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## Study of hydrothermal zinc oxide nanostructures photovoltaic properties

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**Abstract.** Electrical properties of zinc oxide nanostructures were studied in terms of change in the impedance under infrared, red, green, blue, and ultraviolet illumination. Physical interpretation of photoabsorption in ZnO is given, and the prospect of using the synthesized structures as photosensitive elements is shown.

**Keywords:** hydrothermal synthesis, zinc oxide, impedance spectroscopy

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Материалы конференции

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## Исследование фотоэлектрических свойств гидротермальных наноструктур оксида цинка

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**Аннотация.** Исследованы электрические свойства наноструктур оксида цинка по изменению импеданса в условиях ИК, красного, зеленого, синего и УФ освещения. Дана физическая интерпретация фотопоглощения в ZnO и показана перспективность использования синтезированных структур в качестве фоточувствительных элементов.

**Ключевые слова:** гидротермальный синтез, оксид цинка, спектроскопия импеданса

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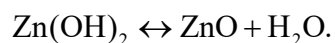
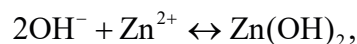
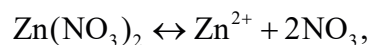
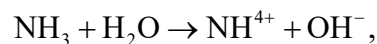
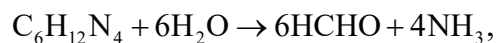
## Introduction

Zinc oxide (ZnO) is a wide-gap semiconductor material with band gap of 3,37 eV at room temperature [1]. This material is inexpensive, widespread, chemically stable, easy to synthesize, and non-toxic. ZnO is widely studied due to applications in light-emitting devices, nanoelectromechanical devices, sensors and others [1-5].

There are plenty of defect states occurring in ZnO that can either ruin the device performance or can be efficiently utilized, so control over the crystallinity is a major factor in ZnO nanostructures fabrication. Typical defects in ZnO are zinc and oxygen vacancies [6], which create levels enhancing non-radiative recombination, which can be used for development of photoabsorbing devices operating in the infrared (IR), visible, and ultraviolet (UV) wavelength ranges. However, the presence of oxygen and zinc vacancies also indicates a low crystalline perfection of the synthesized structures. This work is devoted to development of protocols for control of the morphology of ZnO structures synthesized using hydrothermal method and study of their photoelectric characteristics.

## Materials and Methods

Hydrothermal synthesis is a method of growing various materials and compounds, based on the use of physical and chemical processes that take place in aqueous solutions at slightly elevated temperatures often used to obtain ZnO nanostructures [7]. In our work, silicon substrates Si (111) are used for the hydrothermal synthesis of ZnO nanostructures since this material is known to be the most often used in nanoelectronics. Zinc acetate is used as a seed layer material. The following reactions take place during the growth process:



The growth solution consists of equimolar aqueous solutions of  $\text{Zn}(\text{NO}_3)_2$  and hexamethylenetetramine (HMTA). Sample #1 was synthesized without using surfactants (Fig. 1, *a*). Samples #2 and #3 were synthesized using sodium citrate and polyethylenimine (PEI) respectively (Fig. 1, *b*, *c*) allowing for lateral and vertical growth enhancement, respectively.

The resulting structures are found to possess branched NWs shape with an aspect ratio (length to thickness ratio) of about 10:1 (Fig. 1, *a*), quasi-two-dimensional nanostructures [8] in the shape of hexapods with  $D \sim 5 \mu\text{m}$ ,  $l \sim 1 \mu\text{m}$  (figure1(b)) and NWs with  $D \sim 100 \text{ nm}$  and  $l \sim 1 \mu\text{m}$  (Fig. 1, *c*).

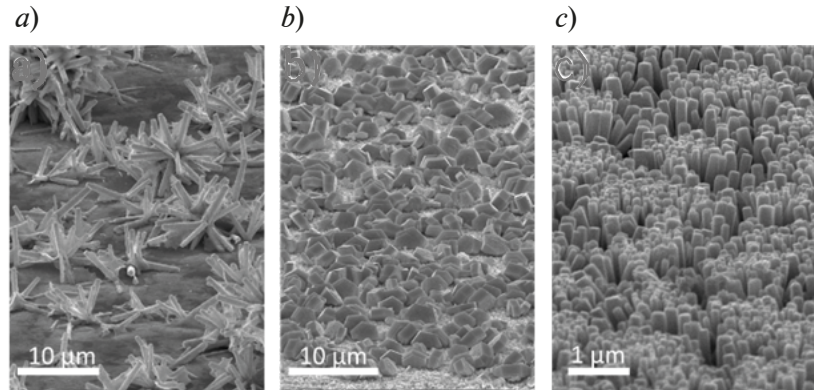


Fig. 1. Scanning electron microscopy (SEM) images of sample #1 (branched NWs) (*a*); sample #2 (hexapods) (*b*); sample #3 (vertical NWs) (*c*)

Electrical properties of the prepared samples were studied using Z500P impedance meter (Elins, Chernogolovka, Russia) in the frequency range from 100 Hz to 500 kHz by impedance spectroscopy. During the experiment, the impedance spectra were obtained under dark conditions, as well as under illumination with IR (850 nm), red (622 nm), green (570 nm), blue (470 nm), and UV (390 nm) LEDs. The power of the LEDs  $\sim 1 \text{ W}$ .

