Structural properties of TiO$_2$-SnO$_2$ thin films prepared by new pyrolysis solid-phase method

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Abstract. Nanoscale TiO$_2$-SnO$_2$ films with the Ti:Sn ratio 1:99, 3:97 and 5:95 mol%, respectively, were obtained by solid-phase low-temperature pyrolysis method. The synthesized materials were studied by X-ray phase analysis and scanning electron microscopy (SEM) analysis. Regardless of the modified agents’ concentration, the structure of cassiterite was observed for all synthesized materials. When studying the effect of synthesis parameters on the materials properties, it was shown that both an increase in the Ti$^{4+}$ concentration and in the calcination temperature leads to an increase in the particle size.

1. Introduction

Nanomaterials based on tin dioxide, doped with different modifying agents, are commonly used to produce optical coatings, gas-sensitive sensors, photocatalysts, etc. [1-2]. Composite materials based on mixed oxides exhibit better optical, electrophysical, and other properties than pure oxide materials, that could be both due to the close ionic radii of tin and titanium and the equal higher valences of these elements. Various studies contain information that the properties of mixed oxides are generally better than those of individual oxides. For example, titanium dioxide nanomaterials with a small addition of tin have higher photocatalytic properties than pure titanium dioxide [3]. The mixture of TiO$_2$-SnO$_2$ oxides is very perspective due to the structural analogy between TiO$_2$ and SnO$_2$: both oxides crystallize in the rutile structure. For example, it was shown [4] that an increase in the tin concentration up to 40% for TiO$_2$-SnO$_2$ materials leads to an increase in the rutile phase of TiO$_2$ due to the similarity of crystal structures, while pure materials crystallize in the cassiterite and anatase phase, respectively. In [5] it was shown that small additions of Ti$^{4+}$ in SnO$_2$ reduce the degradation of SnO$_2$ materials characteristic and increase the density for chemisorption active centers.

To obtain perspective materials with controlled properties different techniques are applied, among them doping and different temperature proceedings are used. The change in the materials films properties is significantly influenced not only by the calcination temperature and the concentration of the additives introduced, but also by the number of layers applied. For example, in paper [6], changes in the optical properties depending on the number of layers (5, 10, 15) of SnO$_2$:TiO$_2$ thin films (Sn:Ti=1:1) synthesized by the sol-gel method were shown. According to the authors, the deterioration of the films transparency with an increase in the number of layers can be associated simultaneously
with a change in the phase composition of the materials (anatase, anatase-rutile and rutile for 5, 10 and 15 layers, respectively), both an increase in the particle size and in the coating density (231, 340, 413 nm).

The synthesis of nanoscale oxide film materials is carried out by various methods, but some of them have certain disadvantages, such as poor reproducibility of the process (sol-gel method), expensive equipment (hydrothermal synthesis, magnetron sputtering, laser sputtering), etc. The spray pyrolysis [7] is the simplest and most economically feasible, widely used method for materials synthesis in large scale. Another perspective method of thin film synthesis is solid-phase pyrolysis [2, 8], which allows one to obtain thin films with a controlled thickness and specified optimal physicochemical properties. Also, solid-phase pyrolysis technique does not include substrates heat treatment (before precursors’ layers applying) in comparison to spray pyrolysis and this technique allows one to obtain sufficiently crystallize films in comparison to sol-gel technology. Comprehensive study of the materials properties synthesized by new technique is an important element for finding methods of their further application.

Thus, the aim of this work was to choose optimal synthesis conditions to obtain high-quality nanoscale films based on tin dioxide containing titanium dioxide in low concentrations by solid-phase low-temperature pyrolysis and to study the structural and morphological properties of the synthesized materials.

2. Experiment
To obtain thin film materials by solid-phase pyrolysis method, stannic chloride pentahydrate SnCl₄·5H₂O, titanium butoxide (C₄H₇O)₄Ti, organic acid, and 1,4-dioxane as a solvent were used as precursors. All chemicals used were of analytical grade or of the highest purity available, were purchased from “ECROS”, Russia. The synthesis was carried out in two stages. At the first stage, intermediate products (organic salts of titanium and tin) were obtained from the SnCl₄·5H₂O and (C₄H₇O)₄Ti in melt. The preparation of the intermediate product was carried out with the introduction of tin tetrachloride required amount (molar ratio Ti:Sn was 1:99, 3:97, 5:95 for materials 1, 2, 3, respectively) in the melt of organic acid and titanium butoxide. After cooling, the synthesized melt was shredded.

The second stage involved dissolving the resulting product in an organic solvent and then applying it to the pre-prepared substrates (soda-lime glass and silicon). To prepare the substrates, chemical cleaning was applied, which include treatment with a hot mixture of K₂Cr₂O₇ and HNO₃ for 10 minutes, three times washing with distilled water and treatment with alcohol. To remove the alcohol residue, the substrates were washed twice in distilled water and dried. Before applying the obtained solution, the substrate was additionally cleaned with acetone for degreasing. The method allows one to obtain films of different thicknesses by applying a precursor’s solution several times using the following technology. Each applied layer was dried in air and then at 120 °C in a drying cabinet. The final heat treatment was carried out in a muffle furnace at 550 °C for two hours, the heating rate was 10°/min. After heat treatment all obtained materials were cooled to the room temperature together with a muffle furnace. This cooling method allows one to obtain uniform coatings without cracks. In this paper, three-layer films applied on the pre-prepared silicon and soda-lime glass substrates were synthesized and investigated.

