The influence of size on the photoluminescence properties of ZnO nanostructures

R.R. Jalolov[*,1], B.N. Rustamova[1], Sh.Z. Urolov[1], Z.Sh. Shaymardanov[1,2]

[1] Institute of Ion-Plasma and Laser Technologies of Uzbek Academy of Sciences, Durmon yuli str. 33, 100125, Tashkent, Uzbekistan
[2] National University of Uzbekistan, University str.4, 100174, Tashkent, Uzbekistan

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* Corresponding author: e-mail rr_jalolov@iplt.uz, Phone: +998 97 427 27 71

В данной работе описаны методы синтеза различных наноструктур ZnO в водных растворах при низких температурах и исследуется влияние размера синтезированных образцов на спектры фотолюминесценции (ФЛ). По мере увеличения диаметра наноструктур наблюдалось уменьшение отношения интенсивности полосы ультрафиолетового излучения к интенсивности полосы желтого излучения в спектре ФЛ. Было обнаружено, что изменение диаметра наноструктур от 15 нм до 1000 нм приводит к уменьшению их ширины запрещенной зоны (E_g) от 3.28 до 3.21 эВ. В наноструктурах с диаметром менее ~400 нм, было обнаружено, что энергия запрещенной зоны сильно зависит от размера наноструктуры и что связи слабее, когда размер наноструктур превышал 400 нм.

Ключевые слова: наноструктуры ZnO, фотолюминесценция, дефекты, размерный эффект.

This paper describes methods for synthesizing different nanostructures of ZnO in aqueous solutions at low temperatures and examines the effect of the size of the synthesized samples on the photoluminescence (PL) spectra. As the diameters of the nanostructures increased, a decrease in the ratio of the intensity of the ultraviolet radiation band to the intensity of the yellow radiation band in the PL spectrum observed. It is found that changing the diameters of nanostructures from 15 nm to 1000 nm leads to a decrease in their bandgap energy (E_g) from 3.28 to 3.21 eV. When the diameters of the nanostructures were less than ~400 nm, it was found that the energy of the band gap was strongly depend on the size of the nanostructure, and that the bond was weaker as the size of the nanostructures exceeded 400 nm.

Keywords: ZnO nanostructures, photoluminescence, defects, scale effect

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I. Introduction

ZnO is a widely studied metal oxide semiconductor, due to its high transparency in the visible region, large bandgap, non-toxic nature, high exciton binding energy and abundant availability in nature makes it a potential candidate for a variety of applications such as gas sensors, transparent electrodes in solar cells, photocatalysts, nanolasers, photoluminescent devices, organic light-emitting diodes, thin-film transistors and et al. [1, 2]. A wide bandgap (3.37 eV at room temperature) makes ZnO a promising material for photonic applications in the UV and blue spectral range, while the high exciton-binding energy (60 meV) allows efficient excitonic emission even at room temperature [1]. Also, ZnO is biocompatible which makes it suitable for biomedical applications. In addition, ZnO is a chemically stable and environmentally friendly material. Consequently, there is considerable interest in studying ZnO in the form of powders, single crystals, thin films, nanorods and nanocrystals. A low-temperature aqueous solution approach offers the potential for a much-lowered

fabrication cost and scale-up production because it can eliminate the complicated issues associated with high-temperature manufacturing and vacuum processing. Moreover, the typical growth temperatures are below 100°C, allowing the fabrication even on substrates such as plastic, which are not allowed to be exposed at higher temperatures.

