Zinc oxide films obtained by sol-gel method from film-forming solutions

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Abstract. Thin ZnO films on silicon and quartz substrates were obtained from a film-enriched ethanolic solution based on $Zn(NO_3)_2 \cdot 6H_2O$ and salicylic acid. The effect of salicylic acid on the processes occurring in the film-forming solution was studied by IR spectroscopy, proton-magnetic resonance, and viscometry methods. The formation of zinc salicylate nitrate in an ethanol solution is established, where salicylic acid exhibits a monodentate property in the carboxyl group. Thermal formation of zinc oxide was determined by thermal analysis and X-ray diffraction. The analysis of optical and electrophysical characteristics of ZnO films was carried out using spectroscopy, ellipsometry and also a block for measuring the electrophysical properties of thin-film materials. It was found that ZnO films were semiconductors of the electronic type, characterized by an optical band gap of 2.91−3.21 eV, a surface resistance of 10^9−10^6 Ω and transparency coefficients in the visible spectral range of 0.80–0.96. It was shown that as the thickness of the ZnO films increased the resistance decreased.

1. Introduction

The proliferation of electronic devices in human life increases the need in autonomous sources of energy. Such sources include solar cells, in which wide-band semiconductor thin-film materials [1-5] are used that have high transparency in the visible region of the spectrum. ZnO-based materials are perspective since ZnO is characterized by a band gap of 3.2−3.8 eV and a transmittance in the visible spectral range of up to 80% depending on the method of preparation. Nowadays, this substance is already being used including in solar cells [6-8]. However, its disadvantages include relatively low transparency, labor-intensive and high-temperature methods of production. These disadvantages can be avoided by using the sol-gel method to obtain thin ZnO films on transparent substrates from film-forming solutions (FFS). This method is the most simple and inexpensive. However, FFS with inorganic zinc salts doesn't have sufficient a film-forming ability due to insufficient viscosity and low adhesion to solid-state substrates. The viscosity and the adhesion of FFS can be increased by introducing an organic ligand with an aromatic ring. A large molecular weight of the organic compound will contribute to the growth of the FFS viscosity value. The delocalized electron density of the benzene ring will participate in the interaction with the solid substrate defects.

The aim of our studies is to determine of influence of salicylic acid on the processes occurring in the in the ethanol solution of zinc nitrate upon the formation of ZnO in the thin-film state and to study its electrical and optical properties.

2. Materials and Methods

A film-forming solution was obtained by dissolving salicylic acid, $Zn(NO_3)_2 \cdot 6H_2O$ in a 96% by weight solution of ethanol. The concentration of organic ligand and zinc nitrate was 0.3 mol/l. Salicylic acid (H_2Sal corresponded chemically pure 99,8 %) was purchased in Aloric (China). The zinc nitrate (pure for analysis) was purchased in TD Reahim (Russia). All reagents were used without further purification. The interaction of salicylic acid with zinc ions in ethanol solution was studied by proton-magnetic resonance (^{1}H NMR), IR spectroscopy and by viscosimetry method. The viscosity of FFS was measured at 25 °C through a glass viscometer VPZH-2 (Russia) with capillary diameter of 0.73 mm. The ^{1}H NMR spectra were acquired at 25 °C on a spectrometer TESLA-BS-497 (Czech) operating at 100 MHz. The ^{1}H NMR spectra were recorded against a 96% ethanol solution. The infrared (IR) spectra of dried FFS were recorded on an Agilent Cary 630 FTIR spectrometer (USA) in the 400–4000 cm^{-1} frequency range, against air. Thermal decomposition of dried FFS was investigated using the thermal analysis method and mass spectrometry. The thermal analysis was carried out on a STA 449 C Jupiter (Germany) in a temperature range of 4…1000 °C in air atmosphere using a QMS 403 Aëlos mass spectrometer. The phase composition of the final product of FFS decomposition was determined by X-ray diffraction on a Rigaku Miniflex 600 diffractometer (CuKα radiation, 2θ = 20°–1200°, scan step of 0.02°, continuous scan rate of 2°/min, Japan).

