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Sensitivity to Ethanol Vapour of Thin Films SnO_2 Doped with Fluorine

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Abstract

Tin dioxide thin films were obtained by centrifuging. Annealing of samples was carried out in a muffle furnace at a temperature of 400 °C for 15 min, 3, 6 and 12 h. The surface resistance of the films was measured by four-force method. The sensitivity to ethanol vapour was determined by experimental setup that allows measurements in the range from room temperature to 300 °C. There is a change in the acidity of the solution with the addition of ammonium fluoride. To take into consideration this change in acidity, three batches of solutions were prepared: one example without additives, another one – with the addition of ammonium fluoride and the last one – with the addition of ammonium hydroxide. Films synthesized from a film-forming solution containing NH_4F have less resistance than films obtained from solutions that do not contain ammonium fluoride. This confirms the presence of fluorine ions in the films as additional sources of free charge carriers. It is found that the pH-indicator of the film-forming solution does not affect the surface resistance of the synthesized SnO_2 films. Annealing of fluoride doped films leads to an increase in surface resistance by two orders of magnitude, which is associated with the removal of fluorine from the films and the formation of a large number of defects. Further annealing leads to a decrease in surface resistance, which seems to be associated with a decrease in defects. It is shown that the change in the hydrogen index of the film-forming solution leads to the formation of films with a thermally stable sensitivity to ethanol vapour.

1. Introduction

Tin dioxide films have good adhesion to the glass surface, high electrical conductivity, transparency (80–90%), mechanical strength and chemical resistance [1–5]. These properties allow them to be used as transparent conductive coatings. Glass with this coating is used for installation in aircrafts and ship cabins, operating in extreme cold, because, passing through the film current capacity of 1 W/cm^2, you can heat the glass to a temperature of 200–400 °C, which allow us effectively deal with icing and fogging.

Tin dioxide films are also intensively used as a sensor sensing element for the determination of various gases in atmosphere [6–9]. The principle of operation of these sensors is based on the modulation of the near-surface region of the space charge and the change in the electrical resistance of the film crystals during the adsorption of gas molecules. In order to occur the physicochemical processes on the surface of the sensitive layer quickly enough, providing a response time of a few seconds, the sensor is heated to a temperature of 100–450 °C, which «activates» its surface. Sensors are used by environmental services, chemical enterprises, oil and gas industry factories – wherever it is necessary to express determination of the concentration of gases such as propane, methane, hydrogen, ethyl alcohol vapour.

The most promising things for development in our days are sensors for ethanol vapour. Since ethanol is not only a highly flammable liquid (ignition temperature is 18 °C) [10], but also a toxic substance, it suppresses the functions of the central nervous system, weakening the physical and mental abilities of the person. The average lethal concentration of ethanol in the working area is more

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than 50000 mg/m^3, the maximum permissible concentration (MPC) is 1000 mg/m^3 [11]. Checking the concentrations of components of a few tenths of MPC is necessary not only for determination the degree of intoxication, but also for the diagnostics of diseases, for example, diabetes [12].

The aim of this work was to analyze the effect of isothermal annealing (400 °C) on the surface resistance and adsorption sensitivity to ethanol vapours of tin dioxide films doped with fluorine ions.

2. Experimental

The experimental part of work used substances that have «especially clean» qualification of «Labhimprom» company (Kazakhstan) production.

Thin films of tin dioxide were obtained by Sol-gel method. The solutions were applied to the surface of the preliminarily purified glass slide fixed on a specially designed table of the rotor of the central centrifuge. After that, the sample was turned at a velocity of 3800 rpm for 3–5 sec, with the aim to remove the excess solution from the substrate surface. The substrate with the remaining thin layer of the solution was heated by infrared radiation up to 80 °C for 1–2 min to vaporize the solvent. The dried sample was annealed in a muffle furnace for 15 min at temperature 400 °C. The cycle was repeated after cooling process. The fifteen layers were applied altogether. The film thickness was estimated by the change in the sample weight. The final thickness was about 250 nm.

Three batches of samples were made to evaluate the effect of fluorine ions on the surface resistance and adsorption sensitivity.

The first batch was made from anhydrous $SnCl_4$ solution. The 95% ethanol was used as a solvent. The pH indicator 0.18 was determined after maturation of the solution, which lasted more than six hours, and increased acidity indicates the release of HCl during the dissolution of $SnCl_4$.

