Sensor Based on Tin Oxide, Obtained from the Solutions of Extracts

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Abstract

Nanocrystalline tin oxide films were obtained on glass and metal substrates by immersing into the solution of tin carboxylate, centrifuging of the substrate with the solution, followed by thermal treatment. A distinguishing feature of the proposed method is the use of extraction for the synthesis of precursors, which allows us to obtain the precursor material free from any impurities. It was established that the sensitivity of tin oxide films to the gases depends on pyrolysis temperature and is maximal for the films pyrolyzed at 400 °C.

INTRODUCTION

Numerous investigations in the area of developing sensors and sensoring procedures are due to the necessity of the ecological provision of vital functions and control of industrial processes. Semiconductor sensors based on SnO_2 (so-called TGS sensors) are used mainly to detect toxic or explosive gases [1–3]. The use of these sensors for medical purposes to analyze human outward breath is promising because some diseases are accompanied by an increase in the concentrations of acetone, ammonia or gases of organic nature [4]. It is most preferable to use SnO_2 in the form of thin layers obtained in different substrates. The value of film resistance depends on measuring temperature. The minimal resistance of tin oxide film and doped compositions was observed at a temperature of 490 °C.

One of the promising directions of improving the activity, selectivity, and time of exposure in gases and other parameters of sensors is to develop new gas sensitive materials based on oxide nanostructures. Investigation involving tin oxide doping with other elements, for example copper, nickel and platinum [5–7], showed that the resistance of the resulting materials increases; however, the response to the presence of gases (hydrogen sulphide, carbon dioxide, carbon monoxide) increases mo re than 100 times, while time of response decreases to 45–60 s.

On the other hand, synthesis method has a substantial effect on the properties of the synthesized material. Among the methods of film technology, those involving solutions are of interest because perfect mixing of the components in solution helps one to obtain homogeneous or uniform mixtures of pyrolysis products and provides the ease of adjustment of components ratio is solution and the introduction of doping elements. Methods of obtaining films from solutions are distinguished by simplicity and involve the processes of self-arrangement and structure forming.

EXPERIMENTAL

In order to obtain tin oxide films, we used the extraction-pyrolysis method based on extraction of the target components from aque-

ous solutions of salts, mixing of the extracts at a required ratio, deposition of the true solution onto a substrate, and thermal treatment [6]. The extracting solvent was a mixture of normal-structured carboxylic acids (caprylic, capric, oenanthic, pelargonic, malonic, succinic). Extraction was carried out according to the cation-exchange mechanism.

At the stage of extraction, tin is isolated from the aqueous solution of $SnCl_2$ into the organic extracting phase; a solution of tin carboxylate in the excess of an organic acid or in a solvent (toluene, hexane) is formed. Systems with monocarboxylic acids are characterized by high separation factors for different metals. Efficient separation of elements in the systems with extracting agents of different classes promotes fine purification of the components of functional materials from impurities at the stage of extraction. It is possible to use the solutions of different composition obtained by processing mineral, industry-related, secondary raw material or industrial solutions from various works. During extraction, the anions of inorganic salts and extrinsic metal cations do not pass into the organic phase. The extraction sequence of metals developed experimentally in [8] illustrates the possibility to use monocarboxylic acids to obtain a metal extract, which would be almost free from impurities.

For extraction of easily hydrolysable metals (Al, Sn, Zr, *etc.*) forming hydrolyzed, usually polymerized carboxylates, the process is essentially complicated. In such a case, it is necessary to add an alkali gradually until the hydrolyzed complexes are formed in the organic phase but without any excess, in order to avoid hydroxide precipitation in the aqueous phase or at the interface. Of course, in this case the metal content of the organic phase should be determined using an independent procedure.

In order to determine the previously given concentration of tin carboxylate more accurately, we carried out re-extraction of 1 ml of carboxylate obtained by extraction into 50 ml of HCl solution. the re-extract was analyzed by means of atomic absorption with AAS-1M instrument. So, a pure organic salt of metal was obtained in the liquid phase with a precise concentration with respect to metal.

