ABSTRACT

of the dissertation for the degree of Doctor of Philosophy (PhD) in the specialty "6D074000 – Nanomaterials and nanotechnology" (chemistry)

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Influence of colloidal characteristics of sol-gel systems based on tin compounds on the structure and thermal stability of nanosized SnO_2 films

The dissertation work is devoted to the study of the influence of colloidal parameters of film-forming systems in the sol-gel process on the structure and thermal stability of nanosized films based on nanosized tin dioxide. The paper presents a study of the influence of the acidity of film-forming systems (pH) on the structural properties of the resulting films. Thermally stable hierarchical micro-nano structures were synthesized from the $SnCl_4$/EtOH/NH_4OH film-forming system basedon the sol-gel technology. A technique for separating a signal from noise for processing the results of X-ray diffraction analysis of nanoobjects on an amorphous substrate has been developed.

The first chapter is devoted to a literature review of semiconductor tin dioxide, the sol-gel method, deposition methods in the sol-gel method and their influence on the structure of the resulting films. The nature of gas sensitivity and the mechanismof electrical conductivity of tin dioxide are considered. The prerequisites for the development of a technique for separating a signal from noise during X-ray diffraction analysis of the resulting films are given.

In the second chapter of the dissertation, the properties of nanosized films of nanosized SnO_2 obtained from lyophilic and lyophobic systems are compared. The structure and properties of the resulting films were studied depending on the pH of the film-forming systems. Changes in the properties of the films depending on the duration of thermal exposure are studied. A technique for conducting an experiment using the sol-gel method for obtaining solutions for further synthesizing nanosized films based on tin dioxide is presented. Modern methods of analysis of the obtained samples were used: X-ray diffraction method, spectral method. The surface of the obtained samples was studied. A technique for studying the electrical conductivity and sensitivity to ethanol vapor of the resulting films is presented.

The third chapter presents the results of the study of the functional propertiesof the obtained nanoscale films of tin dioxide. Based on changes in the parameters of a dispersed system (temperature and reaction time, concentration and chemical composition of precursors), the possibilities of synthesizing materials based on tin oxide with a hierarchical structure are considered.

The fourth chapter describes the developed technology for improving the accuracy of measuring the spectra of nanoobjects on amorphous substrates, based on signal accumulation along the spectrum. The onset of the transition from the amorphous state to the crystalline structure of SnO_2 and the features of the formed crystalline structure as a function of the annealing temperature have been studied.

Relevance of the dissertation topic: Among a large number of promising physical and chemical methods for obtaining materials with different functional properties, the sol-gel technology is of the greatest interest. The common name "sol- gel process" unites a large group of methods for obtaining (synthesis) of materials from solutions, an essential element of which is the formation of a sol and its transition to a gel. Sol-gel

technology is used to produce fire extinguishing foams, to create continuous refractory fibers, to obtain porous and hybrid organic-inorganic materials that are used as sorbents, catalysts, proton-conducting membranes or catalyst carriers. The transformation of sols into gels is the basis of the latest nanotechnologies for the production of light guides, ceramic ultrafiltration membranes, optical, anti-corrosion and electrical insulating coatings, powders with a core-shell structure, photographic materials, luminescent light sources, highly dispersed abrasives and other materials with unique properties and a controlled structure. Such colloidal properties of solutions as lyophilicity and lyophobicity are important factors in obtaining thin films. In works devoted to the preparation of thin films of tin dioxide, either a lyophobic system (sol, suspension, etc.) or a lyophilic system (formation of macromolecules) is usually considered separately. A comparison of these systems makes it possible to reveal the features of the formation of the structure and properties of the obtained films.

