Ion-plasma methods of formation of piezosemiconductor ZnO thin films for acoustoelectronics and optoelectronics

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Abstract. The results of the study of thin nanostructured ZnO films obtained by the method of reactive ion-plasma sputtering are presented. The influence of technological factors on the structural and optical properties of films is considered.

1. Introduction
Zinc oxide belongs to direct-gap semiconductors which have a large band gap $E_g>3.3$ eV, a significant exciton binding energy $E_{ex} = 60$ meV, and also have active piezoelectric properties. The set of these properties defines a wide range of possible applications, including its use in solid-state devices of optoelectronics and functional electronics (acoustooptics, acoustoelectronics) [1–3].

Currently, various methods of growing ZnO thin films are used: gas-phase synthesis from organometallic compounds, pulsed laser ablation of a ceramic target from highly purified ZnO, or electron-beam sputtering in a pulsed mode. In comparison with them, the method of reactive ion-plasma sputtering of a metal target allows to create ZnO films with a large structural perfection of the film, moreover, this method allows doping of the composition of a semiconductor film during its growth [3–5].

2. ZnO thin film synthesis technology by the reactive ion-plasma method
The ZnO films under study were synthesized by the method of reactive ion-plasma sputtering of a metal target. The process of reactive ion-plasma sputtering of a target from high-purity zinc was carried out on a magnetron sputtering unit operating in a constant current mode. The zinc oxide film was synthesized in a gas atmosphere consisting of 20% oxygen and 80% argon. The pressure of the gas mixture in the reactor did not exceed 101 Pa. The substrate temperature varied in the range of 273–523 K. The metal target was made of high purity grade zinc. Wafers of KU grade quartz polished according to the 12th class of purity with a thickness of 2 cm were used as a substrate. The thickness of the synthesized ZnO films was monitored using an interference microscope and was 1.0 μm. The deposition of Al electrodes occurred at the same installation. According to microscopic studies, the thickness of the ZnO film was 1 μm. Al thickness was 0.5 μm. The deposition rate of the ZnO film by the reactive ion-plasma method was within 3–6 nm, which ensured the production of a semiconductor film with a high degree of orientation and the presence of piezo-properties. The ZnO films synthesized by the ion-plasma method on fused quartz and single-crystal LiNbO₃ substrates under completely the
same conditions had completely different degrees of crystallite orientation (figure 1(b), (a)) and a different piezo-response.

**Figure 1.** X-ray diagram of ZnO film synthesized on a different substrate: lithium niobite substrate (a), fused quartz substrate (b).

The dependence of the degree of misorientation of crystallites $\sigma$ on the deposition rate for this pair of substrates, shown in figure 2, indicates a greater effect of the deposition rate on the crystal structure of films on amorphous substrates than on orienting films.

**Figure 2.** Dependence of the degree of misorientation of the crystallites on the growth rate of the ZnO film: 1 – ZnO film on SiO$_2$, 2 – ZnO film on LiNbO$_3$.

In structures used in acoustoelectronics and photonics, a ZnO film is deposited on the surface of Al or Cr of nanoscale thickness. In this case, the orienting effect of the substrate is manifested despite the fact that the film grows on a metallic aluminum sublayer, which, in turn, turns out to be textured on the [111] axis and has a thickness of about 100–500 nm. The sublayer of Al/Cr performs several functions. First, it serves as the internal electrode of the piezoelectric transducer, and, secondly, it participates in matching the acoustic impedances of the piezoelectric transducer and the sound duct. Thirdly, the metal layer contributes to the relaxation of internal stresses arising in a growing zinc oxide film.

On such substrates, the internal stresses did not exceed the tensile strength of zinc oxide at a film thickness of about 20–30 $\mu$m, and in the case of ZnO growth on a SiO$_2$ substrate, the thickness of the
zinc oxide film reached 50 μm before the destruction stage. If the energy of the interface is minimal, then there is a high affinity of the crystal lattices of the film and the substrate, and in this case the growth of the ZnO epitaxial film is possible with high structural perfection and piezo properties.