In order to study thermal decomposition of metal extracts, we carried out thermogravimetric measurements with Q-1000 derivatograph. A weighed portion (50 mg) of metal carboxylate paste was placed in a platinum crucible and heated at a constant rate equal to 10 °C/min.

X-ray phase analysis (XPA) was carried out with DRON-4-07 diffractometer with GUR-9 goniometer (a horizontal goniometer with a radius of 180 mm, with Bregg–Brentato focusing equipped with a graphite monochromator and compatible with a computer). The samples were recorded in the filtered CuK_α radiation rotating the sample around a perpendicular to its plane (in order to increase a number of cases when atomic planes get into the X-ray beam, and to increase the accuracy of the method; the data (angles and intensities) were recorded with a computer. Investigation of the film samples was carried out with the help of a special cell holding the film.

Images of the film were obtained by means of atomic force microscopy (AFM) in the air with the help of a multimode scanning probe microscope Solver P47 (NT-MDT, Russia) in the tapping mode with a silicon cantilever of constant rigidity about 5 N/m. The images were obtained in at least three different points for each sample.

In order to estimate the resistance of films with the help of E6-4d megaohmmeter, flat gold-plated spring-return contacts 3×3 mm in size were made; they were clasped to the film manually.

Measurements of ion and electron conductivity of the films were carried out according to a specially developed procedure using E-7-11 instrument.

The films were deposited on a glass substrate by immersing and centrifuging; the latter procedure allowed us to improve the quality of films. It was established that in the case if the substrate is slowly pulled out of the solution the film is uniform. After depositing the wetting films, it was slightly dried under a heater at 120–140 °C, and then placed into a vertical furnace at the same level as that of a thermocouple controlling temperature through a laboratory autotransformer and a digital voltmeter. After pyrolysis of metal carboxylates for 3–5 min, the substrate with the oxide film was

cooled out of the furnace for 2 min and deposited the next layer.

For controllability of the technology, we developed a procedure to determine film thickness on the basis of disjoining pressure, which is measured from the surface tension of solutions.

RESULTS AND DISCUSSION

It was established that the thickness of wetting film reaches 77–91 nm. The thickness of the solid film was calculated form the data of thermal analysis. The minimal thickness was 10.7 for zinc oxide; the maximal one was 26.4 and 19.2 nm for tin oxide and indium oxide, respectively.

Tin carboxylate decomposes in three stages. At the first stage (120–300 °C) evaporation of solvents occurs (25 %); the second stage (300–370 °C) is accompanied by thermal decomposition of carboxylates and the loss of 40 % of the mass. At the third stage (370–470 °C), due to the combustion of the gas phase, 5 % more is lost. So, tin oxide is formed at a temperature of 400 °C, while the final formation of structure occurs at 470 °C (Fig. 1).

X-ray phase analysis of tin oxide samples showed (Fig. 2) that after pyrolysis at 400 °C the film has a crystal structure; however, broad peaks provide evidence of the small size of crystallites. It is known that the sensitivity of the film increases with a decrease in grain size. The intensity of XPA peaks increases with temperature rise, which is an evidence of an increase in the product crystallinity; the grain size increases, too, as XPA peaks get narrower. The structure of the film evolves during the synthesis; temperature rise promotes crystallization of SnO_2. The film annealed at a temperature within 300–350 °C is crystallized incompletely, while at higher temperature we obtain the materials composed of uniform particles with a size about 20 nm according to the AFM data (Fig. 3). This value may be somewhat overestimated because of a finite size of the cantilever tip. Thermal decomposition of tin carboxylate on a substrate leads to the formation of a large number of nucleation centres, which

