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INTERACTION SnO_2 THIN FILM WITH ORGANIC VAPOURS IN NEUTRAL ATMOSPHERE

The influence of oxygen and organic vapors on SnO_2 thin films conductance has been studied in different conditions. Gas sensitivity for different vapors was researched under different temperatures. It was pointed that oxygen and water presence influenced the sensor sensitivity. The mechanism for interaction of SnO_2 surface with ethanol mixture was proposed. Oxygen role in such processes was discussed. To determine structural peculiarities XRD experiments were provided.

INTRODUCTION

Gas semiconductor sensors have been used to solve gas analysis problems since the sixties. Mostly, thick film sensors were used for these purposes. It have been developed and provided technological details of preparation, testing and improvement these designs. The most widespread materials for sensors were metal oxides such as Fe_2O_3, NiO, TiO_2, and so on. The obtained samples had good stability, high sensitivity and selectivity. Afterwards, there were the attempts to improve the sensor properties by adding different dopants [1].

One of disadvantages in thick film gas sensors is long response time. It's affected by film thickness. There are two processes taking place on surface: adsorption and diffusion of gas species. Indeed, the last is responsible for the response time.

From the eighties till nowadays new trend of sensors based on thin film active layers is developing. The most useful for gas sensors is SnO_2. Sensors, that can be easily prepared and show good sensitive characteristics.

Among many applications of chemical sensors it's worth to pay attention on toxic and explosion vapors control. In industry, especially in technological processes this factor must be taken in account.

This paper describes sensitive parameters of SnO_2 thin films, exposed in different atmospheres,involving mentioned species

EXPERIMENTS

SnO_2 thin films were deposited on alumina substrates (XC 22) from $SnCl_4$-ethanol solution with electrospray pyrolisis method [2]. The deposition was made under constant substrate temperature, reached 450 °C. The principal scheme of the sample is given in Fig. 1. Pt contacts were attached on the substrate with high temperature vacuum evaporation. The surface area and thickness of SnO_2 thin film were 5×7 mm^2 and 200~350 nm respectively.

The sensor has been attached to a resistance heater. The heater can keep the temperature within the range 100—450 °C. Both the sensor and the heater were assembled in the operating chamber, 30 cm^3 volume, which was connected with flowmeter. By means of switching taps one could change atmosphere types from the vapor contained to air.

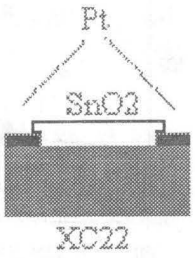

Fig. 1. Scheme of the sample

The sensitive characteristics were measured under different conditions. The sensor has been tested in different atmospheres such as air + acetone, air + ethanol and air + water. After these experiments the sensor was exposed in Ar atmosphere and all experiments were repeated. All experimental data were investigated under constant species concentration, equaled 267 ppm.

EXPERIMENTAL RESULTS AND DISCUSSION

In figures 2—5 there are shown temperature dependences of sensitive an kinetic characteristics of the sensor. As one can see, under oxygen presence the films showed little sensitivity to all ethanol species (fig. 2). More over, nor water neither acetone were detected under oxygen presence. Otherwise, after cleaning surface from oxygen sensor became sensitive to acetone and water. The sensitivity to ethanol raised several times higher. At the same time, response characteristics and maximum sensitivity temperature shifted into range of smaller values from 390—410 to 350—380 °C. Interaction between SnO_2 surface and organic vapor species were studied in [3, 4]. That was verified that the interaction

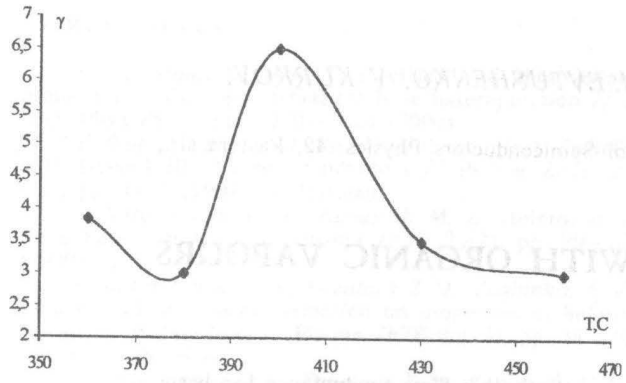

Fig. 2. Temperature dependence of gas sensitivity in air + ethanol atmosphere

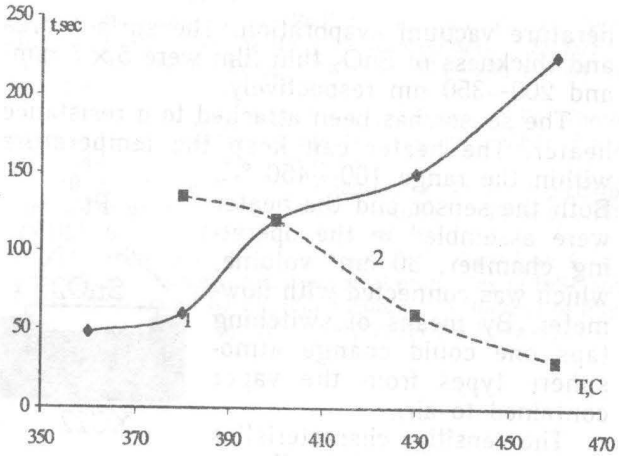

Fig. 3. Temperature dependences of:
1 — response time; *2* — desorption time in air + ethanol atmosphere

