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Influence of plasma and heat treatments on the properties of ZnO nanorods

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Oxide semiconductor nanostructured materials attract considerable attention of researchers due to their efficiency in electronics, optics, photonics, and other applications. One-dimensional semiconductor nanostructures such as nanowires, nanorods, and nanotubes are widely used for both academic research and industrial applications. Such nanostructures are useful materials for investigating of the dependence of electrical, thermal, and mechanical properties on dimensionality and size reduction. Actual study is the effect of postgrowth treatments on the properties of synthesized materials in order to improve their optical and electrical characteristics. In this work, we consider the effect of thermal annealing and treatment in hydrogen plasma on the morphology, optical, structural, and photoluminescent properties of samples consisting of zinc oxide nanorods obtained by chemical solution deposition. It is shown that the passivation of charged oxygen acceptors on the surface of grain boundaries upon short-term treatment in hydrogen plasma followed by thermal treatment in air makes it possible to activate the photoluminescence of ZnO obtained by chemical solution deposition and to obtain conductive transparent layers of ZnO nanorods with intense photoluminescence.

Keywords: zinc oxide, chemical deposition, optical properties, photoluminescence, plasma treatment, heat treatment.
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1 Introduction

Nowadays, nanostructured materials of oxide semiconductors are used as functional units in the manufacture of electronic, optoelectronic, electrochemical, and electromechanical nanodevices [1–3]. Among one-dimensional nanostructures, zinc oxide (ZnO) nanorods are one of the most important nanomaterials actively used in the modern world [4].

Zinc oxide is a semiconductor material with a direct band gap (3.37 eV) and a high exciton binding energy (60 meV) at room temperature [5]. ZnO is also biocompatible, biodegradable, and biosafe for medical and environmental applications [6]. Under normal conditions, ZnO exhibits the hexagonal wurtzite structure. The structure of ZnO can be described as a series of alternating planes consisting of tetrahedrally coordinated O^{2-} and Zn^{2+} arranged alternately along the axis. Due to their characteristics in electronics, optics, and photonics ZnO nanorods are attractive for use in solar cells [7–9], nanogenerators [10], gas sensors [11], photodetectors [12], and other devices. Among these applications ZnO nanorods are increasingly being used as photocatalysts to inactivate bacteria and viruses as well as to decompose environmental pollutants such as dyes, pesticides, and volatile organic compounds with appropriate light irradiation [13-14].

To obtain ZnO layers with the required properties, different types of post-growth treatment of nanorods are used. Among others, heat treatment in atmosphere and hydrogen plasma treatment are often used. The annealing process is one of the most important methods that can greatly affect the properties of ZnO nanostructures. Many researchers report, that ZnO sensor devices become more sensitive to UV after annealing. Annealing as a surface treatment process can remove surface defects and impurities and change the surface absorption and desorption of oxygen molecules, thereby improving the surface condition of ZnO [15]. It is known that photoconductivity in ZnO nanostructures is controlled by the adsorption and desorption of oxygen

on the surface [16]. Consequently, the annealing process can improve the photosensitivity as well as the photoresponse of ZnO by modifying the surface and improving the structure. In turn, annealing in a hydrogen atmosphere is often used to improve the electrical and optical properties of ZnO, since as known hydrogen atoms passivate broken bonds on the surface and energy states in the band gap [17]. During H-plasma treatment several processes occur in ZnO, including the diffusion of thermally and plasma-activated ZnO. Correspondingly, a significant increase in the near edge emission of ZnO was observed in a number of works after treatment with H_2 plasma [18, 19]. The processing leads to the appearance of various hydrogen-related transitions in the NBE emission band. It is assumed that complexes of zinc vacancies with oxygen and hydrogen atoms are responsible for these transitions [20]. It was found that the associated exciton transitions as well as the electronic levels associated with the surface effect on the luminescence spectra of ZnO at the band edge at low temperatures after treatment in H_2 plasma [21] and the emission at the band edge [22]. Another well-known effect caused by surface states in ZnO is the constant photoconductivity, which prevents the dark current from being rapidly restored after UV excitation and is a major drawback for the widespread use of ZnO-based thin-film transistors and photodetectors [23].

In this work we study the effect of thermal annealing, hydrogen plasma treatment, and treatment in hydrogen plasma with preliminary annealing in air on the morphology, optical, structural, and photoluminescent properties of zinc oxide samples, obtained by chemical solution deposition.

