Characterization of nanocrystalline ZnO thin films prepared by new pyrolysis method

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Abstract. To obtain high-quality nanocrystalline transparent ZnO films, a new pyrolysis synthesis method was used. The resulting material was investigated by x-ray diffraction, scanning electron microscopy. Structural analysis of the films shows that they are polycrystalline and have a wurtzite structure. The film structure consists of nanocrystallites about 10–20 nm in size, uniformly distributed over the surface of the substrate and over the thickness of the film. The temperature dependence of the resistance of the obtained films was also investigated. The activation energies of conductivity are determined by the donor conductivity levels existing in zinc oxide, and temperature hysteresis is determined by the effect of charging oxygen adsorbed on the surface of zinc oxide.

1. Introduction
In recent decades, optically transparent electrically conductive nanosized films have been of particular value, since they are widely used in optoelectronics as optically transparent electrodes for photodiodes, displays, solar cells, information display devices, etc. ZnO-based films deposited on glass and polyethylene substrates are used as catalytic systems, deicers in airplanes, automobiles and other modes of transport, transparent conductive coatings in electronic devices, photochemical cells [1, 2], systems for cleaning environmental objects from pollutants [3, 4], etc. In addition, zinc oxide has a high radiation, chemical and thermal resistance, and in the future, it can be widely used to create various transparent electronics devices. Due to the large band gap (Eg = 3.37 eV), ZnO can be used as a detector material for detecting ultraviolet radiation with a wavelength of 320-400 nm [5]. Zinc oxide exhibits pronounced photocatalytic and piezoelectric properties [6, 7].

ZnO-based films can also be used as sputtering of conductive transparent contacts, which are necessary in the manufacture of optoelectronic devices [8], as well as gas sensors [9]. One of the key advantages of zinc oxide is that this material can be easily obtained in the form of both continuous films and arrays of nanostructures with a wide range of different methods [10].

There are many physicochemical methods for the synthesis of zinc oxide thin films, such as sol-gel method, vapor deposition, film casting method, hydrothermal method [11], electrophoretic deposition, magnetron sputtering method, spray pyrolysis, flame-aerosol method, spray deposition, etc. Materials
obtained by various methods have different sizes, structures, phase composition, and, as a result, properties [12]. Therefore, it is necessary to know the advantages and limitations of each method for choosing the synthesis of materials with desired properties, since many methods for producing thin ZnO nanocrystalline films have disadvantages. For example, using the sol-gel method, thin ZnO films can be obtained, but using various stabilizers and technological calcination modes, they are obtained in different thicknesses. Some of the methods are characterized by a high cost of equipment (pulsed laser spraying, hydrothermal method), and a long process time (sol-gel method).

One of the main objectives of materials science is to find methods for producing thin ZnO films from available reagents using inexpensive methods for controlling the thickness, composition, and other characteristics of finished materials. This paper proposes a new method for the synthesis of ZnO transparent films using an organic zinc compound as a precursor, which has several advantages. Thus, the low-temperature pyrolysis method is technologically simpler than the sol-gel method, requires less expensive equipment than the hydrothermal method, and has a relatively low annealing temperature than the oxide method.

2. Experiment

The following chemicals were used to obtain these films: chemically pure zinc acetate dehydrate (Zn(CH₃COO)₂·2H₂O, dioxane, acetone, distilled water and organic acid. Chemicals were purchased from "ECROS" (Russia) and used without additional purification. This method of forming films can be divided into 2 stages. At the first stage, an intermediate product is obtained - an organic zinc compound. In a second step, a solution of the intermediate product is applied to the substrates and the final product is obtained.

The organic zinc compound was obtained by reacting an organic acid with zinc acetate. The amount of organic acid was calculated according to the reaction equation with a 10% excess. As a result of the synthesis, an amorphous powder was obtained, which was used as a precursor for the preparation of film coatings. For this, the organic zinc compound was dissolved in dioxane in a ratio of 1:5, the solution was applied by pouring onto a previously prepared purified substrate (glass, polycor and silicon were used as substrates), dried first at room temperature, and then at 373 K.

The proposed method allows to obtain films of various thicknesses by applying several layers of an precursor organic zinc compound. Samples with a coating of 10 or more layers of the precursor after heat treatment did not have a strong structure, exfoliated, therefore, multiple application of the solution was considered unproductive. It was possible to obtain high-quality multilayer transparent films after two to five layers of applying a precursor solution. For further studies, films were obtained by applying 3 layers of an organic zinc compound solution.

The films were heat treated by heating at a rate of 10 deg / min, with holding at 723 K for 1 h. After calcination, the films were cooled to room temperature in two ways. In the first case, the samples were taken out of the furnace and cooled in a desiccator. In the second case, the films were cooled together with a muffle furnace. Slowly cooled materials had a denser structure, and with faster cooling, defects and cracks were observed in the film coating.

The phase composition of the obtained films was studied by X-ray diffraction (XRD) on an ARLX'TRA, Thermo ARL diffractometer (Switzerland) using CuKα X-rays. Phase composition analysis performed using Crystallography Open Database. The morphology and thickness of the films were studied using a scanning electron microscope (SEM) on an EMXplus 10/12 Bruker apparatus (Germany). To study the temperature dependence of the resistance, nickel contacts (thick - 0,2÷0,3 μm) were formed on top of ZnO films by vacuum thermal spraying. Measurements in the temperature range of 20–340 °C were carried out on an automated test bench for gas calibration at the Microsystems and Integrated Sensors of the Southern Federal University [13].

