Ordering mechanism of silver nanoparticles synthesized in a ZnO:Al polycrystalline film by sol gel method

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Abstract. The optical absorption spectra and structural properties of ZnO:Al films with an intermediate layer of silver nanoparticles with a different number of inserted layers of silver nitrate solution are studied. The study of optical properties showed that with an increase in the number of layers, the intensity of the plasmon absorption peak of nanoparticles increases. Consequently, with an increase in the number of layers, their density increases, it was confirmed by studies of the obtained samples structural properties by transmission electron microscopy.

1. Introduction

Nowadays the production of various semiconductor structures containing ordered nanoparticles of precious metals, such as gold and silver, is being actively developed. Composites based on ZnO, Al\textsubscript{2}O\textsubscript{3}, TiO\textsubscript{2}, SiO\textsubscript{2} matrix are actively in study so the new physical and optical properties are observed in them [1-3]. AZO (ZnO:Al) layers with embedded silver nanoparticles (Ag NP) are very promising for applications in thin-film devices [4-5]. Such thin films have unique optical and electric properties and are good for increasing the efficiency of LEDs emitted light or for increasing the solar cells efficiency due to plasmon effects arising in the composite. And the use of simplicity and cheap technology for their manufacture, for example, sol gel technology, would ensure their industrial applicability [6].

Such composite materials are optically-transparent in the visible spectrum range and at the same time has unique optical and electrical properties associated with the excitation of plasmon resonances in nanoparticles [4, 7-8]. The position of the plasmon resonance in the absorption spectra of nanocomposite is related to the material and shape of the nanoparticles, the distances between them and the material of surrounding matrix [9].

In this work, 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.

2. Fabrication of nanocomposites

For this study, three samples of ZnO:Al (0.5\%) films with involved layers of silver nanoparticles were prepared by sol-gel method and spin-coating deposition. The nanocomposite structure consisted of fused quartz substrate, five layers of AZO, 3, 6, 9, 20 or 30 layers of silver nanoparticles, and five capping layers of AZO. Solvents of AZO and Ag NP were synthesized in 2-methoxyethanol and composed of zinc acetate dehydrate [Zn(O\textsubscript{2}CCH\textsubscript{3})\textsubscript{2}], aluminum nitrate [Al(NO\textsubscript{3})\textsubscript{3}] and silver nitrate [AgNO\textsubscript{3}], respectively. Samples were dried at 300°C and annealed at 570 °C.
Previously, the authors found that when layers of a silver nitrate solution are inserted between the layers of a zinc oxide matrix, an ordered structure of silver nanoparticles is formed in the AZO film [10-11]. An important fact for controlling the obtained composite structure was that the time and temperature of annealing of the film affect the sizes of nanoparticles. Optical measurements showed that the position of the peak of plasmon nanoparticles in AZO also depends on them.

The present work of the authors is devoted to elucidating the influence of technological factors on the density of silver nanoparticles in a zinc oxide matrix.

3. Characterization
The morphology of AZO film with Ag nanoparticles 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 optical absorption spectra measurements were performed with the fiber spectrometer AvaSpec-2048.

4. Model
The composite structure model consisting of an AZO film 100 nm thick with a layer of Ag NP with different distances between them was built in the Comsol Multiphysics software package. Silver nanoparticles diameter has been taken 40 nm, since this is the average size of experimentally obtained Ag NP.

Two different values of the distance between nanoparticles were chosen for simulation, since different plasmon effects are realized in such configurations (figure 1). The absorption spectra of the composite model with a distance between Ag NP comparable of their sizes shows two plasmon peaks at 400 nm and 650 nm. This is due to the fact that the collective interaction of the particles takes effect in such system configuration. If the distance between Ag NP is 110 nm, then in this case the distance between nanoparticles is too large for the collective plasmon resonance to occur, only the own plasmon peak of Ag NP at 550 nm is observed.

Figure 1. Absorption spectra calculated for ordered silver NP with 40 nm diameter for the distance between NP: a - 40 nm, b – 110 nm, simulated by Comsol Multiphysics.
5. Results

It was found that the increase of inserted layers number of silver nitrate solution leads to the intensity of nanoparticles plasmon absorption peak also increases. On the figure 2, it can be seen that the position of the plasmon peak is the same for all samples, the peak wavelength is approximately at 505, 520 and 500 nm, respectively, for samples with 3, 6, 9, 20 and 30 layers of silver nitrate solution. After annealing, the absorption peak is at the 625, 640 and 630 nm, respectively. The absorption peak at 380 nm correspond to AZO crystalline phase.