2 Description of the experiment and discussion of the results

Nanostructured zinc oxide layers were synthesized by chemical solution deposition. A thin seed layer of ZnO (~1–10 nm) was uniformly deposited on spotless glass substrates by the sol–gel method. The sol solution was prepared by dissolving 0.4 g of zinc acetate ($Zn(CH_3COO)_2$) in 10 ml of ethanol with thorough stirring on a magnetic stirrer at room temperature for two hours. Drying at 110°C and final annealing at a temperature of 450°C for 60 minutes in a muffle furnace led to the formation of uniform over the entire surface of the substrates seed layer.

The synthesis was carried out in a glass beaker on a steam bath for two hours on a heated magnetic stirrer at a temperature of 90°C.

The ZnO rods were grown in an equimolar solution containing 75 mM zinc nitrate $Zn(NO_3)_2 \times 6H_2O$ (Sigma Aldrich) and 75 mM hexamethylenetetramine $C_6H_{12}N_4$ (HMTA, Sigma Aldrich) dissolved in distilled water (18.2 MΩ×cm). The samples were placed at a slight angle to the vertical, with their faces facing the walls of the beaker. At the end of the synthesis, the samples were washed with distilled water and then dried in an oven at a temperature of 110–115°C.

Thermal annealing was carried out at atmospheric pressure in air in the temperature range from 100°C to 450°C in a quartz tube furnace. Plasma treatment in a hydrogen atmosphere (H-treatment) was carried out in a quartz cylindrical reactor with an inner diameter of 30 mm. During the hydrogen plasma treatment, the frequency of the high-frequency generator, the power of the high-frequency source and the discharge pressure were maintained at 27.12MHz, 15 W and 70 Pa, respectively. Plasma treatment was carried out at room temperature without intentional heating of the substrate; however, the temperature of the substrate during treatment in hydrogen plasma slightly increased to ~60°C due to high frequency absorption.

The results of the study by electron microscopy of ZnO samples synthesized by chemical solution deposition: initial, subjected to thermal annealing in a muffle furnace at a temperature of 450 ° C for one hour (AT), treated in hydrogen plasma (PT), and also treated in hydrogen plasma with preliminary annealing in air (A + PT), – showed that the synthesized samples are homogeneous layers over the entire surface of the substrate, consisting of rods fused at the base, oriented perpendicular to the substrate (Figure 1).

Initial samples have the highest ratio of crystal length to their thickness (aspect ratio AR), while samples subjected to plasma treatment have the lowest AR (Table 1).

Optical properties, such as optical density spectra and transmission spectra, were studied for all synthesized ZnO samples (Figure 2a, 2b, respectively). The results of the analysis of optical properties allowed us to determine the energy gap of the prepared samples using Tauc's method (Figure 2c).

