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ROOM-TEMPERATURE ULTRAVIOLET LASER EMISSION FROM ZNO HEXAGONAL MICROPRISMS AND NANOWIRES

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We report the observation of optically pumped laser generation in ZnO microprisms and nanowires at room temperature. The ZnO microprisms were grown on the single crystal (100) silicon substrates by a solid-vapor-phase process. The ZnO nanowires were grown on a glass substrate coated with indium tin oxide by the electrochemical deposition. Laser effect was observed at room temperature at the optically pump power higher than 685 kW cm^{-2} for ZnO microprisms and 560 kW cm^{-2} — for ZnO nanowires.
Keywords: zinc oxide, laser emission, ultraviolet photoluminescence, microstructures, nanowires.

УЛЬТРАФИОЛЕТОВОЕ ЛАЗЕРНОЕ ИЗЛУЧЕНИЕ ОТ ZNO ГЕКСАГОНАЛЬНЫХ МИКРОПРИЗМ И НАНОПРОВОЛОК ПРИ КОМНАТНОЙ ТЕМПЕРАТУРЕ

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Мы сообщаем о наблюдении лазерной генерации при оптической накачке в ZnO микропризмах и нанопроволоках при комнатной температуре. Микропризмы ZnO были выращены на монокристаллических (100) кремниевых подложках с паровой фазы. ZnO нанопроволоки были выращены на стеклянных подложках, покрытых оксидным слоем индия с оловом, путем электрохимического осаждения. Лазерный эффект наблюдался при комнатной температуре в тех случаях, когда мощность оптический накачки превышала 685 кВт см$^{-2}$ для ZnO микропризм и 560 кВт см$^{-2}$ для ZnO нанопроволок.
Ключевые слова: оксид цинка, лазерное излучение, ультрафиолетовая фотолюминесценция, микроструктуры, нанопроволоки.

УЛЬТРАФІОЛЕТОВЕ ЛАЗЕРНЕ ВИПРОМІНЮВАННЯ ВІД ZNO ГЕКСАГОНАЛЬНИХ МІКРОПРИЗМ І НАНОДРОТІВ ЗА КІМНАТНОЇ ТЕМПЕРАТУРИ

В. Б. Капустяник, Б. І. Турко, Ю. В. Рудик, В. С. Цибульский, В. П. Рудик, А. П. Васьків

Ми повідомляємо про спостереження лазерної генерації при оптичному нагнітанні в ZnO мікропризмах і нанодротах за кімнатної температури. Мікропризми ZnO були вирощені з парової фази на монокристалічних (100) кремнієвих підкладках. ZnO нанодроти були вирощені електрохімічним осадженням на скляних підкладках, покритих оксидним шаром індію з оловом. Лазерний ефект спостерігався при кімнатній температурі в тих випадках, коли потужність оптичного нагнітання перевищувала значення 685 кВт см$^{-2}$ для ZnO мікропризм і 560 кВт см$^{-2}$ для ZnO нанодротів.
Ключові слова: оксид цинку, лазерне випромінювання, ультрафіолетова фотолюмінесценція, мікроструктури, нанодроти.

1. INTRODUCTION

The current state of optoelectronics requires search of efficient laser materials that would emit light in blue and ultraviolet spectral regions [1]. Zinc oxide is a semiconductor material with a band gap of 3.37 eV at room temperature. The

free excitons in zinc oxide are stable even at room temperature due to their large binding energy (60 meV) [2], As a result, it is possible to obtain the laser effect based on the exciton recombination. The random laser generation was observed in ZnO micron size powder, thin films and nanorods arrays [3–5]. Study of the mechanisms of random lasing in ZnO is of great importance for creating of the high-power semiconductor lasers. This makes the zinc oxide a promising material for creation of the powerful semiconductor lasers in the ultraviolet range with a low threshold pumping. Investigations of the random lasers are performed by the numerous research groups from different countries: USA, Holland, Italy, Ireland, France, Greece, Ukraine, China, Japan and Singapore.

We report the properties of the emitting ZnO micro- and nanostructures. The aim of the work is to define the influence of the resonator shape on the threshold and spatial characteristics of lasing.

