Chapter 4
Carbothermal Synthesis and Characterization of ZnO Nanorod Arrays

N. V. Lyanguzov, D. A. Zhilin and E. M. Kaidashev

An influence of buffer Ar gas pressure and substance-to-source distance on morphometric parameters of vertically aligned ZnO nano- and the microrod arrays synthesized by a carbothermal reduction process on Si (100) substrates covered by ZnO sub-layer is determined. Systematical researches of catalyst-free growth, as well as influence of catalytic agent type (such, as Au and Cu) on formation process and the morphometrical parameters of the produced rods are carried out. It is shown that the catalytic agent plays a role only at the initial stage, and does not participate in the further growth of rods in applied synthesis conditions. Possibility to control the average diameters, lengths and surface distribution density of the rods in the ranges of 100–300 nm, 1.5–9 μm and 2.8×10^8–5.3×10^8 cm^{-2}, respectively, is shown.

4.1 Introduction

Arrays of ZnO filament-like nanocrystals and the nanorods are considered now as basis element of highly efficient electrooptical devices, electrons emitters, sensors for chemical and biological substances, micro- and nanoelectromechanical systems. Morphometric characteristics, such as the characteristic sizes of single elements, the dispersive level, density and homogeneity of surface distribution, mutual spatial orientation are defining for the majority of applications. So far in many presented annuals the possibility to produce the vertically aligned ZnO nano- and microrods arrays with differing morphometric parameters via a very simple gas-phase-technique, such as carbothermal reduction process, is shown. However, comparing these results, it is impossible to create complete and single-digit idea, at least at empirical level, about influence of temperature of synthesis [1],

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concentration in a gas phase [2], operating pressure [3], existence and type of the catalytic agent [4], etc. on morphologies of formed products.

Considering above-mentioned features, the purpose of this work was to research the opportunities of control of the morphometric parameters of ZnO nano- and microrods arrays during their preparation via carbothermal reduction process. As the tasks, we studied the influence of such technological parameters of synthesis, as operating pressure and substrate-to-source distance, on lengths and diameters, on dispersive level, on surface distribution density and homogeneity of produced ZnO nano- and microrod arrays on exact values of level.

4.2 Experiment

ZnO nano- and microrod arrays were produced by a carbothermal reduction process on Si (100) substrates with use of Cu and Au as growth catalyst agents, and also without catalytic agent, respectively, the technique offered in [1, 2, 5, 6]. Substrates were initially exposed to chemical cleaning. Before the catalytic agent deposition and nanorods synthesis the substrates were covered by 80 nm-thick ZnO thin film sub-layers via pulsed laser deposition (PLD) technique under temperature about of 500 °C. The thickness of the catalytic agent layers deposited by magnetron sputtering was about 2–3 nm. Three area-equal fields were distinguished on each sample: the first one was covered with Cu, the second one covered with Au, and the third one without any catalytic agent covering. The pumped quartz tube with inner diameter of 30 mm placed in the horizontal furnace was used as a reaction chamber for synthesis of ZnO-rod arrays. Source of material, or precursor (compacted mixture of ZnO and graphite powders in a weight ratio of 1:1) and the prepared substrates were loaded in the chamber by so way that the precursor was located at the center of furnace. Further the reactor was evacuated and heated up to working temperature. Pressure value (P) in the chamber was regulated by means of changing pumping rate and introducing buffer gas (argon) with the fixed flow of 200 cm^3/min. The substrate-to-source distance (L) was varied stepwise during synthesis, too. Values of substrate temperatures decreased within range 940–920 °C with increasing distance L. The precursor was heated up to 950 °C for 35 min, and duration of the synthesis was 10 min. After synthesis the reactor was naturally cooled down to room temperature. So, the 12 experimental samples of the ZnO rods for $L = 3, 4, 5, 6$ cm and for $P = 150, 50, 15$ Torr were produced.

The morphology of the sintered samples was studied by scanning electronic microscopy on the instrument FE-SEM Zeiss SUPRA 25. Values of average length of rods were determined from micrographs of cross-sections (Fig. 4.1a) under shooting at the angle of 90° to an axis of rods. For determination of average value of rod diameters, the micrographs were registered parallel to a surface (i.e. at the angle of 0° to an axis of rods) (Fig. 4.2). Further, micrographs were computationally processed in ImageJ program [7]. The diameter of circle, whose area was

