DOI 10.1007/s11182-017-1183-7

Russian Physics Journal, Vol. 60, No. 7, November, 2017 (Russian Original No. 7, July, 2017)

PROPERTIES OF SEMICONDUCTOR NANOCRYSTALLINE SENSORS OF CO AND PYROLYSIS PRODUCTS AS A FUNCTION OF TEMPERATURE AND DURATION OF HEATING AND COOLING CYCLES

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UDC 621.382

Time dependences in the thermo-cyclic mode of the conductivity of CO *sensors, constructed in a traditional four-electrode and a planar three-electrode design on the basis of thin nanocrystalline tin dioxide films, are analyzed. The analysis showed that the use of the* $Pt/Pd/SnO_2$:Sb *sensors in a planar design in the thermo-cyclic mode with a long cooling cycle makes it possible to detect smoldering products at a significant reduction of power consumption.*

Keywords: sensors, tin dioxide, carbon monoxide, thermal cycling mode, power consumption.

INTRODUCTION

Development of highly sensitive and high-speed sensors for the detection of gas molecules (CO, H_2, C_xH_y) released during smoldering of various materials is a very urgent task. Miniature gas fire detectors created on the basis of these sensors are of special interest for providing reliable fire safety. Effectiveness of chemical detectors is assessed by their ability to detect carbon monoxide CO at a level of 20-80 ppm. Resistive semiconductor sensors based on thin nanocrystalline tin dioxide films with dispersed layers of palladium and platinum deposited on the surface have become the basis of detectors that meet this requirement [1]. The disadvantage of these sensors is high operating temperature of 300-400°C. Further studies [2-4] have shown that the use of the thermo-cyclic mode during heating for 2 s and cooling for 5 s contributes to a significant increase in the response of the $Pt/Pd/SnO_2$:Sb sensors to low CO concentrations. The results of studying the characteristics of sensors in the conditions of fire tests under smoldering of test materials indicate that the thermo-cyclic mode is promising for increasing the response to the pyrolysis products. Analysis of the shape of the conductivity-time profiles (CTP) provides the possibility of selective recognition of smoldering of wood (cellulose) and polyvinylchloride (PVC) insulation.

The purpose of this work is to study the dependences of properties of the $Pt/Pd/SnO_2$:Sb sensors with different geometries on the temperature and duration of the heating and cooling cycles. Traditional four-electrode sensors and three-electrode sensors in planar design for reducing power consumption were studied.

EXPERIMENTAL TECHNIQUE

Sensors based on the $Pt/Pd/SnO_2$:Sb films from two series (i) and (ii) differing in geometry were studied. For the samples from (i) series, a sensitive layer with an area of 0.3×0.3 mm^2 with platinum electrodes was located on one side of the substrate, and a heater was located on the other side (Fig. 1). In case of sensors from (ii) series, the heater

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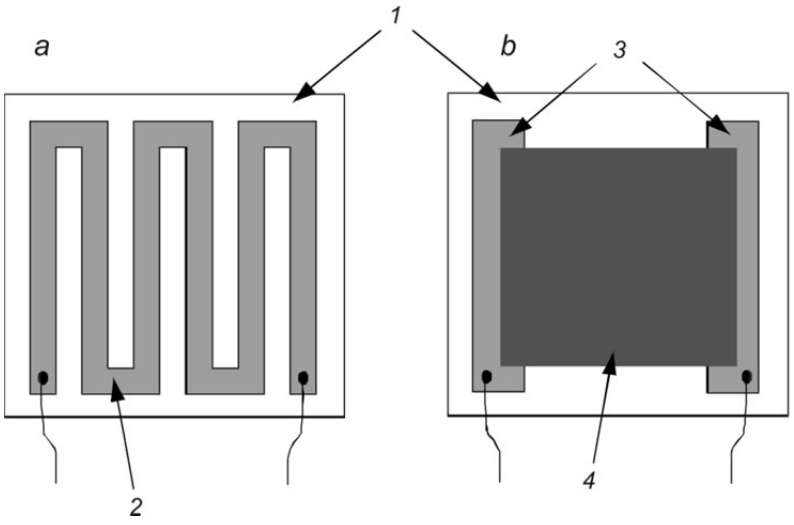

Fig. 1. Schematic representation of the sensor from series (i) from the side of the heater (*a*) and the semiconductor SnO_2 layer (*b*): the substrate (*1*), a platinum heater (*2*), platinum electrodes (*3*), and a sensing element (*4*).

