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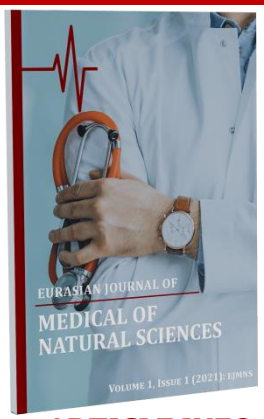

STUDY OF THE PROPERTIES OF THIN FILMS OBTAINED BY THE SOL – GEL METHOD

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ABSTRACT

This paper discusses methods for the synthesis of zinc oxide, which is an important model material for fundamental research in the field of solid state physics. The surface of zinc oxide can dramatically affect the volumetric properties of the material, which is used to make a wide variety of sensors. Heterostructures and p–n heterojunctions based on ZnO, which are obtained by epitaxial growth of ZnO n-type conductivity on other p-type semiconductors with similar crystal lattice parameters, also have broad prospects for practical application.

The relevance of work on developing synthesis methods and studying the properties of ZnO-based materials is due to the broad prospects for the practical application of oxide semiconductors. Zinc oxide is promising for creating transparent and conducting electrodes in the visible region of the spectrum, for use in photovoltaic and photocatalytic converters, in various sensors and other device structures. The physical properties of zinc oxide-based semiconductors make them unique objects for the search for new device solutions and research in the field of high technology. Zinc oxide has a band gap of 3.37 eV at room temperature and an exciton binding energy of about 60 meV, which makes ZnO promising for use in optoelectronics. The synthesis of ZnO p-type conductivity layers and the creation of transparent transistors based on them is relevant for the creation of transparent active display matrices. Research into the processes of synthesis of zinc oxide layers is relevant for finding an alternative to expensive transparent electrodes based on In_2O_3–SnO_2 (ITO), which are used in information display systems and energy-saving technologies. Doping is an effective way to improve the electrical properties of semiconductors. Transparent conductive zinc oxides doped with aluminum (AZO), boron (BZO), and indium (IZO) are promising materials for wide application in optoelectronic devices. Optical transparency in the visible range and high conductivity make zinc oxide a promising material for solar cells and liquid crystal information display systems. Zinc oxide is an important model material for fundamental research in solid state physics. The surface of zinc oxide can dramatically affect the volumetric properties of the material, which is used to make a wide variety of sensors. Heterostructures and p–n heterojunctions based on ZnO, which are obtained by epitaxial growth of ZnO n-type conductivity on other p-type semiconductors with similar crystal lattice

parameters, also have broad prospects for practical application. When synthesizing nanostructures and thin films based on zinc oxide, hydrothermal and sol-gel methods are often used, which have a simple synthesis process, are low-cost, scalable for industrial use, and make it possible to control the morphology, particle size and phase composition of the resulting products. The development of hydrothermal and sol-gel methods for the synthesis of films and nanostructures based on ZnO is an urgent task.

For practical applications, it is important to develop a reproducible technology for producing zinc oxide films with the required properties. In this work, zinc oxide was chosen as the research material, and the object of research is the structure, electrical and optical properties of zinc oxide nanostructures and films. The purpose of this work is to develop low-cost methods for the controlled synthesis of nanostructured layers and thin films of oxide semiconductors, study their structure, optical and electrical properties, develop methods of doping and achieve a high concentration of free carriers and high mobility for the creation of high-quality conductive transparent coatings, electrodes and photovoltaic materials based on their basis.

To achieve this, we have developed a method for depositing thin conductive transparent films based on zinc oxide. The electrochemical and physical properties of the synthesized samples were studied, the optimal parameters of controlled synthesis were determined, as well as the influence of thermal and plasma treatment modes on the optical and electrical properties of the resulting transparent conductive coatings. They created low-resistance conductive ZnO films, as well as films with intense intrinsic photoluminescence.

