Surface morphology of nanostructured zinc oxide materials obtained by plasma-enhanced chemical vapor deposition

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Abstract. Zinc oxide nanostructures have been obtained by plasma-enhanced chemical vapor deposition technique. High-purity elemental zinc was used as the precursor. RF (40MHz) inductively coupled plasma discharge was used for the initiation of the plasma-chemical reactions in the gas phase. Hydrogen-oxygen (H₂-O₂) composition of various ratios was used as the source plasma gas mixture. The optical emission spectroscopy was used as the powerful tool to determine the intermediate excited particles and assume the possible mechanism of the plasma-chemical reactions. The paper also investigates the influence of the substrate’s materials, its temperature, and the power of the heat input into the discharge. The properties of the sprayed materials were characterized by the method of atomic force microscopy.

1. Introduction
Zinc oxide is a promising material for creation of noninvasive human breath sensors with a high analytical response and speed. The large specific surface area of zinc oxide nanostructures allows to absorb organic and inorganic molecules efficiently and selectively, as well as to obtain an amplified signal due to a large number of such molecules. This, as a consequence, gives an opportunity to determine the low concentration of the molecules. In usual conditions wurtzite is the most thermodynamically stable phase of zinc oxide, the structure of which is the reason of its piezoelectric properties [1-5]. The band gap width (E_g = 3.37 eV) allows using ZnO to create emitters and lasers of the visible and UV ranges. The predominance of intrinsic n-type donor defects is observed in ZnO. Therefore, doping in order to achieve p-type of conductivity is not a trivial task until now, although its solution could find its application in the devices based on the p-n junction.

A large number of methods have been proposed for synthesis of nanostructured ZnO. A relatively simple method is to deposit a thin layer of zinc oxide on a substrate using pulsed laser deposition (PLD) or any other physical methods of evaporation of the initial target (zinc-containing precursor) [6-8]. The advantage of PLD is the possibility of doping to control the semiconductor properties of the nanostructures [9-15]. The disadvantages of this method are the complexity of the process scaling, insufficient surface homogeneity and reproducibility of the results. Among the chemical methods of ZnO obtaining from the gas phase it is necessary to mention the MOCVD (metal oxides’ chemical
vapor deposition), as well as the VLC (vapor-liquid-crystal) method. When using the VLC method, thin films made of gold [16, 17] or tin [18] with the thickness of a few tens of nm are preliminarily deposited on the substrate. The disadvantages of the MOCVD method are the use of highly toxic metalorganic volatile precursors, the conversion degree of which never reaches 100%, resulting in the contamination of the final zinc oxide with unreacted derivatives. At present solution methods for the synthesis of ZnO structures are becoming popular due to the use of temperatures from the room temperature to 110–130 °C, due to a comparative simplicity of the procedure, the availability and a low cost of the source precursors [19-22]. Such techniques are, for example, the methods of electrochemical deposition [7] and the sol-gel method [8]. The disadvantages of the synthesis approaches from solutions are the multistage, the need to use high-purity solvents, contamination of the final product with the solvent traces, limited phase composition variations.

The objective of this work is to elaborate a novel approach to the synthesis of the zinc oxide nanostructured materials based on the plasma initiation of the chemical interaction in complex gas mixtures using elemental high-purity zinc as the precursor.

2. Experiment
The installation, schematically depicted in Figure 1, was used for the synthesis of the nanostructured zinc oxide. A detailed description of this installation is also given in [23-27].

![Figure 1. The installation for the synthesis of zinc oxide nanostructures [24].](image)

Zinc of 5N purity (Changsha Rich Nonferrous Metals Co Ltd, China) was used as the source zinc, as well as hydrogen of the special purity (99.9999%, Ar/O2<0.2 ppm, N2<0.2 ppm, H2O <1 ppm, CxHy<0.02 ppm, CO <0.1 ppm, CO2<0.02 ppm) and oxygen of high purity 6.0 (99.9999%, N2<1 ppm, Ar<1 ppm, H2O <0.5 ppm, CH4<0.02 ppm, CO<0.15 ppm, CO2<0.1 ppm) (Horst Technologies Ltd, Russia) were used as the components of the source gas mixture. In the installation with the tubular reactor, as well as during the synthesis of gallium oxide [24], the substrates were placed into the reactor through a stainless-steel vacuum charging flange and assembled perpendicular to the carrier gas flow on a specially developed high-purity quartz substrate holder. For the experiments the substrates made of high-purity monocrystalline silicon, sodium chloride, and c-oriented sapphire 10×10 mm in size were used. Before the start of the experiment the installation was pumped out to the pressure of 1·10⁻³ Pa for several hours for the degassing of the reactor’s inner walls. After that the source with zinc was heated up to 470 °C, while the substrate temperature was set in the range of 250-550 °C, depending on the chosen experimental conditions. Having set the total gas flow through the
plasma-chemical reactor equal to 30 ml/min at the general pressure in the system of 0.1 Pa, the plasma discharge was ignited. Zinc vapors were carried by the carrier gas flow and delivered to the RF discharge zone. Oxygen was supplied directly into the plasma zone through a quartz line mounted perpendicular to the main flow of the carrier gas with zinc. In fact, the formation of the zinc oxide particles occurred in the gas phase in front of the substrate, followed by their deposition on the surface. Hydrogen was used as a terminator and growth regulator. The duration of the experiments was 1 hour.