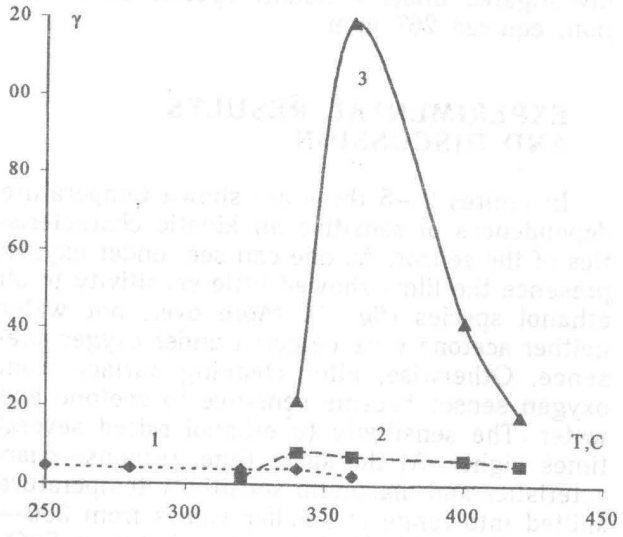

Fig. 4. Temperature dependences of gas sensitivity in:
1 — Ar + water; *2* — Ar + acetone; *3* — Ar + ethanol atmospheres

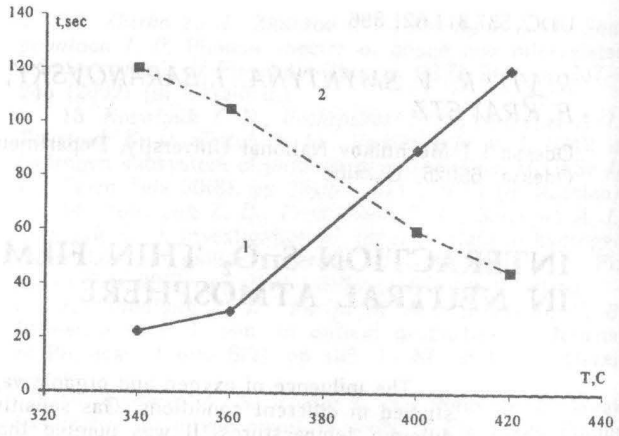

Fig. 5. Temperature dependences of:
1 — response time; *2* — desorption time in Ar + ethanol atmosphere

came via chemisorbed surface oxygen atoms on the following scheme:

$$R + O^- \rightarrow RO + e,$$

which led to conductivity increase. In [2] it was shown that sensitivity value of 2 μm SnO_2 films to ethanol highly increased under oxygen presence and declined in Ar atmosphere.

Results of this paper are the opposite to experimental data obtained in [2]. We appeared that sensitivity to ethanol (fig 4, curve *3*) was higher in Ar-atmosphere than in oxygen (fig 2). As oxygen atoms were desorbed from the film surface by means of high temperature calcinations of the sample in Ar before measurements, ethanol molecules couldn't take part in reaction due to the above described scheme. So, there must be another mechanism of interaction between surface and gas molecules.

One of determinative factors is the film thickness.

The mechanism of interaction between SnO_2 surface and reducing gas molecules in neutral atmospheres and vacuum was discussed in [4]. The proposed mechanism of interaction was the following. Under high temperatures, surface reactions can take place:

$$SnO_2 \rightarrow Sn^{4+} + 2O_\ell^{2-}$$
$$O_\ell^{2-} + R \rightarrow RO + V_{O_2^-},$$

where O_ℓ^{2-} — lattice oxygen atoms, $V_{O_2^-}$ — oxygen vacancies. Oxygen vacancies appeared as interaction result, act as donors [2]. Activation temperature of these donors is about 280 °C [3]. On the base of the above-mentioned verification the sensitivity behavior can be explained.

The sensitivity raises from 300 °C. At the range of 320—340 °C, the rate of electron transfer from donors to conductive band is the highest. However, with temperature increasing there may be desorption of O_ℓ^{2-}, responsible for the sensitivity fall. On the other hand, it is possible that reaction comes via Sn^{4+} states. But it flows

slower, and as result, adsorption time increases (fig. 5 curve *1*).