The destruction of the zinc oxide film is promoted by a sharp change in the temperature of the sample at the end of the evaporation process, since the temperature of additional heating of the sample due to the condensing substance, as a rule, is 70–80 °C. Therefore, when spraying films onto substrates having an initial temperature of 200–250 °C, their temperature rises to 280–330 °C. Therefore, immediately before the end of the evaporation, the temperature of the heater should be increased. This compensated for the parasitic temperature gradient arising at the end of the spraying step. The temperature was reduced at a speed of no more than 3–5 degrees/min.

3. Investigation of the properties of ZnO films

The study of the structure of ZnO films was carried out using the X-ray diffractometry method. The measurements were carried out on an automated DRON-3M X-ray diffractometer, in the range of Bragg angles 2θ from 20 to 80 degrees, with a step Δ2θ = 0.05 degree. The accumulation time of pulses for each measurement point was 10 seconds. The X-ray diffraction patterns of the ZnO films obtained by the reactive ion-plasma method are shown in figure 3, where the evaporation occurred on a heated substrate and in figure 4, where the evaporation occurred without pre-heating the substrate.

![X-ray diagram of a polycrystalline zinc oxide film synthesized on a substrate preheated to 523 K.](image)

**Figure 3.** X-ray diagram of a polycrystalline zinc oxide film synthesized on a substrate preheated to 523 K.

According to X-ray diffraction data, the synthesized films have a polycrystalline structure consisting of nanoscale ZnO crystallites. A diffraction maximum of hexagonal ZnO (002) of high intensity is present on the diffractogram. Therefore, it can be argued that there is a high structural perfection in the synthesized film and the presence of a selected axial texture in the direction of the C axis, perpendicular to the substrate surface.

An increase in the substrate temperature during the synthesis of ZnO films led to the shift of all diffraction maxima toward smaller angles by the same distance along the axis of the angles. This can be explained from the standpoint of increasing interplanar distance due to elastic tensile stresses. During the synthesis of a ZnO film on a preheated substrate, a decrease in the size of zinc oxide crystallite sizes from 25 nm to 11 nm was found. The size of ZnO grains in a film synthesized on a pre-heated substrate up to 523 K, calculated using the Selyakov-Scherrer formula, does not exceed 11nm. In comparing the positions of the diffractogram peaks for films synthesized on hot and cold
substrates, there is a shift in the diffraction pattern towards smaller angles when the film is synthesized on a preheated substrate.

![X-ray diagram](image)

**Figure 4.** X-ray diagram of a polycrystalline ZnO film synthesized on a cold substrate.

The intensity of the peak (110) is higher for the film synthesized on the hot substrate compared to the intensity of the analogous peak present on the X-ray diffraction pattern of the ZnO film synthesized on the quartz substrate without preheating. This fact was discovered by us for the first time and requires additional research involving the EPR method. The study of the transmission spectra of the films was carried out in the wavelength range from 300 nm to 800 nm using a Perkin Elmer Lambda 650 spectrophotometer. In the spectral band of 400–450 nm, the transmittance is at least 65%, and in the range of 450–800 nm, the transmittance of ZnO films increases smoothly to 83%.

The study of the piezoelectric properties of the synthesized ZnO films by an optoacoustic method at a probe radiation wavelength of 340 nm made it possible to determine the main piezoelectric characteristics.

4. **Conclusions**

Synthesis of films by reactive ion-plasma method on pre-heated quartz substrates allows to obtain nanostructured ZnO films with the presence of the hexagonal phase of zinc oxide and structural properties close to the properties of epitaxial ZnO films. The optical and piezoelectric properties of the thin films under study practically coincide with the properties of single-crystal ZnO thin films. Zinc oxide films synthesized by the reactive ion-plasma method have low losses in the visible spectrum and have a strong absorption in the UV spectrum. Also, they have strong piezosemiconductor properties.

These properties allow creating acoustoelectronics, acoustooptics and photonics devices on the thin film ZnO basis.

**References**

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