Films of ZnO on silicon substrates were obtained by centrifugation at a rotational speed of 3000 rpm. ZnO films on quartz and glass substrates were obtained by removing the substrate from film-forming solutions at a speed of 100 mm/s. All the films on the substrates were on one side. The other side quartz and glass substrates were covered with scotch. The structure of oxide films is formed in the process of annealing the film-forming solution on the surface of the substrate and is independent of the coating procedures. To remove the solvent and increase the adhesion of FFS to the substrates, the films were dried in an oven at 60°C for an hour prior to the heat treatment in a muffle furnace at 500°C for an hour. The transmission spectra of ZnO films on quartz and glass substrates were obtained on a spectrophotometer SC5400 (Russia) in the wavelength region of 220…1100 nm. The width of the band gap of ZnO in the thin-film state was determined from the edge of intrinsic absorption band of the sample in the UV spectrum. The optical width of the band gap was found by the formula: $\Delta E = h \cdot \nu$ where h = 6,626070040·10^{-34} J/s, Planck's constant. The thickness and refractive index of oxide films on silicon substrates are determined using the ellipsometry method on an ellipsometer SE400advanced (Germany). Measurements of the resistance of ZnO films on silicon substrates were performed on a laboratory unit including an F-195 ammeter (made in Russia), a V7-40 voltmeter (Russia), a heating element, a control unit and a computer with software. The conductivity type of the films was determined from the temperature dependence of the logarithm of conductivity. The morphology of the samples was studied on a scanning electron microscope Hitachi-3000 (Japan).

3. Results and discussion

In an ethanol solution (96% by weight) of the crystalline $Zn(NO_3)_2 \cdot 6H_2O$ undergoes solvation and hydrolysis. Therefore, in this solution there are solvated ions of $ZnOH^+$, H^+, and NO_3^-. After the adding salicylic acid to zinc nitrate solution, the interaction of $ZnOH^+$ cations with salicylate ion is possible. In the ^{1}H NMR spectra of a solution of salicylic acid, four chemical shifts of protons were detected (table 1). In the spectrum of ^{1}H NMR of FFS on the basis of zinc nitrate with salicylic acid there are only signals of chemical shifts of protons in the benzene ring and hydroxyl group. The chemical shift of protons of a carboxyl group is absent, which indicates monodentate nature of salicylic acid in the reaction: $C_6H_4OHCOOH + ZnOHNO_3 = [ZnC_6H_4OHCOO]NO_3 + H_2O$.

The results of IR spectroscopy also prove the interaction of salicylic acid with zinc ion through the carboxyl group. As can be seen from figure 1, in the IR spectrum of the film-forming solution dried at 60 °C, vibrations of the bonds of crystallization water are present.

Table 1. Chemical shifts of protons in the 1H NMR spectra of salicylic acid and FFS in ethanol.

