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Random lasing in hydrothermal ZnO structures

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Abstract. In this manuscript, we present a study on the optical properties of ZnO nanowires synthesized via hydrothermal method. The nanowires were characterized by low temperature photoluminescence spectroscopy, revealing resonant modes indicative of random lasing behavior provided with scattering by misoriented nanowires. The spectral position of the resonant modes suggests lasing in the region of the P band of exciton-exciton interaction. Our results also indicate a correlation between the surface density of the nanostructures and peak intensity of the emission. Overall, our findings demonstrate the potential of hydrothermal synthesis for fabricating efficient light-emitting devices based on ZnO.

Keywords: zinc oxide, hydrothermal, photoluminescence

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Спонтанная генерация в гидротермальных структурах ZnO

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Аннотация. В данной работе мы представляем исследование оптических свойств нитевидных нанокристаллов (ННК) ZnO, синтезированных гидротермальным методом. ННК были охарактеризованы с помощью низкотемпературной спектроскопии фотолюминесценции, выявившей резонансные моды, указывающие на спонтанную генерацию, обусловленную рассеянием на неориентированных ННК. Спектральное положение резонансных мод предполагает генерацию в области P-полосы экситон-экситонного взаимодействия. Наши результаты также указывают на корреляцию между поверхностной плотностью наноструктур и пиковой интенсивностью излучения. В целом наши результаты демонстрируют потенциал гидротермального синтеза для изготовления эффективных светоизлучающих устройств на основе ZnO.

Ключевые слова: оксид цинка, гидротермальный, фотолюминесценция

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Introduction

Nano- and micro-sized structures find a wide range of applications in various fields from sensors [1] to UV [2,3] and visible range emitters [4]. In the era of information technology and digital multimedia, specific types of light sources based on wide-gap semiconductors, capable of generating violet and ultraviolet (UV) radiation, are becoming increasingly popular in modern optoelectronics and medicine. The high efficiency, rapid switching capabilities, low power consumption, and comparatively low heat dissipation of LEDs based on wide-gap semiconductors have led to their widespread use in both high-end and consumer technologies. For instance, high-efficiency LEDs have replaced traditional backlight units in LCDs.

Zinc oxide (ZnO), which band gap allows using it in UV devices, has attracted significant attention in recent years. Apart from its band gap of 3.37 eV at room temperature, a particularly noteworthy characteristic of ZnO is its large exciton binding energy (60 meV), which is significantly higher than the thermal energy at room temperature (about 26 meV) [5]. This fact indicates that the excitonic effect in ZnO can be maintained up to room temperature, allowing for efficient UV radiation. In addition, ZnO is cheap, relatively abundant, chemically stable, easy to synthesize, and nontoxic. Although there are currently a large number of light-emitting devices based on ZnO, fabrication of low-dimensional, high-performance, and technologically simple solutions remains challenging. This is an area where several unresolved issues exist.

In this study, we employ hydrothermal synthesis [6, 7] of ZnO nanostructures, a method that allows growth of various materials and compounds through physical and chemical processes in aqueous solutions. The advantages of hydrothermal synthesis include the broad ability to control growth conditions, the capability of low-temperature synthesis (below 100 °C), which significantly reduces cost, as well as decreasing the hazard class of the production. In addition, this method enables the synthesis of zinc oxide structures on various substrates, both lattice-matched and not, such as silicon, making this synthesis method suitable for integration with silicon technologies. We synthesized ZnO nanowires with different surface densities directly on a silicon substrate and investigated their low-temperature photoluminescence properties. Our results show that the luminescence properties of the nanowires change significantly with changes in the surface structure distribution. This study demonstrates the potential of this simple and low-cost synthesis method for advancing random laser sources.

Materials and Methods

In our study, we utilize silicon substrate Si (111) for the hydrothermal synthesis of ZnO nanostructures. An aqueous solution of zinc acetate was employed as the seed layer. These seed layers were applied using the spin-coating method. The solution consists of equimolar aqueous solutions of $Zn(NO_3)_2$ and hexamethylenetetramine (HMTA) at a concentration of 50 mmol·l^{-1}. The following reactions occur during the synthesis process:

$$C_6H_{12}N_4 + 6H_2O \rightarrow 6HCHO + 4NH_3, \quad (1)$$

$$NH_3 + H_2O \rightarrow NH^{4+} + OH^-, \quad (2)$$

$$Zn(NO_3)_2 \leftrightarrow Zn^{2+} + 2NO_3, \quad (3)$$

$$2OH^- + Zn^{2+} \leftrightarrow Zn(OH)_2, \quad (4)$$

$$Zn(OH)_2 \leftrightarrow ZnO + H_2O. \quad (5)$$

During the synthesis, a constant temperature of 85 °C was maintained. The synthesis duration for all samples was 3 hours.

The synthesized samples were placed in a closed-cycle helium cryostat (Janis Research Company, USA). The sample temperature was about 10 K. The PL was excited by a He-Cd laser (λ = 325 nm, excitation power W = 50 kW·cm^{-2}) and by an ultraviolet solid-state laser LCM-DTL-374QT (λ = 355 nm).

Results and Discussion

As a result of the synthesis, three characteristic samples with distinctive density were fabricated. SEM images obtained in the selected regions (see Fig. 1) were analyzed, showing the presence of disoriented ZnO NWs with hexagonal faceting and a high aspect ratio of about 10:1 across the entire surface of the sample.

The data on the surface distribution density and the average length of the NWs in different areas are presented in Table 1. It is noted that the distribution density of the NWs decreases towards the edges of the growth substrate, which is likely due to the design features of the sample holder that restrict access to the growth solution.