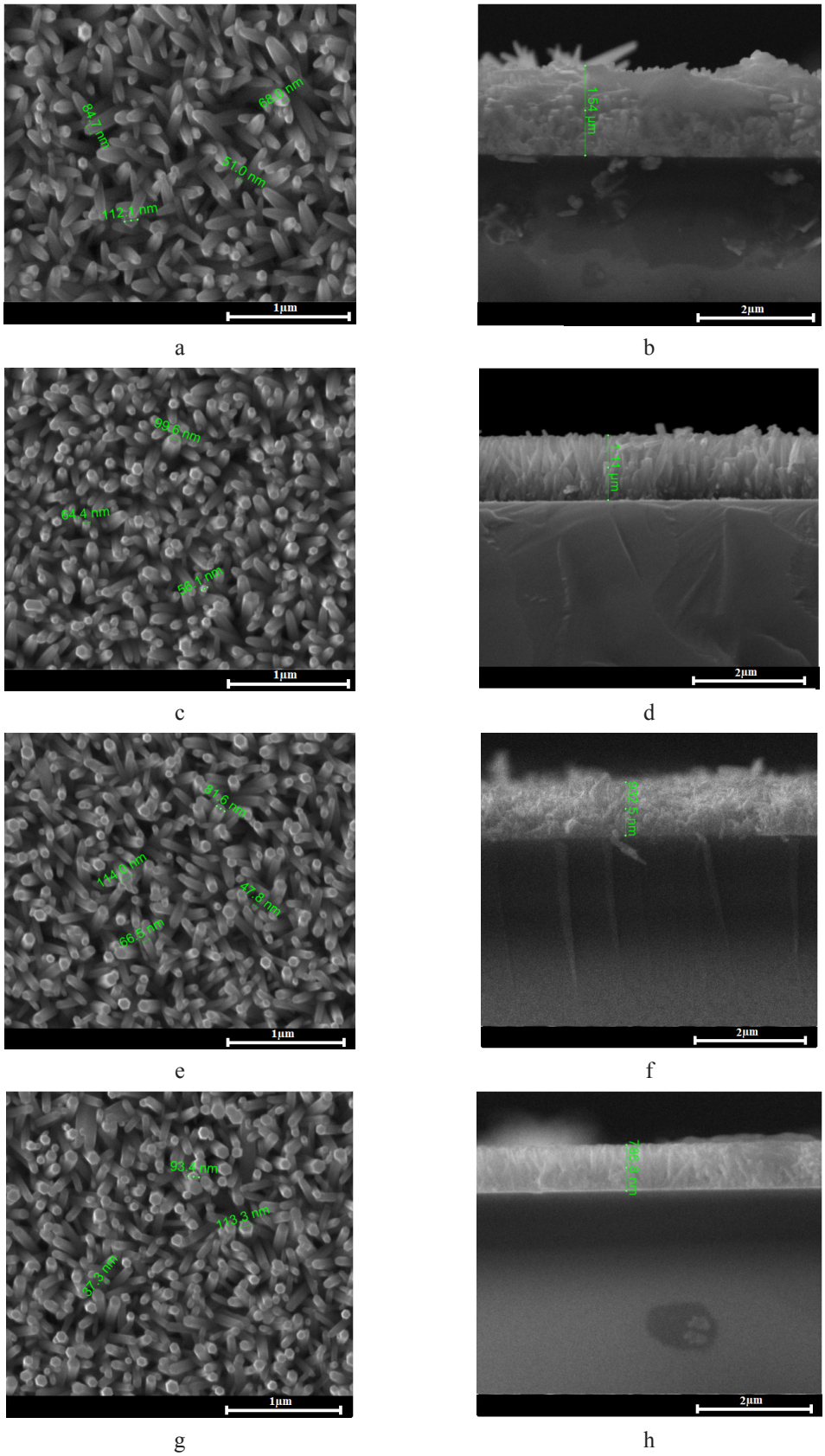

Figure 1 – Morphology of ZnO samples: a, b – initial; c, d – subjected to thermal annealing in a muffle furnace at a temperature of 450 °C for one hour; e, f – treated in hydrogen plasma with preliminary annealing in air; g, h – treated in hydrogen plasma

Table 1 – Physicochemical properties of ZnO nanorods

Sample	FESEM		Length/thickness, l/d	Cell Options, Å		E_g, eV
	Thickness d, nm	Length l, nm		a	c	
Initial	80±30	1540±10	19.25	3.246	5.201	3.125
AT samples	78±20	1100±10	14.1	3.245	5.201	3.15
A+PT-samples	77±20	933±20	12.1	3.246	5.206	3.2
PT samples	78±20	787±10	10.1	3.247	5.204	3.25