The sol–gel method is a non-toxic, low-temperature, low-cost method that simply adds external defects and processes samples to optimize material properties. The spin coating method provides consistent delamination for better control of film uniformity and thickness [1]. To obtain thin ZnO films, it is first necessary to create a homogeneous transparent precursor solution. Several zinc precursors have been used to prepare ZnO thin films, including nitrate, chloride, perchlorate, acetylacetonate, and alkoxides such as ethoxide and propoxide. Despite their chemical advantages, metal alkoxides are not very popular due to sensitivity to moisture, high reactivity and high cost. On the other hand, metal salts are preferred due to their low cost and commercial availability, which seem to be more suitable for large-scale applications. Nitrates, chlorides, perchlorates, and acetates have been used as precursors for sol–gel synthesis, providing thin films with different morphological features and crystallization [1–8]. Films prepared from zinc nitrate show rapid and random crystallization compared to ZnO films prepared from zinc acetate, which also exhibits a smoother surface. The use of zinc perchlorate caused the particles to coagulate and resulted in a cloudy suspension. It was reported that a preparation of zinc chloride or zinc nitrate under similar reaction conditions initially formed clear colloidal suspensions, which, however, coagulated more quickly than in the case of zinc perchlorates. Irreproducible results were obtained from sols prepared using zinc nitrate, while sols prepared from zinc acetate dihydrate resulted in a reproducible system under various experimental conditions [9]. This mixture is heated and stirred until it becomes homogeneous and clear, when it can be used for thin film synthesis. The precursor mixture in solution can significantly influence the properties of the ZnO thin film. For example, ZnO solution can be doped with other metals

such as gallium, copper, cobalt and aluminum to tune the optoelectronic and ferromagnetic properties [10]. Due to their ionic radius, a large number of doping ZnO thin films with group III elements such as aluminum 30 and gallium have been achieved. The ionic radius of Al^{3+} is small than Zn^{2+}, and can easily replace Zn^{2+} in the lattice, but will result in large lattice deformations. Ga3+ has an ionic radius very similar to Zn^{2+}, so it can replace Zn^{2+}, but will produce much less lattice strain than Al^{3+}. Many studies have successfully synthesized Al and Ga doped polycrystalline ZnO thin films with very high transparency and promising electrical properties. These group III elements act as shallow donors when doping ZnO to increase the overall conductivity for use as a transparent conductor [11–14]. Thermal treatment of ZnO thin films can occur at different stages of the sol–gel coating process. Non-reactive electron beam thin film films provide high transparency before and after heat treatment. As the annealing temperature increases, the crystallinity deteriorates and the resistivity improves. ZnO thin films show a shift in band gap with processing temperatures. Understanding how to control heat treatment is important for tuning the material properties of ZnO thin films, leading to promising devices. The application method of sol–gel synthesis can be repeated for the desired number of layers. Typically, a thin film of ZnO is dried between each layer. Drying of thin films usually occurs in an oven ranging from room temperature to 300°C. At temperatures above 100°C, a large percentage of the thin film's mass is lost as the solvent quickly evaporates; after achieving the desired thickness, the ZnO thin film is subjected to other forms of heat treatment at higher temperatures in more controlled atmospheres. Oven annealing has a significant effect on the structure and surface morphology of ZnO thin films. ZnO thin films were annealed over a temperature range of 300 to 500ºC to show an increase in c (002) axis orientation and grain size with increasing temperature. These films still offer high transparency with tunable properties for optoelectronic applications. Sol–gel synthesis and heat treatment of ZnO thin films successively create structured transparent thin films. These films are also subjected to various atmospheric post-syntheses, which can help tune the electrical properties. Hydrogen in semiconductors is electrically active and acts solely as a donor in zinc oxide. It is also known that hydrogen has properties that passivate defects in ZnO and on the surface of quartz. Heat treatment of zinc oxide in a hydrogen atmosphere greatly affects the electrical properties. This additionally allows the addition of hydrogen to create donor vacancies and can passivate zinc vacancies, which is known to increase the overall conductivity of zinc oxide [15]. Research has shown that annealing Al and Ga doped ZnO thin films in air and then in H_2 will produce highly transparent, low resistivity thin films. For thin-film ZnO coatings with 1% aluminum precursor, the minimum resistivity reached 4.06×10^{-3} Om cm with carrier concentrations up to 5.52×10^{19} cm^{-3} after post-annealing in air. ZnO thin films doped with 2% gallium give highly transparent thin films with a resistivity of $3.3\cdot10^{-3}$ Om·cm after post-annealing in an H_2 atmosphere [16].