Through comparison gas sensitivities of figures 2 and 4 one can say that oxygen presence changes reaction rate. Mechanism of reaction between surface chemisorbed oxygen atoms and ethanol was previously well-described in [4] by the following reactions [4, 5]:

$$O_2^- + e \rightarrow 2O$$

$$R + O^- \rightarrow RO + e.$$

Comparing results presented in this paper, one can say that chemisorbed oxygen influences negatively on gas sensitivity. Two reactions can flow on the film surface:

1. Neutral oxygen reaction with oxygen vacancies: $2V_{O^-} + O_2 \rightarrow 2O^-$.

2. Appearance of O^-: $O_2 + 2e \rightarrow 2O^-$.

It leads to conductivity decrease.

The researched films showed rather good selectivity (fig 4). The ruling factor of selectivity was temperature.

The sensitive features of the films may be affected by their surface structure. The thickness

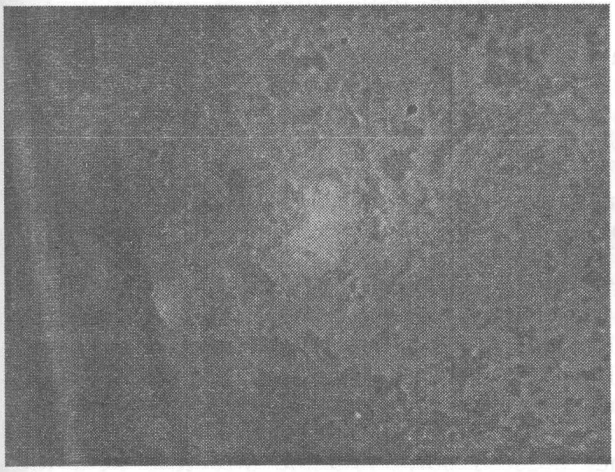

Fig. 6. Image of the film surface before calcinations

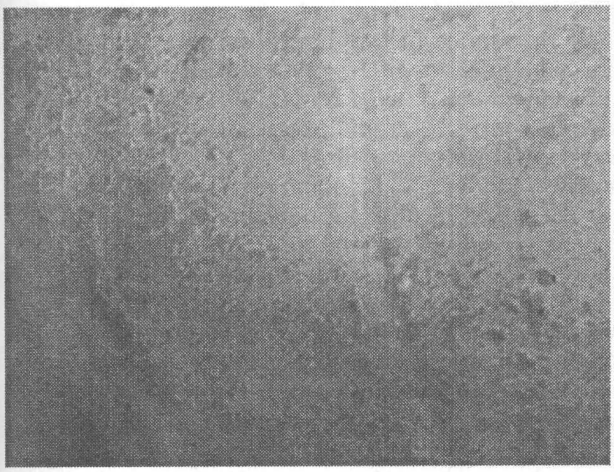

Fig. 7. Image of the film surface after calcinations

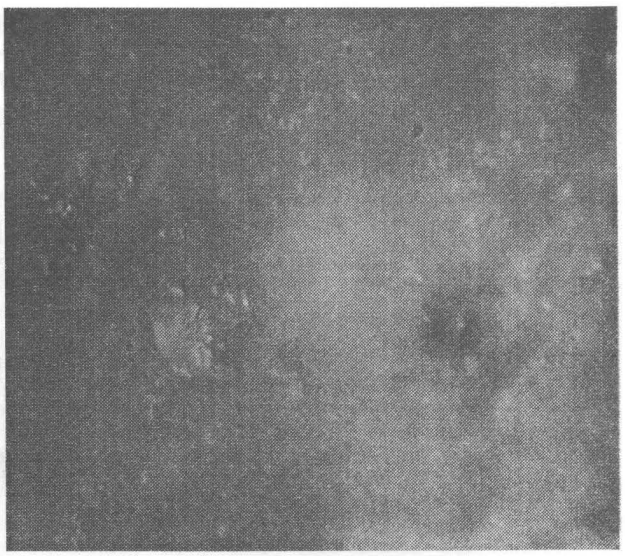

Fig. 8. Image of the film substrate surface

variation can lead to surface reaction activity change. Structural analysis of the films was provided by means of microscope MIM-8M (enlargement 800 times). All the made images in polarized light are shown in figures 6—8. It was defined that the film consists of small crystallites with size 0,2—0,8 μm (here is only evaluation of plane dimensions of crystallite without taking in account the film depth). This fact is proved by the large value of light places. A substrate has many regions of tense. Its crystallite size is much bigger than the film one. After operation, the film becomes more homogenous but its crystallite size doesn't change too much.

CONCLUSION

Temperature dependencies of gas sensitivity to different gases were measured. Sensor showed good sensitivity and selectivity to ethanol in Ar atmosphere. The selectivity ruling factor is an operating temperature. Oxygen adsorption decreased sensitivity to ethanol. Surface reaction doesn't change the film surface structure.

References

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