Composite systems based on tin dioxide have many applications as a functional material. Film coatings are used as active layers in gas analysis equipment. The high chemical homogeneity of the products obtained makes it possible to use SnO_2 coatings as a three-dimensional macroporous anode in lithium-ion batteries. Tindioxide is used as a corrosion protection coating for bipolar 304 stainless steelPEMFC plates. SnO_2 is also used in biomedical applications as a glucose sensor. Tin dioxide is used in ultraviolet photodetectors. In addition, tin dioxide also has antibacterial properties. The antimicrobial properties of SnO_2 thin films were studied by the agar-agar method, and the results confirm the antibacterial activity of SnO_2 against Escherichia coli and Bacillus. Thin films of tin dioxide are transparent in the visible and near ultraviolet regions and, at the same time, can have high electrical conductivity. This combination of optical and electrophysical properties determines the wide application of this material in practice. It is known that the functional properties of oxides are provided by varying degrees of oxygen nonstoichiometricity, which depends on the oxide production technology and its subsequent processing. Animportant role in the formation of the structure and properties of the resulting films is played by the pH of the film-forming systems. In this work, the pH range from 1.4–1.53 was studied. In this range, changes in light absorption and surface resistance are observed, so that there is a transition from the formation of surface to the formation of bulk SnO_2. The advantage of a comprehensive study is the dependence of the transparency of the samples and their resistance on changes in the pH of the film- forming system, which is very important for solar cells and gas sensors.

Obtaining nanomaterials with unique properties, as a rule, is based on the formation of certain structures. In hierarchical structures, useful functions are determined not only at the nano level, but also at other levels of the structure. SnO_2- based hierarchical structures have been intensively researched because of their high surface area, high surface permeability, low density, low cost, environmental friendliness, and stable physicochemical characteristics.

With the development of nanotechnologies, methods for studying nanoobjects are becoming more and more relevant. One of the informative methods is X-ray diffraction analysis. However, it may turn out to be inefficient in the study of thin films containing nanoobjects on amorphous substrates, since the noise level may be higher than the signal level from nanoobjects. Moreover, the contribution to the overall X-ray pattern from the substrate can be much greater than from the films. In this case, the correct subtraction of the background is a rather complicated problem, since the background from an

amorphous substrate is irregular. To solve this problem, the spectrum accumulation method based on N independent background andsample measurements is usually used. The disadvantage of this approach is thesignificant time for measuring the spectra: the more times the spectrum is recorded, the higher the signal-to-noise ratio. It takes 100 measurements to increase the signal- to-noise ratio by a factor of 10. Therefore, the development of an optimal method for express processing of X-ray spectra from nanoobjects on amorphous substrates is an urgent scientific and practical task.

The purpose of the study: Development of scientific bases for the creation of nanosized films of nanosized SnO_2 and methods for their analysis based on the study of the influence of colloidal parameters of solutions in the sol-gel process on the structure and properties of the resulting films.

Research objectives:

1) Obtain lyophobic and lyophilic film-forming systems and investigate the properties of nanoscale films obtained from these systems. Investigate the change in the properties of nanosized films depending on the duration of thermal exposure.

2) To study the structure and properties of nanoscale films depending on the pH of film-forming systems.

3) To develop a method for improving the accuracy of measuring the spectra of nanoobjects on amorphous substrates.

Research methods:

The sol-gel method was used to obtain solutions for further synthesis of nanosized films based on tin dioxide. Modern methods of analysis of the obtained samples were used: X-ray diffraction method, spectral method. The surface of the obtained samples was studied. A technique for studying the electrical conductivityand sensitivity to ethanol vapor of the resulting films is presented. The properties of thin SnO2 films obtained from lyophilic and lyophobic systems are compared. The structure and properties of the resulting films were studied depending on the pH ofthe film-forming systems. Changes in the properties of the films depending on the duration of thermal exposure are studied.

The main provisions of the dissertation submitted for defense:

1. The sensitivity to ethanol vapor of nanosized films obtained from $SnCl_4$/EtOH/NH_4OH and $SnCl_4$/EtOH/NH_4F at the same acidity coincides within the measurement accuracy.

2. In the $SnCl_4$/EtOH/NH_4OH film-forming system at a ratio of ammonium ions to tin ions equal to 2 (pH=1.49), thermally stable dendritic micro-nano structures with the longest first-order axes are formed.

3. In the spectrum of nanoobjects on amorphous substrates, using the method of signal accumulation along the spectrum, the background from the substrate is qualitatively subtracted, and the signal-to-noise ratio increases by a factor of $\sqrt{2L+1}$ (where the parameter $L \leq 0.165 \cdot L_{FWHM}$, L_{FWHM} is the number of spectrum recording channels corresponding to full width of the diffraction line at half amplitude).