![Figure 2. Optical density spectra of polycrystalline ZnO:Al (0.5%) films with 3, 6, 9, 20 and 30 layers of silver nitrate solution, after drying at 300 °C (a) and annealing at 570 °C (b).](image)

Before annealing, during which polycrystalline AZO grains are formed in the composite, in samples with 6, 9, 20 and 30 layers, collective plasmon resonance at a frequency of 440 nm, as well as a thinner peak of own plasmon resonance presents are observed. After annealing, in the samples, except the sample with 30 layers of nanoparticles, only the peak of own plasmon resonance is observed, the width of which increases.

To find out the reasons for this optical behavior property, a series of samples consisting of AZO oxide films with an intermediate layer of silver nanoparticles with a different number of layers will be studied by TEM.

TEM observation showed that the AZO films have a polycrystalline structure with grains sizes of 10-12 nm. The total thickness of the composite film is about 90-100 nm. The TEM image shows that the Ag nanoparticles formed an ordered structure in AZO film (Figure 3). In samples with 3 layers of silver nitrate solution the NP size was 40-50 nm, the distance between them was about 300 nm. In samples with 9 layers of silver nitrate solution the NP size was slightly larger and amounted to 40-60 nm, the distance between them was much smaller - about 80-90 nm. It was found that the increase of inserted layers number of silver nitrate solution leads to the density of nanoparticles increases while maintaining their size.

Since the peak position of plasmon absorption does not move with increasing of silver nitrate solution layers, all samples have intrinsic plasmon oscillations of the nanoparticles. Apparently, the interaction effect between the particles begins to predominate at the distance between the nanoparticles be less than or equal to the nanoparticles diameter [10-11]. Thus, the observed behavior of the samples is confirmed by the fact that, in order to observe own plasmon resonance, it is necessary to increase the number of layers and, consequently, the Ag NP concentration.
Figure 3. Bright-field TEM image of cross-section (002) of polycrystalline ZnO:Al (0.5%) films with 3 (a) and 9 (b) layers of silver nitrate solution after annealing at 570 °C.

6. Conclusions
The optical and structural properties of ZnO:Al films with different number an intermediate layer of silver nitrate solution are studied. The study of optical properties showed that with an increase in the number of layers, the intensity of the plasmon absorption peak of nanoparticles increases. Consequently, with an increase in the number of layers, their density increases. It was found that at a high concentration of nanoparticles, at which the distance between the nanoparticles becomes comparable with their size, in addition to own plasmon resonance, a plasmon peak from a system of interacting particles is observed in the optical absorption spectrum. The transmission electron microscopy investigation of the obtained coatings showed that the Ag nanoparticles in the AZO film form an ordered structure. TEM investigation confirmed the Ag nanoparticles density increasing.

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References
[1] Atwater H, Polman A 2016 Nature materials 9 865
[2] Sk M M, Yue C Y, Ghosh K, Jena R K 2016 Journal of Power Sources 308 121-140
[3] Ge M, Cao C, Huang J, Li S, Chen Z, Zhang K Q, Lai Y 2016 Journal of Materials Chemistry A 4 (18) 6772-6801
[4] Szabó O, Flickyngerová S, Ignat T, Novotný I, Tvarožek V 2016 Facta Universitatis, Series: Electronics and Energetics 29 (1) 77-88
[5] Inamura R, Toyoda T, Tanaka T, Uzumaki T 2009 Journal of Applied Physics 105 (3) 034314
[6] Bochkareva S S 2016 Proceedings of Universities. Applied Chemistry and Biotechnology 6 81-93
[7] Hong C S, Park H H 2006 Thin Solid Films 515 (3) 957960
[8] Toyoda T, Tsugawa S 2009 Journal of Applied Physics 105 (3) 034314
[9] Noguez C 2006 The Journal of Physical Chemistry: C 111 (10) 380619
[10] Shirshneva-Vaschenko E V, Sokura L A, Baidakova M V, Yagovkina M A, Snezhnaia Zh G, Shirshnev P S, Romanov A E 2019 Journal of Physics: Conference Series 1410 (1) 012170