Groups	δ, ppm, $C_6H_4OHCOOH$	δ, FFS
–CH–	6.83–6.95 ppm	6.74–6.93 ppm
–CH–	7.31–7.48 ppm	7.29–7.49 ppm
–OH	7.80–7.88 ppm	7.76–7.85 ppm
–COOH	8.20–8.30 ppm	–
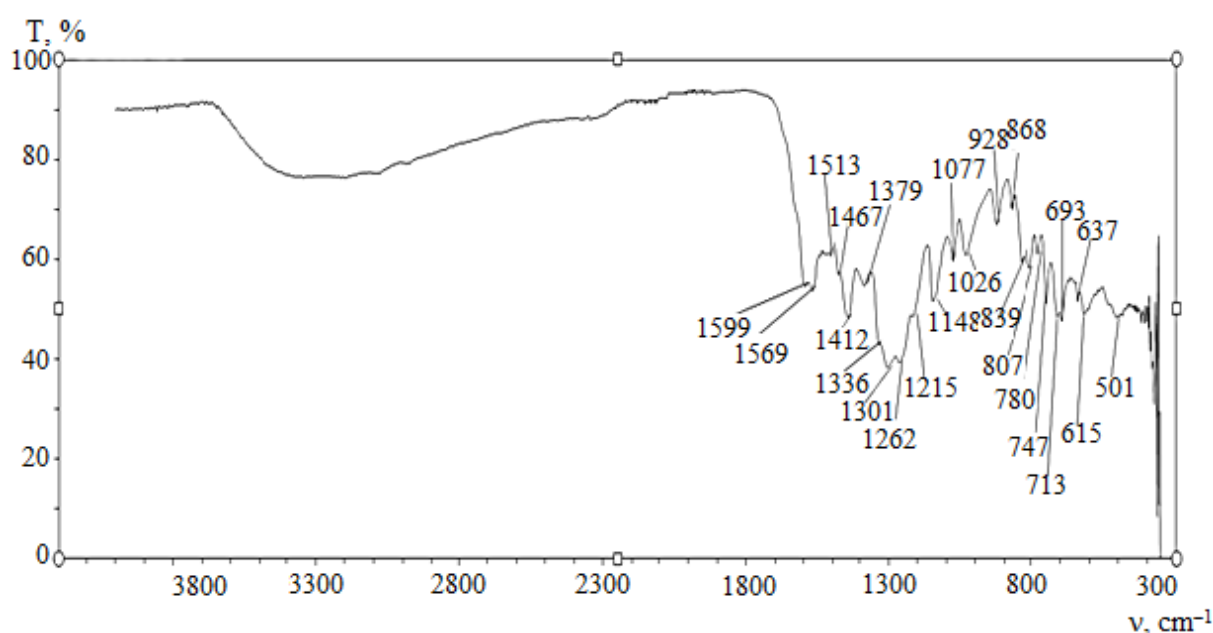
Figure 1. IR spectrum of FFS based on $Zn(NO_3)_2 \cdot 6H_2O - H_2Sal - C_2H_5OH$ dried at 60 °C.

Antisymmetric and symmetric vibrations of –OH groups are observed in the frequency range of 3550–2800 cm^{-1}, deformation vibrations of H–O–H – at 1599 cm^{-1} [9]. The absorption at 1070–900 cm^{-1} corresponds on the flat deformation vibrations of C–H in the 1,2-; 1,4-substituted ring; the absorption at frequencies of 800–650 cm^{-1} correspond to nonplanar deformation vibrations of C–H in the 1,4-; 1,2-substituted ring. In the IR spectrum there are frequencies with maxima at 1569, 1513, 1442, 1379, and; 1336 cm^{-1}, characterizing the symmetric and asymmetric valence vibrations of C=O bonds in the carboxyl group. Valent vibrations of the C–OH bonds of the phenol group are observed at frequencies of 1148, 1077, and 1026 cm^{-1}. When comparing the frequencies characterizing the vibrations of the C=O and C–OH bonds in the film-forming solution with the frequencies of these same groups in the solution of salicylic acid (figure 1), it can be seen that the frequencies of C=O groups are strongly shifted to the lower frequency region and their number decreased. The position and number of frequencies of C–OH group does not change, which indicates the participation of only the carboxyl group in the formation of bonds with zinc ion. Absorption with a maximum at 501 cm^{-1} indicates the presence of a Zn–O bond and at frequencies of 1379; 1301; 1262; 1215 cm^{-1} –NO$_3$ groups. On the basis of the foregoing, it follows that the FFS, dried at 60 ° C, is a

$[ZnC_6H_4OHCOO]NO_3 \cdot xH_2O$. As can be seen from figure 2, FFS based on $[ZnC_6H_4OHCOO]NO_3$ acquires stable properties (viscosity does not change) after keeping it for 5 days.
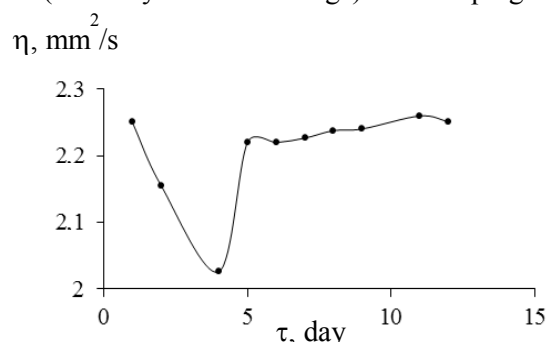

Figure 2. Time-related fluctuation of FFS' viscosity.