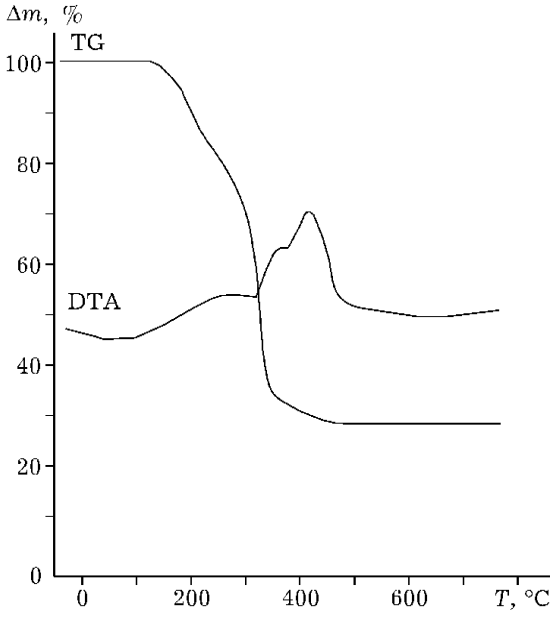

Fig. 1. Thermal oxidation of tin carboxylate.

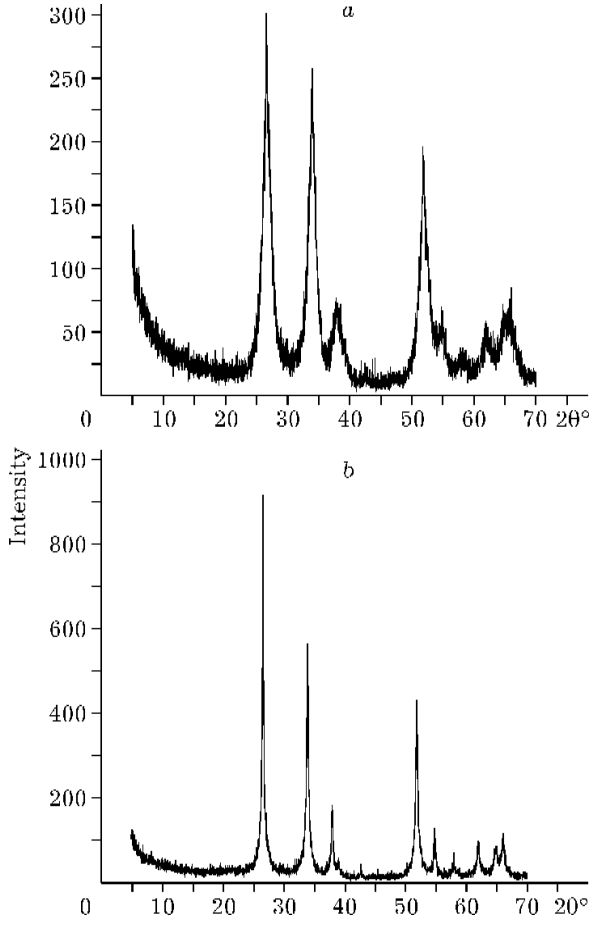

Fig. 2. X-ray phase analysis of SnO_2 films obtained after pyrolysis at 400 °C (*a*) and annealing at 500 °C (*b*).

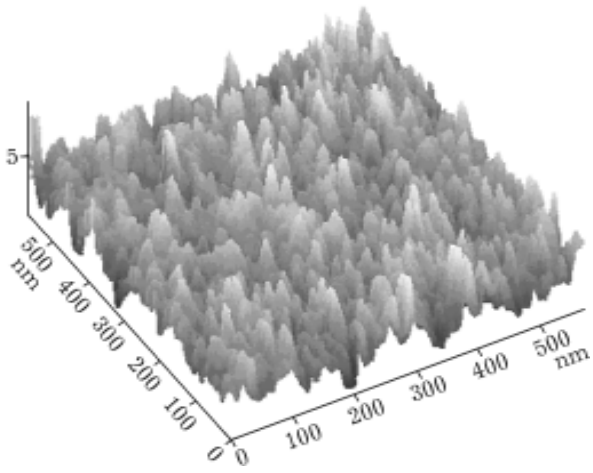

Fig. 3. AFM image of the surface of SnO_2 film.

promotes the formation of the nanocrystalline film structure after annealing at 300 °C.

