Growth of zinc oxide nanostructures by mass transfer through a micro-sized vacuum zone in a temperature gradient field

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Abstract. This paper presents the results of studies on the controlled production of ZnO nanostructures with specified physical properties. It has been shown experimentally that by using the mass transfer of a substance through a micro-sized vacuum zone in a temperature gradient field, it is possible to grow quasi-one-dimensional ZnO nanostructures stochastically or orderly located on a substrate. The density of deposition of quasi-one-dimensional ZnO nanostructures is determined depending on the substrate material. It was found that the resulting ZnO nanostructures have good crystal perfection and stoichiometric compositions, and also have pronounced piezoelectric properties.

1. Introduction
Zinc oxide is a direct-gap semiconductor material and can exhibit pronounced semiconductor, optical, acoustic, electrical, and magnetic properties [1-3]. These properties of ZnO can be used to create high-performance LEDs, lasers, optical and acoustic waveguides, photo- and thermoelectric converters, piezoelectric devices, gas sensors [4,5], luminescent emitters, catalysts, etc. There are many methods for obtaining ZnO in the form of bulk single crystals, nano- and micro-sized powders, poly- and single-crystal films, whiskers grown on orienting and non-orienting substrates. However, all of them do not have a sufficient level of technology to ensure the guaranteed creation of a material with specified geometric parameters, mechanical properties, optical and electrical characteristics. The search for ways to obtain zinc oxide with desired properties is an urgent physical and technological problem. Within the framework of this work, research has been carried out to develop the scientific foundations for obtaining crystalline ZnO nanostructures with specified properties by mass transfer in a micro size vacuum zone (MSVZ) in a temperature gradient field.

2. Hardware design of the MSVZ method
To build a model of the deposition of zinc oxide nanostructures using a micro size vacuum zone, the theory was used, described in detail in [6-8] as applied to the classical semiconductor materials Si and Ge. In the simplest case, the considered MSVZ method is characterized by the use of mutually parallel plates - a substrate and a sublimating source (Figure 1), the presence of a given temperature difference between them $\delta T = T - T_S > 0$ and the fulfillment of the conditions:
where \( l \) is the thickness of the vacuum zone between the source and the substrate, \( T \) is the source temperature, \( T_s \) is the substrate temperature; \( R \) is the radius of the position; \( \lambda_0 \) is the free path of molecules in the zone between the source and the substrate.

\[
\begin{cases}
\frac{l}{R} << 1, \\
\frac{\lambda_0}{l} >> 1
\end{cases}
\]  \hspace{1cm} (1)

3. Experimental

A specific feature of zinc oxide is a significant difference in the volatility of its components: oxygen is in a gaseous state even at room temperature, and zinc intensively sublimes only at temperatures near the melting point (419 °C). This circumstance causes technological difficulties in the growth of zinc oxide structures by sublimation of its vapors from the surface of a crystalline source. In the present work, these difficulties are overcome due to two stages of the growth of ZnO nanostructures. At the first stage, a zinc layer on substrates (silicon, zinc oxide, sapphire, molybdenum, graphite) was grown by the MSVZ method. The source was zinc plates 1.5 mm thick and 70 mm in diameter (Figure 2). The zinc source was previously cleaned with a hydrochloric acid solution (30%), then washed with acetone, isopropyl alcohol, and distilled water. The substrates were cleaned in an ethyl alcohol solution in an ultrasonic bath, washed in distilled water, and purified in Ar plasma. The planar dimensions of the vacuum zone during zinc deposition were <100 μm. Residual gas pressure in the working chamber of the unit <10\(^{-1}\) Pa.
Experiments on the preparation of homogeneous zinc layers were carried out in the temperature range 450-680 K. At higher temperatures, the deposition of zinc on the substrate is not uniform, and the resulting layer has a developed cellular microstructure. The temperature control of the MSVZ process was carried out using a PtRh–Pt thermocouple. The temperature drop between the source and the substrate was 150 K. The thickness of the obtained zinc layers was set by the process time and the source temperature and did not exceed 5 μm. At the second stage, the grown zinc layers were oxidized in an oxygen flow. It is known that zinc practically does not oxidize in air due to the presence of the formed thin carbonate film - ZnCO$_3$. To obtain ZnO nanostructures, it was proposed to use the MSVZ method in the version shown in Figure 3.

The flow of oxygen molecules inside the growth zone was obtained by heating substances that contain oxygen in a bound state: potassium permanganate and potassium chlorate. Potassium permanganate releases molecular oxygen by means of the following reaction:

$$2\text{KMnO}_4 = \text{K}_2\text{MnO}_4 + \text{MnO}_2 + \text{O}_2$$

When potassium chlorate is heated, decomposition occurs with the release of three oxygen molecules (MnO$_2$ was used as a catalyst.):

$$2\text{KClO}_3 = 2\text{KCl} + 3\text{O}_2$$

When potassium permanganate was used, the temperature of the oxygen vapor source varied in the range 370-430 K. Oxidation using potassium chlorate was carried out in a higher temperature range of the oxygen source 470 - 600 K. It was revealed that the process of zinc oxidation with the use of potassium chlorate is more intensive due to the higher temperature and higher concentration of oxygen molecules. The time of the second stage of the experiment was 60 minutes. After the completion of the oxidation process, the sample was removed from the working chamber and cooled in air. As a result of forced oxidation, zinc oxide nanostructures are formed on the substrate surface, the geometric properties of which can be controlled using the substrate and source temperatures, as well as the temperature field.
gradient in the mass transfer zone. It should be noted that the zinc oxide layer can be separated from the substrate together with the zinc sublayer and used separately from the substrate without degradation of properties.