Typically, a photoluminescence (PL) spectrum of ZnO nanostructures consists of two parts: a near band edge (NBE) emission centered at around 380 nm and defect-related emission bands in the visible range [1]. The PL characteristics of ZnO nanostructures strongly depend on their crystalline quality, which in turn are determined by their size and growing conditions and methods and post-grown treatment history. The defect-related emission bands can appear in violet-blue (390–460 nm) or/and green (500–520 nm) or/and yellow-orange (560–600 nm) or/and red (650 nm) ranges. The interstitial oxygen or complexes formed with oxygen have been ascribed to yellow-orange band [3-7]. Yellow-orange band is frequently observed in ZnO nanomaterials grown from water-contained solutions of Zn compounds at relatively low temperatures.The most obvious trend versus particle size is that the surface-to-volume ratio increases for smaller particles and the transport distance from any interior point to surface traps and recombination sites decrease in the same trend. In addition to the correlations between the defects and the optical properties, one should also notice that at the nanoscale the size not only directly impacts the defect contents but also the optical properties of materials. Examining PL spectra of various ZnO nanostructures provide a way for us to understand the roles of size and defects in the earlier photoexcited processes. Despite the large body of research devoted to size effect in ZnO nanostructures, many questions remain regarding the optical and electronic properties of these centres. The size of nanostructures has a major impact on their optical, crystalline, and electrical properties. There are many contradictions in published scientific articles. Sharma et al. [8] noted that when thickness of the film increases, crystalline quality of ZnO thin films improves, in contrast to Ref [9, 10] as the size of the nanostructures increased, their optical quality decreased.

This work reports a systematic study of dependence of the morphological and optical properties of various ZnO nanostructures grown over glass substrates. We have synthesized different 1D ZnO nanorods using a low-temperature hydrothermal method and ZnO nanocrystals using a chemical bath deposition method. The relationships between size of ZnO nanostructures and PL properties are revealed and discussed. Our studies show that as the size of ZnO nanostructures synthesized in aqueous solution at low temperatures increased, the number of defects formed in them increased and the maximum redshift of the PL intensity occurred.

II. Experiment

ZnO nanorods have been synthesized through hydrothermal route. Before ZnO nanorods are grown, a seed layer was formed on the surface of the substrates. Dip coating method has been applied to prepare ZnO seed layer on substrates because of its low cost and easy approach. All the reagents (Sigma-Aldrich, 99%) used in the experiment were analytically pure and were used without further purification. 5 mM of zinc acetate dehydrate ($ZnC_4H_6O_42H_2O$) was dissolved into 40 ml of ethanol with stirring for 1 hour at room temperature for obtaining a clear homogenous solution. The stirred solution was taken in a beaker and the substrates were dipped in the solution with different velocities using a handmade automatic dip coating system and dried in air at room temperature. The substrates with zinc acetate seed layer were annealed at 200°C for 30 min in air to decompose zinc acetate into ZnO nanocrystals.

Growth of ZnO nanorods is carried out in the following order: the aqueous solutions of zinc nitrate hexahydrate ($Zn(NO_3)_26H_2O$) and hexamethylenetetramine ($C_6H_{12}N_4$) were first prepared separately and then they were mixed together. The resulting suspension was transferred into a Teflon-lined stainless steel autoclave. The substrates with the ZnO seed layer were placed face-down and without seed layer substrates were placed on the bottom of the autoclave. Finally, the autoclave was sealed and put into the water thermostat bath. The hydrothermal reaction was carried out at 90°C for 5 hours.

ZnO nanocrystals were synthesized by chemical bath deposition method. The growth procedure was designed as follows: 0.6586g zinc acetate dihydrate ($Zn(CH_3COO)_22H_2O$) was dissolved in a 30 ml methanol solution under vigorous stirring at room temperature (RT), then ultra-sonicated for 10 min. DI water (10 ml) was added into the solution under stirring. Glass substrates were placed in a row in the bottom of the conical flask with the prepared solution. The conical flask then was put into a water tank at a constant temperature of 63℃ for 24 h. After the expi-

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ration of the ZnO particle deposition process, the conical flask was taken out and cooled to RT.

The emission spectra of ZnO nanorods were obtained using a photoluminescence set-up coupled to a 0.75 m monochromator with diffraction grating and high sensitive photomultiplier tubes. As excitation source, a longitudinally pumped nanosecond pulse N_2 laser emitting at 337 nm (pulse duration ~6 ns, P ~15 kW, repetition rate 100 Hz) was used. Emission spectra were recorded using a boxcar integrator with a gate width of 40 ns.

The morphology of the ZnO nanostructures was examined using a scanning electron microscope (SEM) PHILIPS XL-30.

