Electrophysical and photocatalytic properties of SnO$_2$-ZnO thin films prepared by sol-gel method

V Yu Storozhenko$^1$, M G Volkova$^1$, Yu N Varzarev$^2$, A P Starnikova$^2$, V V Petrov$^2$ and E M Bayan$^1$

$^1$Department of Chemistry, Southern Federal University, Rostov-on-Don, 344090, Russia,
$^2$Research and Education Centre “Microsystem technics and multisensory monitoring systems”, Southern Federal University, Taganrog, 347922, Russia

vstorozhenko@sfedu.ru

Abstract. Electrophysical properties of SnO$_2$-ZnO thin films prepared by sol-gel method have been studied. The resistance of thin films have a temperature hysteresis, the films resistance decreases up to two times when the temperature reaches 210-300 °C and returns to its initial value when cooling down to 90-30 °C. That phenomenon can be explained by the processes of thermal generation - recombination of electrons, and adsorption - desorption of oxygen on the surface of the films.

1. Introduction

Thin films of semiconductor oxide materials are widely used in microelectromechanical systems, electronic devices, etc [1]. One of the most used is a composite material based on mixed oxides of Zn(II) and Sn(IV) due to the combination of their high chemical stability, non-toxicity, and unique electrophysical properties [2].

In [3,4] thin films of SnO$_2$-ZnO were applied by ultrasonic spray pyrolysis technique. With an increase in the tin content in the sample, the thickness of the films increased too, and the resistivity decreased. These works showed that the obtained ZnO-SnO$_2$ films can be used in photovoltaic devices. In [5], ultrasonic spray pyrolysis technique was used to obtain films based on zinc tin oxide. It was shown that an increase in zinc concentration reflects a deterioration in crystallinity in terms of a decrease in grain size. This is explained by an increase in the number of lattice dislocations due to the larger number of dangling bonds formation with an increase in the zinc content. In [6] SnO$_2$-ZnO thin films prepared by radio-frequency magnetron sputtering. The effect of the substrate temperature on the morphology and properties of the films was shown. It was found that with an increase in temperature, the particle size increases too, and the resistivity decreases.

In addition to unique electrophysical properties, materials based on zinc and tin oxides have photocatalytic activity [7]. The photocatalytic activity of SnO$_2$-ZnO thin films obtained by the sol-gel method was quantified by the degradation of methylene blue via ultraviolet irradiation. It was found that films containing a mixture of ZnO and SnO$_2$ exhibit a higher photocatalytic activity in comparison to pure phases SnO$_2$ and ZnO [8].

In addition to studying the properties of zinc and tin oxides thin films, an important stage is the synthesis of thin-film materials. Several methods of preparation are described in the literature, the
main of them are spray pyrolysis, co-precipitation method and sol-gel method [9, 10]. In physical methods of obtaining, complex devices and conditions that differ from standard ones are most often used. Therefore, in recent years, much attention has been paid to chemical methods for obtaining film materials from solutions, since they are simpler, more economical, and does not include expensive equipment using. The sol-gel method is the simplest method for producing films of complex composition [11].

The aim of this work was to synthesize SnO$_2$-ZnO thin films with a Sn:Zn molar ratio from 0.5:99.5 to 5:95 by the sol-gel method and study their electrophysical and photocatalytic properties.

2. Experiment
To obtain thin film materials by the sol-gel method, SnCl$_4$·5H$_2$O, Zn(NO$_3$)$_2$·6H$_2$O and isopropanol as a solvent were used. The Sn(IV):Zn(II) molar ratio in solutions was 0.5:99.5, 1:99, 5:95 by mole. Calcination was carried out for 2 hours at 550 °C. The phase composition of the obtained films was studied by the X-ray diffraction (XRD) using a diffractometer ARLX'TRA, Thermo ARL (Switzerland) with CuKα X-rays. The morphology and thickness of the films studied by scanning electron microscopy (SEM) on a Nova Nanolab microscope. The photocatalytic activity of obtained thin film was studied in the reaction of a model pollutant (methyl orange) photodegradation under the illumination of UV light [12]. The study of the electrophysical properties of the film samples was carried out according to the previously described method [13]. The measurement results were compared with pure ZnO obtained earlier [14].