In the film–forming solution a fluoride agent-NH_4F was added in the manufacture of the second batch. The ratio of tin ions to fluorine ions was 10/4. NH_4F crystals were dissolved during 2 h stirring at a speed of 140 rpm and parallel heating at a temperature of 35 °C on the orbital rotation shaker LAB-PU-01. The acidity of the final solution was controlled by pH-Meter (pH-150M) and it was pH = 1.80.

The change in the acidity of the solution is due to the hydrolysis of ammonium fluoride. According to the scheme:

$$NH_4F + H_2O \rightarrow NH_4OH + HF$$

A weak base of NH_4OH and strong acid HF are formed. The total acidity of such a solution is «acidic», that is, below 7. What we observe. However, the presence of NH_4OH in the solution leads to a change in pH from 0.18 to 1.8.

Since the acidity of the solution decreased significantly after the addition of ammonium fluoride and became close to the pH of the tin acid deposition (pH = 2.0), the third batch of samples was made. This batch was obtained from a solution with pH = 1.80, but containing no fluorine ions. The NH_4OH was selected as a reagent, increasing the basic properties of the solution, because heating breaks down into products ($NH_3 + H_2O$) which are easily removed from the film. Alcoholic ammonia solution was added dropwise to the matured alcoholic solution $SnCl_4$ was added with constant stirring until pH = 1.80.

The final concentration of tin ions in solutions was 0.13 mole/l.

$SnCl_4$ forms gel-like tin acid $xSnO_2 \cdot yH_2O$ in contact with water, and easily removes hydrochloric acid HCl from the film, in accordance with the reaction:

$$xSnCl_4 + (y + 2x)H_2O \rightarrow xSnO_2 \cdot yH_2O + 4xHCl$$

Drying and subsequent annealing of the films removes water from tin acid.

$$xSnO_2 \cdot yH_2O \rightarrow xSnO_2 + yH_2O$$

The films obtained in this way consisted of amorphous SnO_2 and did not contain other tin oxides [13].

Annealing of samples was carried out in a muffle furnace SNOL 6.7/1300 at a temperature of 400 °C for 3, 6 and 12 h.

The surface resistance of the films was measured by four-force method. The sensitivity to ethanol vapours was determined by the experimental setup that allows measurements in the range from room temperature to 300 °C.

3. Results and discussion

3.1. Surface resistance

The surface resistance of thin SnO_2 films was determined by 5 measurements with confidence probability of P = 0.95 and Student's coefficient of $t_{0.95.4}$ = 2.776. The results of measurements are presented in Table 1.

Table 1
Surface resistance of SnO_2 films after isothermal annealing

Composition of film-forming solution	Surface resistance of films after annealing at 400 °C			
	15 min, kOm/square	3 h, kOm/square	6 h, kOm/square	12 h, kOm/square
$SnCl_4$ in ethanol	15.6±1.3	90±10	120±10	245±38
$SnCl_4$ in ethanol + NH_4F	6.7±0.9	912±77	834±88	522±125
$SnCl_4$ in ethanol + NH_4OH	15.4±1.6	63±8	150±15	1450±49

One can be see from Table 1 that films synthesized from a film-forming solution containing NH_4F have less resistance than films obtained from solutions that do not contain ammonium fluoride. This confirms the presence of fluorine ions in the films as additional sources of free charge carriers. The surface resistance of films synthesized from solutions without additives and with addition of NH_4OH differs within the accuracy of the measurements. Consequently, the pH of the film-forming solution does not affect the surface resistance of the synthesized SnO_2 films.

Three-hour annealing at 400 °C leads to an increase in the surface resistance of films doped with fluorine by two orders of magnitude. The surface resistance of fluorine-free SnO_2 films also increased, but not so much. The increase in resistance of fluoride doped films is probably due to the removal of fluorine from the films and the formation of a large number of defects. Further annealing leads to a decrease in surface resistance, which indicates a decrease in the concentration of defects in these films.

The surface resistance of films without fluorine ions increases with the annealing time. The spread of surface resistance values increases also, that is the heterogeneity of the films in the structure increases, micro-cracks and other defects appear.

3.2. Film sensitivity to ethanol vapor

The sensitivity of synthesized thin SnO_2 films to ethanol vapour was studied during two stages. At the first stage the temperature, at which the maximum sensitivity of the studied film to ethanol vapour is achieved, was determined. At the second stage at the found temperature, the change in the resistance of the film was measured under the influence of different concentrations of ethanol vapour.

