Synthesis and characterization of ZnO nanorods obtained by catalyst-free thermal technique

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Abstract. ZnO nanorod arrays have been synthesized on silicon wafers by catalyst free thermal vapor deposition with different temperature values. Vertical-aligned ZnO nanostructures were grown at the quite low temperatures by this method. Modification of the method allowed to place silicon substrates in areas with different ratios of concentrations Ar and O$_2$ molecules in the vapor phase. Photoluminescence spectroscopy and electron microscopy studies have shown that morphologies and optical properties of nanorods depends on different ratios of concentrations of the molecules in the vapor phase.

1. Introduction

Zinc oxide, is a promising semiconducting and piezoelectric material with direct wide-band gap (3.37 eV at room temperature) and large exciton binding energy (60 meV). During the last years one-dimension nanocrystalline ZnO structures such as nanowire, nanorods, nanobelts and nanocables attract much attention of various research groups, due to their unique physical properties and potential applications in nanoscale devices. Of particular interest are well-oriented arrays of ZnO nanorods in connection with the combination of excellent electronic and optoelectronic properties of each nanorod. These ZnO nanorods arrays can be used as active elements of nanodevices, such as LEDs [1], nanosensors [2], UV lasers [3] photodetectors [4], etc. For practical applications the main objective is to obtain arrays of nanostructures ZnO, with the necessary morphology and physical properties.

There are various methods of producing arrays of nanorods ZnO: hydrothermal method, pulsed laser deposition, chemical vapour deposition and metalorganic chemical vapour deposition, thermal evaporation and etc. One of the promising methods for the growth of ZnO nanorods is the thermal technique of synthesis from Zn vapor, which implemented in this paper. In our work we obtained ZnO nanorod arrays by means of catalyst free thermal evaporation technique under different temperature values and investigated properties of the structures.

2. Experiment

The technique used during the synthesis of ZnO nanorod arrays have been based on thermal evaporation of metallic granule Zn in Ar and O$_2$ gas mixture, transferring vapor precursors to the
substrate and subsequent deposition of ZnO nanorods on the substrate from the vapor phase without the use of any metal particles as catalysts.

ZnO nanorods grew at a quite low temperature without any catalysts on the ZnO (100nm) / (100) silicon substrates 10x10 mm² in size. The thin ZnO buffer layer was prepared by pulsed laser deposition technique on the Si substrate. Laser radiation of KrF laser (λ = 248 nm, E = 300 mJ) was focused on the surface of rotating ZnO ceramic. Distance between target and substrate was 50 mm. The repetition frequency of the laser pulses was 10 Hz. The substrate temperature was 500°C. ZnO film was deposited at 2,000 laser pulses, the oxygen pressure was 2 × 10⁻² mbar.

It was found the morphology and optical properties of ZnO rods on the substrates are very sensitive to the Zn vapor supersaturation. Our reactor used for the synthesis comprised a horizontal tube furnace, a pumped quartz tube and an argon and oxygen gas supply. In our work, the precursor (Zn granule) and substrates placed in a small quartz tube. In contrast to works [5-7], we use a small quartz tube opened on both sides. This tube is placed in a reaction chamber - a quartz tube 32 mm in diameter, located in a resistive heater. Using this modification could be achieved different ratio values of concentrations of the zinc and oxygen molecules in the vapor phase in different areas of reactor. Pressure value in the experimental setup was controlled by the means of changing pumping rate and flow of Ar buffer gas.

**Figure 1.** Experimental setup used for the growth of nanostructures.

In the first series of experiments zinc granule (purity 99.9999%) weighing 500 mg was placed in the center of the small quartz tube. Substrate ZnO / (100) Si was placed on a distance of 0.5 cm from the Zn granule between zinc precursor and input aperture of gas mixture. After the quartz chamber was pumped to 2 mbar, Ar gas was flowed at a flow rate of 240 sccm, and the deposition pressure was set 11 mbar. Next the substrate and Zn granule are heated to a synthesis temperature in 35 minutes. When the necessary temperature was achieved, gas also started flow in the reactor at 8 sccm. Well-aligned ZnO nanorod arrays have been grown at the furnace temperature 600°C in 15 minutes.