3. Results and discussion
According to XRD data, all of obtained materials are nanosized, insufficiently crystallized. For all materials, the main phase is the wurtzite. The analysis of diffraction peaks showed the presence of hexagonal wurtzite structure of ZnO for all the thin films. The cassiterite phase appears in samples with a tin content of 0.5 mol% or more. The low intensity of the peaks can be a consequence of both the crystallites small size influence and the insufficiently crystallization of the material. As the content of tin in the sample increases, the degree of crystallinity and the intensity of the peaks increase too. The lowest peak intensity is observed for the sample with the lowest tin addition (0.5 mol. %).

![XRD patterns of the synthesized SnO$_2$-ZnO films, calcined at 550 °C (*) – wurtzite structure, ■ – cassiterite structure.](image)

Figure 1. XRD patterns of the synthesized SnO$_2$-ZnO films, calcined at 550 °C (* – wurtzite structure, ■ – cassiterite structure).
SEM data showed that the films surface and thickness are inhomogeneous. The cross section shows that nanoscale films have a porous structure and an average thickness of about 120-130 nm. The thickness reaches 400-500 nm in some places, which is typical for films formed by the sol-gel technology.

Temperature dependences of the resistance (R) measurements showed that the resistance of pure ZnO is 20% higher than that for films 0.5SnO$_2$:99.5 ZnO and 1SnO$_2$:99ZnO, and 30% higher than that for material 5SnO$_2$:95ZnO (Figure 1), which correspond with the another research works [14, 15].

The temperature hysteresis is observed in all the presented dependences of resistance on temperature – the heating and cooling curves do not coincide. When the temperature increases from 30 to 210-240 °C, the resistance of the films changes insignificantly. With further heating up to 300 °C, resistance decreases almost twice. When the temperature decreases from 300 °C to 100-90 °C, the resistance reaches the minimum value (and even slightly decreases), and when cooling down to 30°C, increases to the initial value.

This difference in the heating and cooling curves may be due to the competition of two processes – thermal generation and recombination of electrons, on the one hand, and adsorption-desorption processes of oxygen on the films surface, on the other, which also lead to a change in the charge carriers concentration.

The values of the activation energy of conduction estimated by the Arrhenius equation for the temperature ranges in which the resistance changes significantly were 0.15-0.19 eV for the range of 240-300 °C upon heating and 0.07-0.09 eV for the range of 90-30 °C upon cooling, respectively. These energy values correspond to two levels that are electron donors. The fact that they appear separately at the heating and cooling stages can be explained by the intermediate capture of electrons by oxygen adsorbed on the surface at high temperatures. In areas with a slight change in resistance, the activation energy is sufficiently small. However, the presence of a section with negative activation energy on the cooling curve can also indicate the effect of adsorbed oxygen.

The photocatalytic activity study for all materials showed that all materials, regardless of their composition, exhibit photocatalytic properties. It was noted that SnO$_2$-ZnO films had higher catalytic properties than pure zinc oxide films. At the same time, the material containing the minimum amount of SnO$_2$ (0.5SnO$_2$:99.5 ZnO) has the best photocatalytic activity. In 60 minutes, when exposed to UV light irradiation, the degradation of the model pollutant methyl orange was 40%.
4. Conclusion
Thin films of SnO₂–ZnO, including the wurtzite and cassiterite phases, were synthesized by the sol-gel method. It was shown that the material containing the minimum amount of tin dioxide (0.5SnO₂:99.5ZnO) exhibits the lowest degree of crystallization. The resistance of thin SnO₂–ZnO films have a temperature hysteresis, the films resistance decreases up to two times when the temperature reaches 210-300 °C and returns to its initial value when cooling down to 90-30 °C. SnO₂–ZnO thin films efficiently utilized for photocatalytic degradation of methyl orange dye under UV light.