3. Results and discussion

3.1. Optical emission spectroscopy of the plasma process

First of all, the influence of the ratio (oxygen/hydrogen) in the initial gas phase on the mechanism of the plasma-chemical process was studied [28-30]. Figure 2 shows the optical emission spectra of the Zn-H2-O2 plasma mixture at various ratios of hydrogen and oxygen, measured in the range of 180-1080 nm.

![Figure 2](image)

During the experiments the gas ratios of O2/H2 - 2/1, 1/1 and 1/2 (the ratios are given in moles) were used. The spectrum of the binary mixture (Zn-H2) is shown in Figure 2a for comparison. Without oxygen the plasma spectrum includes emission bands of zinc atoms Zn (I) at 258.25, 260.86, 277.06, 280.07, 328.24, 330.26, 334.51 and 468.03 nm, and also molecular and atomic emission lines of hydrogen in the range of 460-950 nm.

Addition of oxygen to the Zn-H2 mixture in the ratio 2/1 (Figure 1b) is accompanied by a significant decrease in the intensity of the Zn (I) and H2 (I) lines. In addition, the intensity of the atomic lines of hydrogen H (I) at 486.1, 656.3 nm slightly increases, and weak lines from oxygen-containing fragments O (I), O (II), OH (I) appear in the areas of 450 - 500 nm and 680 - 950 nm. It is necessary to mention that in the conditions of our experiment the emission lines of Zn (II) atoms are not observed. Besides, the plasma spectrum contains lines at 228.78 (P), 326.08 (P), 615.15 (M), 652.15 (P), 668.98 (P) nm, which are probably related to [Zn-O-]* excited particles, and which become the units of the initial structure formation of the lattice. With the increase of the plasma power the growth of the intensity of all the emission lines in the plasma spectrum is observed. In addition, the relative intensities of the lines at 228.78, 326.08, and 615.15 nm increase, this is probably associated with the increase in the yield of zinc oxidation reaction products.
3.2. Study of the obtained samples by the atomic force microscopy (AFM)

The obtained samples were studied by the atomic force microscopy. The dependence of the samples’ morphology on the temperature of the zinc source is shown in Figure 3.

$$R_a = 0.37 \text{ nm}, R_z = 2.25 \text{ nm}$$

$$R_a = 1.27 \text{ nm}, R_z = 14.87 \text{ nm}$$

$$R_a = 3.55 \text{ nm}, R_z = 15.50 \text{ nm}$$

Figure 3. Dependence of the samples’ surface morphology on the temperature of the zinc source.

The increase in the temperature of the zinc source leads to both increase in the size of structure-forming fragments and increase in the surface roughness of the material. This is connected with the increase of the zinc concentration in the gas phase. An average surface roughness $R_a$ increases from 0.37 nm at 425 °C to 3.55 nm at 475 °C almost by a factor of ten. Along with this the height of the roughness of the profile $R_z$, characterizing an average size of the structure-forming crystallites, increases from 2.25 nm at 425 °C to 15.50 nm at 475 °C.

The dependence of the samples’ surface morphology on the power supplied to the plasma discharge is shown in Figure 4.

$$R_a = 0.76 \text{ nm}, R_z = 8.71 \text{ nm}$$

$$R_a = 0.67 \text{ nm}, R_z = 3.36 \text{ nm}$$

Figure 4. The dependence of the samples’ surface morphology on the power supplied to the plasma discharge.

The increase of the plasma power from 50 to 100 W leads to decrease of the materials’ surface roughness. We observe a similar tendency in the examples of other oxide materials, for instance, gallium oxide. The increase of the plasma power affects the relaxation conditions of the excited particles on the substrate; this allows varying the growth regimes of the solid phase.

The dependence of the surface morphology of the samples on the substrate temperature (the zinc source temperature was 420 °C, the plasma power was 50 W) is presented in Figure 5. The increase in
the temperature of the c-sapphire substrate from 25 °C to 250 °C leads to the decrease in the roughness of the materials.

\[
\begin{array}{c|c|c}
R_a & 0.76 \text{ nm} & R_a & 0.37 \text{ nm} \\
R_z & 8.71 \text{ nm} & R_z & 2.25 \text{ nm}
\end{array}
\]

**Figure 5.** Dependence of the samples’ surface morphology on the substrate temperature.

4. Conclusion

The paper presents a fundamental possibility of synthesis of zinc oxide materials with different surface morphology by plasma-enhanced chemical vapor deposition in complex oxygen-hydrogen plasma-forming mixtures. The plasma-chemical process was investigated by the optical emission spectroscopy at different ratios of the source components in the gas phase and at different energy input. The excited particles existing in the plasma in the experimental conditions have been determined. It was found out that the increase of the plasma power results in the increase of the intensity of all the emission lines in the emissive spectrum. In addition, the relative intensity of the lines at 228.78, 326.08, and 615.15 nm increase, this is probably connected with the increase of zinc oxide materials’ content. The obtained samples were studied by the atomic force microscopy. It was found out that the increase in the temperature of the zinc source leads both to the increase in the size of structure-forming fragments and the increase in the surface roughness of materials. On the contrary, the increase of the plasma power from 50 to 100 W leads to the decrease in the surface roughness of the materials.

5. References

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