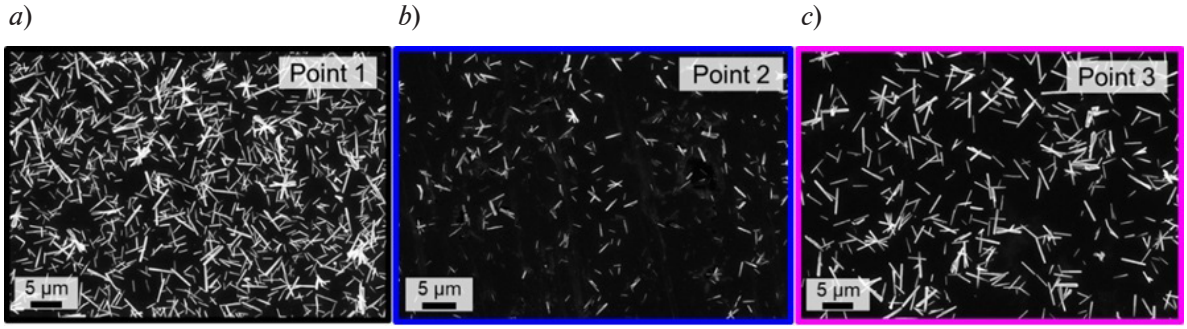

Fig. 1. SEM images showcasing three characteristic morphologies

Table 1

Data on distribution of NW density and their average length in different areas of the sample

Area	Distribution density, %	Average length, μm
Point 1	22.6	1.74
Point 2	4.3	1.24
Point 3	12	2.16

The optical properties of the synthesized ZnO were investigated using photoluminescence (PL) spectroscopy. The results of the PL measurements of the samples shown in Fig. 1 are depicted in Fig. 2, *a* and demonstrate UV emission centered near 372 nm for all of the samples. Remarkably, upon excitation narrow lines in the region $\lambda \simeq 373-376$ nm are observed in the PL spectra (Fig. 2, *a*). Such a behavior is a manifestation of the resonant action of the grown structures leading to the amplification of the resonant modes. Fig. 2, *b* shows the change in the luminescence intensity with increasing optical pumping. The obtained plot demonstrates a transition between two linear regimes which is typical for the occurrence of a stimulated emission. The threshold value is found at 140 kW·cm^{-2}. We believe that a cluster of disoriented ZnO crystals forms an optical structure that acts as a resonator providing peculiar scattering and stimulating occurrence of a closed optical circuit, which leads to selective amplification of the optical modes. The spectral position of the corresponding lines indicates that laser generation probably occurs in the P band region of the exciton–exciton interaction [8]. A correlation is observed between the density distribution and the intensity of peaks in the photoluminescence spectra. At Point

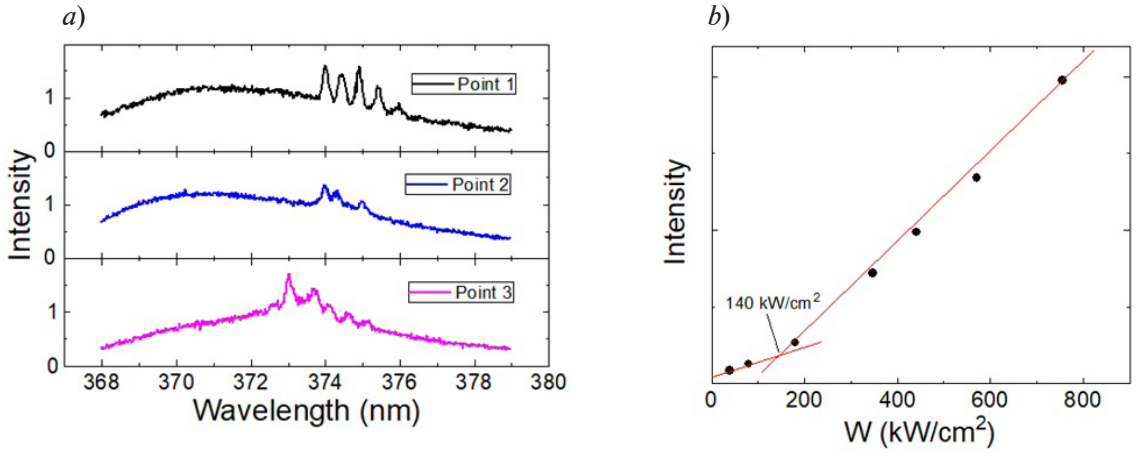

Fig. 2. Photoluminescence spectra taken at different points of synthesized sample (*a*); change in luminescence intensity with increasing excitation laser power *W* (*b*)

1, the NWs have the highest density, which leads to distinctly pronounced intense peaks in the spectra. Presumably, the high surface density leads to the formation of a greater number of closed circuits acting as resonators, resulting in an increased intensity of the PL. Based on the data obtained, it can be concluded that formation of lasing structures is feasible through the modification of structures density on the sample surface. Such a change in structures density can be implemented at the synthesis stage by adjusting seed layers' number and precursors concentration in the growth solution.

Conclusion

We synthesized via hydrothermal method and studied optical action of ZnO nanowires. Low temperature PL spectra revealed occurrence of the resonant modes observed at different points of the sample. Pump-power dependence of the intense modes demonstrate threshold behaviour typical for the stimulated emission. The spectral position of the resonant modes indicates that lasing most likely occurs in the region of the P band of the exciton–exciton interaction. We also observe correlation between the surface density of the nanostructures and peak intensity of the emission. The results show that a simple hydrothermal synthesis method is promising for fabricate efficient light-emitting devices based on ZnO.

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