The Effect of Vacuumization on the Photoluminescence and Photoresponse Decay of ZnO Nanostructures Grown by Different Methods

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Abstract – The effect of vacuumization on photoluminescence (PL) spectra and photoresponse decay of ZnO nanostructures fabricated by different methods was investigated. The visible band of photoluminescence and ultraviolet (UV) photosensitivity of the samples grown from the vapor phase was associated with the surface defects such as oxygen vacancies, and for the samples grown by hydrothermal method - with presence of the surface hydroxyl groups. The experimental results show that ZnO nanostructures grown from the vapor phase would be promising for producing of the low cost and effective UV detecting devices.

Key words – zinc oxide, nanostructures, photoluminescence, detectors of ultraviolet, defects.

I. Introduction

In recent years, extraordinary multifunctional properties of ZnO nanostructures were demonstrated. In particular this concerns transistors, nanogenerators, solar cells, light-emitting diodes, optically pumped lasers, chemical and biological sensors, detectors of ultraviolet and optical switches based on these materials. However, there is still no clear understanding of nature of the luminescence bands and the sensor parameters dependence on the type and number of defects in ZnO.

II. Experimental

ZnO nanostructures were grown on sapphire substrates with pre-deposited Au electrodes by two different methods. The distance between Au electrodes did not exceed 100 µm. ZnO nanowires (Fig. 1) were produced by the method of gas-transport reactions [1]. ZnO nanorods (Fig. 2) were grown by hydrothermal method [2]. Morphology of the samples was examined using REMMA-102-02 Scanning Electron Microscope-Analyzer. The room-temperature PL spectra 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 nm). (266 The measurements of the current-voltage (I-V) characteristics were carried out using Keithley Model 2401 Low Voltage SourceMeter multimeter.



Fig. 1. Microphotographs of ZnO nanowires



Fig. 2. Microphotographs of ZnO nanorods

The photoresponse decay was measured at 360-nm wavelength line obtained from a Xe lamp (1 kW) using the monochromator. All experimental measurements were made either in air and in vacuum at the pressure of 0.5 Pa.

III. Results and discussion

The morphology of ZnO nanowires and nanorods is shown in Figs. 1 and 2, respectively. ZnO nanowires were with diameter of 150-200 nm and a length of 5 μ m. ZnO nanorods are characterised by an uniform length of about 1 μ m with an average diameter of about 100 nm.

The room-temperature PL spectra of ZnO nanowires (Fig. 3) and nanorods (Fig. 4) obtained in vacuum and air consists of the two bands in the UV and visible regions.



Fig. 3. PL spectra of the ZnO nanowires in vacuum and air

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. The wide band from approximately 450 nm to 750 nm are caused by defects, first of all, by uncontrolled impurities and stoichiometry defects. For both types of samples after evacuating of air to the pressure of 0.5 Pa there occurred a slight increase of the ultraviolet band intensity, whereas the intensity of the visible band was changed in a different way. In the case of ZnO

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nanowires in vacuum the integrated intensity of the visible band increased by about 6%, whereas in the case of nanorods - vice versa, decreased by 17%. On the basis of these data, one can conclude that the green peak around 520 nm for ZnO nanowires arises due to radiative recombination of a photogenerated hole with an electron attributed to an oxygen vacancy [3]. The emission peak near 600 nm for ZnO nanorods originates from the hydroxyl groups attached to the ZnO nanorods [4]. These groups were also found to be removed upon evacuation, suggesting that there is a physical adsorption on the surface of the nanorods. When the PL spectrum was recorded again at the atmospheric condition, the intensity of the visible band is recovered almost to its original value. Since there is a substantial amount of water molecules in air, thay can be considered as source for the hydroxyl groups creation.



Fig. 4. PL spectra of the ZnO nanorods in vacuum and air

Fig. 5 presents the current-voltage (I-V) characteristics of the samples with ZnO nanowires and nanorods placed between two Au electrodes in darkness. A linear *I-V* characteristics indicate the ohmic nature of the contacts.



Fig. 5. I-V characteristics of Au-ZnO contacts in darkness

Photoresponse decay for the samples was measured under 5 V bias at room temperature in vacuum and air (Figs. 6 and 7). In the case of detecting of the ultraviolet radiation at the wavelength of 360 nm there was found that the recovery time of the sample with nanostructures grown by hydrothermal method is much higher then the recovery time of the sample with nanostructures grown from a vapor phase. After evaporating of air to the pressure of 0.5 Pa and switching off the Xe lamps the recovery time increased for the detector with ZnO nanowires and was not changed for the detector based on the nanorods. Filling with air had a little impact on the photocurrent relaxation time for the detector with nanorods, and led to a rapid decrease in the case of detector with ZnO nanowires. UV detector based on ZnO nanorods show a much higher rise time of photocurrent value upon illumination in comparison with the detector with ZnO nanowires. The high rise time indicates that the traps in the ZnO nanorods are involved into the photocurrent generation process.



Conclusion

We investigated the effect of vacuumization on the photoluminescence spectra and photoresponse decay of ZnO nanostructures fabricated by different methods. It was confirmed that the surface states play a crucial role in formation of PL spectra and UV detector properties of the nanomaterials. We associated a visible photoluminescence band and UV detecting properties of the samples grown from a vapor phase with the surface defects such as oxygen vacancies, and for the samples grown by hydrothermal method - with presence of the surface hydroxyl groups. Our results clearly show that ZnO nanostructures grown from the vapor phase would be promising for creation of the low cost and effective UV detecting devices.

References

- M. R. Panasiuk, B. I. Turko, V. B. Kapustianyk, O. P. Stanko, A. V. Mandryka, R. Y. Serkiz, Y. H. Dubov, "Photo- and thermostimulated luminescence of ZnO nanowires," J. Appl. Spectrosc., vol. 80, pp.240-243, Mar. 2013.
- [2] W. M. Choi, K.-S. Shin, H. S. Lee, D. Choi, K. Kim, H.-J. Shin, S.-M. Yoon, J.-Y. Choi, S.-W. Kim, "Selective growth of ZnO nanorods on SiO2/Si substrates using a graphene buffer layer," Nano Res., vol. 4, pp.440-447, May 2011.
- [3] D. Banerjee, J. Y. Lao, D. Z. Wang, J. Y. Huang, D. Steeves, B. Kimball, Z. F. Ren, "Synthesis and photoluminescence studies on ZnO nanowires," Nanotechnology, vol. 15, pp.404-409, Jan. 2004.
- [4] A. Sharma, B. P. Singh, S. Dhar, A. Gondorf, M. Spasova, "Effect of surface groups on the luminescence property of ZnO nanoparticles synthesized by sol–gel route," Surf. Science, vol. 606, pp.L13-L17, Sep. 2012.

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