Study of the influence of the ZnO:Al polycrystalline film morphology on the silver nanoparticles formation

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Abstract. The paper presents the results of the optical and structural properties studies of samples consisting of ZnO:Al (AZO) oxide films with an intermediate silver nanoparticles layer. Obtaining samples were carried out by the method of sol-gel technology using different types of composition, and the conditions for drying and final annealing of the samples were varied. The study of the samples optical properties consisted of the optical absorption spectra measurements, and their structural properties were determined by X-ray diffraction and small-angle X-ray scattering. Comparison of data obtained from measurements of optical and structural properties of samples confirmed the results obtained from modeling in the Comsol Multiphysics software. X-ray diffraction demonstrated that the AZO films have a polycrystalline structure and are highly textured in the [002] direction. Zinc oxide grains are 10-15 nm. Silver nanoparticles are the comparable with AZO grains and have dimensions of several tens of nanometers. An increase in the annealing temperature of the films leads to a redistribution of silver nanoparticles in the AZO film, the distance between the particles increases. Consequently, the effect of the plasmon eigenmodes of the nanoparticles prevails over the effect of the system of particles oscillations interacting with each other. The analysis of the coatings obtained by the method of small-angle X-ray scattering showed that nanoparticles in the AZO film form an ordered structure.

1. Introduction

Thin-film transparent conductive materials are essential to optoelectronic devices technologies. These days the most widely used oxides are of In, Sn, and Zn [1]. ZnO is interesting for its low stability, low toxicity and chemical resistance. Aluminum-doped zinc oxide (AZO) films attracts particular attention, due to its transparency of about 90% in the visible and near IR ranges and low specific electrical resistance. AZO films are widely used in thin film solar cells [2-4], gas sensors [5], transducers [6], luminescent materials [7], heat mirrors [8], and other optoelectronic devices.

Besides AZO films, the nanocomposites, representing AZO layers with embedded noble metal nanoparticles, are of special concern [9, 10, 11]. Such nanocomposite is optically-transparent in the visible spectrum range and simultaneously has unique optical and electrical properties associated with the excitation of plasmon resonances in metal nanoparticles. At the boundaries between the silver particles and the AZO environment, Schottky contacts formed that leads to an increase of nanocomposite electric conductivity due to thermal (thermionic emission) or photoinduced (an internal photoeffect) electron transfer [12, 13, 14]. In addition, the local amplification of the electromagnetic field occurs upon excitation of localized plasmon resonance in nanocomposite structure [15, 16, 17]. In AZO polycrystalline films, the carrier transport is carried out along the grain boundaries [18, 19]. In [20], it was found that the existence of silver nanoparticles in AZO film led to an increase of the composite dark
surface resistance, while at the same time the action of resonance light excitation on composite film significantly reduced its resistance. The temperature dependences of dark current and photocurrent in AZO films and in AZO films with embedded silver nanoparticles have revealed activation dependences, but the activation energies are different. The difference in the values of activation energies indicates various channels upon which conductivity and photoconductivity are carried out. In the cause of the illumination absence, silver nanoparticles play a role of defects preventing the carrier transport along the AZO grain boundaries. Ten time conductivity increase in case of illumination is associated with the excitation of plasmon resonances in nanoparticles and the generation of hot electrons by damping of plasmon oscillations and their subsequent transition to the conduction band of the surrounding semiconductor. For applied Optoelectronics, it is important to have the control over the physical properties of plasmon nanostructures, to obtain an enhancement of the electromagnetic field by selective light illumination. For example, to realize the Purcell effect in LED structures. [21, 22, 23] The position of the plasmon resonance in the absorption spectra of nanocomposite is related to the material and the shape of the nanoparticles, the distances between them and the material of surrounding matrix [24]. The display regularities of nanoparticles formation and controlled obtaining of resonance peaks in absorptions spectra, i.e. obtaining of ordered nanostructures, will take materials science to a new level in the creation of new smart materials for Optoelectronics. To study the possibility of nanocomposite structures with controlled physical characteristics synthesis, the sol-gel method is most suitable. This method combines the simplicity of the technological process with the possibility of varying the composition and heat treatment of the material.