Study of the properties of thin films and nanostructures obtained by the sol–gel method

The morphology and optical properties of AZO and BZO films were studied. Electron microscopy studies have shown that the resulting films are continuous and homogeneous over the entire surface of the sample. Figures 1a and 2a show the optical density spectra of AZO and BZO samples obtained by the sol–gel method with 12 and 11 layers, respectively. At

wavelengths less than 380 nm, an increase in optical density occurs, associated with interband absorption of light when electrons are excited from the valence band to the conduction band of zinc oxide.

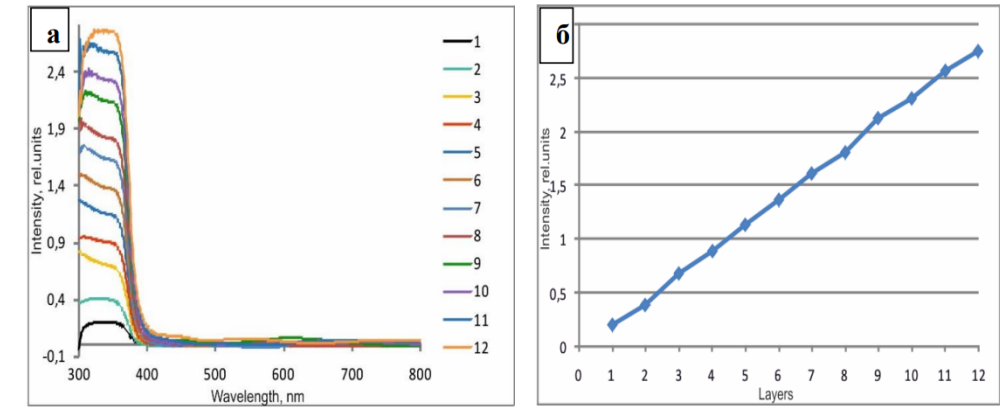

Figure 1. Optical density spectra of a ZnO:Al sample obtained by the sol–gel method, 12 layers. a – optical density spectra of AZO samples, b – dependence of the intensity of the absorption spectrum on the number of layers

The linear increase in the absorption coefficient maxima (Figures 1b and 2b) allows us to judge the almost constant thickness of the doped ZnO films deposited in one cycle. As can be seen in Figures 3 and 4, the resulting samples have high transparency from 99% for one layer and up to 85% for 12 layers, almost identical to the transparency of the glass substrate on which the film was applied.

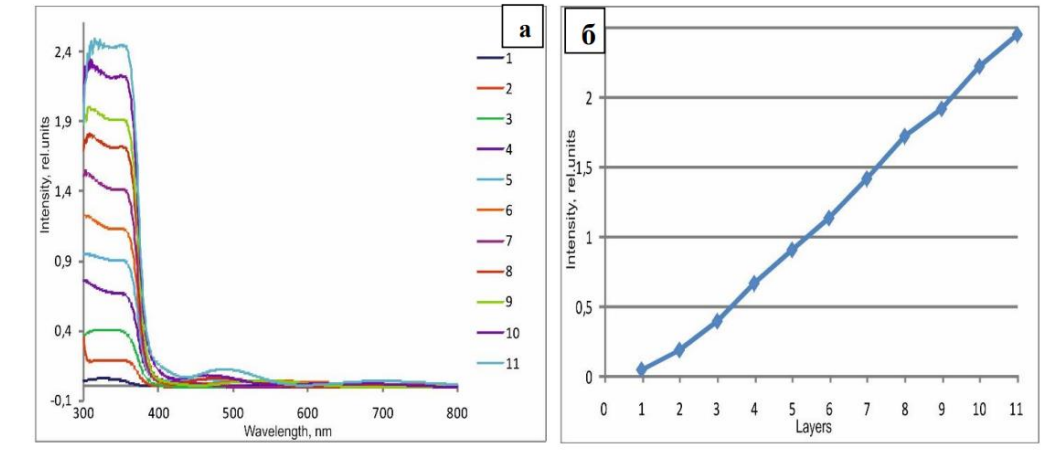

Figure 2 – Optical density spectra of the ZnO:B sample obtained by the sol–gel method, 11 layers. a – optical density spectra of BZO samples, b – dependence of the intensity of the absorption spectrum on the number of layers

Interference vibrations in the transmission spectra indicate a high uniformity of the thickness of the resulting films. Figure 1 a – optical density spectra of AZO samples, b – dependence of the absorption spectrum intensity on the number of layers Figure 1 – Optical density spectra of a ZnO:Al sample obtained by the sol-gel method, 12 layers a – optical density spectra of BZO samples, b – intensity dependence absorption spectrum depending on

the number of layers Figure 2 – Optical density spectra of the ZnO:B sample obtained by the sol-gel method, 11 layers.