III. Results and discussion

Morphology and particle size of the synthesized ZnO nanostructures are shown in Fig. 1. Crystallized the seed particles of ZnO deposited on substrates have a similar shape with an average size of 10–20 nm as shown in Fig. 1a.

Figure 1b displays SEM images of the as-grown ZnO nanorods grown on the substrate with seed layer. As can be seen, the hydrothermal growth method provided to synthesis a high density of uniform hexagonal nanorods approximately 50–70 nm in diameter and the length around 0.9–1.1 μm. Simultaneously with the vertically aligned ZnO nanorod grown on the seed layer, homogeneous nanostructures of ZnO were also deposited on glass substrate placed on the bottom of the autoclave.

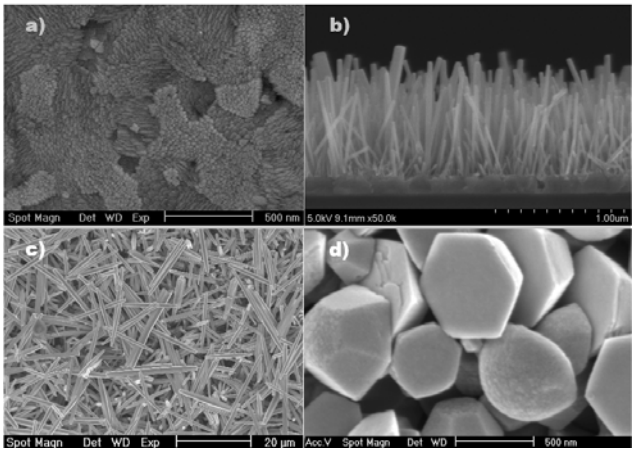


Figure 1. SEM images of ZnO nanostructures obtained by scanning electron microscope: a) crystallized the seed particles, b) nanorods, c) microrods, d) nanocrystals.

These ZnO microrods possesses spindle-shaped and hexagonal form and their length and diameter are 18−20 and 0.5−1 μm, respectively. Microrods are located chaotically and have predominantly horizontal positions on the substrate. The ZnO nanocrystals deposited on quartz substrates have the same regular cone form with the average sizes of 300–500 nm as shown in Fig. 1d.

Fig. 2 shows the decomposition of PL spectra of as-grown ZnO nanostructures grown by aqueous solution methods at low temperatures into Gaussian components. The PL spectrum of crystallized the seed particles contains only a strong band in the ultraviolet range and no emission bands in the visible range were observed. However, PL spectra of ZnO nanostructures except only seed particles consist of two peaks: narrow and strong in the UV range with weak and broad emission bands in the visible range

The deconvolution of PL spectra into Gaussian components helps to obtain more complete information about the radiation bands in the spectrum. The Gaussian deconvolution shows that The PL spectra contain a sharp ultraviolet (UV) peak located at 378–386 nm and weak violet band (VB) 391–402 nm and a broad yellow emission band (YB) around 558–568 nm [11]. The UV peak was attributed to near band edge emission or free exciton of ZnO. The yellow and blue luminescence bands can be attributed to intrinsic defects and/or their complexes, considering that ZnO nanostructures were synthesized without extraneous additions. At the hydrothermal synthesis method, the reaction runs in an aqueous medium with excess oxygen, which facilitates the formation of zinc vacancies. Theoretical studies predict that under ZnO-synthesis conditions with excess oxygen the zinc-vacancy and interstitial oxygen formation enthalpy is smaller than that for other defects [12]; therefore, zinc vacancies can be dominant defects. Taking into account these data and our results, we can suggest that the violet PL band near 395–405 nm in ZnO nanostructures is also due to defects related to zinc vacancies or their complexes. As was theoretically predicted, the (0/−1) transition level for a zinc vacancy lies above the top of the valence band by ~0.45 [12] or ~0.3 eV [13] and the (−1/−2) transition level lies above the top of the valence band by ~0.8 [12] or 0.7 eV [13]. Hence, electron transitions from the conduction band or a shallow donor level to a singly charged acceptor level of a zinc vacancy can provide luminescence with a wavelength of 395 450 nm [14].