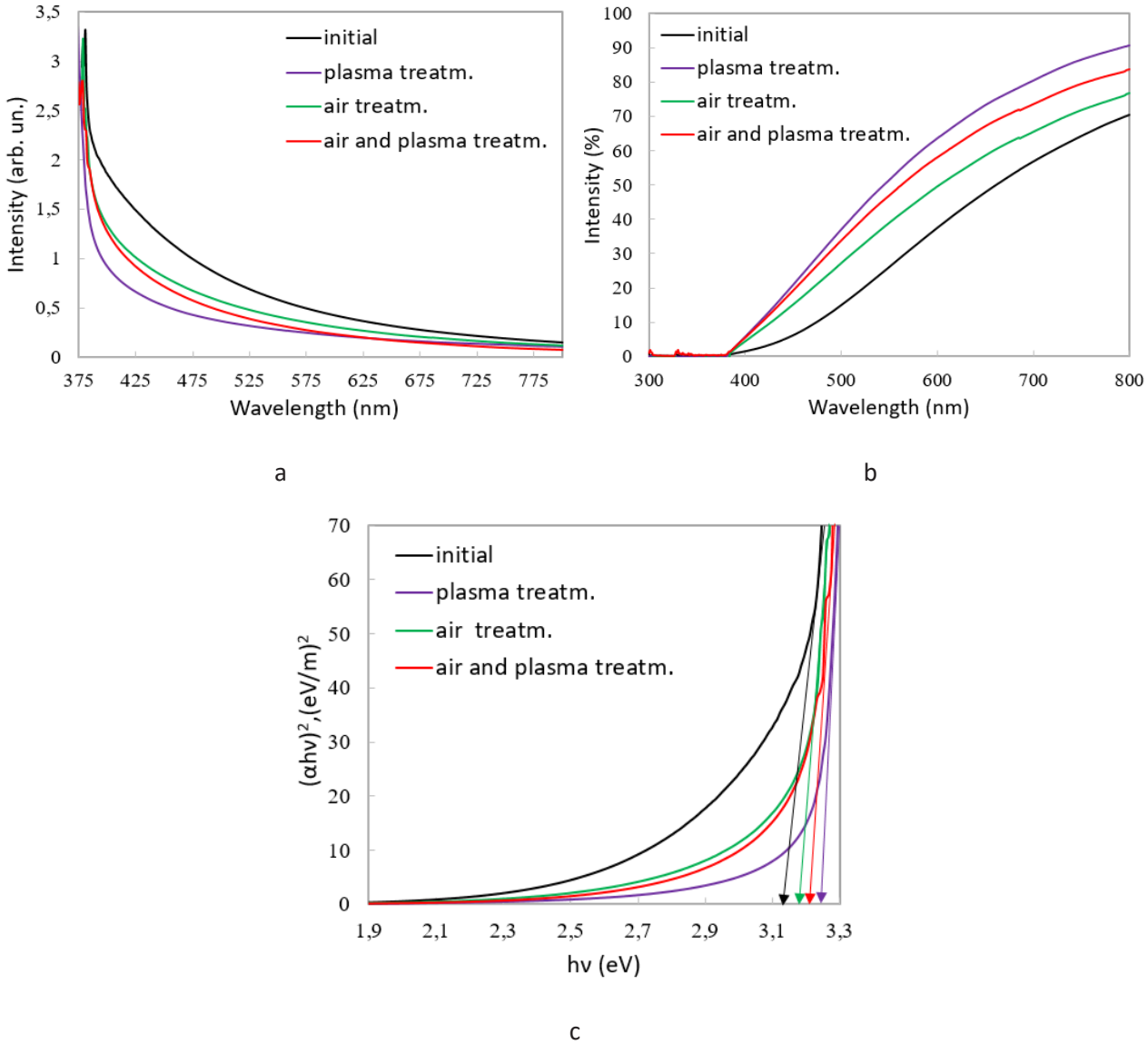

Figure 2 – Optical properties of ZnO films obtained by chemical deposition:
(a) absorption spectra, (b) transmission spectra, (c) Tauc Plot diagram

The optical absorption spectra near the band gap of the sample annealed in air and also annealed in air followed by treatment in hydrogen plasma are similar. Samples treated in hydrogen plasma had the lowest absorption. This suggests that grown ZnO has numerous large number of electronic levels that are involved in light absorption, and the optical activity of these levels can be passivated by H-treatment. The highest absorption was noted for the original samples. It was found that the optical band gap is Eg = 3.125 eV for the original samples, 3.15 eV for the samples subjected to thermal annealing, 3.2 eV for the samples annealed in air followed by treatment in hydrogen plasma, 3.25 eV for samples treated with hydrogen plasma only (Table 1).

The XRD measurements were carried out under the same conditions. The diffraction peaks present indicate the hexagonal structure of the wurtzite of all samples under study. An analysis of the diffraction patterns showed a high crystallinity of all samples with a predominant (002) orientation with a slight difference in the intensity of the diffraction peaks. No significant effect of treatments on the structural properties of the samples was noted. The cell parameters of all samples are given in Table 1. Figure 3 shows the X-ray diffraction pattern of the original ZnO sample.