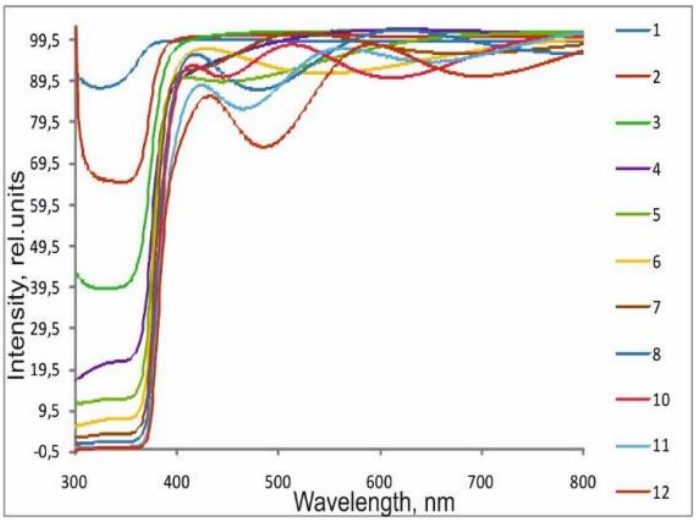

Figure 3 – Transmittance of a ZnO:Al sample obtained by the sol-gel method, 12 layers

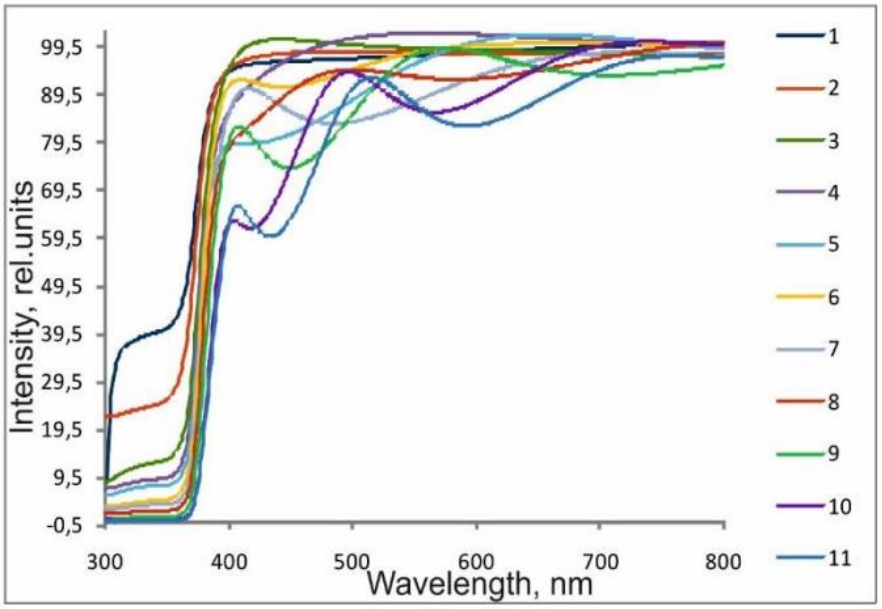

Figure 4 – Transmittance of the ZnO:B sample obtained by the sol-gel method, 11 layers

After applying 10 layers of the sol-gel method, SEM images of the cleavage of the AZO sample were taken (Figure 4). Since there is a close to linear dependence of the increase in the intensity of optical absorption in the intrinsic region of the spectrum on the number of layers, we can assume that each deposited layer leads to an increase in thickness by the same amount ~ 30 nm.