Acknowledgments
The present study was performed with financial support of RFBR, project number 20-07-00653 A.

References
[1] Chang Y-J, Lee D-H, Herman G S, Chang C-H 2007 High-Performance, Spin-Coated Zinc Tin Oxide Thin-Film Transistors Electrochem. Solid-State Lett. 10(5) 135-138
[2] Schmidt-Mende L, MacManus-Driscoll J L 2007 ZnO–nanostructures, defects, and devices Materials today 10(5) 40-48
[3] Jazmati A K, Kakhia M, Abdallah B 2018 Physical, optical and sensing properties of sprayed zinc doped tin oxide films Optik 158 1113–1122
[4] Atay F, Akyuz I, Durmaz D, Kose S 2019 Characterization of ZnO-SnO₂ oxide systems produced by ultrasonic spray pyrolysis Solar Energy 193 666–675
[5] Hegazy A R, Salameha B, Mathaie M, Alsmadi A M 2020 Morphology and optical analysis of defect levels in ultrasonically-sprayed zinc tin oxide thin films Ceramics International 46 13151–13158
[6] Zhao J, Ni J, Zhao X, Xiong Y 2011 Preparation and characterization of transparent conductive zinc doped tin oxide thin films prepared by radio-frequency magnetron sputtering Journal of Wuhan University of Technology-Mater. Sci. Ed. 26(3) 388–392
[7] Hamrouni A, Moussa N, Parrino F, Di Paola A, Houas A, Palmisano L 2014 Sol-gel synthesis and photocatalytic activity of ZnO-SnO₂ nanocomposites Journal of Molecular Catalysis A: Chemical 390 133-141
[8] Torres Martinez D Y, Castanedo Pérez R, Torres Delgado G, Zelaya Ángel O 2012 Structural, morphological, optical and photocatalytic characterization of ZnO–SnO₂ thin films prepared by the sol–gel technique Journal of Photochemistry and Photobiology A: Chemistry 235 49–55
[9] Krunks M, Mellikov E 1995 Zinc oxide thin films by the spray pyrolysis method Thin Solid Films 270 33-36
[10] Yang Z, Lv L, Dai Y, Xv Z, Qian D 2010 Synthesis of ZnO–SnO₂ composite oxides by CTAB-assisted co-precipitation and photocatalytic properties Appl. Surf. Sci. 256 2898–2902
[11] Chenb W-J, Liua W-L, Hsieh Sh-H, Hsu Y-G 2012 Synthesis of ZnO:Al Transparent Conductive Thin Films Using Sol-gel Method Procedia Engineering 36 54 – 61
[12] Bayan E M, Lupeiko T G, Pustovaya L E, Volkova M G 2020 Synthesis and photocatalytic properties of Sn–TiO₂ nanomaterials, Journal of Advanced Dielectrics 10(01n02) 2060018
[13] Petrov V V, Plugotarenco N K, Nazarova T N, Korolev A N 2007 Preparation of Sols from Water–Alcohol Solutions of Tetraethyl Orthosilicate and SnCl₄ and the Effect of Sol Composition on the Surface Morphology of Sol–Gel Films Inorganic Materials 43(9) 1010–1014
[14] Petrov V V, Bayan E M, Khubezhov S A, Varzarev Yu N, Volkova M G 2020 Investigation of Rapid Gas-Sensitive Properties Degradation of ZnO–SnO₂ Thin Films Grown on the Glass Substrate Chemosensors 8(2) 40
[15] Petrov V V, Varzarev Yu N, Abdullin Kh A 2019 Temperature Dependence of Electrical Properties of ZnO Nanorods Array IOP Conf. Series: Materials Science and Engineering 703 012040