2. EXPERIMENTAL

The ZnO microprisms (Fig. 1) were grown on the single crystal (100) silicon substrates by a solid-vapor-phase (VLS) process in a horizontal tube furnace in air at 600 °C using Zn powder.

ZnO nanostructures on a glass substrate coated with indium tin oxide (ITO) were synthesized by the two-step process. Firstly, the seed layer of ZnO nanoparticles was deposited on the substrate by SILAR (Successive Ionic Layer Adsorption and Reaction) method [6]. For this purpose the substrate was immersed for 15–20 sec. into 0.5 M distilled water solution of zinc salt and $Zn(CH_3COO)_2$ and hexamethylenetetramine (HMT) at room temperature, then washed in a distilled water, and dipped for 15–20 sec. into a distilled water at the temperature about 80 °C. This cycle was repeated 20–25 times. The nanowires (Fig. 2) were synthesized by electrodeposition from an aqueous solution in the electrochemical cell with two electrodes [7]. To obtain the nanostructures we used 20 mM nitrate hexahydrate zinc $Zn(NO_3)_2 \cdot 6H_2O$ and hexamine solution in a distilled water at the temperature of 70 °C. The substrate with a seed layer of ZnO nanoparticles was used as working electrode-cathode, and as the second electrode-anode we used a graphite plate. The potential of –0.9 V was applied to the substrate that was kept in a cell for 1 hour. After the process of synthesis the substrate with nanowires was washed in distilled water and dried in air.

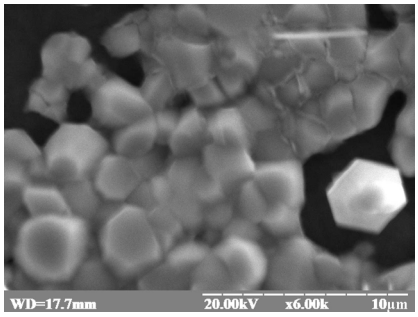

Fig. 1. SEM images of ZnO microprisms

Morphology of the samples was examined using REMMA-102-04 Scanning Electron Microscope-Analyzer.

The room-temperature photoluminescence spectra (PL) were measured using automated monochromator/spectrograph M266 connected with CCD camera, based on Hamamatsu S7030-1006S sensor. The samples were excited by FQSS266-Q2 Nd:YAG laser (266 nm).

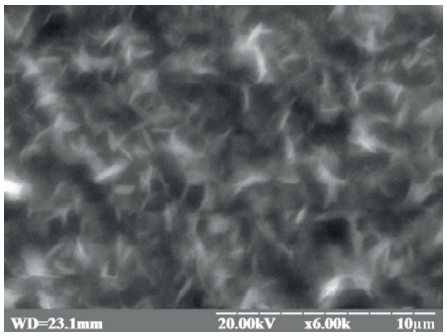

Fig. 2. SEM image of ZnO nanowires

To obtain the room-temperature ultraviolet laser emission from the experimental samples the laser beam was focused by quartz lens with a focal length of 7.5 cm.

3. RESULTS AND DISCUSSIONS

The morphology of the investigated samples is presented in Fig. 1 and Fig. 2. As one can see, the ZnO microprisms with a diameter of about 2–4 μm, length of ~4 μm and pronounced hexagonal cut were grown on the (100) silicon substrate. The undoped ZnO nanowires are characterised by the uniform length of about 1 μm with the average diameter of about 100 nm. The room-temperature PL spectra of the ZnO

microprisms (Fig. 3) consists of the intense bands both in the ultraviolet (UV) and visible regions. The band at 388 nm is typical for ZnO and arises due to recombination of free excitons, bound excitons and transitions in donor-acceptor pairs [8, 9]. The bands at 520 nm and 650 nm are caused by defects, first of all, by uncontrolled impurities and stoichiometry defects [8–11]. As it is shown in Fig. 3, at low pump power the emission spectra in the UV region consists of a single broad emissions peak. Its full width at half maximum (FWHM) is 18.1 nm.

