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To cite this article: B R Ilyassov and N Kh Ibrayev 2016 *IOP Conf. Ser.: Mater. Sci. Eng.* **110** 012060

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Synthesis of nanostructured films of zinc oxide and a study of its structural and luminescent properties

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Abstract. ZnO nanorod array were synthesized on sol-gel prepared ZnO seed layer over quartz substrates by hydrothermal method. X-ray diffraction results show that nanorods are the typical hexagonal wurtzite structure without any other new phase and preferentially oriented along the c-axis perpendicular to the substrate surface. The scanning electron microscopy (SEM) of the surface of the ZnO film showed vertical ZnO nanorods with hexagonal cross-section. The luminescence spectrum of ZnO nanorod array consisted of a narrow UV band and a broad band in visible region of spectrum and its temporal characteristics were measured.

1. Introduction

ZnO is a multifunctional semiconductor material having direct wide band gap of 3.37 eV and high excitonic binding energy of 60 meV at room temperature. These properties make it a promising semiconducting material for transparent electronics, solar cells and other optoelectronic devices [1-3]. Synthesis of ZnO nanostructures such as one-dimensional rods, wires, tubes etc., has got increasing attention for its specific properties and for the fabrication of nano-scale devices. Many different techniques were used for the synthesis of nanostructures; they include vapor-liquid-solid (VLS) epitaxy [4], chemical vapor deposition (CVD) [5], pulse laser deposition (PLD) [6], thermal decomposition [7], hydrothermal synthesis [8], etc. The hydrothermal method is a more simple and cost effective process for the synthesis of ZnO nanorods. It has very low synthesis temperature below 100°C, catalyst free process and is suited for the uniform synthesis of ZnO nanorods over large area of the substrates. The structural and optical properties of the nanorods obtained by hydrothermal process exhibits strong dependence on conditions such as seed layer crystallinity, choice and concentration of surface-active agent used and reaction time for synthesis. Some authors [9] had reported the effect of annealing substrates on the density of ZnO nanorod array. Other authors [10] had studied the influence of addition of NaOH on the diameter of ZnO nanorods prepared by hydrothermal method. Liu et al. [11] had synthesized ZnO nanorods on sputtered ZnO seed layer.

In this work we have synthesized ZnO nanorod array on sol-gel prepared ZnO seed layer [1] over quartz substrate. The structural properties of the nanorods were studied by X-ray diffraction (XRD). The nanorods in array showed c-axis orientation perpendicular to the substrate and had structure of wurtzite. The surface morphology of the nanorods was studied by Scanning electron microscopy

(SEM). The surface of the ZnO film exhibits vertical ZnO nanorods with hexagonal cross-section. The optical properties of the samples were studied by UV-Vis spectrophotometer. The reflectance of the nanorod showed an absorption edge at the band gap of ZnO. The photoluminescence of nanorods showed UV emission at room temperature.

2. Experiment procedure

ZnO nanorods arrays were synthesized on quartz substrates by hydrothermal method [11], initially on the surface of the cleaned quartz substrates were coated thin seed layer of zinc oxide ZnO by sol-gel method [12]. The sol is prepared by dissolving zinc acetate dehydrate in isopropyl alcohol (with concentration of 20 grams per liter of solvent) at 20 °C with intensive stirring on a magnetic stirrer for 1-2 hours. Preparation of the clear solution at high concentrations of zinc acetate was achieved by adding a few drops of lactic acid. The resulting solution remains clear for a long time, it allows to obtain high-quality seed layers.

Uniform distribution of the sol on the substrate surface is achieved by dripping several drops of the solution onto the substrate mounted on a chuck of a spin-coater (VTC-200 Spin Coater, MTI), and then the substrate spun at ~ 3000 rpm for 30 seconds. Later, the substrate is placed on a hot oven and kept at a temperature of 300 °C for 10 minutes. Final annealing at a temperature of 450 °C for one hour leads to the formation of thin transparent layers on the substrate surface. This method allow us to synthesize ZnO multi-layered films on the substrate with area of 1-1.5 cm², having uniform properties and a high optical transmission factor in the visible range.