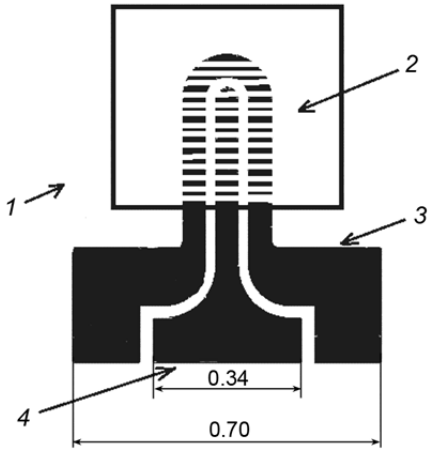

Fig. 2. Schematic representation of the sensor with three electrodes from series (ii): the substrate (*1*), a sensing element (*2*), a platinum heater (*3*), and an electrode to the sensing element (*4*).

and the contact to the sensitive layer were formed on one side of the substrate by platinum deposition followed by photolithographic engraving (Fig. 2). Then, a photoresist was applied to the surface with the platinum heaters and contact areas, in which windows were open to form a sensitive element with an area of 0.4×0.4 mm^2. A technology similar to [5, 6] was used for the production of tin dioxide films doped with antimony using magnetron sputtering of a Sn + Sb alloy target and subsequent explosive photolithography.

Time dependences of the sensors' conductivities $G_0(t)$ and $G(t)$ in pure air and under the influence of gases (CO and cellulose smoldering products), respectively, were measured. The measurements were carried out with the help of a specially designed stand that made it easy to rebuild and stabilize the working temperature of the sample, measure the relative humidity in the chamber, and ensure the operation of the sensors in the modes of constant heating and thermal cycling. The ratio $G(t) / G_0(t)$ was used as the adsorption response. The time, in which conductivity reached 0.9 of the stationary value G_{st}, was considered as the response time t_r. To measure characteristics under the influence of CO, four

TABLE 1. Dependences of the Responses G_{CO}/G_0 of Two Sensors (1) and (2) from Series (i) and (ii) on the Time of Introduction of 100 ppm of CO into the Chamber after the Start of the Cooling Cycle with the Duration t_1 = 30 min.

t_s, min	G_{CO}/G_0			
	(i) – 1	(i) – 2	(ii) – 1	(ii) – 2
5	1.08	1.13	2.14	1.53
10	1.06	1.10	1.95	1.72
15	1.04	1.07	1.54	1.44
20	1.03	1.05	1.38	1.29
25	1.03	1.04	1.35	1.27

sensors were simultaneously placed in a 1-liter quartz chamber, the experimental procedure was similar to [6, 7]. The volume of the chamber, in which the fire tests were conducted, was 150 liters. The time dependence of the sensors' conductivity was measured using an aspirational test mode (a fan was turned on in the chamber).

Calculations showed that the used weight of the test substance of 0.52 g/l cellulose is about 0.3 of the weight of the corresponding material, as specified in GOST R 50898-96 [8]. The test substance was placed inside the helix, through which current was passed. The value of the current was chosen in such a way that the process of smoldering, but not the burning of materials, was going on. The duration of the current transmission was 20-30 s. During this time, there was a complete pyrolysis of both samples with the emission of smoke. The measurements were carried out on the samples that were tested for 8-10 days, since this period is sufficient to stabilize the parameters of the CO sensors [6, 9].

RESULTS AND DISCUSSION

Preliminary calculations showed that to reduce power consumption by 3 orders of magnitude, it is necessary to select a certain ratio between the heating and cooling cycles during thermal cycling. To this end, studies were carried out of the CO sensors in the mode with a heating cycle t_2 = 2 s and a cooling cycle t_1 = 30 min with the supply of 100 ppm of CO. The measurements were carried out 5 times when CO was supplied into the measuring chamber, each time at different moment after the start of the cooling cycle t_s = 5, 10, 15, 20, and 25 min. The chamber was pumped with pure air 5 minutes after the CO was supplied. As shown in [4, 6], adsorption and oxidation of CO molecules to CO_2 predominate in the cooling cycle with the participation of oxygen ions in atomic form O^- preliminarily chemisorbed in the heating cycle. The conductivity (and the response) reaches the maximum value of G_{CO}/G_0 = 40–50 at the end of the 5th second of the cycle with the duration t_1 = 5 s.

In case of conventional four-electrode sensors from series (i), with an increase in the cooling cycle duration up to 30 min in pure air, the conductivity increases in this cycle during the first 500-600 s. The increase is caused by an increase in the density of ions O_2^- and a decrease in the density of atomic oxygen on the surface of tin dioxide.

After the introduction of 100 ppm of CO into the chamber, a short-term increase (for ~ 5 min) is observed, and then, the conductivity decreases, the response values decrease substantially, the more noticeable, the closer to the end of the cooling cycle CO is introduced (Table 1).

When using the three-electrode sensors from (ii) series after heating for 2 s, heating was switched off and the sensors were cooled naturally to room temperature (Fig. 3, curves *1*). The time dependences of the conductivity were measured only in the cooling cycle. After introduction of CO into the measuring chamber, a noticeable increase in the conductivity is observed, and the value of G_{CO} does not decrease until the end of the cycle (Fig. 3, curves *2*). The response G_{CO}/G_0 decreases at t_s > 15 min, but it remains high enough up to t_s = 25 min (Table 1).