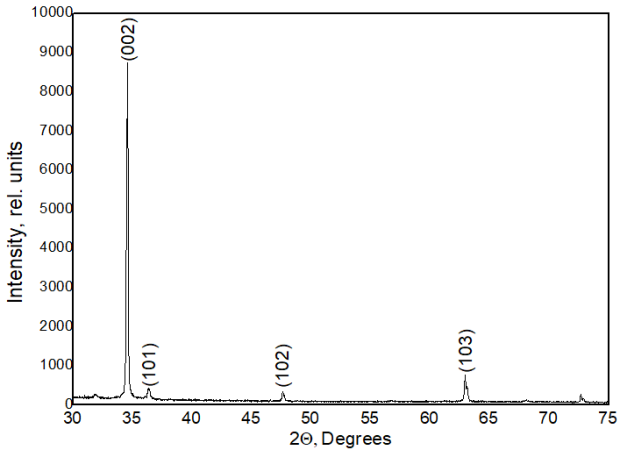

Figure 3 – Diffractogram of the initial ZnO sample

The photoluminescence spectra of ZnO samples synthesized by chemical solution deposition were studied (Figure 4). The photoluminescence spectra were measured at room temperature under excitation with light with a wavelength of 300 nm. As can be seen from Figure 4, immediately after synthesis the PL spectra show mainly an impurity band with a maximum at ~620 nm, and the intrinsic PL band almost does not appear. After annealing in air for an hour the maximum of the impurity PL band shifts by ~560 nm. Plasma treatment leads to a change in the ratio of the intensities of intrinsic and impurity photoluminescence bands. Preliminary annealing in the atmosphere followed by plasma treatment promotes a sharp increase in the intrinsic PL band.

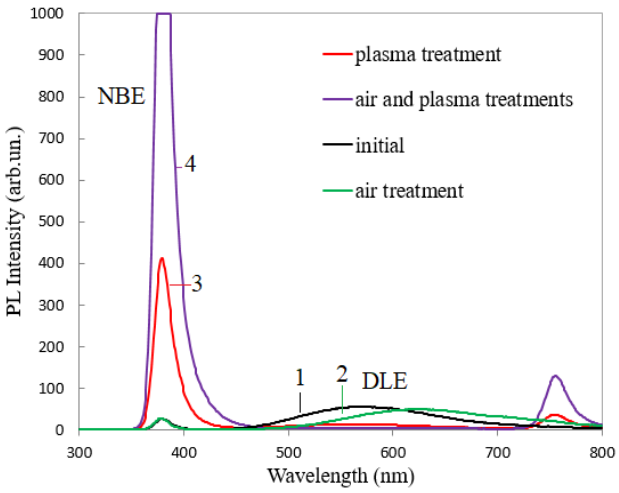

Figure 4 – Photoluminescence spectra of ZnO samples: 1. initial; 2. thermally annealed in a muffle furnace at 450°C for one hour; 3. treated in hydrogen plasma; 4. treated in hydrogen plasma with pre-annealing in air

A difference was noted in the photoluminescence spectra of the initial samples and after treatments [24]. The DLE band, which in the original samples had approximately the same intensity as the NBE band (Figure 4, spectra 1, 2), was completely passivated after treatment in hydrogen plasma (Figure 4, spectra 3, 4). The intensity of the NBE band in PT samples increased after treatment in hydrogen plasma (Figure 4, spectrum 3) by ~17 times compared to the initial spectrum (Figure 4, spectrum 1). An increase in the PL intensity may be associated with the passivation of recombination centers on the surface and in the bulk, the introduction of shallow donors, and others. For example, specific chemisorbed oxygen and various radicals obtained during synthesis are present on the surface of ZnO, which significantly effect on the surface recombination and can be passivated hydrogen [25].

Samples annealed at 450°C followed by treatment in hydrogen plasma showed an increase in NBE intensity by a factor of ~65 compared to the initial PL spectrum (Figure 4). This increase can

be explained by a change in the structure of surface defects during thermal annealing, since it is known that the photoluminescent properties of nano- and microcrystalline ZnO are largely determined by surface effects [26]. It is known that the adsorption of oxygen forms causes the quenching of UV radiation of ZnO nanoparticles and the restoration of visible radiation [27].

3 Conclusions

The optical, structural, and photoluminescent properties of samples consisting of zinc oxide nanorods vertically oriented with respect to the substrate, synthesized by chemical solution deposition, initial, subjected to thermal annealing in a muffle furnace at a temperature of 450 °C for one hour, treated in hydrogen plasma, as well as processed in hydrogen plasma with preliminary annealing in air, were compared. It is shown that samples processed in hydrogen plasma had the lowest absorption coefficient, and the initial ZnO samples had the highest. The optical band gap for initial samples was 3.125 eV, 3.15 eV for samples subjected to thermal annealing, 3.2 eV for samples annealed in air followed by treatment in hydrogen plasma, 3.25 eV for samples processed only with hydrogen plasma. It is noted that the synthesized ZnO samples subjected to thermal annealing followed by treatment in hydrogen plasma had the highest photoluminescence intensity.

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