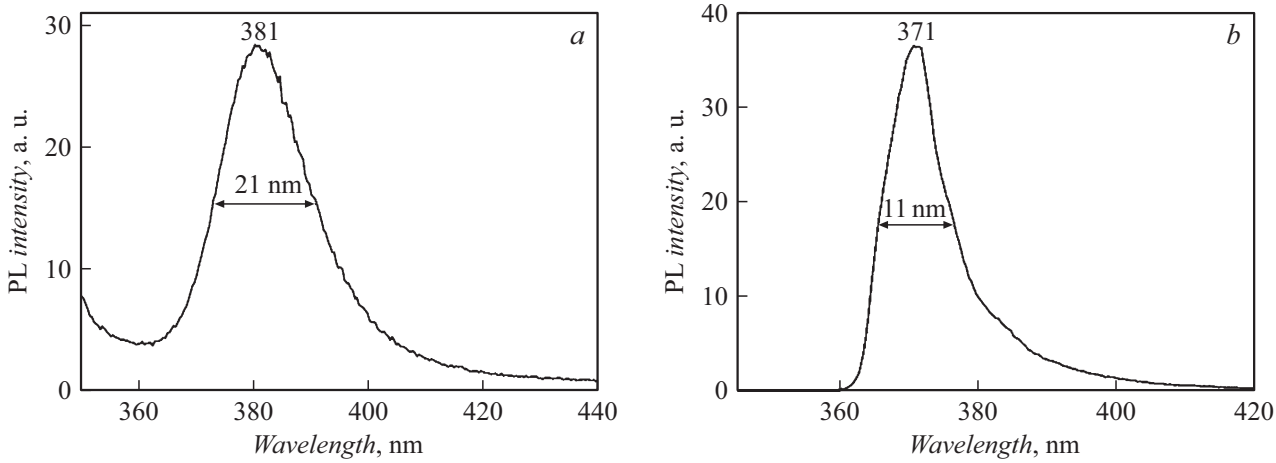

Figure 2. Photoluminescence spectra of powder ZnO during UV-excitation with wavelength $\lambda_{ex} = 337$ nm at room (a) and nitrogen (b) temperatures.