Scientific novelty of the results obtained:

It has been shown that the addition of a fluorinating agent to lyophilic systems leads to the fixation of fluorine ions in the structure of the resulting xerogel. And in lyophobic systems, separate phases of nanosized SnO_2 and NH_4F are formed. It was found that the sensitivity to ethanol vapor of nanosized films obtained from $SnCl_4$/EtOH/NH_4OH and $SnCl_4$/EtOH/NH_4F at the same acidity coincides within the measurement accuracy. Thermally stable hierarchical micro-nano structures are

synthesized from the $SnCl_4$/EtOH/NH_4OH film-forming system using the sol-gel technology. A classification of the shape and size of the synthesized structures depending on the pH of the solution is given. It was found that when the ratio of ammonium ions to tin ions is equal to 2 (pH=1.49), dendritic structures with the longest first-order axes are formed. It has been shown that the properties (transmission coefficient, surface resistance, sensitivity to ethanol vapor) of films obtained from the $SnCl_4$/EtOH/NH_4OH film-forming system are stable upon prolonged exposure to temperature. A technique has been developed for improving the accuracy of measuring the spectra of nanoobjects on amorphous substrates based on signal accumulation along the spectrum. In the $SnCl_4$/H_2O film-forming system, the onset of the transition from the amorphous state to the crystalline structure of SnO_2 was studied. It has been established that the crystal begins to form already at a temperature T = 50˚C along the SnO_2(211) plane. The crystal structure of the obtained nanosized SnO_2 films significantly depends on the annealing temperature. The main characteristics of the spectrum (the number of peaks, their width, and their relative amplitudes) are different at different annealing temperatures.

Practical significance of the obtained results:

The use of the $SnCl_4$/EtOH/NH_4OH film-forming system makes it possible to create hierarchical micro-nano structures with a controlled (depending on the pH of the solution) size. The discovered relationship between technological factors and the film structure is of significant practical value for the formation of gas-sensitive material layers. The synthesized hierarchical structures make it possible to increase the gas sensitivity and are thermally stable. Due to the greater stability of the properties of films obtained from this film-forming system, with prolonged temperature exposure, the service life of the gas sensor is increased. Film-forming systems $SnCl_4$/EtOH/NH_4OH compared to $SnCl_4$/EtOH/NH_4F have a lower cost, environmental friendliness and stable physical and chemical characteristics. The doping of tin dioxide films with fluorine obtained by the sol-gel method leads to a significant increase in the electrical conductivity of the films and an increase in their transparency. The developed method of signal and noise accumulation along the spectrum makes it possible to significantly reduce the noise level in the diffraction study of nanoobjects on amorphous substrates. This makes it possible to significantly reduce the processing time of the spectra and to study the onset of the transition from the amorphous state to the crystalline structure of tin dioxide. In the $SnCl_4$/H_2O film-forming system, it was found that the crystal begins to form already at a temperature T = 50˚C along the SnO_2(211) plane. The crystal structure of the obtained nanosized SnO_2 films significantly depends on the annealing temperature. The main characteristics of the spectrum (the number of peaks, their width, and their relative amplitudes) are different at different annealing temperatures.

Approbation of the work: The results are presented at the following conferences and forums: International scientific conference of students and young scientists "Farabi Alemi" Almaty, Kazakhstan, 2019 and 2020; INESS The 7th Internation Conference on Nanomaterials and Advanced Energy Storage Systems, Almaty, Kazakhstan, 2019; II International Scientific Forum "Nuclear Science and Technology", Almaty, Kazakhstan, 2019.

Publications: Based on the dissertation materials, 14 scientific papers (5 articles, 3 patents, 6 theses) were published, including 5 in journals indexed byScopus and Web of Science, and 2 in publications recommended by CCFES.

Compliance with the directions of scientific development or state programs:

The research carried out within the framework of the dissertation work was carried out under the project AP05134263 "Influence of colloidal parameters of solutions in the sol-gel process on the structure and thermal stability of the properties of thin SnO_2 films" and under program-targeted funding BR05236404 "Development of scientific foundations for the creation new nanomaterials and methods for their analysis to obtain films with desired useful properties.

Structure and scope of the dissertation: The dissertation consists of an introduction, four chapters, a conclusion and a list of sources used. The volume of the dissertation is 111 pages, including 11 tables and 65 figures.

Personal contribution of the doctoral student: In the process of carrying out these studies, the author performed most of the experiments, made a significant contribution to the development of analysis methods, and also took an active part in the discussion and publication of the results.