The yellow band is often observed in zinc oxide nanomaterials grown from aqueous solutions at

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relatively low temperatures and is usually attributed to interstitial oxygen or complexes formed with the participation of oxygen. A ratio of the intensity of the ultraviolet emission to the intensity of the broadband emission indicates an optical quality of nanostructures. It is remarkable in Fig. 2 that the ratio of the intensity of the ultraviolet emission to the intensity of the broadband (visible) of PL emission bands depends significantly on the size of the nanostructures. As the diameters of the nanostructures increased from 70 nm to 1000 nm,

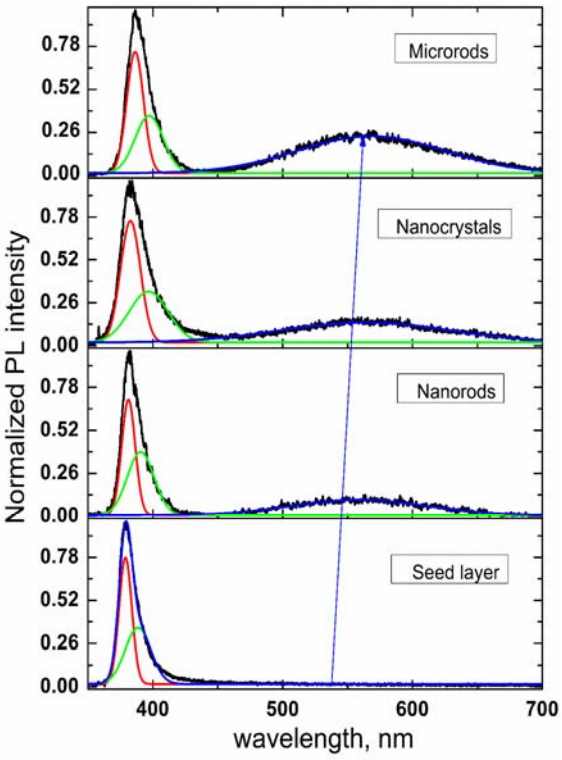


Figure 2. PL spectra of ZnO nanostructures and their Gaussian components.

the ratio of the intensity of the ultraviolet radiation band to the intensity of the yellow radiation band decreased from 7.5 to 3.2. This indicates that the size of the as-grown nanostructures increases, the concentration of defects in them increases and their quality deteriorates [9, 10]. According to the authors in Ref. [15], the yellow luminescence from ZnO structures was not sensitive to the surface modifications of the nanostructures and could be originated from the defects localized in the bulk, not on the surface. Thus, changes in the surface-to-volume ratio of ZnO nanostructures should affect the violet and yellow luminescence intensities in opposite directions. The surface-to-volume ratio N can be expressed as:

$$N = \frac{S}{V}$$

For the a) crystallized seed particles, b) – nanorods c) – nanocrystals d) – microrods, the surface-to-volume ratio is ~200, ~30, ~11, ~6. Obviously, the crystallized seed particles have more advanced surface but small volume than that the other nanostructures and the yellow luminescence band will dominate in the PL spectrum ascribed from the randomly deposited ZnO microrods.

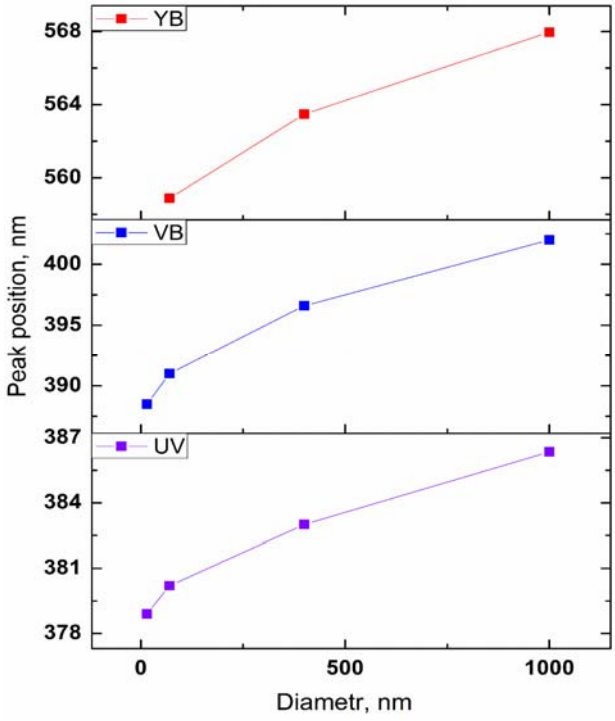


Figure 3. Variation of the maximum of the emission bands depending on the size of ZnO nanostructures.

