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The Formation of ZnO-Based Coatings from Solutions Containing High-Molecular Polyvinylpyrrolidone

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Abstract—A method for deposition of transparent nanosize ZnO-based coatings on the glass surface from solutions containing high-molecular polyvinylpyrrolidone is described. The method can be used to form transparent homogeneous coatings based on ZnO with an increased energy gap width. It does not require any intricate technological equipment.

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Thin coatings based on zinc oxide serve as transparent electrodes for various photoelectronic devices and parts in solar power engineering and optoelectronics and are used in low-E glazing. The properties and morphology of these coatings and the development of methods for their deposition are currently the object of intense research [1–8].

Wet methods for obtaining coatings based on zinc oxide [1, 2, 8, 9] are promising because of the flexibility and versatility of the technological process, and their practical implementation does not require any intricate technological equipment.

It was shown in [10, 11] that highly uniform transparent oxide coatings can be formed by using solutions of metal nitrates and high-molecular (M_s = 1300000, Sigma-Aldrich) polyvinylpyrrolidone (PVP). In the first stage of the process, a thin uniform composite coating is formed on the substrate surface composed of a polymer and close-packed salt particles 10–15 nm in size [11]. In the subsequent thermal treatment, metal nitrates and PVP are fully decomposed and gaseous residues are removed.

Zinc oxide coatings constituted by rather coarse (0.7–1.1 μm) aggregates of nanocrystals were deposited in a similar way in [9] from solutions of zinc acetate and substantially lower molecular PVP (M_s = 40000) (PVPK-30, Himedia).

A significant difference of the wet method with water-soluble polymers from the widely known sol-gel techniques for coating deposition [1, 2, 8, 9] is that it has no stage in which a colloid solution (sol) is formed. This precludes formation of aggregates of colloid particles in the film-forming solution and makes it possible to significantly improve the uniformity of the coatings.

The goal of the present study was to examine the possibility of using the wet method with water-soluble polymers for obtaining ZnO-based transparent coatings and to analyze specific features of the morphology and spectral properties of the resulting coatings. The role of the starting materials was played in the study by an aqueous solution of $Zn(NO_3)_2$ and a solution of high-molecular (M_s = 1300000, Sigma-Aldrich) PVP in propanol-2. After the zinc nitrate solution was added to the PVP solution, the mixture was agitated at room temperature for 15 min. The resulting film-forming solution contained 3.8×10^{-6} M of PVP and 5.7×10^{-2} M of $Zn(NO_3)_2$ and had the form of a transparent homogeneous liquid.

Coatings were deposited onto the surface of an alkali-silicate glass (Menzel-Glazer, item no. 021102) by dipping it at room temperature into a film-forming solution and subsequent removal and drying at 80°C for 3 h. This procedure yielded thin uniform composite coatings on both sides of a glass substrate. In its chemical composition, the coating was a PVP film containing zinc nitrate.

Glass samples with coatings were thermally treated in air at a temperature of 550°C or 2 h, which nearly

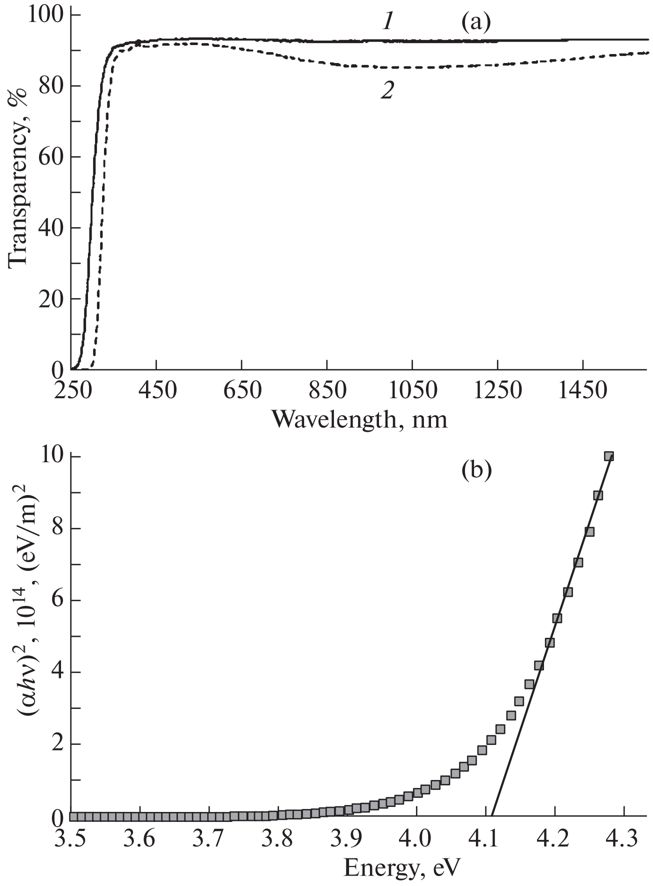

Fig. 1. (a) Transmission spectra of the starting alkali-silicate glass (curve *1*) and glass having zinc oxide coatings on both of its opposite surfaces (curve *2*). (b) $(\alpha h\nu)^2 = f(h\nu)$ dependence for the material of the coating.

fully coincided with the thermal treatment conditions used in [9]. The transmission spectra of the samples were measured in the range 200–2000 nm on a Shimadzu UV3600 spectrophotometer. The morphology of the coatings was studied by scanning electron microscopy (SEM) on a Carl Zeiss SUPRA 25 instrument.

