The formation of nanoparticles, ceramics, and thin films of ZnO in the environment of zinc vapor

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Abstract. The investigations of formation mechanisms of ZnO nanoparticles, ZnO ceramic materials sintering and synthesis of ZnO thin films in zinc vapor-containing atmosphere shown that increase in "zinc/oxygen" relation (P\textsubscript{Zn}/P\textsubscript{O\textsubscript{2}} ratio) leads to a significant change in the structure and formation mechanisms of ZnO ultrafine particles, thin films and bulk materials. We observed that ZnO whiskers growth occurs in the direction of the optimal ratio of partial pressures of Zn and O\textsubscript{2}. Growth of ZnO tetrapods during the ejection of Zn vapor in an oxygen atmosphere occurs in two stages: the formation of the ZnO\textsubscript{1-x} seed and subsequent growth of ZnO whiskers from it. It was also shown that the synthesis of ZnO films by magnetron sputtering in the Zn vapor excess environment can occur by the "vapor-liquid-solid" (VLS) mechanism. Also sintering of Ga-doped ZnO ceramic targets in the atmosphere containing desired pressure of Zn vapor leads to increase in target density and oxygen deficiency. These targets were used for deposit transparent conductive oxide (TCO) thin films onto glass substrate by direct current (dc) magnetron sputtering. The relationship between the structural perfection and electrical characteristics of Ga doped ZnO (GZO) films as a function of synthesis temperature and Ga content (3-6 at.%) were investigated.

1. Introduction
The development of new materials and devices based on zinc oxide is currently experiencing an unprecedented boom in solar energetic, industry of displays and light-emitting diodes. Applied research in developing new ceramic materials for the formation of transparent electrodes and their deposition technologies [1], dye-sensitized photovoltaic cells [2], etc is hence in high demand. Numerous studies show that an important factor in determining the conditions of nucleation and formation of ZnO-based nanoparticles, thin films and bulk ceramic materials is the ratio of pressure of Zn vapor and partial pressure of oxygen (P\textsubscript{Zn}/P\textsubscript{O\textsubscript{2}}) in the chamber during the synthesis [3]. In this study we attempted to examine the effect of the P\textsubscript{Zn}/P\textsubscript{O\textsubscript{2}} on the structure of ZnO nanoobjects and films deposited by magnetron sputtering, as well as on the processes of sintering of ceramic targets for the formation of transparent electrodes.

2. Experiment and materials
We investigated the influence of P\textsubscript{Zn}/P\textsubscript{O\textsubscript{2}} ratio on the structure of ZnO nanoobjects (whiskers, tetrapods) and ZnO films, as well as on the sintering of TCO ceramic targets. Synthesis of ZnO nanoobject materials was carried out by various methods: 1) the annealing in the air of the zinc films (thickness ≈ 1000nm), synthesized by thermal evaporation of zinc from a Knudsen cell on the Si or glass substrates;
the gas-phase synthesis of ZnO aggregates by means of effusion of the overheated Zn vapor through a thin channels into oxygen atmosphere.

To investigate effect of Zn vapor excess environment on the properties of ZnO films, a series ZnO films were grown by dc magnetron co-sputtering ZnO ceramic target and Zn metal target at different substrate temperatures and various discharge currents of magnetron with Zn target. Also the synthesis of ceramic targets was carried out by sintering of ZnO-based compacted materials with doping in the atmosphere containing Zn vapor [4,5]. To study the properties of the ZnO-based TCO thin films, ZnO targets with the gallium content of 3 to 6 at% were manufactured. The thin films were synthesized by dc magnetron sputtering at a constant pressure of Ar in the chamber (0.5 Pa), while substrate temperature varied from room temperature to 280 °C.

Morphology of samples surface and film thickness was studied using scanning electron microscope LEO 1450 (Carl Zeiss). The structural properties of the samples were investigated using X-ray diffractometer Shimadzu XRD-7000, with CuKα radiation. Precise XRD measurements were performed in order to estimated the full width at half maximum (FWHM) of the (002)ZnO XRD peak. The resistivity, Hall mobility and free carrier concentrations for Ga-doped ZnO TCO thin films were estimated by the four-point probe method and Hall-effect measurement.

3. Results and discussions

3.1. Formation of nanoobjects in the atmosphere of Zn - O₂.

Previous studies [6,7] have shown that the formation of ZnO whiskers at Zn vapor excess occurs by the mechanism of "vapor-liquid-solid" (VLS), moreover “liquid”-forming agent is ZnO_{1-x} phase. The model of zones of the growth of ZnO whiskers and tetrapods is shown in Figure 1a. The nucleation of the ZnO whiskers occur at the edge of the nozzle, and the further formation of whiskers is directed along the axis of the cone, i.e. along the lines of a certain optimal \( \frac{P_{Zn}}{P_{O2}} \) ratio.