In this work, the coupling of the optical and structural properties of AZO oxide films with involved layers of silver nanoparticles nanocomposites prepared by the sol-gel technology have been studied. The influence of polycrystalline grains growth in AZO film on the formation and reformation of silver nanoparticles embedded in the film has been investigated.

2. Fabrication of nanocomposites

For this study, two 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 [$\text{Zn(O}_2\text{CCH}_3)\text{]_2 ZnAc}$] and aluminum nitrate [$\text{Al(NO}_3\text{)]_3}$] was dissolved in 2-Methoxyethanol with concentration of 0.2 M. Monoethanolamine (MEA) was used as a stabilizer. The molar ratio of MEA/ZnAc was 1:1; the molar ratio of Zn/Al was 1:0.03. The solution of silver nanoparticles consisted of silver nitrate [$\text{AgNO}_3$] in 2–Methoxyethanol with concentration of 0.03 M (AgEGME).

For results interpretation we have suggested to introduce the samples classification. 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 (NA); the second one, where layers of silver nanoparticles were deposited on annealed at 650°C AZO layers (A). In each series the non-annealed samples of nanocomposite (NA-0-AgEGME, A-0-AgEGME), annealed at 580°C (NA-1-AgEGME, A-1

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 study of structural property of samples series was carried out by X-ray diffraction (XRD) with the use of Bruker D2 Phaser diffractometer (Cu Kα radiation λ=0.154 nm). Phase and crystallographic structure identification were realized using wide-angle X-ray scattering (WAXS). Small-angle X-ray scattering (SAXS) allowed determining the periodicity in the ordering Ag nanoparticles system.

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

4. Results

4.1. Morphological analysis

Figure 1 presents the cross-section TEM image of sample № A-1-AgDMF. The total thickness of the composite is about 90-100 nm. The separate monolayers of AZO with grains from up 9 to 12 nm in size were clearly observed. It can be seen that silver nanoparticles with sizes of about 40 nm are formed in the sample. Particles are located at the same distance from each other, this distance is 90-100 nm.

Figure 1. a) Cross-section TEM image of Sample A-1-AgDMF; b) Optical density spectrum of Sample A-1-AgDMF.

4.2. Optical characterization

The optical density spectra with the wavelength from 200 nm to 900 nm of Sample A-1-AgDMF and series of NA-AgEGME and A-AgEGME samples are presented in Figure 2. In all spectra, an absorption band in the UV region was observed, corresponding to the absorption of AZO. The presence of a pronounced absorption step with an absorption limit of 380 nm indicates that the formation of the AZO crystalline phase begins in non-annealed films.
In the spectra of optical density of nanocomposite structures, migration of the resonance peak was observed depending on the temperature regimes of the samples post-processing. Thus, it can be said that in the process of annealing the films, silver nanoparticles are reformed with varying distances between them. Optical absorption of a structure of silver nanoparticles embedded in an AZO film as a function of the distance between nanoparticles was simulated in Comsol Multiphysics software. In Figure 3 the cross section absorption spectra obtained from composite structures with a distance between nanoparticles of 110 nm and 40 nm and a nanoparticle size of 40 nm are shown. It is clear that at a distance of 110 nm, the eigenmodes of silver nanoparticles in the AZO environment at 400 nm prevail, and when the distance between nanoparticles is less than 100 nm, the interaction effect between nanoparticles begins to predominate, and the plasmon resonance shifts to 550 nm. With a further decrease in the distance between the particles, an increasing number of neighboring particles will influence each other, which further shifts the resonance position to the long wavelength region. Comparing the data of the experimentally obtained spectra with the modeling data, we can conclude that annealing at 700°C of the initially non-annealed sample leads to the formation of silver nanoparticles removed from each other at the distance of more than 100 nm. The minimum optical density in the visible range from 450 nm to the IR region indicates a good crystalline texture of AZO and the absence of silver absorption centers, i.e. there was an enlargement, ordering of silver nanoparticles. Wide
resonances at intermediate annealing temperatures are associated with the integration of silver nanoparticles that occurs during the growth of AZO grains within the crystallization process.