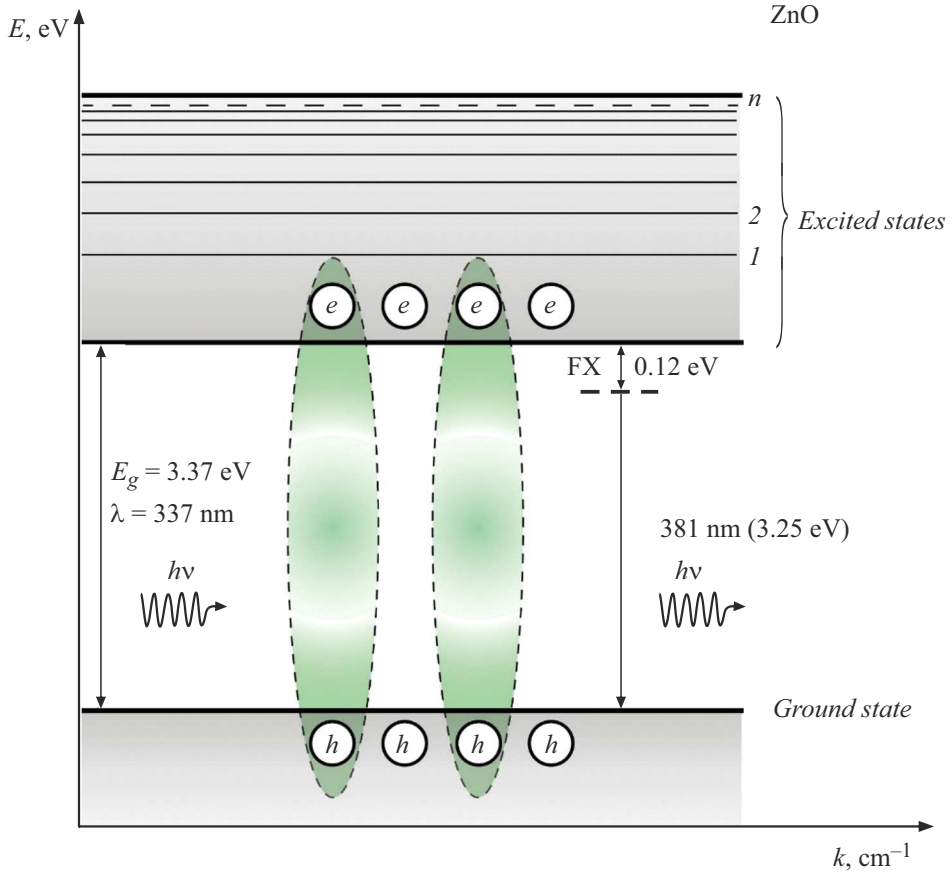

Figure 3. Schematic diagram of energy transitions in UV-region of spectrum at room temperature in powder ZnO.

nitrogen temperatures. Fig. 2, *a* and *b* shows that in the photoluminescence spectra of sample the characteristic short-wave bands of radiation near the absorption edge of ZnO, or so called near-band-edge luminescence, are observed. The occurrence of the observed short-wave bands at wavelength of 371 nm (3.333 eV) and 381 nm (3.246 eV) (Fig. 2, *a* and *b*) is explained by several possible causes. In particular, one of the causes of the observed bands appearance can be a direct interband transition of electron from a conduction band into a valence band or transition from level of zinc interstitial defect (Zn_i) into the valence band. It was previously stated [13] that the observed photoluminescence band corresponds to exciton radiation and is due to rcombination of free excitons.

From the shown spectra (Fig. 2, *a* and *b*) it is obvious that dependence of sample photoluminescence intensity on temperature is observed. Decrease in sample temperature to temperature of liquid nitrogen results in intensity increasing.

Besides, it is identified that temperature decreasing affects the peak width: peak narrowing occurs (Fig. 2, *b*). Full width at half maximum (FWHM) of the photoluminescence bands during nitrogen temperature is ~ 11 nm, which is by about 2 limes below the room temperature (~ 21 nm). As it is stated in [19], radiation in UV-region with full width ~ 15 nm relates to the recombination of free excitons, which is relatively close to full width of the sample studied herein.

Besides, temperature decreasing of the sample to temperature of liquid nitrogen affects the radiation band position. Fig. 2, *b* shows that band shifts towards the short-wave region of spectrum by ~ 10 nm (blue shift). Paper [17] studied the effect of concentration of free electrons n_e (in range $10^{13}-10^{18}\,\mathrm{cm}^{-3}$) on the peak position of near-band-edge luminescence of ZnO bulk crystals at room temperature. It was shown that at temperature of 300 K the photoluminescence band shifts from ~ 3.312 eV ($n_e = 10^{13}\,\mathrm{cm}^{-3}$) to ~ 3.27 eV ($n_e = 10^{18}\,\mathrm{cm}^{-3}$). At low value of n_e the band gap of the crystal is $E_g = 3.372$ eV. It is assumed that band shift towards low energies upon n_e increasing is associated with band gap decreasing. As it can be observed in Fig. 2, *b*, for the studied sample the same behaviour of the photoluminescence band is observed, and the observed effect is associated, may be, with the band gap increasing at nitrogen temperature.

The energy diagram of ZnO powder is presented in Fig. 3. For ZnO sample the level of free excitons (FX) is by 0.12 eV below the conduction band bottom (Fig. 3). As it is already known, the mechanisms of band gap increasing and decreasing in ZnO are complicated processes which depend on some factors, such as temperature, size of crystallites and type of doping elements [20].

So, the photoluminescence in ZnO powder was obtained at UV-excitation with wavelegth 337 nm. In photoluminescence spectra the near-band-edge luminescence in UV-range of wavelength was identified. It was determined that decrease in sample temperature to temperature of liquid nitrogen results in position shift (blue shift) and increase in intensity of photoluminescence band. So, under low temperature it is possible to increase band gap of electron.

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Conflict of interest

The authors declare that they have no conflict of interest.

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