For sensor materials operating on the basis of changes in resistance under exposure to gases, it is important to achieve the minimal resistance, which is determined by the crystal structure of the film, by the presence of extrinsic phases and doping elements. In order to determine optimal conditions for the synthesis of sensor materials, experiments were carried out to measure SnO_2 film resistance depending on synthesis temperature. The dependence of film resistance R on annealing temperature is shown in Fig. 4. Within temperature range 200–300 °C, the film contains the organic phase; resistance at a temperature of 250 °C is about 3 MW. Within temperature range 300–400 °C, the resistance of the film decreases because of the formation of the oxide layer, and reaches its minimal value (1.2–2.3 kW) at 350–470 °C, since, according to DTA, a solid tin oxide with defect-bearing structure is formed within this temperature range. Temperature rise to 470–550 °C is accompanied by structure stabilization; resistance increases to 0.5–1 MW as a consequence of an increase in grain size and possibly film crippling.

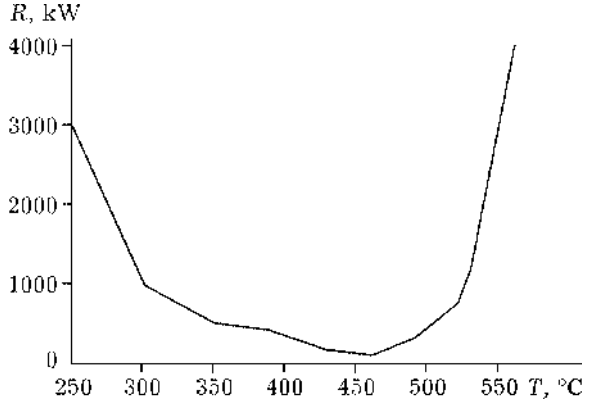

Fig. 4. Dependence of resistance R of SnO_2 film on a glass substrate on the synthesis temperature.

Changes in the surface layer of the films occur with time; resistance increases to 6–8 MW within 2–3 days. Isothermal annealing of aged films at 450 °C for 30 min resulted in a decrease in resistance to 1 MW, for 1 h to 0.6–0.7 MW.

An increase in film thickness due to an increase in the number of layers in wetting-pyrolysis cycles had no effect of film resistance.

The use of probes does not allow one to measure the conductivity of thin films correctly because one cannot eliminate the effect of the substrate and operator carrying out the mea-

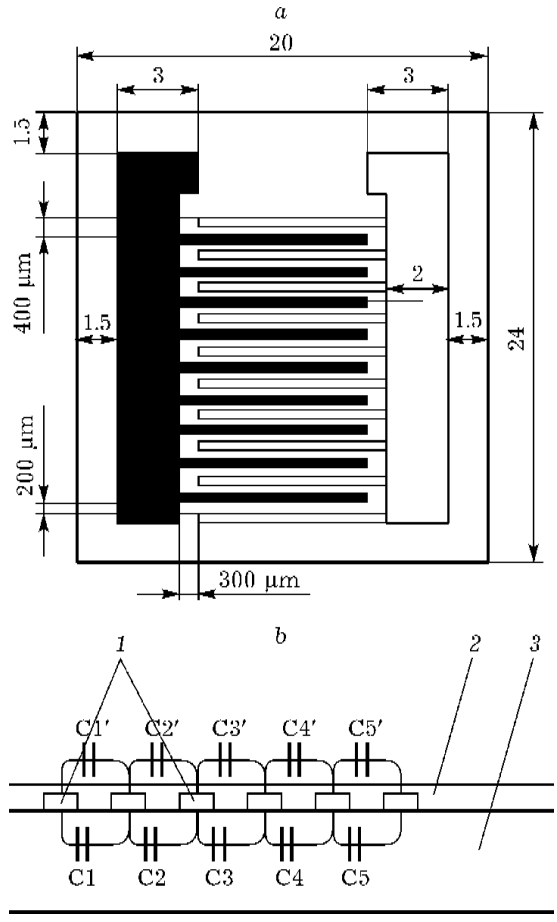

Fig. 5. Topological layout of the measuring capacitor (*a*) and a capacitor structure of the film under measurement (*b*): *1* – evaporated electrodes, *2* – ferroelectric film under investigation, *3* – substrate.

surements. We proposed an efficient method to measure the conductivity of thin oxide films with the help of a capacitor composed of two combs deposited on a substrate.