**Figure 3.** Cross-section absorption spectra: Left spectra corresponding to the structure model (insert image) simulated by Comsol Multiphysics: a - the distance between silver nanoparticles is 110 nm, b - the distance between silver nanoparticles is 40 nm. The diameter of the silver particles is 40 nm. Right spectra corresponding to the experimental samples: a - A-1-AgEGME, b - NA-3-AgEGME.

For samples with AZO layers annealed before deposition of silver nanoparticles, the optical absorption spectra have different dynamics with increasing annealing temperature. Two resonance peaks were observed in the optical density spectra, indicating the presence of two types of nanoparticles: nanoparticles of different shapes, and nanoparticles of the same shape and size, but having different periodicity in different planes (directions). When annealing at 700°C, one resonant peak was smoothed, the second was weakly expressed, and «shelf» was demonstrated in the visible spectrum. It can be assumed that the initial annealing of the AZO layers sets the orderly embedding of silver nanoparticles between the grains. The subsequent annealing of the upper layers does not allow re-forming of the nanoparticles imbedded between the AZO grains of the lower layers, as a result, at 700°C there is a percolation of silver nanoparticles at the interface of the AZO layers.

4.3. Structural characterization

According to X-ray diffraction data, a decrease in the sol aging time (from 3 days to 2 hours) results in a formation of AZO film with higher crystalline perfection, with a more pronounced pattern in the (002) direction (samples № A-0-AgEGME(1), A-0-AgEGME(2), Figure 4). In its turn, an increase in the time and temperature of samples annealing leads to an increase in the size of the polycrystalline grains AZO. Samples annealed at maximum temperature (700°C) exhibit a pronounced AZO pattern, characteristic for the texture crystals with preferred crystallographic orientation of the grains (samples № A-1-AgEGME, A-3-AgEGME, Figure 4). However, it has been found that annealing of AZO films with Ag nanoparticles at a temperature of 700°C leads to the vanishing of silver peaks in the XRD diffractogram (samples № A-1-AgEGME, A-0-AgEGME, A-3-AgEGME, Figure 4).
Figure 4. WAXS data from samples № A-0-AgEGME(1), A-0-AgEGME(2), NA-0-AgEGME, A-1-AgEGME, A-0-AgEGME, A-3-AgEGME. The WAXS spectrum demonstrates the lines corresponding to (100), (002), (101), (102) reflections of ZnO and (111), (200) reflections of Ag. These lines are consistent with the hexagonal and cubic crystal lattice of ZnO and Ag, respectively.

Samples research by the SAXS method revealed that samples with plasmon peaks in the absorption spectrum demonstrate periodicity with specific dimensions of 85, 50 and 25 nm (Figure 5). These system dimensions were estimated using the Bragg law according to the approach described, for example, in [25, 26].

This fact may point out that an ordered system of silver nanoparticles spaced 85, 50 or 25 nm apart from each other is formed in such samples, the specific size of 85 nm may also correspond to the thickness of the ZnO film. Moreover, samples with a weakly pronounced AZO pattern have an internal periodicity (samples № A-0-AgEGME, A-1-AgDMFA, NA-0-AgEGME, Figure 5).

Figure 5. SAXS data from samples № A-0-AgEGME, A-1-AgDMFA, NA-0-AgEGME. It is displayed by logarithmic unit for better visualization. Curves indicate the periodicity in the system with the given characteristic dimensions.

5. Discussion
Based on the X-ray diffraction analysis and optical spectroscopy results, we can make a conclusion that AZO phase nucleation process begins at 300°C, which was also discussed in [27]. As it can be seen
from Figure 5 for NA-0-AgEGME, the grains sizes in non-annealed composite are small and the grain pattern is not pronounced. After the deposition of silver nanoparticles on such surface, they start to penetrate into the AZO layers, embedding between the grains (Figure 6). Due to the fact that there are a lot of deposited silver nanoparticles, the overlapping of silver nanoparticles occurs, which manifests itself in continuous metal absorption in the visible range of optical absorption spectrum. The silver existence was also observed in X-ray analysis spectrum. With deposition of upper AZO layers on the structure, the migration of silver nanoparticles in the upper AZO layers arises, which leads to the orderly mixing of nanoparticles with AZO grains and the appearance of the pronounced plasmon peak at 500 nm (Figure 6, c; Figure 2). The increase of the film annealing temperature results in the increase of the grain size and the appearance of a pronounced crystalline texture. The optical absorption spectrum (Figure 2) depicts that silver nanoparticles have been re-formed, and the broadening of the resonance peak indicates the fusion of nanoparticles into particles with fuzzy shape. The annealing at 700°C leads to the appearance of the resonance peak at 410 nm in absorption spectrum, corresponding to the eigenmodes of silver nanoparticles in AZO medium. We associate this result with the formation of large round-shaped silver nanoparticles at a distance more than 100 nm from each other.

