Electron-microscopy study of ordered silver nanoparticles synthesized in a ZnO:Al polycrystalline film

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Abstract. The optical absorption spectra and structural properties of samples series consisting of AZO oxide films with an intermediate layer of silver nanoparticles with different sol compounds were investigated. TEM analysis of the obtained coatings showed that the nanoparticles in the AZO film form an ordered structure, and the distance between them depends on the sol composition and the film annealing temperature. Optical measurements showed that a position of the nanoparticle plasmon peak in AZO also depends on them.

1. Introduction
Developing the approaches for obtaining ordered nanostructured composites with controlled physical properties remains a major challenge for photonics, biosensors, nanofluidics [1-4]. New physical properties were observed by use of ZnO, Al$_2$O$_3$, TiO$_2$ and SiO$_2$ as functional matrix materials in the preparation of metal–oxide nanocomposites [5-8]. For dispersed phases in nanocomposites silver and gold are among the most interesting metals because of their remarkable chemical reactivity in solution [9].

ZnO:Al oxide films (AZO) with metal nanoparticles (NP) exhibit unique optical and electrical properties induced by excitation of plasmon resonances [10-13]. The ability to manage these properties via varying film structure gives rise to many important features and applications.

In this work, composite coatings consisting of AZO films with an intermediate layer of silver NP obtained by sol-gel technology were investigated. The advantages of the sol-gel method are a low temperatures synthesis, a high degree of homogeneity in a multicomponent system, and the possibility of obtaining noncrystalline systems, which synthesis by traditional methods leads usual either to phase separation or crystallization [14]. The main aim was to reveal correlation between optical and structural properties of films produced from different sol compounds and for different annealing temperatures.

The correlation of the optical and structural properties of composite coatings consisting of ZnO:Al oxide films (AZO) with an intermediate layer of silver nanoparticles obtained by the sol-gel technology were investigated. The introduction of silver nanoparticles with dimensions of several tens of nanometers leads to the appearance of an additional peak in the optical absorption spectrum of AZO, corresponding to the plasmon peak of nanoparticle absorption [10]. A shift of the nanoparticle plasmon peak in AZO was observed depending on the AZO sol composition and the film annealing temperature with the same concentration of silver introduced into the sol.
For a series of samples consisting of AZO oxide films with an intermediate layer of silver nanoparticles with different sol compounds, optical absorption spectra were measured, and their structural properties were determined by transmission electron microscopy (TEM). The comparison of optical and structural properties measurements data of the samples allowed to derive some regularities of the silver nanoparticles formation in the AZO matrix that were consistent with the results of the optical properties of model structures (Figure 1, part 1-3) obtained from the simulation [15].

2. Fabrication of nanocomposites
For this study, series of AZO films with involved layers of silver nanoparticles samples were prepared. To fabricate nanocomposite structure five monolayers of AZO were deposited on a fused quartz substrate, than four layers of silver nanoparticles dissolved in the solvent were deposited. Finally, the obtained structure was covered by five monolayers of AZO. The series of samples were distinguished by temperature treatment conditions. All layers were deposited by spin-coating method. Each layer was dried at 300 °C.

The sol solution for AZO consisted of zinc acetate dehydrate [Zn(O\(_2\)CCH\(_3\))\(_2\), ZnAc] and aluminum nitrate [Al(NO\(_3\))\(_3\)] was dissolved in 2-Methoxyethanol with concentration of 0.2 M. The solution of silver nanoparticles consisted of silver nitrate [AgNO\(_3\)] in 2-Methoxyethanol with concentration of 0.03 M.

In this work, two series of samples have been investigated: the first one, where layers of silver nanoparticles were deposited on non-annealed layers of AZO; the second one, where layers of silver nanoparticles were deposited on annealed at layers. In each series the non-annealed samples of nanocomposite, annealed at 570 °C, 650 °C and 700 °C have been studied.