The layout of the capacitor is shown in Fig. 5, *a*. The film to be measured is deposited on the surface of the capacitor structure forming miniature capacitors between the electrodes of the comb (see Fig. 5, *b*). The measurements are carried out with a Wheatstone bridge in which a substrate without a film located in the same temperature field is switched in parallel to the film to be measured. In this case the bridge offset is due only to the film parameters. Such an arrangement allows us to decrease the effect of substrate parameters on measurement results optimally. The data obtained in measurements are shown in Table 1 and in Fig. 6.

So, since the dependence of resistance on temperature is observed only with alternating current, while no motion of charge carriers is observed at temperature increase with direct current, the electron conductivity is absent in SnO_2 films, while the ion conductivity increases with temperature rise to 400 °C. The conductivity of the film is maximal at 350 °C, then decreases (see Fig. 6). A decrease in the conductivity at high temperature is likely to be connected with the additional oxidation of the film under investigation.

It was established in the investigation of the dependence of changes in film capacity on temperature that the capacity of SnO_2 film decreases with temperature rise and approaches zero at 400 °C. This is also connected with an increase in film conductivity at increased temperature.

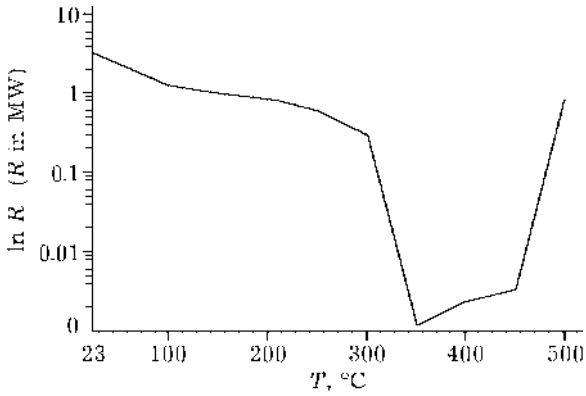

Fig. 6. Dependence of resistance on temperature at the measuring cell.

Certification of the sensor properties of tin dioxide films in gases was carried out by passing the gases synthesized in chemical reactions into a cell in which the film under measurement was placed. In order to obtain the necessary gases, we added the required amount of an acid to powdered or granulated Zn or $CaCO_3$ in a Würtz flask. The calculated amount of H_2 or CO_2 was obtained as a result of the interaction of these compounds.

The sample was placed in a quartz cell 20 mm in diameter and 300 mm long through which the air flow was passed. The flow rate (10–12 l/h) was driven by PRG-2B gas flow booster. The temperature dependence of resistance and adsorption response was studied

TABLE 1

Electric characteristics of SnO_2 film on measuring cell

Temperature, °C	Resistance, Ω		Capacity, F
	direct current	alternating current	
23	$3.12 \cdot 10^6$	$8.38 \cdot 10^6$	$2 \cdot 10^{-9}$
100	$1.20 \cdot 10^6$	–	$1.1 \cdot 10^{-9}$
150	$1.00 \cdot 10^6$	–	$0.15 \cdot 10^{-9}$
200	$0.80 \cdot 10^6$	–	$60 \cdot 10^{-12}$
250	$0.57 \cdot 10^6$	–	$30 \cdot 10^{-12}$
300	$0.29 \cdot 10^6$	–	$10 \cdot 10^{-12}$
350	$1.20 \cdot 10^3$	–	$0.1 \cdot 10^{-12}$
400	$2.30 \cdot 10^3$	–	–
450	$3.20 \cdot 10^3$	–	–
500	$1.00 \cdot 10^6$	–	–

