

SEMICONDUCTOR SENSORS FOR QUICK ANALYSIS OF GASEOUS POLLUTANTS IN THE ATMOSPHERE

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The results of investigation into some properties of thin SnO₂ films aimed at the development of sensitive elements for an analysis of carbon monoxide and hydrocarbons are presented in this paper. The production technology and temperature dependence of film conductivity have been studied. It has been shown that combination of volume doping with silver and surface doping with platinum of the films produced by cathode sputtering allows one to decrease the working temperature of sensors and to extend the range of the measurable values of the concentration of investigated gases. The design of a small-size CO analyzer is described.

The problem of ecological monitoring of gaseous atmospheric pollution from industrial emissions stimulated both the development of remote sensing techniques and investigations aimed at the development of relatively cheap and technically reliable methods for analysis of gaseous pollutants harnessing different physicochemical processes of gas interaction with matter.

One unique property of metallic oxide semiconductors, for example, SnO₂, ZnO, and TiO₂, is the possibility of reversible chemisorption of active gases CO, H₂S, CH₄, and so on at their surface accompanied by the change of the electrical conductivity of semiconductor. This fact is of interest to investigators (see Refs. 1–11).

Let us consider the chemisorption phenomena in the example of the *n*-type semiconductor characterized by the oxygen deficit. Oxygen is adsorbed into the surface of semiconductor in air. Having captured electrons, oxygen changes to the state O⁻ thereby decreasing the number of free charge carriers. The space charge region (SCR) depleted of free electrons is formed and conductance of semiconductor decreases. When semiconductor is in the investigated gas, it is adsorbed into the semiconductor surface having captured the preionisorbed oxygen O⁻. The decrease of the adsorbed oxygen concentration leads to narrowing of the SCR and increasing the conductance of the sensitive element.

For example, CO is oxidized to CO₂, which desorbs from the surface. Methane adsorption is accompanied by molecular dissociation CH₄ ↔ CH₃ + H, and then the methyl group CH₃ and H₂ atom interact with oxygen adsorbed into the semiconductor surface. The above-considered phenomena are widely used abroad for the development of the sensitive elements of gas sensors on the basis of metallic oxide semiconductors, because under certain conditions the charge concentration varies practically linear with the gas concentration in the medium to be analyzed.

The data on some semiconductors and conditions at which they can be used for detection of different gases are summarized in Table I.

TABLE I.

Gas to be analyzed	Sensitive element	Working Temperature, °C	Reference
Carbon monoxide CO	ceramic SnO ₂ : Sb ₂ O ₃ +Pt,	10–100	9
	filmly SnO ₂ : Cu,	250–450	3
	ceramic ZnO:Pt	250–400	9
Nitrogen oxide NO _x	filmly SnO ₂ ,	400	9
	ceramic Al ₂ O ₃ + V ₂ O ₅ ,	450–500	6
Hydrogen sulfide H ₂ S	ceramic SnO ₂ + ZrO ₂ + Al ₂ O ₃	600	6
	ceramic SnO ₂ + ZrO ₂ ,	175	10
	ceramic SnO ₂ + Sb ₂ O ₃ ,	200	10
	Ca and Mg oxides, filmly SnO ₂ :Al ₂ O ₃	150	7
Hydrocarbons (methane CH ₄ , propane C ₃ H ₈ , izobutane C ₄ H ₁₀)	ceramic SnO ₂ (ZnO):Cr, Ru	500	6
	filmly ZnO:Jn	410	9
	ceramic SnO ₂ :Pt(Pd)	500	6
Ethanol vapor C ₂ H ₅ OH	thin filmly SnO _x :Pd, Au	250	9
	ceramic SnO ₂ :Mg(NO ₃) ₂ , CaCl	450–500	9

Industrial technology of development of sensitive elements and series production of such devices are lacking in Russia, although such investigations are carried out in a number of organizations (see Refs. 5 and 7–10) and are of interest for atmospheric optics applications, for example, for the development of remote sensing methods for ecological monitoring of gaseous environmental pollution. Small-size high-sensitive semiconductor sensors can be irreplaceable for

lidar complexes as reference devices in the process of lidar calibration as well as for measurement of local atmospheric pollution in the ground layer, including initial data acquisition in the construction of the vertical profiles of gas concentration, etc.