Scanning electron microscopy (SEM) and photoluminescence (PL) was used to characterize optical and morphological properties of the ZnO nanorod arrays. SEM images and PL spectra of synthesized nanorods shown in Figure 2. SEM and PL researches was carried out on different areas of the substrate to study the effect of the atmosphere supersaturation by Zn vapor on the properties of produced zinc nanorods. The size of crystals depends on distance to the edge of a small quartz tube that shown in scanning electron microscope images. It is found that the ratio values of zinc and oxygen molecules concentrations in the vapor phase influences on size and optical properties of ZnO.
nanostructures. Average diameter of the rods is about 50 nm. Average height of rods increases with increasing substrate-to-source distance from 200 nm to 800 nm. Nanorods from various areas had different concentrations of point defects related to oxygen vacancies according to the red-shift of the PL peak corresponding to exciton transitions.

In the second series of experiments substrate was placed on a distance of 4.5 cm from the zinc granule downstream of gas mixture. The deposition pressure was set 11 mbar. Next the substrate and Zn granule were heated to a synthesis temperature in 25 minutes. When the necessary temperature was achieved, gas also started flow in the reactor at 5 sccm. At the final stage of the synthesis process the pressure in the chamber was rapidly increased from 10 mbar to 50 mbar by changing the pumping rate. ZnO nanorod arrays with sharp tips have been grown at the furnace temperature 600°C in 30 minutes.

SEM and PL researches was carried out on different areas of the substrate to study the effect of the Zn vapor supersaturation on the properties of obtained zinc nanorods. The sharpened form of nanorods (Fig. 3) is similar to the shape of the nanostructures obtained in work [8]. The rapid increase of pressure value leads to a change in the rate of generation of zinc vapor and molecular mobility. Consequently were grown the rods with various form of the tips in different areas of the reactor. Photoluminescence spectra show that obtained structures have a high intensity peak in the ultraviolet spectrum range at a wavelength of ~ 380nm, and a low intensity peak in the visible spectrum, which corresponds to low concentrations of point defects related to oxygen vacancies.
3. Conclusion

A method of synthesis one-dimensional ZnO nanostructures by thermal evaporation technique at the quite low temperature (550°C -600°C) is proposed. The configuration used in this work allows us to localize the substrate in areas of reactor with different ratio values of concentrations of the zinc and oxygen molecules in the vapor phase. SEM images and PL spectra have shown that physical properties of synthesized structures depend on Zn vapor supersaturation values. Using our modification presented in this work, makes it possible to obtain the nanocrystals with the necessary morphological and excellent optical properties. Such rods are very interesting in quantum optoelectronics. Particularly they can be used in ultraviolet photodetectors and light-emitting diodes.

4. Literature

[1] Sun X W, Huang J Z, Wang J X, Xu Z 2008 Nano Lett. 8 №4 1219–1223
[2] Kim D Y, Son J Y 2009 Electrochemical and Solid-State Letters 12 №12 109-111
[3] Huang M H, Mao S, Feick H, Yan H, Wu Y, Kind H, Weber E, Russo R, Yang P 2001 Science 1897-1899
[4] Chien Y L, Shouou-J C, Sheng P C, Ching T L, Che F K, Hong M C 2006 Applied Physics Letters 89 153101
[5] Park J, Choi H, Siebein K, Singh R 2003 Journal of Crystal Growth 258 342–348
[6] Chang P, Fan Z, Wang D, Tseng W, Chiou W, Hong J, Lu J 2004 Chem. Mater 16 5133-5137
[7] Red’kin A N, Makovei Z I, Gruzinsev A N, Dubonos S V, Yakimov E E 2007 Inorganic Materials 43 №3 253-257
[8] Pan N, Wang X, Zhang K, Hu H, Xu B, Li F, Hou J 2005 Nanotechnology 16 1069–1072