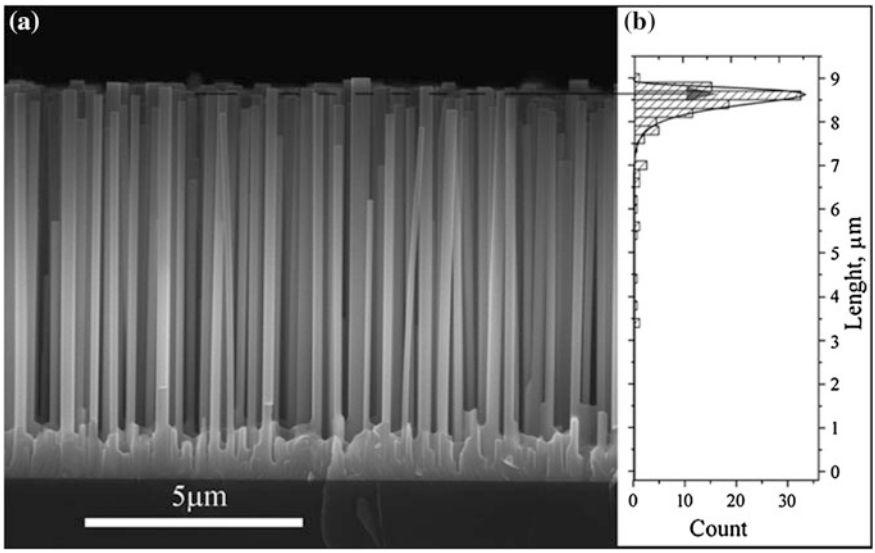

Fig. 4.1 The SEM image of cross-sections of the ZnO-rod array synthesized on Si (100) substrate with pressure of 50 Torr at substrate-to-source distance of 4 cm without the catalytic growth agent (**a**). The histogram of statistical distribution of rods on length for this sample (**b**)

equal to the area of cross-section of the rod, was selected as a value of diameter. Based on obtained data, the histograms of statistical distribution of rods on lengths (Fig. 4.1b) and on diameters (Fig. 4.3) were plotted. These histograms were approximated by logarithmically normal distribution function. As average length or diameter of rods for each sample the maximum of approximating distribution function was accepted. The dispersion level of length or diameter of rods was defined as the expressed in a percentage ratio of FWHM value for correspondent approximating distribution function to the average value.

The XRD studies of the synthesized samples were carried out on the Rigaku ULTIMA IV Theta–Theta Type diffractometer (Cu $K\alpha_1$ radiation).

4.3 Result and Discussion

Electron microscopy showed that all of the samples were the arrays of ZnO-rods, which vertically aligned to the substrate. The average length of the rods varied in a non-linear way with increasing substrate-to-source distance, reaching the maximum values at $L = 4$–5 cm. Similar regularity is observed for dependence of the rod length on pressure, namely the rods produced at $P = 50$ Torr have the greatest average length. So, values of average lengths of ZnO-rods sintered without the catalytic growth agent under pressure of 15 Torr, reached of 4.5, 7, 8.7 and

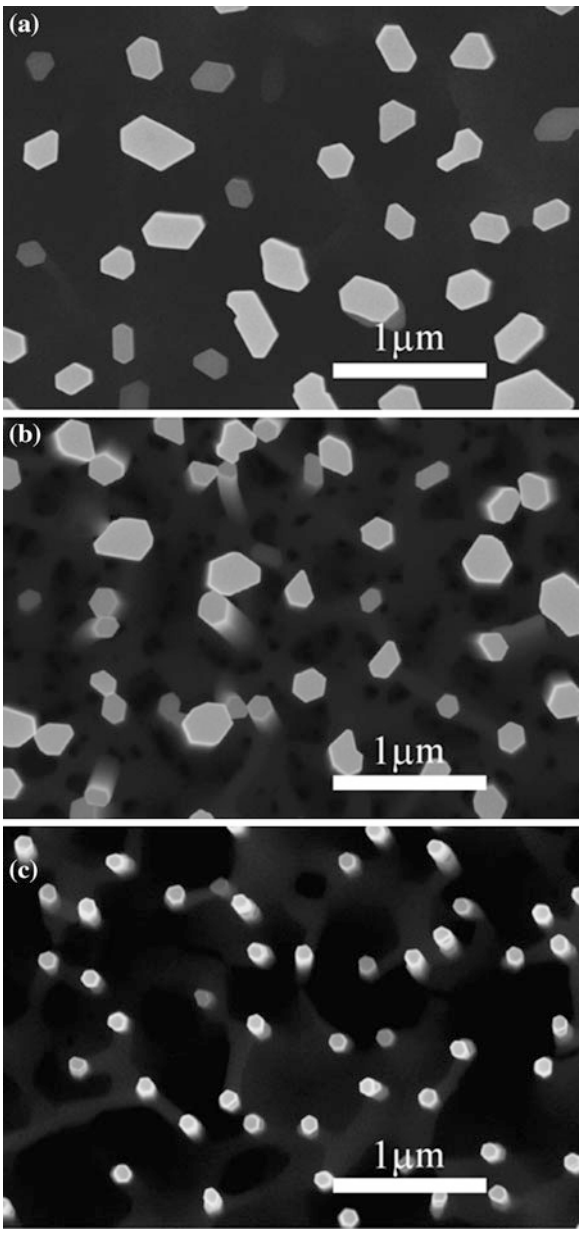

Fig. 4.2 SEM images (*top view*) of ZnO-rod array synthesized on Si (100) substrate at substrate-to-source distance of 4 cm without the catalytic growth agent with pressure of 150 Torr (**a**), 50 Torr (**b**), and 15 Torr (**c**)