The results of investigations aimed at the development of sensitive elements based on SnO_2 thin films for an analysis of carbon monoxide and hydrocarbons are presented in this paper, and the design of a small-size CO analyzer is described.

PROPERTIES OF SENSITIVE ELEMENTS AND THEIR PRODUCTION TECHNOLOGY

Because the process responsible for the change in conductance occurs on the surface of the sensitive element, thin films from metallic oxides doped with different additions (see Table I) have had their greatest impact.

We produced SnO_2 films using the group technology of microelectronics which provided the high productivity and allowed us to produce several sensitive elements with the reproducible parameters in one technological cycle.

We used standard polycore plates 500 μm thick having polished and grinded sides as a substrate. Pectinated electrodes for the sensitive element and heater were produced by sputtering of solid platinum layer with subsequent photolithographic etching of the layout on the polished and grinded sides of the substrate. Sensitive SnO_2 film was sputtered in the oxygen-argon plasma. Then plates containing six sensors were cut by laser and annealed for three hours at 600°C in order to stabilize the sensor parameters.

Usually SnO_2 sensors for CH_4 should be heated up to 500°C. We have succeeded in the decrease of the working temperature down to 350–400 °C by doping of a film volume with silver with subsequent sputtering of a thin semi-transparent platinum layer which played a role of catalyst in chemical reactions taking place on the semiconductor surface in the process of CH_4 adsorption.

The decrease of the working temperature and increase of the sensitivity of sensors for CO were reached by the volume doping of SnO_2 films with copper and surface doping with platinum.

The investigation of the volt-ampere characteristics (VAC) of the SnO_2 films has shown that they are ohmic in the temperature interval from room temperature to 450°C. This means that energy barriers higher than KT (where K is the Boltzmann constant and T is the temperature) are absent in the grain-boundary regions. The temperature dependence of film resistance was investigated for more detail study of the film conductance. Typical $\ln R$ dependence on $10^3/T$ for films doped with silver is shown in Fig. 1. The resistance decreases as the temperature increases from 20 °C to ~260–280°C, with two linear portions being identified in the curve.

The activation energy calculated with the use of experimental data in the temperature range 20–180°C (the portion of the curve from A to B) constitutes $E_{a1} = 0.18$ –0.28 eV, which corresponds to the energy of ionization of donor levels in SnO_2 ($E_D < 3$ eV). When the temperature is 180–280°C (the portion of the curve from B to C), the activation energy is $E_{a2} \approx 0.58$ –0.62 eV. We may assume that ionization of deep levels due to silver occurs. However, their unambiguous identification is difficult, because the data on energy levels initiated by silver in the forbidden SnO_2 zone are unavailable. An analysis of our data shows

that the thickness of the SCR is less than the film thickness and the film conductance is primarily determined by the volume conductance of the layer undepleted to charge carriers.

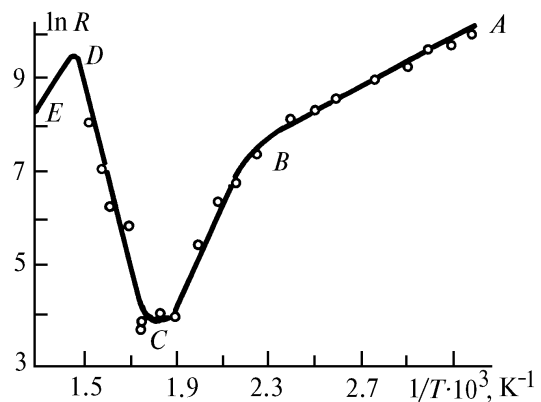


FIG. 1. Temperature dependence of the SnO_2 : Ag, Pt film resistance upon heating.

The increase of the SnO_2 film resistance is observed in the temperature interval 300–400°C (the portion of the curve from C to D in Fig. 1) due to evaporation of water (see Ref. 2).