The decrease in viscosity by 4 days of keeping FFS can be associated with the destruction of the structure of the ethanol solvent under the influence of the electric field of dissolved salt ions [10]: $[ZnC_6H_4OHCOO]^+$ and NO_3^-. FFS viscosity growth (up to 2.23 mm^2/s) is associated with the orientation of the solvent molecules in the electric field of the dissolved substances. Compared with the ethanol solution of zinc nitrate, the viscosity of the of zinc salicylate FFS nitrate is higher by 0.59 mm^2/s. A higher value of the viscosity of FFS makes it possible to obtain more uniform films of zinc oxide. The use of a FFS after the fifth day (η = 2.24 mm^2/s) of its aging makes it possible to obtain films with stable properties. The annealing temperature of the film-forming solution for the production of ZnO was determined by thermal analysis using mass spectrometry. As can be seen from figure 3, the process for the formation of ZnO occurs in three steps.
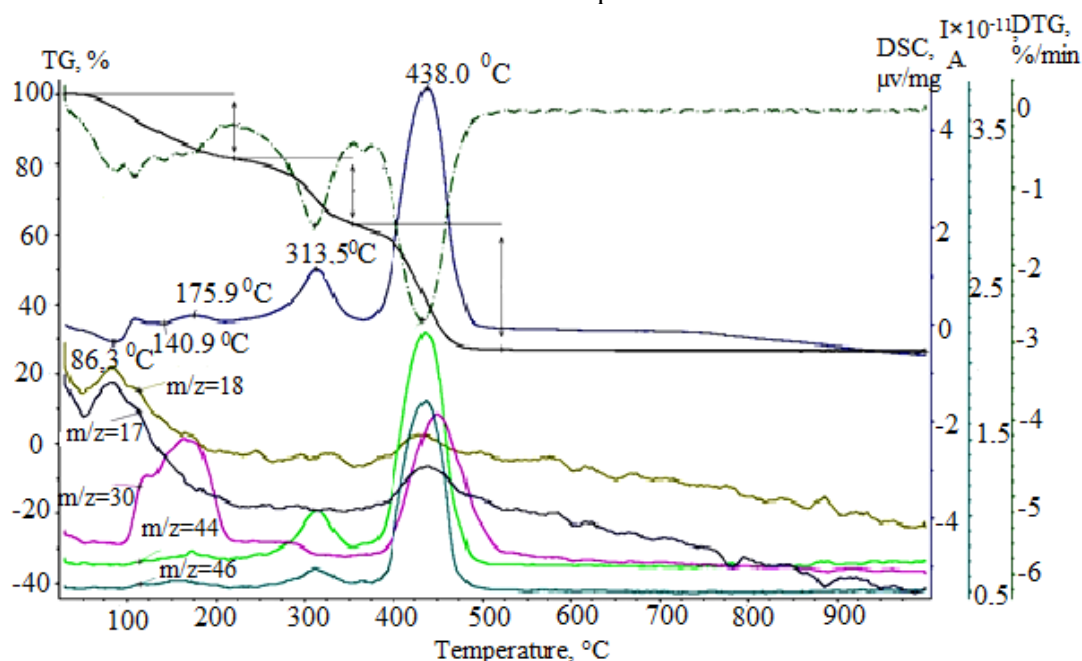

Figure 3. The thermal analysis data of the FFS dried at 60 °C with mass spectrometry data of the products of its decomposition.