Hydrothermal synthesis of ZnO nanorods was carried out in the aqueous solution of zinc nitrate dehydrate and hexamine (C₆H₁₂N₄) in a glass beaker; the substrates with the seed layer of ZnO were placed at the fluoroplastic holder into the upright position. The synthesis was carried out in the temperature range 90-95 °C for 3 hours with intensive stirring. The resulting samples were washed with deionized water and dried.

3. Results and discussion

Studies of as-grown ZnO films on the scanning electron microscope (FEI Quanta-250) exhibited that the ZnO film is an array of hexagonal nanorods predominantly oriented perpendicular to the substrate (Fig. 1). X-ray patterns of as-grown ZnO films exhibited that ZnO nanorods have a hexagonal wurtzite structure with unit cell parameters $a = 3.260 \text{ \AA}$, $c = 5.214 \text{ \AA}$ and predominantly oriented along the direction of the crystallographic c-axis (Fig. 2).

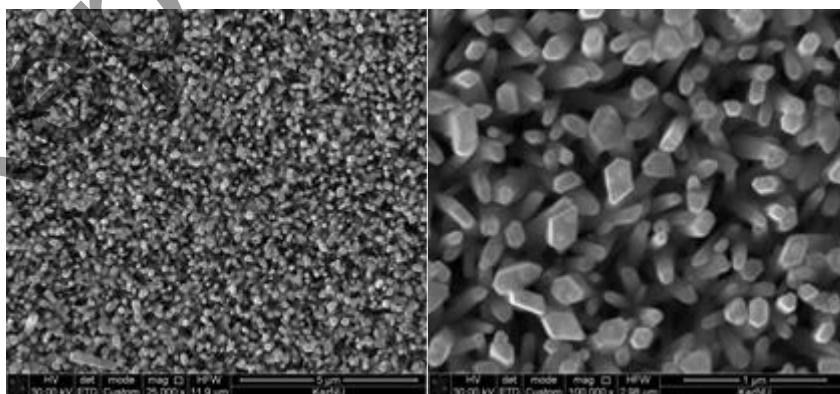


Figure 1 - SEM image of surface microstructure of ZnO film prepared by hydrothermal method at different magnification.

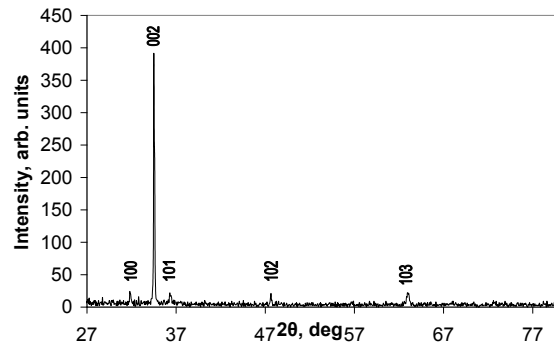


Figure 2 - X-ray pattern of ZnO films prepared by hydrothermal method.

The luminescent properties of zinc oxide nanorods array were investigated. The luminescence spectra of ZnO nanorods array was measured on a highly sensitive fiber-optic spectrophotometer AvaSpec-2048 at room temperature, photoexcitation of samples was performed the third harmonic of a neodymium laser LCS-DTL-374QT ($\lambda = 355$ nm, $\tau = 7$ ns, $E = 5$ mJ). The luminescence spectra of the films ZnO (Fig. 3) exhibited two bands: a narrow band in the UV with a maximum at 370-372 nm and a broad band in the visible region. The broad band in the visible region had several peaks with a maximum of 524 nm in the green region, 572 nm and weak peaks in the orange and red region. UV band has exciton nature, the main luminescence centers are free and bound excitons [13]. Visible luminescence of zinc oxide nanostructures related to point defects mainly with oxygen vacancies on the surface and inside the crystal, for the less defective ZnO nanostructures it covers mainly the green region of the spectrum [14].