Figure 1a schematically shows also the change of partial pressure of oxygen and pressure of Zn vapor in the direction from nozzle. During the effusion of zinc in oxygen atmosphere, in addition to the growth of whiskers, also observed the gas-phase formation of ZnO tetrapods (inside the cone generator). ZnO tetrapods, formed in the flow of zinc, shown in Figure 1b.

![Figure 1. a – the model of zones for the growth of ZnO whiskers and tetrapods; b – SEM photos of ZnO tetrapods; c – SEM photo of as-deposited Zn layer; d – SEM photo of Zn layer after annealing in air.](image-url)
Numerous observations confirm the fact that the formation of tetrapods occurs during the expansion of zinc in a two-stage scheme.
- A forming of ZnO$_{1-x}$ crystallization seeds into field with relatively high pressures of zinc.
- Subsequent growth of four whisker legs during the expansion of the seed material.

The formation mechanism of whiskers along the lines of a certain optimal P$_{Zn}$/P$_{O_2}$ ratio is also confirmed by our experiment on the oxidation of metallic Zn layers. Figure 1c shows a SEM micrograph of the surface of the as-deposited Zn film.

The annealing of the Zn layer at 380 °C in air results in the formation of a dense web of whiskers on the surface of Zn hexagonal grains (Figure 1d). Analysis of the morphology shows that the whiskers are directed predominantly parallel to the original surfaces of Zn grains, i.e. again along the lines of optimum pressure ratio of oxygen (O$_2$ comes from the outside) and zinc vapor (Zn comes from the film due to evaporation). The formation of two-dimensional web-like structure of the ZnO dendritic branches was also reported in [8].

However, saturated vapor pressure of elemental zinc at 380 °C corresponds to 10 Pa, i.e. doesn’t match conditions for whisker growth. One can propose, that due to autoignition of zinc vapor at 380 °C, near-surface regions of the film reach boiling temperature and higher zinc vapor pressure. This zinc flame front moves deeper within the layer parallel to the surface of crystallites. Thus, whisker growth occurs in zinc flame front plane within the region of optimal ratio of P$_{Zn}$/P$_{O_2}$.

3.2. DC magnetron synthesis of ZnO films via VLS mechanism.

Previously we have shown that the columnar structure of ZnO thin films was suppressed by dc-magnetron co-sputtering of ZnO and Zn at the substrate temperature 450 °C [9]. In this paper we study the structure of films synthesized at 300, 500 and 800 °C, as well as different flows of Zn vapors. Figure 2a-c shows micrographs of ZnO films cross-section view at different substrate temperature (T$_{sub}$). At a T$_{sub}$ < 400 °C the films have a typical columnar structure (Figure 2a). Figure 2b shows that

![Figure 2](image_url). SEM photos of the ZnO films, deposited at different substrate temperatures (a-c) and different discharge currents of Zn target (d-g).
suppression of the formation of columnar structures occurs at $T_{\text{sub}} > 400^\circ C$. This is due to the formation of ZnO$_{1-x}$ low-melting phase on the growing surface under the environment of Zn vapor excess [10,11]. In this case, as in the growth of whiskers, the growth of thin films proceeds in accordance with the VLS model [7]. Further increase in $T_{\text{sub}}$ is the result of decrease in the number of crystallization centers on the surface and forming an array of separate columnar structures (Figure 2c). Dependence of the structure on the Zn sputtering intensity is shown on Figure 2d-g. Increasing the flow of Zn does not increase the thickness of the films. This shows that the excess of Zn is not incorporated into the film and only provides a low-melting phase on the growing surface.

3.3. ZnO based TCO ceramic materials.

One of the most important areas of applied research is the development of advanced TCO ceramic targets for magnetron sputtering. It should be noticed that the requirements for the front (color filter, C/F) and back (thin film transistor, TFT) transparent electrode in the liquid crystal displays (LCD), as well as to the electrodes in organic light emitted diodes (OLED) structures and solar converters, vary significantly. Obviously, adaptation of the target to the specific requirements will significantly improve the performance of devices. In addition, targets must possess high density (not less than 95% of theoretical) to prevent nodules formation. To address these requirements, we developed a method of synthesis of ceramic targets in the atmosphere with excess vapor pressure of zinc [5]. Completed studies show that an increase in shrinkage rate is the result of formation of liquid phase ZnO$_{1-x}$ on the grains surface, leading to a significant increase in diffusion. Synthesizing ceramics have a density of at least 99% of the theoretical value and a deficiency of oxygen in the ceramics of about 8%.

We investigated the relationship between the perfection of the films and electrical characteristics of Ga doped ZnO (GZO) films as a function of synthesis temperature and Ga content (3-6 at.%) in high-density ceramic targets, sintered in an atmosphere containing zinc vapour.

The investigation of the resistivity of GZO films as a function of the Ga content show that the behavior of this dependence with increasing substrate temperature can be divided into three characteristic temperature regions (Figure 3a):
- resistivity decreases monotonically with increased Ga content in temperature range $T_{\text{sub}} < 150^\circ C$;
- the curves reach minimum at Ga content $\sim 4-5$ at% at $150^\circ C \leq T_{\text{sub}} \leq 200^\circ C$;
- the resistivity increases monotonically in the range of 3 to 6 at% Ga at $T_{\text{sub}} \geq 250^\circ C$.