The first stage is accompanied by two endothermic (86.3 °C, 140.9 °C) and one exothermic effects (175.9 °C). At this stage, in the temperature range of 25…225 °C, the molecules of adsorbed and crystallized water (m/z =17, 18) are sequentially removed, as well as the decomposition of nitric acid molecules (m/z = 30, 46), which is confirmed by mass spectrometry (figure 3). The second and third

stages of FFS destruction are characterized by two exothermic effects with maxima at 313.5 °C and 438.0 °C. According to the mass spectra at these stages, the presence of NO_2 (m/z = 46, m/z = 30), as well as CO_2 (m/z = 44) and H_2O (m/z = 18, m/z = 17). Therefore, at the temperature above 225 °C, $[ZnC_6H_4OHCOO]NO_3$ decomposes as a result of the oxidation of the salicylate ion and decomposition of NO_3^--ion. The decomposition process ends at a temperature of 500 °C. A TG curve at this temperature shows no change in mass. The final product of the decomposition FFS is ZnO. As can be seen from X-ray patterns (figure 4), in the sample obtained after annealing the film-forming solution at 500 °C are only peaks belonging to ZnO of structure wurtzite .
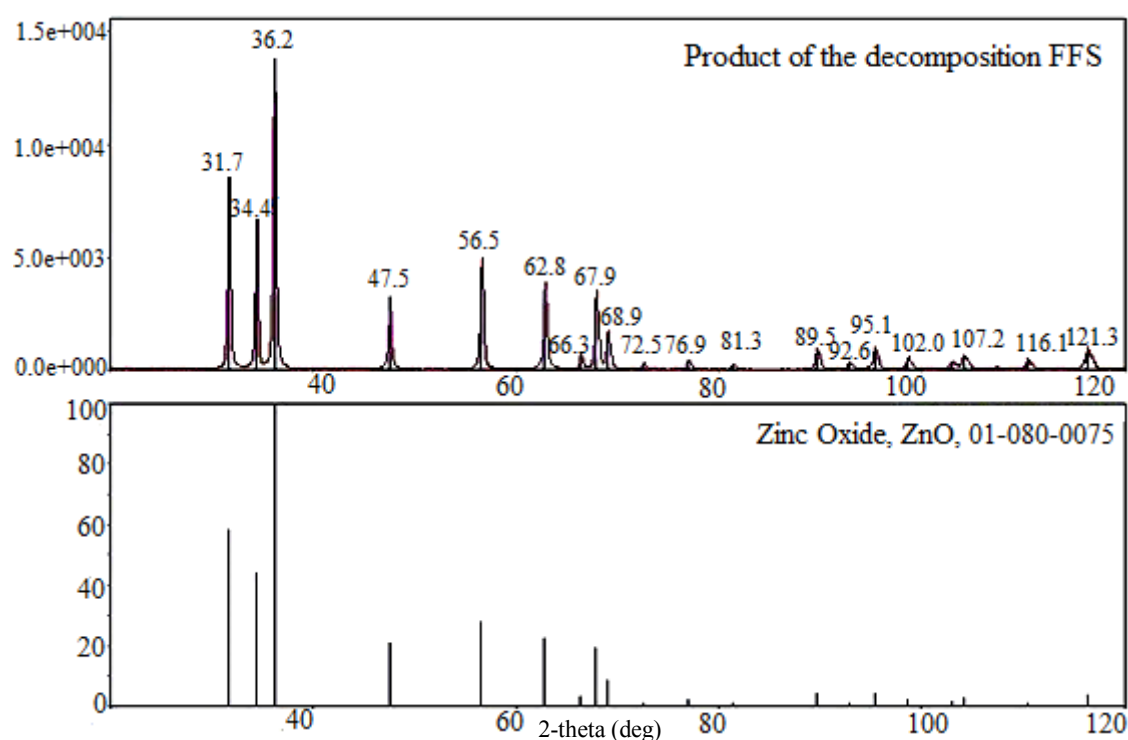

Figure 4. X-ray patterns of decomposed product of dried FFS obtained at 500 °C.