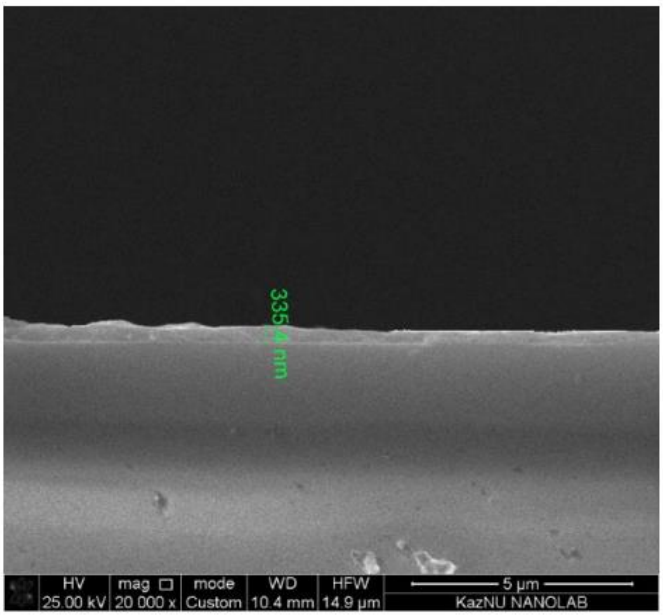

Figure 5 - SEM image of a side cleavage of a sample with ZnO:Al, obtained by the sol-gel method with 10 layers

Figure 3 - Transmittance of a ZnO:Al sample obtained by the sol-gel method, 12 layers Figure 4 - transmittance of a ZnO:B sample obtained by the sol-gel method, 11 layers As experiments have shown, adding 0.2 g of polyethyleneamine to a 10 ml sol solution at At constant concentrations of the remaining components, it allows you to increase the thickness of the deposited film by 2 – 2.5 times (Figure 6).

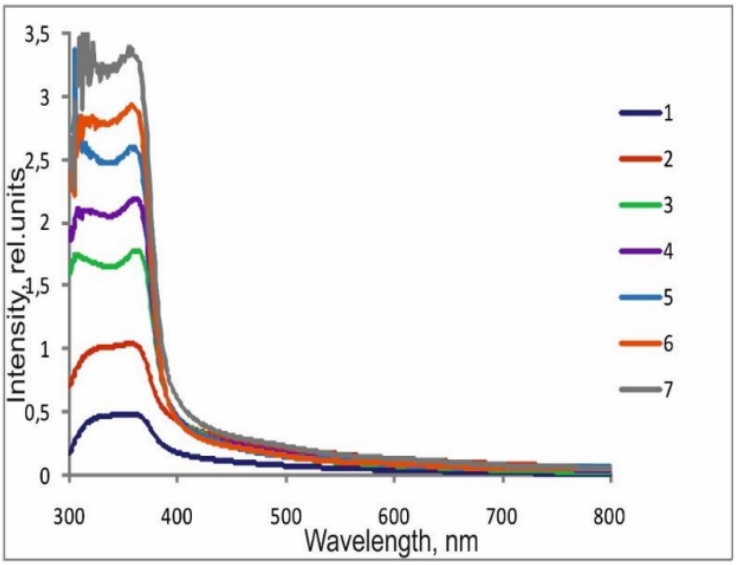

Figure 6 – Optical density spectra of a ZnO:Al sample obtained by the sol-gel method with the addition of PEI, 7 layers

The electrical characteristics of the obtained AZO and BZO samples were studied using the Hall effect and electrical resistance in a van der Pauw four-probe configuration. The initial resistance of all synthesized samples was high (1 – 6) MOm, and the carrier mobility was low.

In order to improve the electrical characteristics of the samples, they were thermally treated in a vacuum of 0.04 Torr at temperatures of 350, 450 and 550°C for 1 hour. Tables 1 and 2 present the average changes in the electrical characteristics of AZO and BZO samples obtained by the sol–gel method before and after annealing. Figure 5 - SEM image of a side cleavage of a sample with ZnO:Al, obtained by the sol-gel method with 10 layers. Optical density spectra of the ZnO:Al sample obtained by the sol-gel method with the addition of PEI, 7 layers

Table 1 - Change in the resistance of AZO and BZO samples obtained by the sol-gel method after annealing in a vacuum at a temperature of 550°C for 1 hour

Sample	Resistance, Ом	
	Original	After annealing
AZO	$1.2 \cdot 10^3$	298
BZO	$6 \cdot 10^3$	700

Sample resistance, R, Initial Om after annealing AZO $1.2 \cdot 10^3$ BZO $6 \cdot 10^3$.