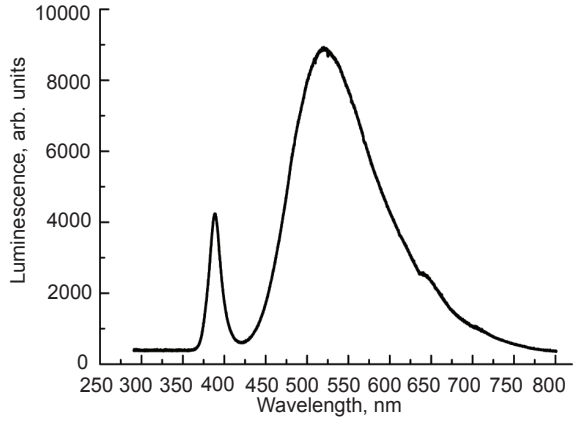

Fig. 3. Room-temperature PL spectra of the ZnO microprisms

The emission spectra of the ZnO nanowires (Fig. 4), in contrast to the PL spectra of the microprisms, is characterized by the very intense band in the ultraviolet region wavelengths of light and much less intense one — in the visible range.

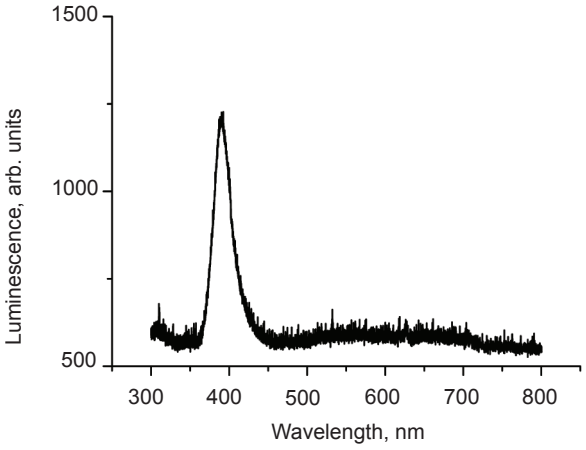

Fig. 4. Room-temperature photoluminescence spectra of the ZnO nanowires

Fig. 5 presents the evolution of the edge luminescence spectra for the excitation intensity increasing from 120 kW cm^{-2} to 1.3 MW cm^{-2}. For the pumping power of 1.3 MW cm^{-2} FWHM of the emission band was found to be 2.5 nm. The emission spectra of ZnO microprisms at the optical pumping 1.3 MW cm^{-2} consists of the two maxima at 388 nm and 390 nm.

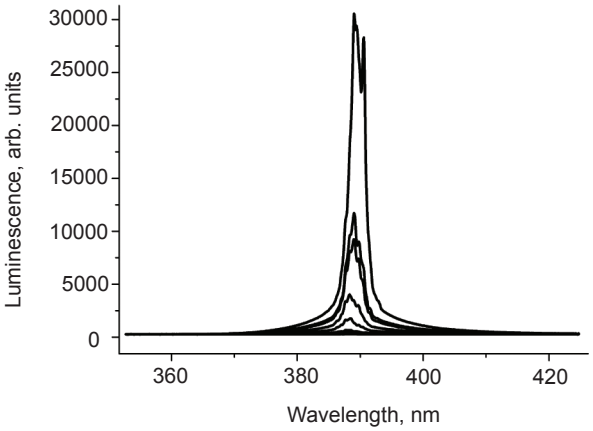

Fig. 5. Evolution of the room-temperature edge luminescence spectra of the ZnO microprisms at the excitation intensity increasing from 120 kW cm^{-2} to 1.3 MW cm^{-2}

Fig. 5, 6 present a clear evidence of the stimulated emission with the threshold of I_{th}~685 kW cm^{-2}.