The sensitivity of tin dioxide films was defined as in research work [13]. Figure 1 shows the temperature dependence of the sensitivity of SnO_2 thin film to ethanol vapours (1 mg/l). It is seen from Fig. 1 that the maximum sensitivity of ethanol vapour shifted from 230 °C with increasing duration of annealing of the films to 15 min and it leads to 260 °C with annealing for 12 h. It is also seen from the figure that with the increase of annealing duration, the sensitivity to ethanol vapours with the concentration of 1 mg/l of films synthesized from the $SnCl_4$ solution in ethanol without additives changes (Fig. 1a). There is a significant increase in the sensitivity of the obtained films after annealing at 400 °C for 3 and 6 h (curves 2 and 3 of Fig. 1a). After annealing for 12 h (curve 4 of Fig. 1a), sensitivity decrease is observed, which can be caused by a significant increase in crystallite sizes from ~6.5 to ~11 nm [14].

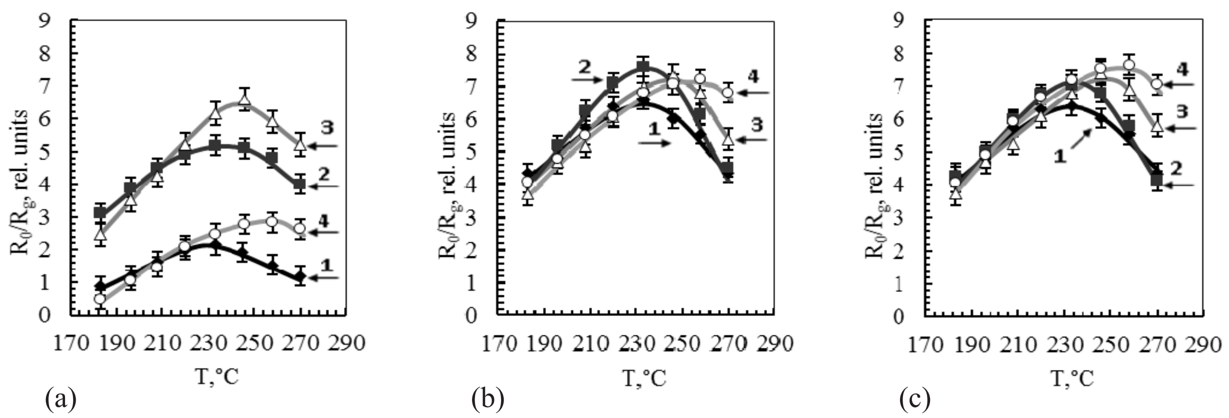


Fig. 1. Temperature dependence of sensitivity to ethanol vapour (1 mg/l) of thin SnO_2 films: (a) – synthesized from solution of $SnCl_4$ in ethanol; (b) – with the addition of NH_4F; (c) – with the addition of NH_4OH. (1 – film sensitivity after deposition; 2 – after 3 h of annealing; 3 – after 6 h of annealing; 4 – after 12 h of annealing).

Table 2

Response time of SnO_2 films to the presence of 1 mg/l ethanol vapour

Composition of film-forming solution	The response time of the films after annealing			
	15 min	3 h	6 h	12 h
$SnCl_4$ in ethanol	< 4 s	~2 s	< 2 s	~1 s
$SnCl_4$ in ethanol + NH_4F	< 2 s	~1 s	~2 s	< 2 s
$SnCl_4$ in ethanol + NH_4OH	< 2 s	~2 s	~1 s	< 2 s

For the films synthesized from solutions of tin tetrachloride in ethanol with addition of NH_4CI and NH_4OH, the maximum sensitivity to ethanol vapour is also shifted by 30 °C to higher temperatures. Annealing of films within 3 h leads to an increase in sensitivity, but not as significant as that of films, obtained from solutions without additives. It should be noted that the sensitivity of these films to ethanol vapour with a concentration of 1 mg/l at a substrate temperature of 230–240 °C with a further increase in the annealing time varies within the accuracy of the measurements.

The response time of the films to ethanol vapours was defined as in research work [15].