3. Characterization
The morphology of AZO film with Ag nanoparticles (NP) was determined through transmission electron microscope (TEM) technique using a JEOL JEM-2100F with the accelerating voltage of 200 keV. The sample was prepared in a cross section in accordance with the standard procedure, including preliminary mechanical thinning and further polishing with an ion beam (argon ion beam energy - 4 keV).

The structure of samples also was investigated by scanning electron microscope (SEM) LYRA3 TESCAN with the accelerating voltage of 10-20 keV.

The optical density spectra measurements were performed with the fiber spectrometer AvaSpec-2048.

4. Results
The optical density spectra (Figure 1.1a-1.11a), the cross-section TEM images (Figure 1.1b-1.11b) and images of model composite structures corresponding to the investigated samples (Figure 1.1c-1.11c) are presented. Comparing the optical spectroscopy and TEM results for each sample, one can derive the following regularities of composite structures formation.

After several monolayers of silver nanoparticles solution deposition and their heat treatment at 300 °C the nanoparticles coalescence is observed. The size and shape of the formed nanoparticles depends on the heat treatment conditions of the AZO layers, on which they are deposited, and on the annealing conditions of the entire composite. At temperature drying of 300 °C, the nucleation of polycrystalline grains in AZO films occurs, the size of the grains is about 3-5 nm (Figure 1.3b, 1.3c, 1.8b, 1.8c). An increase in the annealing temperature of the AZO films leads to an increase in the grain size (Figure 1.2b, 1.2c, 1.5b, 1.5c, 1.6b, 1.6c). The diffraction pattern for AZO films annealed up to temperature of 650 °C, corresponds to a polycrystalline structure (Figure 2a). Upon annealing at 650 °C, a single-crystal thin-film structure or a structure with equal oriented AZO grains is formed (Figure 2b). In the case, when silver nanoparticles are deposited on the non-annealed AZO layers, silver nanoparticles coalesce into spherical particles of about 20–35 nm in size on the granular boundary of the layers (Figure 1.8b, 1.8c). An increase of the annealing temperature leads to the AZO grains and nanoparticle
Figure 1. (part 1) Optical density spectra (a), light-field cross-section TEM image (002) (b) and model structures (c) of samples № 1, 2, 3, 5 polycrystalline AZO films with silver nanoparticles:

1.1, a-c correspond to the structure: fused quartz substrate - ZnO:Al (3%), 5 layers, annealing 580 °C - NP Ag, 5 layers without annealing - ZnO:Al (3%), 5 layers, annealing 580 °C;

1.2, a-c correspond to the structure: fused quartz substrate - ZnO:Al (3%), 5 layers, without annealing - Ag, 4 layers without annealing - ZnO:Al (3%), 5 layers, annealing 700 °C;

1.3, a-c correspond to the structure: fused quartz substrate - ZnO:Al (3%), 5 layers, annealing 650 °C - NP Ag, 4 layers, without annealing - ZnO:Al (3%), 3 layers, without annealing;

1.5, a-c correspond to the structure: sapphire substrate - ZnO:Al (3%), 5 layers, without annealing - NP Ag, 4 layers, without annealing - ZnO:Al (3%), 5 layers, annealing 570 °C;
Figure 1. (part 2) Optical density spectra (a), light-field cross-section TEM image (002) (b) and model structures (c) of samples № 6, 8, 10, 11 polycrystalline AZO films with silver nanoparticles:

1.6, a-c correspond to the structure: fused quartz substrate- ZnO:Al (3%), 5 layers, annealing 650 ºС - NP Ag, 4 layers, without annealing-ZnO:Al (3%), 5 layers, annealing 570 ºС;

1.8, a-c correspond to the structure: fused quartz substrate- ZnO:Al (3%), 5 layers, without annealing- NP Ag, 5 layers, without annealing- ZnO:Al (3%), 5 layers, without annealing;

1.10, a-c correspond to the structure: fused quartz substrate- ZnO:Al (3%), 5 layers, without annealing- ZnO:Al (3%), 5 layers, annealing 700 ºС;