Figure 1a shows transmission spectra of the starting glass and one with a coating. It can be seen that the deposition of the coating noticeably changes the transmission of the glass in two spectral ranges: in the UV part (280–350 nm) and in the near-IR part (800–1300 nm).

The energy gap width was determined for the synthesized systems of ZnO nanosize particles by the procedure suggested by Tauc [12] from the dependences

$$(\alpha h\nu)^2 = A(h\nu - E_g). \tag{1}$$

Here, $h\nu$ is the photon energy, E_g is the energy gap width of the semiconductor, A is a constant, and α is the absorption coefficient. Plotting in the $(\alpha h\nu)^2 = f(h\nu)$ coordinates makes it possible to determine E_g in the coatings under study as the point of intersection of the linear extrapolation of the dependence from the high-absorption region to that characterized by low absorption of light.

Figure 1b shows the $(\alpha h\nu)^2 = f(h\nu)$ plot for a zinc oxide coating fabricated by using high-molecular PVP. It can be seen that the energy gap width of ZnO in the coating is ~4.1 eV, which is close to the E_g obtained in [9] for similar coatings deposited by using low-molecular PVP. These values substantially exceed the energy gap width of the bulk macroscopic zinc oxide (3.36 eV) and E_g in ZnO coatings produced by ion-beam sputtering (3.21–3.26 eV) [13] and those synthesized in a low-temperature plasma discharge (3.26–3.32 eV) [14]. It is noteworthy that the energy gap widths in ZnO nanostructures produced by deposition from aqueous solutions were 3.2–3.3 eV, depending on the temperature at which the material was thermally treated [15]. These values are close to E_g of the macroscopic material and are substantially smaller than those in the coatings we obtained.

Thus, based on the data we obtained and on the results of [9], we can conclude that, with both high- and low-molecular PVP, ZnO coatings with a substantially wider energy gap, compared with the conventional macroscopic material, can be deposited by the solution method.

It is noteworthy that deposition of an even thin nanosize coating noticeably reduces the transmission of a glass sample in the near-IR spectral range. As is known, coatings that are transparent in the visible spectral range and exhibit increased absorption or reflection of light in the near-IR spectral range are widely used in the industry for manufacture of modern low-E glasses [16]. The transmission spectra in Fig. 1a show that the technologically simple method for deposition of zinc oxide coatings developed in the study can be used in development of the low-E glass technology.

Figure 2a shows a plan-view SEM image of the coating surface. It can be seen that the coating is constituted by nanoparticles that are, as a rule, less than 25 nm in size and have a density on the order of 3×10^{10} cm^{-2}. Analysis of the nanoparticle size distribution by means of DIAnaTEM software [17] (Fig. 2b) demonstrated that the scatter of sizes does not exceed 10 nm. The observed small size of the nanoparticles constituting a coating is presumably an important factor that could make the energy gap width of the material larger due to the quantum-confinement effect [18].

Comparison of the data in Fig. 2a with the results reported in [9] shows more structurally uniform zinc oxide coatings can be formed by using high-molecular PVP.

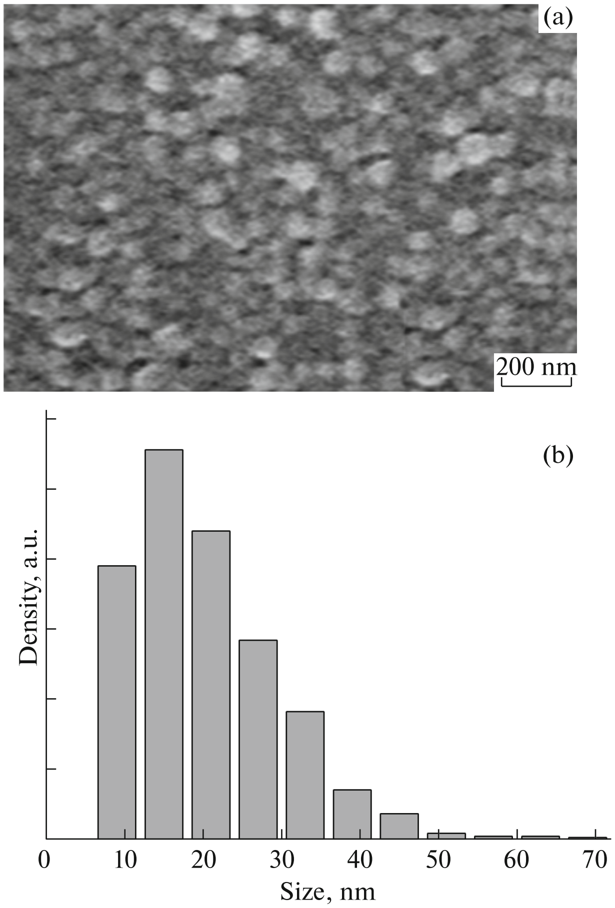

Fig. 2. (a) Plan-view SEM image of the coating surface. (b) Analysis of the nanoparticle size distribution in the coating by DIAnaTEM software [17].

Thus, it was shown that thin uniform zinc oxide coatings can be formed on the surface of glass from solutions containing high-molecular polyvinylpyrrolidone. The coatings are constituted by nanoparticles with a characteristic size of about 20 nm and density on the order of 3×10^{-2} cm^{-2}. The solution method developed in the study can form ZnO-based coatings with increased energy gap width and does not require any intricate technological equipment.

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