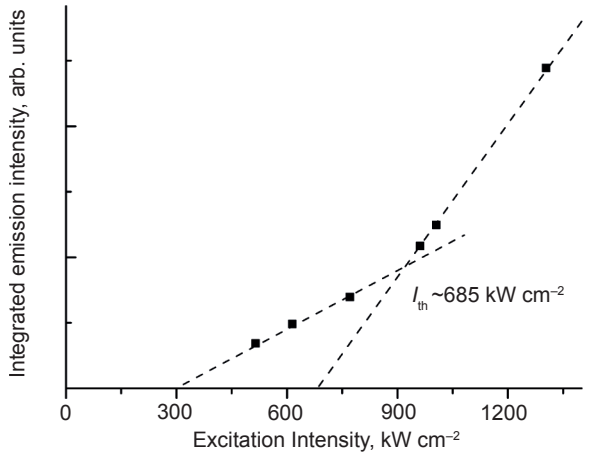

Fig. 6. The room-temperature dependence of integrated output intensity on excitation intensity of the ZnO microprisms

Although the alignement of the ZnO nanowires is quite chaotic, it is possible to select the regions of their prevailing orientation along the direction parallel to the electric field determined by excitation with the polarized light of a Nd:YAG laser. For ZnO nanowires the stimulated PL appears starting from the pumping powers of 560 kW cm^{-2} as the narrow lasing line with a maximum at 388 nm (FWHM 1.8 nm) (Fig. 7, 8).

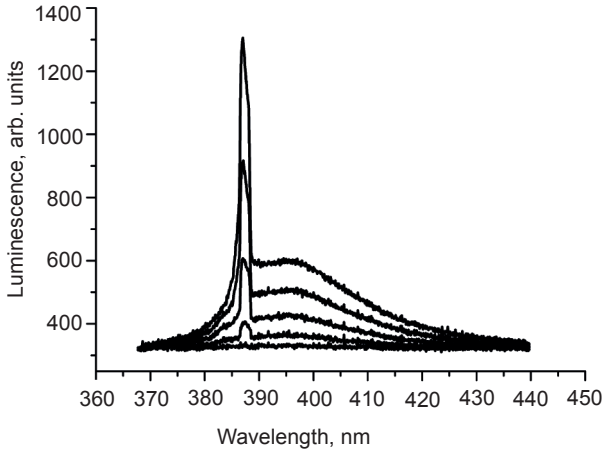

Fig. 7. Evolution of the room-temperature edge luminescence spectra of the ZnO nanowires at the excitation intensity increasing from 120 kW cm^{-2} to 1.2 MW cm^{-2}

Fig. 9 shows the high polarization dependence of the emission intensity of ZnO microprisms. The emission above the threshold is found to be strongly TE polarized (parallel to the growth plane) for both types of samples.

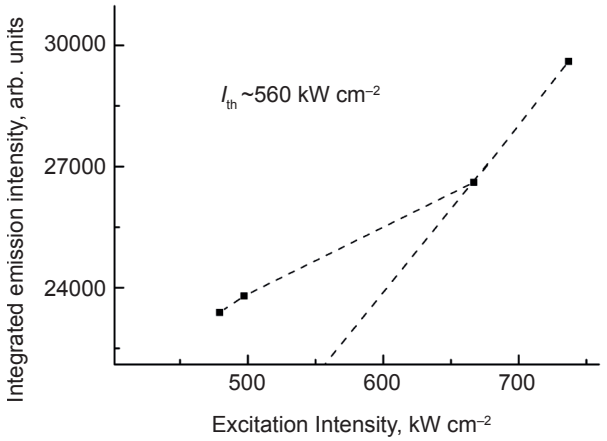

Fig. 8 The room-temperature dependence of the integrated output intensity on excitation intensity for the ZnO nanowires

According to the theoretical calculations the stimulated luminescence line caused by recombination of the interacting excitons at room temperature should have a maximum in the range of 384–386 nm, and for the recombination of the electron-hole plasma — in the range of 393–397 nm [8, 12–14]. For our samples both mechanisms occur as it follows from the observed stimulated luminescence spectra.

The obtained data confirm that excitonic emission may be used for realization of efficient lasing on the basis of ZnO due to its larger exciton binding energy (60 meV) compared to other wide-band-gap semiconductors.