Fig. 3 shows the variation of the maximum of the emission bands depending on the size of the nanostructures. Maxima of the UV emission peak belong to the near band edge transition level shifted from 378 to 386 nm. This result indicates that when the size of the structure increases from 15 to 1000 nm, the values of bandgap energy (E_g) decreased from 3.28 to 3.21 eV. According to the bandgap energy (E_g) of the bulk ZnO, these results can be attributed to the optical confinement effect correspond to the size and length of nanostructures [16, 17]. This results show that as the size of the nanostructures increases, the maxima of all emission peaks also move toward larger wavelengths at the same time.

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The fact that the shifts of the maximums of all the emission bands occur under the same law also confirms that the values of bandgap energy is shrinking.

The position of the maximum of the emission peaks varies inversely with the size of the nanostructures (Fig. 3). When the size of the nanostructures ranged from 0 to 400 nm, the width of the energy band gap became strongly dependent on the size of the nanostructure, and as the size of the nanostructures increased from 400 nm, the width of the energy band gap became weakly dependent on the size of the nanostructures.

IV. Conclusion

We have successfully synthesized various nanostructures of ZnO in an aqueous solution at low temperatures. ZnO nanostructures ranged in diameter from 15 to 1000 nm and exhibited a hexagonal structure. It was found that the photoluminescence spectra of nanostructures are strongly dependent on their size. As the ratio of nanostructures to the volume of water increased, so did the number of defects in them. At the same time, the optical quality of nanostructures deteriorated.

It was found that the position of the maximum of the observed radiation bands in the photoluminescence spectra of nanostructures is inversely related to their diameters. When the diameter of the nanostructures ranged from 0 to 400 nm, the width of the energy band gap became strongly dependent on the size of the nanostructure, and as the size of the nanostructures increased from 400 nm, the width of the energy band gap became weakly dependent on the size of the nanostructures. The maximums of all the emission bands occur under the same law.

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ZnO наноструктурининг фотолюминесценция хоссаларига ўлчамнинг таъсири

Р.Р. Жалолов[1], Б.Н. Рустамова[1], Ш.З. Уролов[1], З.Ш. Шаймарданов[1,2]

[1]Ион-плазма ва лазер технологиялари институти, ЎзР ФА, Дўрмон йўли кўчаси, 33, 100125, Тошкент, Ўзбекистон
[2]Ўзбекистон Миллий Университети, Университет кўчаси 4, 100174, Тошкент, Ўзбекистон

Ушбу ишда паст ҳароратда сувли эритмаларда ZnO нинг турли хил наноструктураларини синтез қилиш усуллари баён қилинган бўлиб, синтез қилинган намуналар ўлчамларининг фотолюминесценция (ФЛ) спектрларига таъсири тадқиқ қилинган. Наноструктураларнинг диаметрлари ошиб бориши билан ФЛ спектридаги ултрабинафша нурланиш полосаси интенсивлигининг сариқ нурланиш полосаси интенсивлигига нисбати камайиши кузатилди. Наноструктураларнинг диаметрлари 15 нм дан 1000 нм гача ўзгариши уларнинг тақиқланган зона энергиясининг (E_g) 3,28 эВ дан 3,21 эВ гача камайишига олиб келиши аниқланди. Наноструктураларнинг диаметрлари ~400 нм дан кичик бўлганида, тақиқланган зона энергияси наноструктураниг ўлчамига кучли боғлиқ эканлиги, ноструктуралар ўлчами 400 нм дан катталашган сари бу боғланиш кучсиз еканлиги аниқланди.

Калит сўзлар: ZnO наноструктуралари, фотолюминесценция, нуқсонлар, ўлчам эффекти.

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