The parameters of the crystal lattice of the formed ZnO are a = b = 3.250898 Å, c = 5.20827 Å, $\alpha = \beta = 90°$, and $\gamma = 120°$. On the basis of the foregoing, it follows that the film-forming solution based on zinc nitrate and salicylic acid is an ethanol solution of zinc salicylate nitrate. After it is dried of FFS at a temperature of 60 °C, the solvent and HNO_3 are removed and in the residue remains $[ZnC_6H_4OHCOO]NO_3$, which decomposes at a temperature of 500 °C to ZnO:

$$4[ZnC_6H_4OHCOO]NO_3 + 23O_2 = 4ZnO + 24CO_2 + 10H_2O + 4NO_2.$$
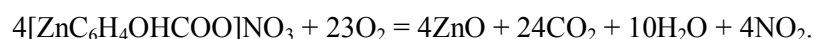
ZnO films on silicon substrates obtained from FFS at 500 °C are characterized by a thickness value of 12.6 ± 0.4 nm and a refractive index of 2.34 ± 0.07, herewith the surface resistance (R) of the films is $10^9\Omega$, and the optical band gap is 3.21 ± 0.04 eV. With an increase in the films thickness from 12.6 to 200.0 nm, the surface resistance reduces from 10^9 to 10^6 Ω. The decrease in resistance may be due to higher concentration of charge carriers for thicker film. The optical width of the forbidden band is not higher than 2.91± 0.03 eV. As can be seen from figure 5, the obtained oxide film has an electronic type of conductivity.
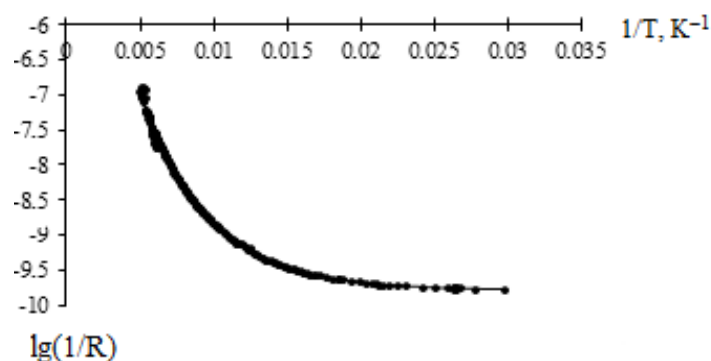
Figure 5. Temperature dependences of the conductivity of thin films ZnO.

From the data obtained for the dependence of (log (1/R)) on (1/T) from the Arrhenius equation for the ZnO films, the value of the activation energy (Ea) of the charge carriers was calculated, which amounted to Ea = 1.0 ± eV. This value is much lower than the optical band gap (3.21 ±0,04) eV, which is explained by the curvature of the energy bands with the formation of a random potential relief [11, 12].

It is known, that the transparence of films in the visible region of the spectrum is affected by the degree of their crystallinity, stoichiometry and concentration of charge carriers. High roughness films and a large thickness increase the absorption losses light and reduce their transmittance in visible light [13]. As can be seen from figure 6, ZnO films having a larger thickness are more uneven.
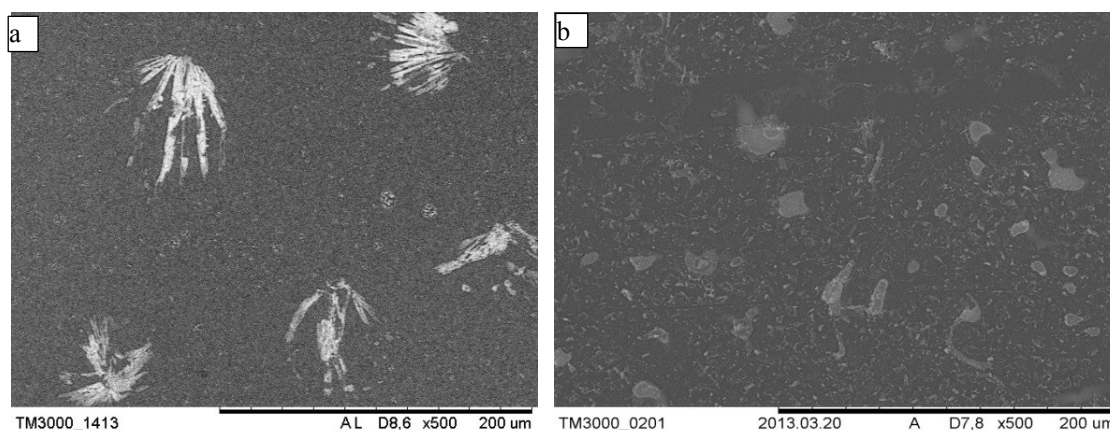

Figure 6. Morphology of ZnO films surface with thickness: a) 12.6±0.4 nm; b) d = 215±2 nm.