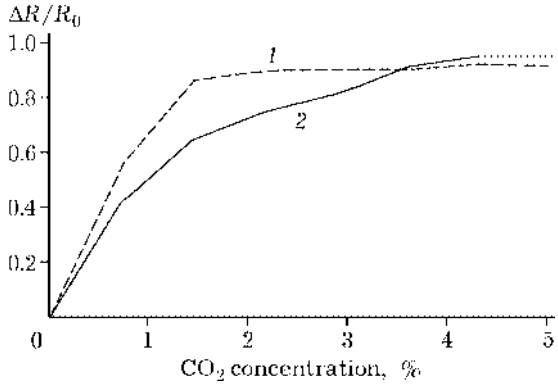

Fig. 7. Dependence of SnO_2 film resistance on CO_2 concentration at the measuring cell at 400 (*1*) and 350 °C (*2*). ΔR is the difference between the resistance of the film in oxygen and in CO_2 gas, R_0 is the resistance of the film under investigation without CO_2 at T = 350 °C.

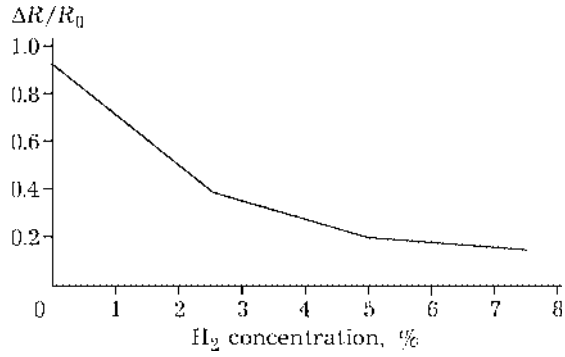

Fig. 8. Dependence of the resistance of SnO_2 film in H_2-containing gas on the concentration of H_2.

with the cell placed in a furnace. Gas mixed with air was supplied to the inlet of the measurement cell.

Measurements of the film resistance under exposure to CO_2 allowed us to obtain the dependence of SnO_2 film resistance on gas concentration at 350 and 400 °C (Fig. 7). One can see that a direct dependence of resistance on gas concentration is observed at a temperature of 350 °C. It is concluded that the sensor for CO_2 detection operates with the highest efficiency within temperature range 300–350 °C. At lower temperature the response of the sensor to CO_2 is unsatisfactory.

It was established in the experiments on H_2 detection that the resistance of films increases in the atmosphere of H_2 while in the atmosphere of CO_2 it decreases. Measurements with H_2 gas were carried out at a temperature of 300 °C. The dependence of sensor response to H_2 for SnO_2 films at different temperatures is shown in Fig. 8.

It is known that the resistance of sensors based on tin oxide changes in the presence of oxidant gases due to their adsorption or desorption [7]. The surface electron density changes in this process. The adsorbed gases are captured by grain boundaries, and the grain boundary potential barrier increases, which result in an increase in the resistance of the material. For reducing gases, adsorption results in the depletion of charge carriers, so resistance decreases due to the lowered potential barrier at grain boundaries.

Active sensor characteristics of tin oxide are due to non-stoichiometry and lack of oxygen atoms [7]. Along with Sn^{4+} ions, neutral tin oxide (bearing no charge) contains Sn^{2+} ions. Divalent tin ions Sn^{2+} act as electron donors in the reduction-oxidation process. With temperature rise, adsorption of the atmospheric oxygen takes place mainly on the surface of SnO_2 crystallites; oxygen accepts the electrons rendered by the semiconductor SnO_2 crystallites of n type. That is why oxygen atoms at the surface are ionized with the formation of anions O_2^-, O^-, O^{2-}. These anions form active chemical centres providing sensor properties to the structure.

In the absence of a reducing gas, electrons leave the bound states during the reduction of molecular oxygen thus forming O^- ions, so SnO_2 gets high resistance. Reducing gases, such as hydrogen, petrol vapour, react with oxygen anions O^-, and the electron return to the bound states, which results in an increase in the resistance of films.

CONCLUSIONS

So, tin oxide films obtained with the help of a simple and cheap technology exhibit good sensor properties. The use of a solution-involving technology helps one to obtain a nanocrystalline material. In addition, it is possible to obtain nano-sized coatings uniform in morphology, on the substrates of different shapes and sizes. The optimal conditions of obtaining the films with the maximal sensitivity to carbon dioxide, hydrogen and ethanol were obtained.

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