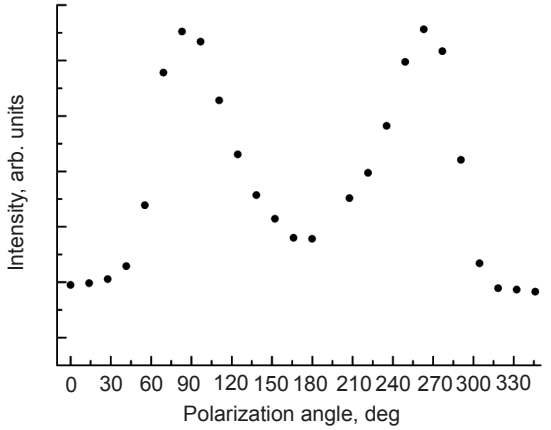

Fig. 9. Polarization dependence of laser emission of ZnO microprisms

Exciton-exciton scattering-induced stimulated emission is very important for the realization of low-threshold lasers since it occurs at the threshold lower than that for the electron-hole plasma recombination. The demonstration of stimulated emission with excitonic origin paves the way for the realization of blue-violet laser diodes based on ZnO [8].

As it is shown in Fig. 10, the laser emission spectra of the ZnO nanowires varied depending on the observation angle. At lower values of the observation angles (α ~ 18°) laser emission spectra of the ZnO nanowires also contains a band with a maximum at 383 nm corresponding to recombination of free excitons [12].

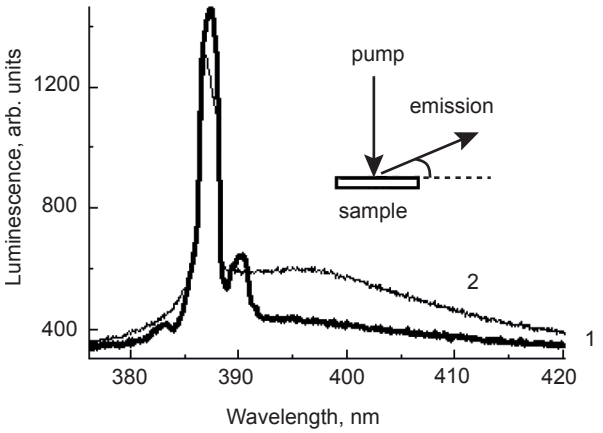

Fig. 10. The room-temperature spectra of laser emission of the ZnO nanowires for two directions: 1 — observation angle α = 18° from the sample surface, 2 — observation angle α = 70° from the sample surface. The excitation intensity is 1.2 MW cm^{-2}. The insets illustrate the experimental configuration

In the case of ZnO microprisms there is possible the emergence of optical feedback

connected with reflection of light from the upper and lower their parallel faces (Fabry-Perot resonator structure).

The Fabry-Perot resonance mode spacing can be determined by the equation [15]:

$$\Delta\lambda = \frac{\lambda^2}{2nl}, \qquad (1)$$

where l is the cavity length, n is the refractive index (~2.3), λ is the resonant wavelength.

For a ZnO microprisms with a length of 4 μm, the resonant mode is expected to be at 388 nm (or 390 nm). The resonant mode spacing for the cavity length of 4 μm is around 8 nm. Therefore, it can be deduced that only one single Fabry-Perot mode exists in the ultraviolet photoluminescence range of ZnO microprisms.

4. CONCLUSIONS

The structure and photoluminescence of ZnO microprisms and nanowires were studied. The laser generation was obtained in the ultraviolet spectral range in vicinity of 388 nm. We presented an evidence of the lasing effect in the ZnO microprisms and nanowires. The threshold intensity for ZnO microprisms and nanowires was found to be approximately 685 kW cm^{-2} and 560 kW cm^{-2}, respectively. The coherent feedback in ZnO microprisms can be provided by two basic mechanisms. In the first case the coherent feedback is provided by multiple reflections from the end facets of the microprisms serving as a Fabry-Perot resonator. In the second case, the coherent feedback is provided by multiple scattering events (random lasing from ZnO). In contrast to this for the ZnO nanowires it is possible to realise only random laser generation. The mechanism of laser emission for ZnO microprisms and nanowires would be connected with the exciton-exciton scattering at intermediate intensities but may be switched to the electron-hole plasma emission at higher intensities [12, 13]. The ZnO nanowires and microprisms grown using the methods patented by authors manifest effective ultraviolet stimulated luminescence at room temperature and are promising for creation of the short-light laser sources.

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