Zinc oxide particles in films 215 nm thick have different forms with length from 1 to 30 microns and therefore the surface is more rough. Thin zinc oxide films (d = 12.6 ± 0.4 nm), despite the dendritic inclusions up to 60 μm, are more uniform. The particles located between these inclusions of similar size are 0.5–3 μm.

The obtained spectra of optical transmission of zinc oxide films of different thickness on quartz substrates (figure 7) show that the average transmittance in the visible region of the spectrum of thinner zinc oxide films is 0.90–0.96.
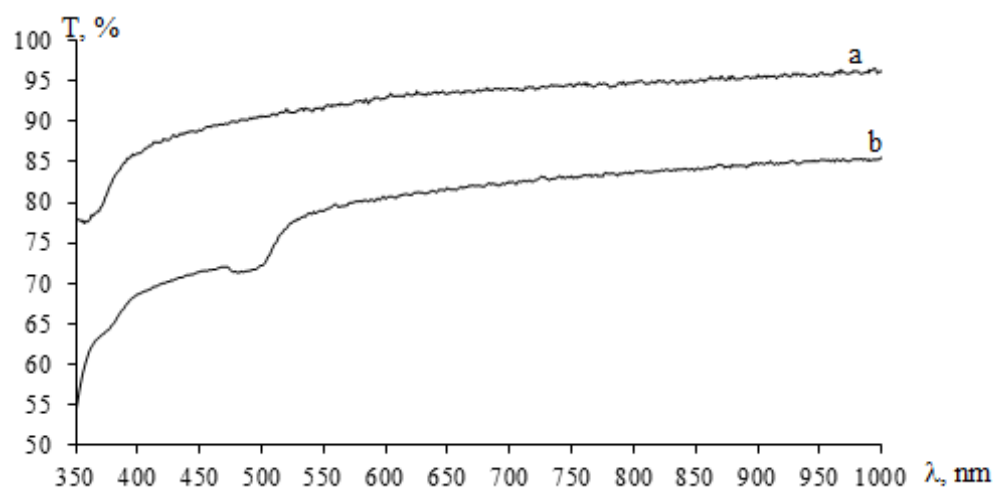
Figure 7. Transmission (T,%) spectra of zinc oxide films on glass substrates: a) 12.6±0.4 nm; b) d = 215± 2 nm.

It has been established that their edge optical absorption at 77% of the transmission has a wavelength of about 360 nm. An increase in the thickness of the films to 215 ± 2 nm shifts the edge optical absorption (55%) to 350 nm.

4. Conclusion

Salicylic acid is involved in the formation of the film-forming ability of a solution of zinc nitrate in ethanol. For the first time it was shown that salicylic acid exhibits a monodentate character by complexation with zinc cation in ethyl alcohol. Zn^{2+} interacts with carboxyl group of salicylic acid. The formation of a complex compound $[ZnC_6H_4OHCOO]NO_3$ in solution leads to an increase in viscosity, due to which the film-forming ability increases.

It was established that to obtain zinc oxide films with stable properties, it is necessary to maintain film-forming solutions for five days after its preparation. Zinc oxide from the dried film-forming solution is formed through the stage of removing of the ethanol solvent and subsequent thermal destruction of zinc nitrate hydroxoxalicylate, accompanied by the burning of the ion salicylate and decomposition of the nitrate of the ion to nitric (IV) oxide and oxygen. ZnO is formed at an annealing temperature 500 °C. The structure of ZnO is wurtzite. Films of zinc oxide of the electron type are characterized by a high-resistance surface. The thickness of the films affects their conductivity and transparency. When the thickness of the films is increased in 15−16 times, the resistance decreases by 1000 times due to a decrease in the width of the forbidden band. However, the transparency of the films is reduced by 10−15%, which is explained by the increase in the charge carriers, as well as by the increase in the unevenness of the thin film coating.

Acknowledgments

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