The phase composition of the obtained films was studied by X-ray diffraction (XRD) using an ARLXTRA diffractometer, Thermo ARL (Switzerland) with CuKα X-rays. Phase composition analysis performed using Crystallography Open Database. The morphology, quality, particles size in the volume and on the surface as well as thickness of the obtained film materials on the silicon substrates were studied by scanning electron microscopy (SEM) using a scanning electron microscope Nova Nanoab 600. The size of the coherent scattering regions (D) was estimated by XRD analysis data using the Scherrer equation: D = kλ/(β·cosθ), where k is the geometric shape coefficient, λ is the X-ray wavelength constant (λ = 0,154 nm), and β is the full width at half the maximum of the diffraction line and θ-diffraction angle.
3. Results and discussion

The results of the XRD analysis showed that all synthesized materials are nanoscale, sufficiently crystallize and contain cassiterite phases (Figure 1). The absence of additional peaks on the XRD pattern suggests a high quality of the films obtained by low-temperature solid-phase pyrolysis technique. With an increasing of the modifying agents concentration the peaks intensity also increased.

![Figure 1. XRD patterns of SnO$_2$-TiO$_2$ materials calcined at 550 °C (explanations are presented in text) and SnO$_2$[9].](image)

With increasing of the modifying agents’ concentration, an increase in the particle size calculated according to the Scherrer equation was also observed (19, 23 and 29 nm for materials 1, 2, 3, respectively). According to the calculations, for materials 1, 2, and 3 the crystallinity was 47, 45, and 43%, respectively. This change may be related to the fact that films containing a high tin ions concentration crystallize even at room temperature in rutile or cassiterite type, while an increase in the titanium dioxide concentration leads to an increase of the amorphous phase [5].

According to SEM analysis (Figure 2a), the films obtained by pyrolysis have relatively smooth surfaces, homogeneous in the volume and solid. The thickness of the films is about 70 nm for three-time application. The presented SEM images do not have clear borders despite the three layers application. This indicates a possibility to synthesize high-quality thin oxide films of the controlled thickness by low-temperature pyrolysis technique.

![Figure 2. SEM images (a) and particles size distribution (b) of thin film on the silicon substrate (Ti:Sn=1:99) calcined at 550 °C.](image)
All of obtained films materials are consisted from particles almost round in their shape. Statistical analysis of the SEM data showed that the average particle size is 8 and 13 nm, for materials 1 and 3, respectively. For the material Ti:Sn=1:99 (Figure 2b), most of the grains are in the size range of 8-10 nm.

The slightly excessive data obtained by the Scherrer equation compared to the data obtained from the statistical SEM analysis may be due to differences in the determination methods. The XRD method estimates the entire volume of the material, whereas the statistical SEM analysis is a more accurate method, estimating the surface of the synthesized film (table 1).

| Materials | Particles size, nm (XRD) | Particles size, nm (SEM) | Crystallinity, % |
|-----------|--------------------------|--------------------------|-----------------|
| 1 (Ti:Sn=1:99) | 19 | 8 | 47 |
| 2 (Ti:Sn=3:97) | 23 | 10 | 45 |
| 3 (Ti:Sn=5:95) | 29 | 13 | 43 |

4. Conclusion
Homogeneous thin film nanomaterials TiO2-SnO2 were obtained by solid-phase low-temperature pyrolysis technique. The described method allows one to obtain film coatings of different thicknesses by varying the applied layers number of the precursor’s solution with good reproducibility. It was shown that the particle size increases with both increasing of the modifying agents’ concentration and the calcination temperature. With an increase in the concentration of the introduced additives, the synthesized materials crystallinity decreases. The best crystallinity degree was shown for film material doped with the minimum Ti4+ concentration (1 mol.%). The presented method makes it possible to obtain homogeneous films of controlled thickness with uniform and smooth surface, which allows one to recommend it to produce semiconductor film materials as promising electrode or gas-sensing material.

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References
[1] Al-Hamdi A M, Rinner U and Sillanpää M 2017 Process Safety and Environmental Protection 107 190-205
[2] Petrov V V, Bayan E M, Khubezhov S A, Varzarev Y N and Volkova M G 2020 Chemosensors 8(2) 40
[3] Bayan E M, Lupeiko T G, Pustovaya L E and Volkova M G 2020 Journal of Advanced Dielectrics 10 (1,2) 2060018
[4] Medjdali F, Bouabellou A, Bouachiba Y, Taabouche A, Bouatia K, and Serrar H 2020 Mater. Res. Express 7 016439
[5] Zakrzewska K, Radecka M, Przewoźnik J, Kowalski K and Czuba P 2005 Thin Solid Films 490 (1) 101-7
[6] Sönmezoğlu S, Arslan A, Serin T and Serin N 2011 Physica Scripta, 84(6) 065602
[7] Leng J, Wang Z, Wang J, Wu H-H, Yan G, Li X, H Guo, Liu Y, Zhang Q and Guo Z 2019 Chem. Soc. Rev. 48 3015-72
[8] Volkova M G, Storozhenko V Y, Petrov V V and Bayan E M 2020 J. of Phys.: Conf. Ser. 1695(1) 012023
[9] Downs R T and Hall-Wallace M 2003 Am. Mineral. 88 247-250