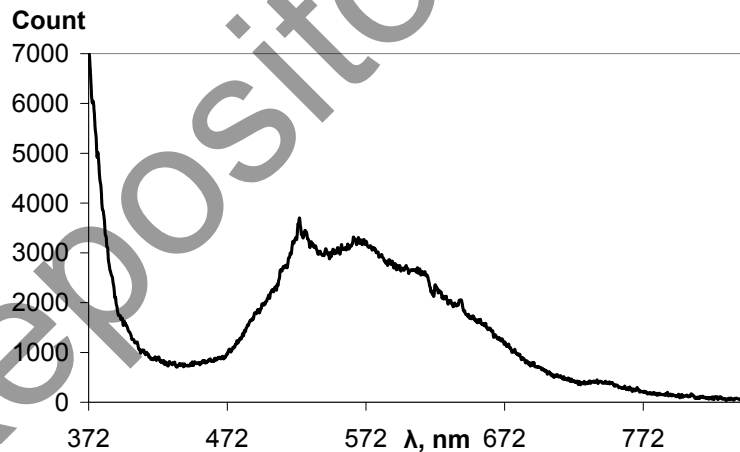


Figure 3 - The photoluminescence spectra of ZnO films prepared by hydrothermal method.

The temporal characteristics of luminescence of ZnO in subnanosecond and nanosecond time ranges were measured (Fig. 4 and 5). The samples were excited by a picosecond pulse semiconductor laser (BDL-SMC) with repetition rate of 50 MHz and pulse duration of 50 ps. The detection of luminescence carried out by a picosecond spectrometer using mode time-correlated single photon counting. All curve of kinetics of UV luminescence decay is not an exponential function (Fig. 4). However, the initial part of the kinetic decay curve (up to 10 ns) is described by an exponential. Lifetime calculated from this exponential part of curve is ~ 0.2 ns. All curve of kinetics of luminescence decay in the visible region is also not an exponential function (Fig. 5). Lifetimes of the emission bands with maxima at 524 nm and 572 nm calculated from the initial part of the exponential curve decay are the same and approximately 60 ns.

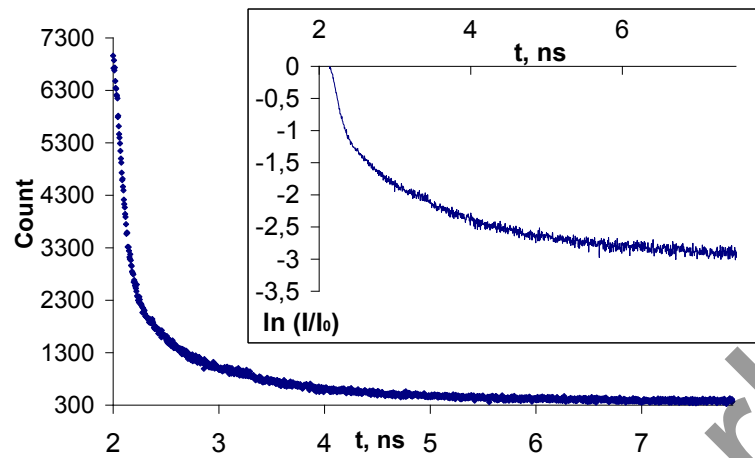


Figure 4 - The ultraviolet luminescence decay of zinc oxide films prepared by hydrothermal method.

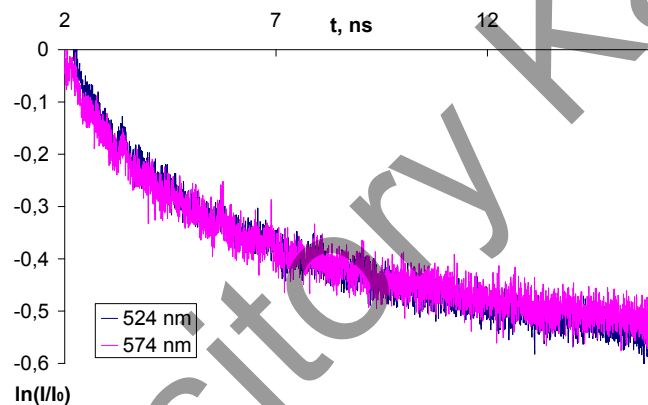


Figure 5 - Kinetics of luminescence decay of zinc oxide films in the visible region prepared by hydrothermal method.

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