3. Results of experimental studies and discussion

Figure 1 (a) shows an X-ray picture of a finished thin ZnO film deposited on a glass substrate. The main phase of the obtained films is the crystal structure of wurtzite, as expected for zinc oxide. All
materials at diffraction maxima: (100), (002), (101), (102), (110), (103), (200), (112) and (201) can be indexed as single-phase, corresponding to the hexagonal structure wurtzite ZnO (Crystallography Open Database, COD ID 1011259 [14]). Diffraction maxima of other phases were not detected.

The size of the coherent scattering regions (D) was estimated using the Scherrer equation: \( D = k \cdot \lambda / (\beta \cdot \cos\Theta) \), where \( k \) is the geometric shape coefficient, \( \lambda \) is the X-ray wavelength constant \( (\lambda = 0,154 \text{ nm}) \), and \( \beta \) is the full width at half the maximum of the diffraction line and \( \Theta \)-diffraction angle. The values of \( \beta \) and \( \Theta \) were taken from 3 intense peaks (101) (100) (002) of the ZnO wurtzite phase. The average crystallite size was 12,6±0,9 nm.

SEM analysis revealed a fairly uniform surface morphology. Nanocrystallites are uniformly distributed over the surface and thickness of the film, the film has a porous structure. Analysis of crystallite sizes from SEM images showed that their average size is 13,5±4,4 nm, which correlates with the sizes of coherent scattering regions. The average thickness of three-layer films is 90 nm. Despite the fact that the film was formed during the deposition of three layers, their SEM images were not observed boundaries. This indicates a high-quality technology for the formation of thin films of zinc oxide of different thicknesses.

**Figure 1(a, b).** (a) X-ray diffraction patterns of synthesized ZnO film; (b) SEM images of ZnO film.

Figure 2 shows the temperature dependence of the resistance of the ZnO film grown on a polycor in the temperature range 30-340 °C. The resistance of the films varies from 7∙10\(^9\) Ohm to 1,2∙10\(^8\) Ohm in the indicated range. The dependences of the resistance of the zinc oxide film R during heating and cooling do not coincide, which indicates the presence of temperature hysteresis.
Figure 2. Temperature dependence of the resistance of the ZnO film.

ZnO films exhibit lower conductivity upon cooling than upon heating. The presence of hysteresis is usually associated with the appearance of adsorbed oxygen on the surface during heating and cooling. Oxygen molecules in the atmosphere are adsorbed on the surface of zinc oxide and become negatively charged due to the capture of electrons from the surface layers of ZnO. As a result, a depletion layer is formed in the surface region of the film; its conductivity decreases [15]. Figure 2 shows that both curves have two characteristic regions — low-temperature region 1 (30–130 °C) and high-temperature region 2 (170–300 °C), which are characterized by different activation energies of conductivity. It is known that the conductivity of zinc oxide is determined by oxygen vacancies, which are electron donors [16], and, accordingly, the activation energy of conductivity is determined by donor levels formed by vacancies in the forbidden zone of ZnO. Based on the presented dependences using the Arrhenius equation, the activation energies of conductivity $E_a$ were calculated:

$$R = R_0 \exp \left( \frac{E_a}{kT} \right),$$

where $R_0$ is the preexponential factor; $k$ is the Boltzmann constant; $T$ is the temperature.

Calculations of the activation energy ($E_a$) showed that in region I, when heated, $E_a$ is 0.10 eV, and when cooled, 0.02 eV. For region II, $E_a$ is 0.71 eV upon heating and 0.88 eV upon cooling.

The conductivity of zinc oxide in region I is most probably determined by the oxygen vacancies existing in zinc oxide [17], which are located 0.05 eV below the conduction band. The conductivity in region II is determined by vacancies $V^2$ (Zn$^{2+}$), which have a donor energy level below the level of the conduction band from 0.4 to 0.7 eV. The conductivity in region II can also be explained by the existence of interstitial Zn$^+$ ions with a donor energy level of 0.4-0.5 eV.

The effect of adsorbed oxygen and its charging processes lead to a hysteresis in the temperature dependence of the conductivity of the ZnO film and some variations in the values of activation energy. The origin of the temperature hysteresis of the resistance can be explained by two competing processes — the thermal generation of electrons and the adsorption of oxygen particles on the ZnO surface [18].

4. Conclusion
The proposed new method for producing thin films of zinc oxide is an economical and simple method that does not require expensive equipment and non-toxic reagents and has a relatively low calcination temperature. This method allows one to obtain nanoscale films of controlled thickness, which include crystallites $13.5 \pm 4.4$ nm in size. The temperature dependence of the resistance of the zinc oxide film in...
the studied temperature range is characterized by temperature hysteresis. The activation energies of conductivity are determined by the donor conductivity levels existing in zinc oxide, and temperature hysteresis is determined by the effect of charging oxygen adsorbed on the surface of zinc oxide.

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