Table 2 – changes in the electrical characteristics of AZO and BZO samples obtained by the sol–gel method after annealing in vacuum at different temperatures

Sample	Characteristic	Annealing temperature		
		550 °C	450 °C	350 °C
AZO	Concentration n, cm^{-3}	$1{,}289 \cdot 10^{20}$	$3{,}93 \cdot 10^{19}$	$6{,}005 \cdot 10^{19}$
	Mobility μ, $cm^2/V \cdot s$	9,152	9,561	7,271
	Resistivity ρ, Om·cm	$5{,}323 \cdot 10^{-3}$	$1{,}663 \cdot 10^{-2}$	$1{,}537 \cdot 10^{-2}$
BZO	Concentration n, cm^{-3}	$3{,}381 \cdot 10^{19}$	$2{,}883 \cdot 10^{19}$	$1{,}869 \cdot 10^{19}$
	Mobility μ, $cm^2/V \cdot s$	12,52	3,693	8,596
	Resistivity ρ, Om·cm	$1.481 \cdot 10^{-2}$	$6{,}139 \cdot 10^{-2}$	$4{,}108 \cdot 10^{-2}$

Sample characteristics; annealing temperature T, (°C) 550 450 350 AZO, concentration n, cm^{-3} $1.289 \cdot 10^{20}$, $3.93 \cdot 10^{19}$, $6.005 \cdot 10^{19}$, mobility μ, cm^2 /V·s, 9.152, 9.561, 7.271. Conductivity ρ, Om·cm $5.323 \cdot 10^{-3}$, $1.663 \cdot 10^{-2}$, $1.537 \cdot 10^{-2}$ BZO. Concentration n, cm^{-3} $3.381 \cdot 10^{19}$, $2.883 \cdot 10^{19}$, $1.869 \cdot 10^{19}$. Mobility μ, $cm^2/V \cdot s$, 12.52, 3.693, 8.596. Conductivity ρ, Om·cm $1.481 \cdot 10^{-2}$, $6.139 \cdot 10^{-2}$, $4.108 \cdot 10^{-2}$ Annealing in vacuum contributed to an increase in the concentration and mobility of charge carriers, as well as a decrease in resistivity. The best indicators $\rho = 5.323 \cdot 10^{-3}$ Om·cm were obtained on samples of zinc oxide doped with aluminum subjected to heat treatment at 550°C.

Thus, annealing in a vacuum under certain conditions and temperature ranges is an effective way to increase the concentration of free carriers and mobility in ZnO films without

leading to a deterioration in the optical characteristics of the films, and therefore can be used to obtain transparent conductive coatings

From the results of the study, the following conclusions were drawn:

- The determining role of the atmosphere during annealing on the electrical properties of ZnO samples was discovered: in an oxidizing atmosphere, the electrical conductivity sharply decreases with increasing annealing temperature in the range of 200 – 550°C, and when annealing in a vacuum, the electrical conductivity increases significantly.
- To achieve activation of the electrical activity of small donors (boron, aluminum) in ZnO samples, thermal annealing is required in a reducing atmosphere at temperatures of 450 – 550ºC.
- The intensity of intrinsic PL in the original ZnO samples increases ~10–100 times after plasma treatment in a hydrogen atmosphere, however, keeping the samples under normal conditions leads to degradation of the PL intensity within several days.
- To achieve a stable PL intensity that is not subject to the aging effect, it is necessary to subject the samples to preliminary annealing in air in the temperature range of 300 – 500ºC, followed by plasma hydrogen treatment, which leads to an increase in the PL intensity by 300 – 1000 times compared to the PL in the original samples.

The research results can be used to specifically change the electrical and luminescent properties of films and arrays of ZnO nanorods. The resulting ZnO films with high transparency in the visible region and high electrical conductivity can be used as TCO substrates. The optimal synthesis modes determined in this work can be used to obtain highly oriented ZnO films and nanorod arrays. The results on the processes of activation of the electrical activity of small donor impurities in ZnO films can be used to select optimal heat treatments for obtaining transparent conductive layers of ZnO doped with boron or aluminum impurities. The results on the dependence of electrical and luminescent properties on the state of the surface can be used to create various sensors and sensors that operate on surface effects.