In the case, when silver nanoparticles are deposited on the annealed AZO film, the nanoparticles are embedded between texture polycrystals (grains) and their arrangement is initially more regulated, but less homogeneous.

Consequently, based on the pursued technology purposes, we can choose sequencing of layers deposition and temperature treatment.

6. Conclusions
Comparison of the study results of the optical and structural properties of AZO films samples with Ag nanoparticles obtained under different conditions has demonstrated that the worse the AZO crystalline texture and the smaller the size of silver nanoparticles (up to a certain limit) is the more homogeneously the nanoparticles are distributed throughout the sample. Further temperature treatment of the samples results in the integration and coarsening of the nanoparticles. An ordered system of silver nanoparticles located 85, 50, or 25 nm apart from each other was formed in the samples. The different values of the periodicity in the system, obtained from SAXS, may be due to the different distances between Ag particles in two perpendicular directions in the ZnO film. It happens because polycrystalline AZO grains
with the wurtzite structure separate the particles from each other. The deposition of nanoparticles on an annealed film with a pronounced AZO crystalline texture determines their periodicity, but prevents their homogeneous distribution in different directions in the film plane. An increase in the annealing temperature of the films leads to the reorganization of silver nanoparticles in the AZO film, the distance between the particles increases, the effect of the eigenmodes of the nanoparticles over the interaction effect between the particles begins to predominate.

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 and XRD studies were performed using equipment owned by the Joint Research Center “Material science and characterization in advanced technology” (Ioffe Institute, St.-Petersburg, Russia).

References
[1] Yu X, Marks T J and Facchetti A 2016 Metal Oxides for Optoelectronic Applications Nature Materials 15 (4) p 38396
[2] Selvan J A A, Keppner H and Shah A 1996 The Growth of Surface Textured Aluminium Doped ZnO Films for a-Si:H Solar Cells by RF-Magnetron Sputtering at Low Temperature MRS Online Proceedings Library Archive p 426
[3] Matsubara K, Fons P, Iwata K, Yamada A, Sakurai A, Tampo H and Niki S 2003 ZnO transparent conducting films deposited by pulsed laser deposition for solar cell applications Thin Solid Films pp 431-432
[4] Minemoto T, Matsui T, Takakura H, Hamakawa Y, Negami T, Hashimoto Y, Uenoyama T and Kitagawa M 2001 Theoretical analysis of the effect of conduction band offset of window/CIS layers on performance of CIS solar cells using device simulation Solar Energy Materials and Solar Cells 67 (1) pp 83-88
[5] Weisenrieder K and Muller J 1997 Conductivity model for sputtered ZnO-thin film gas sensors Thin Solid Films 300 (1-2) pp 30-41
[6] Belt R F and Florio G C 1968 Preparation of ZnO Thin-Film Transducers by Vapor Transport Journal of Applied Physics 39 (11) pp 521-523
[7] Bethke S, Fan H and Wessels B W 1988 Luminescence of heteroepitaxial zinc oxide Applied Physics Letters 52 (2) p 13840
[8] Jin Z C, Hamberg I and Granqvist C G 1987 Optical properties of transparent and heat reflecting ZnO:Al films made by reactive sputtering Applied Physics Letters 51 (3) p 14951
[9] Seon C S, Park H H, Moon J H and Park H H 2006 Effect of metal (Al, Ga, and In)-dopants and/or Ag-nanoparticles on the optical and electrical properties of ZnO thin films Thin Solid Films 515 (3) p 95760
[10] Szabo O, Flickyngerova S, Ignat T, Novotny I and Tvarozek V 2016 Gold nanostructures sputtered on zinc oxide thin film and corning glass substrates Facta Universitatis, Series: Electronics and Energy 29 (1) pp 77-88
[11] Toyoda T, Tsugawa S and Shen Q 2009 Photoacoustic spectra of Au quantum dots adsorbed on nanostructured TiO$_2$ electrodes together with the photoelectrochemical current characteristics Journal of Applied Physics 105 (3) pp 034314
[12] Atwater H A and Polaman A 2010 Plasmonics for improved photovoltaic devices Nature Materials 9 (3) p 20513
[13] Mubeen S, Hernandez-Sosa G, Moses D, Lee J and Moskovits M 2011 Plasmonic Photosensitization of a Wide Band Gap Semiconductor: Converting Plasmons to Charge Carriers Nano Letters 11 (12) p 554852
[14] Du L, Furube A, Hara K, Katoh R and Tachiya M 2013 Ultrafast plasmon induced electron injection mechanism in gold–TiO$_2$ nanoparticle system Journal of Photochemistry and Photobiology C: Photochemistry Reviews 15 pp 21-30