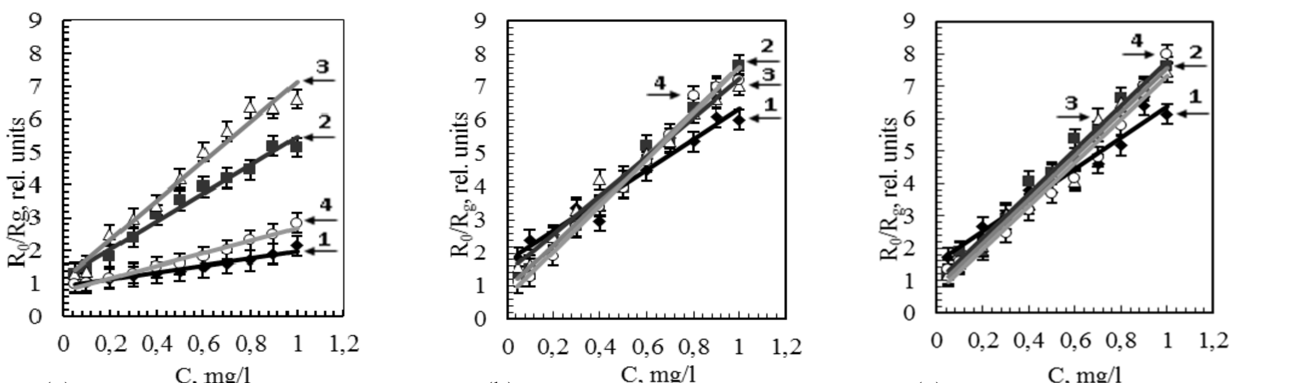
Table 2 shows the response time of SnO_2 thin films to the presence of 1 mg/l ethanol vapour. According to Table 2, it can be seen that for SnO_2 films obtained from solutions without additives, with an increase in the annealing time, the response time decreases, which is associated with the formation of micro-cracks, leading to an increase in the surface on which the interaction with the analyzed gas occurs. The response time of films synthesized from solutions with the addition of NH_4F and NH_4OH, with increasing annealing time varies slightly and ranges within 1–2 sec.

Figure 2 shows the dependence of the sensitivity of SnO_2 films on the concentration of ethanol vapour.

It is seen from Fig. 2 that for films synthesized from $SnCl_4$ solution in ethanol without additives (Fig. 2a) there is an increase in sensitivity to ethanol vapour with an increase in the annealing time of samples up to 6 h and a decrease in annealing from 6 to 12 h.

Films obtained from solutions with addition of NH_4F and NH_4OH, immediately after synthesis are highly sensitive to ethanol vapour Fig. 2b and c. Three-hour annealing results in a slight increase in sensitivity, and further annealing does not lead to noticeable changes in sensitivity. A three-hour film annealing leads to the removal of solvent residues and reaction by-products (HCl, H_2O, HF, NH_4OH) from the films. Microcracks appear on the surface of the films. This increases the contact surface between tin dioxide and the gas to be detected – sensitivity increases. An increase in the duration of annealing does not lead to a further increase in sensitivity to ethanol vapor, since an increase in cracks leads to a breakdown in contact between the tin oxide particles.

Moreover, the sensitivity of these films varies within the accuracy of the measurements. Consequently, the increase in the adsorption sensitivity to ethanol vapour is associated with a change in the hydrogen index of the film-forming solution, which leads to the formation of a more porous film structure.



(a) (b) (c)

Fig. 2. Dependence of sensitivity of SnO_2 films on the concentration of ethanol vapour: (a) – synthesized from solution of $SnCl_4$ in ethanol; (b) – with the addition of NH_4F; (c) – with the addition of NH_4OH. (1 – film sensitivity after deposition; 2 – after 3 h of annealing; 3 – after 6 h of annealing; 4 – after 12 h of annealing).

4. Conclusions

A comparative study of the isothermal annealing (400 °C) effect on the surface resistance and adsorption sensitivity to ethanol vapours of tin dioxide films doped with fluorine ions and films obtained without the addition of a fluorinating agent was carried out.

An increase in the surface resistance from 6.7 ± 0.9 kOm/square to 912 ± 77 kOm/square after 3 h of annealing of fluorine doped films was found. The increase in surface resistance by two orders of magnitude is probably due to the removal of fluorine from the films and the formation of a large number of defects. A decrease in point defects with an increase in the annealing time leads to a decrease in the surface resistance of these films from 912 ± 77 kOm/square to 522 ± 125 kOm/square.

It is shown that films, obtained from solutions with pH = 1.80, have a more thermostable sensitivity to ethanol vapor than films, obtained from a solution with pH = 0.18.

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