![Figure 3](image_url)

Figure 3. The temperature dependence of GZO films resistivity at different Ga content (a); resistivity ($\rho$), carrier concentration ($n$) and Hall mobility ($\mu$) of GZO films vs. gallium content in the target (b - $T_{\text{sub}} = 50^\circ C$; c – $T_{\text{sub}} = 250^\circ C$).
These data show that minimum resistivity is reached at low value of Ga contents with increased substrate temperature. Figure 3b&c shows measurements of Hall parameters of the GZO films synthesized at temperatures of 50 and 250 °C from the targets GZO with 3, 4, 5 and 6 at% Ga. At substrate temperature $T_{\text{sub}} = 50$ °C, carrier concentration increases linearly as Ga content is increased, reaching saturation at 6 at%. At temperature of 250 °C maximum of carrier concentration is achieved when Ga content reaches $\sim$ 3 at%. Further increase of Ga leads to the localization of an excess of Ga at the grain boundaries and reduction of mobility. These data are consistent with the results of X-ray analysis (Figure 4). It is observed that the GZO films are predominantly in (002) ZnO orientation and do not reveal any other phases.

In the insert of Figure 4 shows the profiles reflections (002) ZnO for GZO films with 3-6 at% Ga deposited at substrate temperature of 50 and 250 °C. It is noteworthy that the intensity of the peak (002) at 250 °C has a pronounced maximum at 4 at% Ga, and at 50 °C is a monotonically increasing up to 5-6 at% Ga. FWHM measurements, shown on Figure 4, demonstrate that growth of intensity peaks is coupled with increased grain size. Observed increase in the perfection of GZO films for the temperature of 50 °C may be associated with the reduction of the concentration of native defects due to incorporation of trivalent gallium in ZnO lattice. As concentration continues to increase, gallium excess on the growing surface creates new centers of crystallization, leading to a decrease in grain size.

Next we compared the data of Hall measurements of GZO films (3 at%), synthesized at different temperatures. Resistivity, concentration and mobility of the films are shown in Figure 5a. Of particular interest is the anomalous behavior of the mobility at 100-150 °C. In this case, carrier concentration increases with increasing $T_{\text{sub}}$. At temperatures above 150 °C mobility and concentration steadily increase and show signs of saturation at a temperature of about 250 °C. In the temperature range 50 ÷ 150 °C Hall parameters vary in opposite directions: concentration increases while mobility decreases. With further increase in temperature observed anomalous mobility around 100 ÷ 150 °C can be associated with non-stoichiometry of targets. According to [12], presence of zinc vapor excess in the flow leads to the formation of metal clusters on the surface at temperatures below 150 °C. We
propose that sputtering of targets with a deficit of oxygen leads to the presence of zinc vapor in the
cell and consequent deterioration of the crystalline perfection of the films. Increase of carrier
concentration in the range up to 150 °C is then due to thermal activation process of embedding an
impurity in the lattice.

Figure 5. Resistivity, carrier concentration and Hall mobility of GZO films with 3 at% Ga
deposited at various substrate temperatures (a); the temperature coefficient of resistance of GZO
films with 3 at% Ga deposited at various substrate temperatures (b).

Also, measurements of the temperature coefficient of resistance (TCR) show that the GZO films,
synthesized at temperatures below 150 °C, have a negative TCR, whereas the films, deposited at
T_{sub} ≥ 200 °C, TCR becomes positive, i.e. high synthesis temperatures lead to degenerate
semiconductor behaviour (Figure 5b).

4. Conclusions
The effect of the P_{Zn}/P_{O2} ratio on the formation and structure of ZnO nanoparticles as well as ZnO-
based thin films and ceramics was investigated. The experimental results are summarized in the
following.

(1) The ZnO whiskers grow along the lines of a certain optimal P_{Zn}/P_{O2} ratio.
(2) The formation of ZnO tetrapods occurs during the expansion of zinc in a two-stage scheme:
the formation of the ZnO_{1-x} seed and subsequent growth of ZnO whiskers from it.
(3) The increase in P_{Zn}/P_{O2} Ratio at dc magnetron co-sputtering of Zn and ZnO targets leads to a
significant change in the structure of ZnO films at T_{sub} > 400 °C according to the VLS
mechanism.
(4) The Ga-doped ZnO ceramic targets, sintered in the environment of zinc vapour, have have a
density of at least 99% of the theoretical value and a deficiency of oxygen in the ceramics of
about 8%. The presence of oxygen deficiency in the sputtered ceramic improves the structural
and electrical characteristics of the deposited ZnO-based TCO films. With increasing of
substrate temperature the minimal value of resistivity of Ga-doped ZnO thin films is achieved
at lower concentrations of gallium.

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