The relative variation of the sensor resistance $\Delta R/R$ by action of the mixture of air and methane as a function of the temperature of sensitive element and of the methane concentration is shown in Figs. 2 and 3. The general behavior of these curves agrees with the data from Refs. 4 and 11. The $\Delta R/R$ dependence on the temperature is a curve with maximum; however, this maximum occurs at $T = 450$ –460°C for SnO_2 films doped with silver, while for ceramic SnO_2 sensors doped with platinum it occurs at $T = 500$ °C (see Ref. 11).

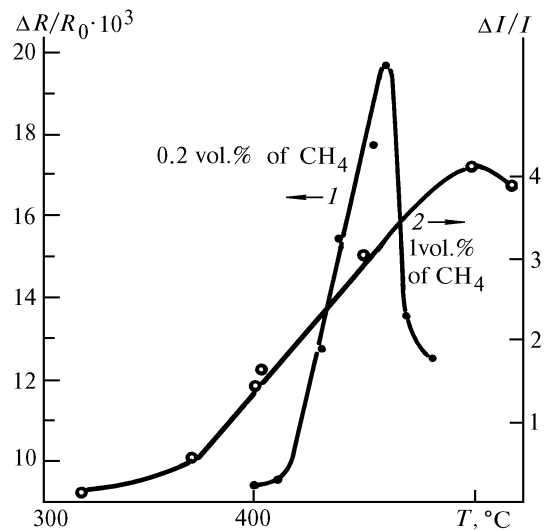


FIG. 2. Relative variation of resistance of the SnO_2 : Ag, Pt film as a function of temperature by action of the mixture of about 0.2 vol. % of CH_4 and air (curve 1). Data from Ref. 11 shown for comparison were measured with the sensor based on ceramics (curve 2) by action of the mixture of 1 vol. % of CH_4 and air by the method of measuring the relative variation of the current $\Delta I/I$ in bridge circuit.

The concentration sensitivity of the examined sensors points to the signal saturation at rather high content of methane in air (0.2–0.4 vol. %). For the SnO₂ films subject to surface doping with palladium the saturation was observed at 200 ppm of CH₄ in air,⁴ what makes an analysis of practically important values of concentration close to dangerously explosive ones (0.2–0.5 vol. %) difficult.

Thus, the combination of volume doping with silver and surface doping with platinum of the SnO₂ films produced by cathode sputtering allows us to decrease the working temperature and to extend the range of measurable values of concentration of examined gases in air when measurements are carried out without rarefication of a sample.

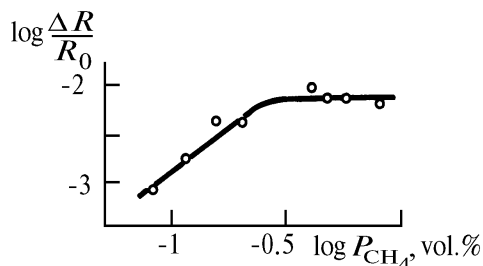


FIG. 3. Relative variation of the SnO₂:Ag, Pt film resistance by action of methane—air mixture as a function of the CH₄ concentration. Measurements were performed at a temperature of 450°C.

ANALYZER DESIGN

A small-size analyzer developed on the basis of the above-considered properties of semiconductors comprises the following components (see Fig. 4): the system of air intake from the volume being analyzed 1, 2, and 3; the device for measurement and output of information 4; and, the power supply unit 5.

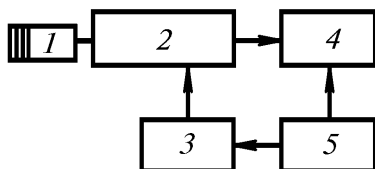


FIG. 4. Block diagram of gas analyzer.

The system of air intake is used to pump the controllable volume of examined gas through the sensitive element. It consists of a flexible tubing and filters 1 intended for purification of a medium from aerosol component and water vapor, the sampling aspirator 3, and batcher of original design 2. Its scheme is shown in Figs. 5 a and b.

The sampling aspirator is the small-size compressor for air pumping through the batcher and sensitive element.