References:

1. Kamaruddin, Sharul Ashikin, Kah – Yoong Chan, Ho – Kwang Yow, Mohd Zainizan Sahdan, Hashim Saim, and Dietmar Knipp. Zinc Oxide Films 97 Prepared by Sol–gel Spin Coating Technique // Apl. Phys. A Apl.ied Physics A. – 2010. – №104(1). – P. 263 – 268.
2. Bahadur H., Srivastava A. K., Sharma R. K., Chandra S. Morphologies of Sol – Gel Derived Thin Films of ZnO Using Different Precursor Materials and their Nanostructures // Nanoscale Res Lett. – 2007. –№2. – P. 469 – 475.
3. Murali K.R. Properties of sol – gel dip – coated zinc oxide thin films // Journal of Physics and Chemistry of Solids. – 2007. – №68. – P. 2293 – 2296.
4. Sahal M., Hartiti B., Ridah A., Mollar M., Marı B. Structural, electrical and optical properties of ZnO thin films deposited by sol – gel method // Microelectronics Journal. – 2008. – №39. – P. 1425 – 1428.
5. James B., Miller Hsin – Jung H., Bret H. Howard, Esteban B. Microstructural эBolution of sol – gel derived ZnO thin films // Thin Solid Films. – 2010. – №518. – P. 6792 – 6798.

6. Detlef W. Bahnemann., Claudius Kormann, and Michael R. Hoffmann, Preparation and Characterization of Quantum Size Zinc Oxide: A Detailed Spectroscopic Study // J. Phys. Chem. – 1987. – №91. – P. 3789 – 3798.
7. Znaidi L. Elaboration of ZnO Thin Films with Preferential Orientation by a Soft Chemistry Route // Journal of Sol – Gel Science and Technology. – 2003. – №26. – P. 817 – 821.
8. Guo, Dongyun, Kuninori Sato, Shingo Hibino, Tetsuya Takeuchi, Hisami Bessho, Kazumi Kato. Low – temperature Preparation of Transparent Conductive Al – doped ZnO Thin Films by a Novel Sol–gel Method // Journal of Materials Science J Mater Sci. – 2014. – Vol. 49, №14. – P. 4722 – 4734.
9. Wu S. Z., Yang H. L., Xu X. G., Miao J., Jiang Y. Ferromagnetism Studies of Cu – doped and (Cu, Al) Co – doped ZnO Thin Films // J. Phys.: Conf. Ser. Journal of Physics: Conference Series. – 2011. – №263. – P. 012022.
10. Foo K.L., Kashif M., Hashim U., a Ali M.E. Fabrication and Characterization of ZnO Thin Films by Sol – Gel Spin Coating Method for the Determination of Phosphate Buffer Saline Concentration // Current Nanoscience CNANO. – 2013. – Vol. 9, №2. – P. 288 – 292.
11. Znaidi, Lamia, Tahar Touam, Dominique Vrel, Nacer Souded, Sana Yahia, Ovidiu Brinza, Alexis Fischer, Azzedine Boudrioua. AZO Thin Films by Sol – Gel Process for Integrated Optics // Coatings. – 2013. – Vol. 12, №3(3). – P. 6 – 39.
12. Liu Yanli, Yufang Li, Haibo Zeng. ZnO – Based Transparent Conductive Thin Films: Doping, Performance, and Processing // Journal of Nanomaterials. – 2013. – №121 – P. 1 – 9.
13. Wang, Fang – Hsing, Ching – Tien Chou, Tsung – Kuei Kang and Chia – Cheng Huang. Structural, electrical, and optical properties of carbon nanotube – incorporated Al – doped zinc oxide thin films prepared by sol – gel method // Journal of Ceramic Processing Research. – 2013. – №45. – P. 149 – 152.
14. Raoufi, Davood, Taha Raoufi. The Effect of Heat Treatment on the Physical Properties of Sol–gel Derived ZnO Thin Films // Apl.ied Surface Science. – 2009. – Vol. 255, №11. – P. 5812 – 5817. 98
15. Salam, Shahzad, Mohammad Islam, and Aftab Akram, Sol–gel Synthesis of Intrinsic and Aluminum – doped Zinc Oxide Thin Films as Transparent Conducting Oxides for Thin Film Solar Cells // Thin Solid Films. – 2013. – №529. – P. 242 – 247.
16. Nayak Pradipta K., Jinwoo Kim, Seungjun Chung, Jaewook Jeong, Changhee Lee. Yongtaek Hong Spin – coated Ga – doped ZnO Transparent Conducting Thin Films for Organic Light – emitting Diodes // Journal of Physics D: Apl.ied Physics J. Phys. D: Apl. Phys. – 2009. – Vol. 42, №13. – P. 139801.