5.9 μm, with the dispersion level of 13, 7, 4 and 2.5 %, for distances of $L = 3$, 4, 5, and 6 cm, respectively. In the case of the same values of L, average lengths of the rods synthesized with $P = 50$ Torr, reached of 7.5, 8.7, 6.7 and 2.1 μm, with

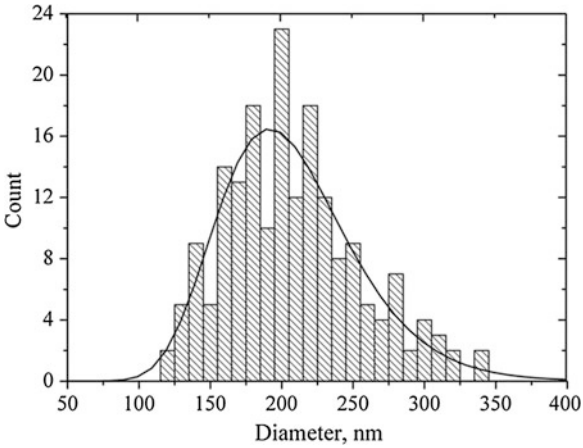

Fig. 4.3 The histogram of statistical distribution on diameters for the ZnO-rods produced with pressure of 50 Torr at substrate-to-source distance of 4 cm without the catalytic growth agent

the dispersion level of 2, 3, 3.5 and 7 %, and with $P = 150$ Torr they were 3.2, 5.6, 2.9 and 1.3 μm, with the dispersion level of 5, 4.5, 3.5 and 3 %, respectively.

Average diameter of rods increases with evaluation pressure and increasing substrate-to-source distance. So, average diameters of ZnO-rods produced with the pressure of 15 Torr, reached of 100, 110, 155 and 195 nm, with a dispersion level of 5, 4.5, 3 and 33 % for distances of $L = 3$, 4, 5, and 6 cm, respectively. For the same values of L, diameters of the rods synthesized with a pressure of 50 Torr, reached of 180, 195, 225 and 240 nm, with a dispersion level of 8, 28, 29 and 25 %, and with $P = 150$ Torr, they reached of 225, 230 (Fig. 4.2a), 270 and 300 nm, with a dispersion level of 24, 28, 30, 32 %, respectively. The average length and diameter of the rods depending on pressure value and substrate-to-source distance are plotted in Fig. 4.4. In the presence of catalytic growth agents, Au or Cu, the increase of average length on 7–15 % and reduction of average diameter of rods on 2–10 % (depending on specific conditions for each sample) were observed.

Surface distribution density of rods for all fabricated samples changed in the range from 2.7×10^8 to 8×10^8 cm^{-2}, being homogenous for each sample along the surface. The rods in the transverse sections have a shape of the close-to-regular hexagons, if their diameters are no more than 150 nm, and of more complex polygons formed by combination of hexagon-like figures in the case of bigger diameters.

In $\theta/2\theta$-patterns (Fig. 4.5) there are only the reflexes relating to Si (100) substrate, and reflexes like (00 l) attributed to zinc oxide, such as (002) and (004). This unambiguously testifies to mutual crystallographic orientation of [001] ZnO ‖ [100] Si in the normal to the substrate direction. The FWHM of rocking curve for ZnO-(002) reflex is obtained about 0.5°. The φ-scans for asymmetrical ZnO-(114) reflex approved that the ZnO-rods showed full azimuthal disorientation in the plane.