The batcher is intended for pumping of the examined gas (air) volume through the sensitive element and gas mixing with clear air to decrease the gas concentration at high levels of pollution in order to prevent the destruction of the sensitive element. In addition, the batcher is used to make the sensitive element serviceable by pumping of the clear air through it. The batcher operates in two stages. The first stage includes the air intake through the opening 1 (see Fig. 5 a) and filling the connecting tube 2 of known

volume. Simultaneously the air purified with filters through the opening 3 is pumped through the sensitive element thereby making it serviceable. The second stage of operation begins after displacement of the rod 4 up to the stop (see Fig. 5 b). The analyzed air from the volume 2 is pumped through the sensitive element to perform measurements. It should be noted that the volume 2 containing the purified air operates not only as a connecting tube, but also as a mixer thereby decreasing the gas concentration in the predetermined proportion (what is taken into account by introducing the corresponding correction in the process of calibration of this device), and protects the sensor against overloading.

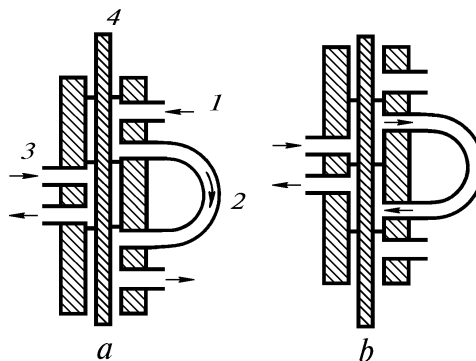


FIG. 5. The batcher.

The voltage supply unit transforms a direct voltage of 12 V in direct supply voltage for each system. As a heater of the sensor, the switching transformer-free voltage convertor is used based on the NE 555 timer comprising a voltage doubler, in which the output stage of the timer is modeled by switch, a generator of negative voltage, and its efficient continuous voltage regulator. The power supply unit of the recording system is bipolar and comes in single-ended transformer circuit design with two parametric voltage regulators. The transformer has a large output resistance. For this reason, to weaken the dependence of the output voltage on a load, stabilotron is included that additionally stabilize the output voltage.

The measuring unit is based on double-cascade operational amplifiers, synchronously changing their parameters and having a large amplification coefficients, and an integral analog-to-digital converter (ADC) of the K 572 PV2 type, harnessing the principle of double integration over 3.5 decimal bits with the output for control of seven-segmented photodiode indicators. Measurement error due to zero and temperature drifts of the ADC is rather small (no more than 10 μV). A clock pulse generator, whose pulse repetition frequency is chosen from the typical series 40, 50, 100, and 200 kHz, and internal voltage supply unit are also included in the ADC. The measuring system is a digital voltmeter with maximum input voltage of 200 mV. Specifications of the developed gas analyzer are listed below.

Gas-analyzer specifications

Supply voltage, V	12 ± 1.2 1.8
Maximum consumed power, W	3.5
Working temperature of the sensor, °C	150–200
Voltage applied to the sensitive element, V	0.4
Power consumed by the heater, W	3
Time required to make the sensitive element serviceable, s	20

Time constant of measurement, s	5
Overall dimensions:	
Electronic unit, mm	200×100×70
Air intake system, mm	∅ 10×100
Mass of gas analyzer, kg	0.9

Measurable parameters

Mass concentration sensitivity, g/m ³	no less than 10 ⁻⁶
CO concentration sensitivity, g/m ³	0.1–1.0
Relative measurement error, %	10

Thus, we have obtained the characteristics of the filmy sensitive elements that are highly competitive on a global scale and decreased the working temperature of SnO₂ sensors down to 350–400 °C and 150–200 °C for detection of CH₄ and CO using the combination of the volume and surface doping. In addition, ways are shown to extend the range of measurable values of the gas concentration without rarefaction of a sample. It should be noted that the design proposed here and the production technology are highly competitive on a global scale by sensitivity, temperature regimes, and specifications, but further efforts are necessary to improve the stability of the parameters of sensitive elements and to increase their working time under real atmospheric conditions.

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