4. Results and Discussion
In the course of the experiments on the preparation of ZnO nanostructures by the MSVZ method, it was found that when using ZnO powder as a source, at a distance of less than 100 μm from the substrate, the formation of stochastically oriented nanowires of various thicknesses is observed (Figure 4).

![Figure 4. Stochastically oriented ZnO nanowires obtained on different substrates by the MSVZ method as a source was an ultrafine ZnO powder: a) Si (100) substrate; b) Al2O3 (100) substrate](image)

The diameter of nanowires depends on the temperature of the sublimating source and ranges from 25 nm (T = 1090 K) to 80 nm (T= 1250 K). An increase in the diameter of nanowires with increasing source temperature is due to an increase in the rate of growth of the growth substance. The areal density of nanowires is determined by the type and material of the substrate. When silicon substrates were used, the surface density reached 140-180 nanowires/μm². For sapphire substrates, at comparable rates of growth substance supply, the surface density of nanowires is significantly reduced and lies in the range of 20-40 nanowires/μm². The experiments were carried out under the following technological conditions: vacuum zone thickness l~100 μm, substrate diameter D~70 mm, source temperature T~1150 K. Data on the surface density of nanowires formed on substrates of various nature are presented in Table 1.

**Table 1. Surface density of ZnO nanowires depending on the substrate material**

| Substrate material | Surface density of ZnO nanowires, (pcs./μm²) |
|--------------------|---------------------------------------------|
| Zinc Oxide         | 140-180                                     |
| Silicon            | 70-100                                      |
| Sapphire           | 20-40                                       |
| Molybdenum         | 50-70                                       |
| Graphite           | 30-50                                       |

The MSVZ method also allows one to obtain ensembles of quasi-one-dimensional ZnO nanostructures (nanowhiskers). ZnO nanowhiskers differ from nanowires in shape, location and radius of curvature of the tip. Nanowires, as can be seen from Figure 4, are predominantly oriented in the plane of the substrate.
surface on which they are formed. The diameter of ZnO nanowires changes insignificantly along the entire length. ZnO nanowhiskers (Figure 5) predominantly grow normally or at a small angle to the crystallite surface on which they are formed. In the direction from the base to the top, their section decreases. The growth of quasi-one-dimensional nanosized ZnO structures by the MSVZ method also occurs in two stages. Stage 1 - sublimation deposition of pure zinc on a silicon or sapphire substrate, stage 2 - annealing of the obtained layer of pure zinc in an oxidizing medium. To obtain ZnO nanowhiskers, in the course of the experiment, a layer of pure zinc is deposited on a preliminarily prepared silicon wafer using the MSVZ method (at a substrate temperature \( T_S = 570 \) K). Next, a zinc film, together with a substrate and an oxygen source, is placed in a chamber and annealed in an oxygen atmosphere at a pressure of \( P = 10^5 \) Pa and a temperature 30 degrees less than the melting point of zinc \( T = 660 \) K, for 20 minutes. As a result of annealing in an oxygen atmosphere, misoriented quasi-one-dimensional ZnO nanostructures are formed on the surface of the zinc layer (Figure 5).

![Figure 5. SEM image (mag. 20 kX) of disordered quasi-one-dimensional ZnO nanostructures](image)

To obtain ordered ensembles of quasi-one-dimensional ZnO nanostructures with a given orientation, the two-stage MSVZ method was also used under the same pressure conditions described above. However, in order for the growth of ZnO whiskers to become orderly, special zinc layers were selected with a certain shape of crystal grains. The annealing temperature was changed, the process time was increased to 40 minutes. As a result, ensembles of quasi-one-dimensional ZnO nanostructures were obtained, which in the process of growth were arranged in an orderly manner along the normal to the corresponding face of zinc crystallites (Figure 6, a), except for the regions near the change in the orientation of the crystallite faces (Figure 6, b).
The quasi-one-dimensional ZnO nanostructures obtained by the two-stage MSVZ method have thicknesses in the range from 30 to 150 nm (Figure 6, c) with a section decreasing from the base to the top and a length from 1.5 to 5 μm (Figure 6, d). Studies have shown that these quasi-one-dimensional ZnO nanostructures have high mechanical strength, which is explained by their high structural perfection associated with a low probability of trapping liquid microinclusions by the crystallization front, leading to the growth of dislocations during solidification. Using X-ray microanalysis, it was found that the quasi-one-dimensional ZnO structures obtained by the MSVZ method have a high stoichiometry (Figure 7). A feature of such ZnO nanostructures is a pronounced piezoelectric effect [9,10].
Figure 7. Elemental composition of ZnO nanostructures obtained by MSVZ method

5. Conclusion
In this work, it is experimentally shown that the MSVZ method allows one to obtain ZnO nanostructures with specified properties and parameters. Controlling and setting the desired properties of the resulting ZnO nanostructures is achieved by varying the temperature, geometric, and pressure conditions of the MSVZ method. The mass-transfer method considered in this work in a micro-sized vacuum zone has not been previously used for the controlled growth of quasi-one-dimensional ZnO nanostructures. However, it has significant potential advantages over the methods currently used for these purposes. Compared to magnetron sputtering and a number of other evaporation methods [11,12], the MSVZ method is equilibrium and practically isothermal, which makes it possible to grow defect-free nanostructures with a high degree of ZnO stoichiometry.

Compared to the classical MBE, the MSVZ method is technically simpler and provides complete transfer of the matter to the crystallization front. Unlike pulsed laser deposition, the MSVZ method is not associated with the uncontrolled ingress of molten zinc droplets and solid source particles erupting from the molten material microcrater onto the growing layer.

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