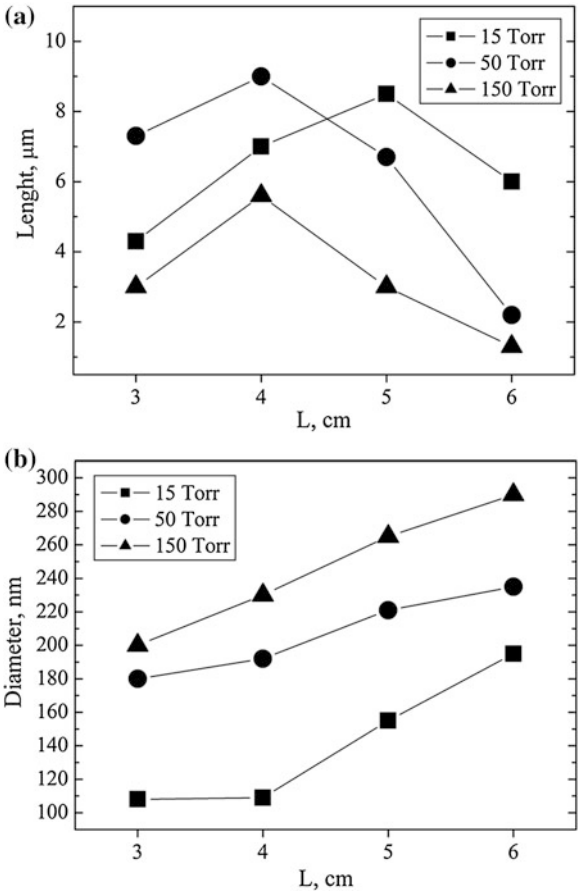

Fig. 4.4 The graphical representation of dependences of average length (**a**), and average diameter (**b**) on pressure value and substrate-to-source distance

From electron microscopy data for Au-covered areas of the samples it might be supposed the presence of gold nanoparticles with average diameter about of 30 nm concentrated near the interface of ZnO-rods with ZnO-sublayer. XRD also confirmed the existence of gold nanoparticles. In the areas covered with Cu, metal particles were absent. This may confirm that copper is evaporated, or embed into crystalline structure of the ZnO-rods during their formation. Also metal particles were absent on lateral surfaces and peaks of rods in the case of use both Au, and Cu as catalyst. These results, along the facts, that rods grow in absence of the catalytic agent, and only insignificant difference of morphometric parameters, argue that the catalytic agent plays a role only at the initial stage (forming preferential growth centers), and does not participate in the further growth of rods under existing synthesis conditions.

Also, an additional series of samples was synthesized with pressure of 50 Torr at distances of $L = 3$, 4, 5 and 6 cm, when the temperature was lowered by 50 degrees, i.e. the precursor was been heated up to 900 °C. Preparation of substrates

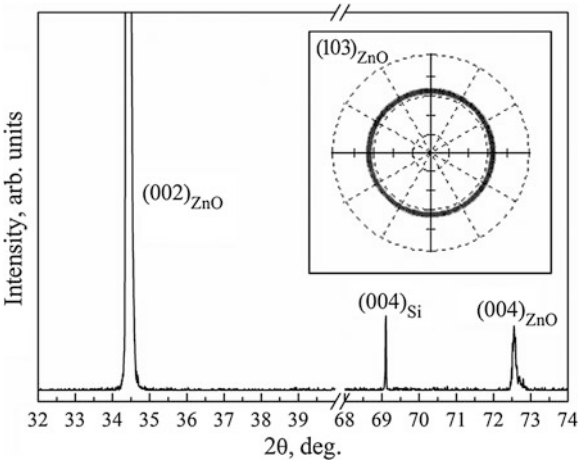

Fig. 4.5 $\omega/2\theta$-pattern array of the rods ZnO on Si. In insertion, it is shown a pole figure of a reflex ZnO-(103)

here was carried out in a way similar explained earlier. ZnO-rods were not produced on each of these samples. A zinc oxide layer (no more than 20 nm thick) formed on surface of the initial ZnO-sublayer was only one resulting product formed during this experiment.

From the facts of the dependence of rod length and their average diameter on changing substrate-to-source distance and buffer Ar pressure, it is evident to assume that by varying with distance and pressure, the gas-phase parameters and the rate of surface-related processes on a substrate might be changed. Such values, as partial pressure of Zn vapors, rate of diffusion, oxidation of Zn adatoms and pressure of residual oxygen in each point of the reaction chamber might depend on two technological parameters: substrate-to-source distances and buffer pressure of Ar. By changing and manipulating these two parameters, it is obviously possible to change and control the kinetic and thermodynamic conditions of growth and, therefore, the morphometric parameters of formed structures.

4.4 Conclusion

The possibility to control the average diameters, lengths and surface distribution density of ZnO-nanorod arrays produced by carbothermal reduction process (or carbothermal synthesis) is shown in the ranges of 100–300 nm, 1.5–9 μm, 2.8×10^8–5.3×10^8 cm^{-2}, respectively. The dispersion level of the synthesized rods did not exceed of 33 % in diameter and 13 % in length. The growth of rods was observed in both cases of Cu or Au existence, and without of the growth catalytic agent. The morphometric parameters of ZnO-rod arrays varied no more than on 15 % in dependence on the one of these two cases. From the existence of gold nanoparticles near the interface of ZnO-rods with ZnO-sublayer, it is concluded that the catalytic agent plays a role only at the initial stage of growth.

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