1.11, a-c correspond to the structure: fused quartz substrate - ZnO:Al (3%), 5 layers, without annealing - NP Ag, 8 layers, without annealing - ZnO:Al (3%), 5 layers, annealing 700 ºС;
Figure 1. (part 3) Optical density spectra of samples № 4, 7, 9 polycrystalline AZO films with silver nanoparticles:

1.4, a correspond to the structure: fused quartz substrate - ZnO:Al (3%), 5 layers, annealing 650 °C - NP Ag, 4 layers, without annealing - ZnO:Al (3%), 4 layers, annealing 700 °C;

1.7, a correspond to the structure: fused quartz substrate - ZnO:Al (3%), 5 layers, annealing 650 °C - NP Ag, 4 layers, without annealing - ZnO:Al (3%), 5 layers, without annealing;

1.9, a correspond to the structure: fused quartz substrate - ZnO:Al (3%), 5 layers, without annealing.

sizes increase. In the case, when silver nanoparticles are deposited on the annealed AZO layers, they have the form of oblate ellipsoids (Figure 1.3b, 1.3c). The ellipsoidal observed in two plasmon peaks in the spectrum of optical density (Figure 1.3a). Annealing of the composite leads to the formation of a more spherical shape factor nanoparticles (Figure 1.2b, 1.2c). Upon annealing at 700 °C, silver drifts through composite with the release of spherical nanoparticles in a fused quartz substrate (Figure 1.1b, 1.1c, 1.11b, 1.11c). The drift of nanoparticles into a substrate at a temperature of 700 °C can be associated with the diffusion of silver along the grain boundaries due to the melting of the particles [16]. The peak in the optical absorption spectrum at 420 nm (Figure 1.1a, 1.11a) corresponds to the plasmon resonance wavelength for spherical silver nanoparticles surrounded by the quartz. For several samples, the effect of silver nanoparticles formation on the surface of AZO was observed (Figure 1.6b, 1.6c, 3).

Figure 3 presents the SEM image corresponding to the sample of Figure 1.6b. In this case, the particles of a spherical shape, with a size of 90 nm and a distance between them of 150-200 nm, are formed. A similar effect was observed in [17] during heat treatment in water vapor of glass with silver ions in the near-surface layer. Conceivable in our case, the AZO films were not sufficiently annealed, oxygen species at grain boundaries of AZO remained [18], and similar conditions were formed for the formation of nanoparticles on the surface of the composite. Although the mechanism for obtaining such structures is not yet completely clear, the composites with partly project out metal nanoparticles from the surface are nevertheless of interest as a sensor due to the surface enhanced Raman scattering activity [19].
Figure 2. Diffraction pattern of samples № 1 (a) and № 5 (b) with mono- and polycrystalline AZO films, respectively.

Figure 3. SEM image (002) corresponds TEM image 1.6b of polycrystalline AZO films with silver nanoparticles.

5. Conclusion
TEM analysis of the obtained coatings showed that the nanoparticles in the AZO film form an ordered structure, and the distance between the particles depends on the sol composition. The relationship determined between the sizes of AZO grains and silver particles in the AZO and the distance between them allowed to obtain controlled the ordered plasmon structures by varying the composition and synthesis mode of the AZO films.

An annealing process results in a gradual decrease and broadening of Ag NP absorption peak. This phenomenon corresponds to the reorganization of NP in the AZO film in a more disordered way and even silver escape into the substrate.

Acknowledgments
The work was supported by the Ministry of Education and Science of the Russian Federation within the framework of the Federal target program “Research and development in priority directions of the scientific-technological complex of Russia for 2014–2020”, code 2017-14-576-0003, agreement № 14.575.21.0127 from September 26, 2017, unique ID RFMEFI57517X0127. The TEM studies were performed using equipment owned by the Joint Research Center “Material science and characterization in advanced technology” (Ioffe Institute).

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