### Results and Discussion

The spectra of samples under different conditions are presented in Nyquist coordinates – the dependence of the imaginary part of the electrical impedance on the real one (Fig. 2). Spectra of samples can be visually divided into two parts: low-frequency (large impedance values) and high-frequency (10 kHz–500 kHz) in the form of a semicircle [9, 10], which is well described by an equivalent RC circuit, and the diameter of the semicircle corresponds to the resistance  $R$  of the material [11]. Analyzing the experimental data, we approximated the high-frequency part of the spectrum by a semicircle with the center lying on the x axis, which makes it possible to find the active electrical resistance of the zinc oxide structures lying between the electrical contacts. The change in the diameter of the approximating semicircles during the transition from dark conditions to illumination with a certain wavelength indicates a change in the active resistance of zinc oxide structures due to photoexcitation of carriers.

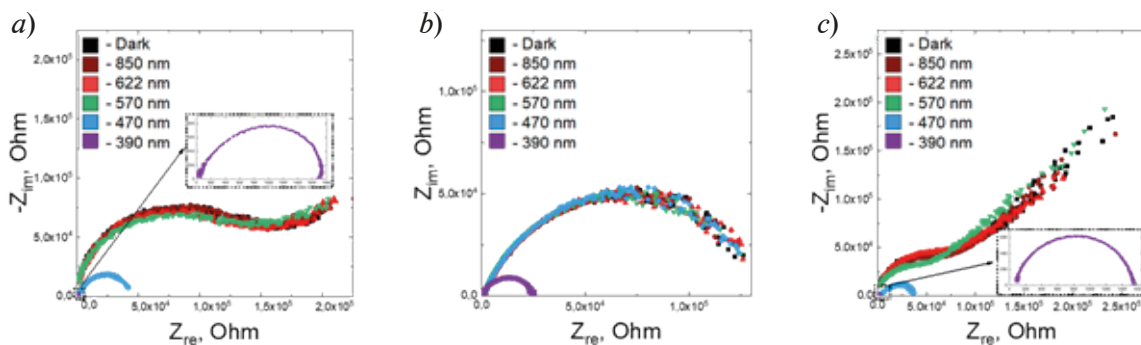


Fig. 2. Impedance spectra of sample #1 (*a*); sample #2 (*b*); sample #3 (*c*)



Figure 2 shows that no change in the resistance is observed for any of the samples when exposed under IR (850 nm) and red (622 nm) illumination. This is generally expected, due to wide-gap structure of ZnO. All the samples show high absorption when exposed near the absorption edge (390 nm). Table 1 shows the changes in resistance during illumination, obtained as a result of the analysis of the dependences shown in figure 2.

Table 1.

**Photoresistive response in three types of synthesized structures**

	570 nm	470 nm	390 nm
No surfactants	–	70%	99%
Sodium citrate	–	–	81,5%
PEI	26%	59,5%	98%

Structures synthesized without surfactants and using PEI also show photoconductivity under blue illumination ( $\lambda = 470$  nm). This behavior may be due to the presence of defect levels – zinc vacancies [7, 12, 13] in the band gap. The absence of absorption at a wavelength of 470 nm in the structures synthesized using sodium citrate indicates a high crystalline perfection of the structures. The sample synthesized using PEI also exhibits absorption at a wavelength of – 570 nm, which may be due to the presence of oxygen vacancies and interstitial Zn atoms [7, 14]. Further investigation of the nanostructures crystallinity will allow detailed interpretation of the demonstrated effects.

**Conclusion**

As a result of the work, samples of three morphology types were obtained: branched NWs, hexapods, vertical NWs. The change in photoabsorption depending on the wavelength of the LED radiation was studied by impedance spectroscopy. These changes are related to the crystallinity of the synthesized ZnO structures. The results obtained indicate that changing the hydrothermal growth chemistry is an effective way to control the optical properties of ZnO.

Thus, the zinc oxide structures synthesized in the course of this work are promising for their use as photosensitive elements.

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