[15] Maier S A and Atwater A H 2005 Plasmonics: Localization and guiding of electromagnetic energy in metal/dielectric structures Journal of Applied Physics 98 (1) p 011101

[16] Maier S A, Brongersma M L, Kik P G, Meltzer S, Requicha A A G, Koel B E and H. A. Atwater. 2003 Erratum: Plasmonics - A route to nanoscale optical devices Advanced Materials 15 (7-8) p 562

[17] Knight M W, Sobhani H, Nordlander P and Halas N J 2011 Photodetection with Active Optical Antennas Science 332 (6030) p 7024

[18] Ohyama M, Kozuka H and Yoko T 2005 Sol–Gel Preparation of Transparent and Conductive Aluminum-Doped Zinc Oxide Films with Highly Preferential Crystal Orientation Journal of the American Ceramic Society 81 (6) p 1622-32

[19] Schuler T and Aegerter M A 1999 Optical, electrical and structural properties of sol gel ZnO:Al coatings Thin Solid Films 351 (1) p 12531

[20] Shirshnev-Vaschenko E V, Sokura L A, Shirshnev P S, Kirilenko D A, Snehnaia Zh G, Bauman D A, Bougrov V E and Romanov A E 2018 Preparation of transparent n-ZnO:Al/p-CuAlCrO$_2$ heterojunction diode by sol-gel technology Reviews on Advanced Materials Science 57 (2) pp 167-74

[21] Koenderink A F 2010 On the use of Purcell factors for plasmon antennas Optics Letters 35 (24) pp 4208-10

[22] Yeh D M, Huang C F, Chen C Y, Lu Y C and Yang C C 2008 Localized surface plasmon-induced emission enhancement of a green light-emitting diode Nanotechnology 19 (34) p 345201

[23] Sung J H, Kim B S, Choi C H, Lee M W, Lee S G, Park S G, Lee E H and Beom-Hoan O 2009 Enhanced luminescence of GaN-based light-emitting diode with a localized surface plasmon resonance Microelectronic Engineering 86 (4-6) pp 1120-23

[24] Noguez C 2007 Surface Plasmons on Metal Nanoparticles: The Influence of Shape and Physical Environment The Journal of Physical Chemistry C 111 (10) pp 3806-19

[25] Agbabiaka A, Wiltfong M and Park C 2013 Small Angle X-Ray Scattering Technique for the Particle Size Distribution of Nonporous Nanoparticles Journal of Nanoparticles 2013 p 11

[26] Matsui H and Tabata H 2017 Infrared Solar Thermal-Shielding Applications Based on Oxide Semiconductor Plasmonics Nanoplasmonics - Fundamentals and Applications Chapter 8 IntechOpen

[27] Zaretskaya E R, Gremenok V F, Semchenko A V, Sidsky V V and Yushkanes R L 2015 Structural properties of ZnO:Al films produced by the sol–gel technique Semiconductors 49 (10) pp 1253-1258