Further, the characteristics of the three-electrode sensors were studied in the course of the cellulose smoldering in the thermo-cyclic modes for various cooling cycle durations. The heating time was 2 s. In case of t_1= 5 s, at the end of the cooling cycle, the response G_c/G_0 = 25–30. Under prolonged cooling t_1 = 30 s, there is a sharp decrease in the

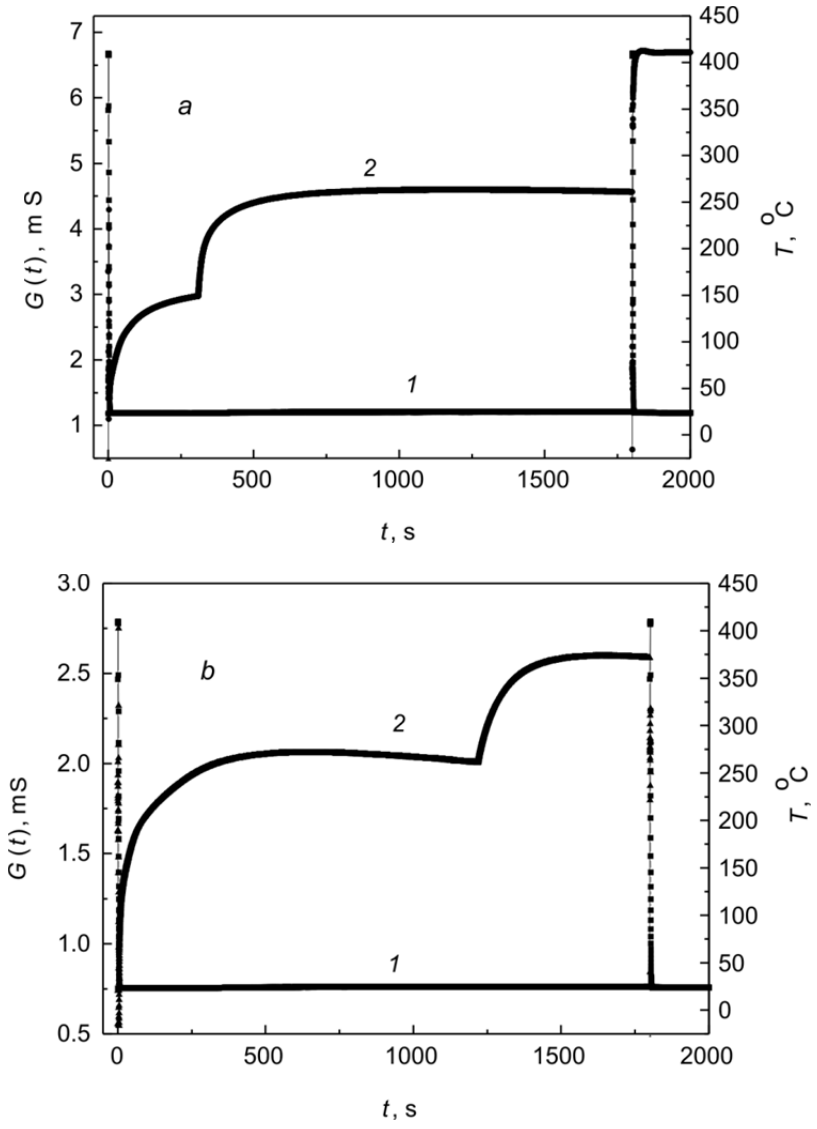

Fig. 3. Time dependences of the temperature (*1*) and conductivity (*2*) of the sensors from series (ii) with 100 ppm of CO supplied after 5 min (*a*) and 20 min (*b*) after the start of the cooling cycle in the modes of heating up to 410°C for 2 s and cooling down to 30°C for 30 min.

response of the sensors to the effect of the cellulose smoldering. However, these values G_e/G_0 = 1.95–2.1 are almost 2 times higher than those under exposure to CO and do not depend on the moment of the beginning of the cellulose smoldering process (Fig. 4).

It is interesting that a noticeable response of the sensors from series (ii) to the effect of the cellulose smoldering products is observed with further increase in the duration of the cooling cycle to 60 min.

It is established that the use of the Pt/Pd/SnO_2:Sb sensors in planar design in the thermo-cyclic mode with long cooling cycle t_1 = 30 min or more provides the ability to detect the smoldering products at a significant reduction of power consumption. On their basis, it is possible to create low-temperature fire detectors.

This work was performed as a part of the State Task of the Ministry of Education and Science of the Russian Federation (Task No. 3.9661.2017/ 8.9).

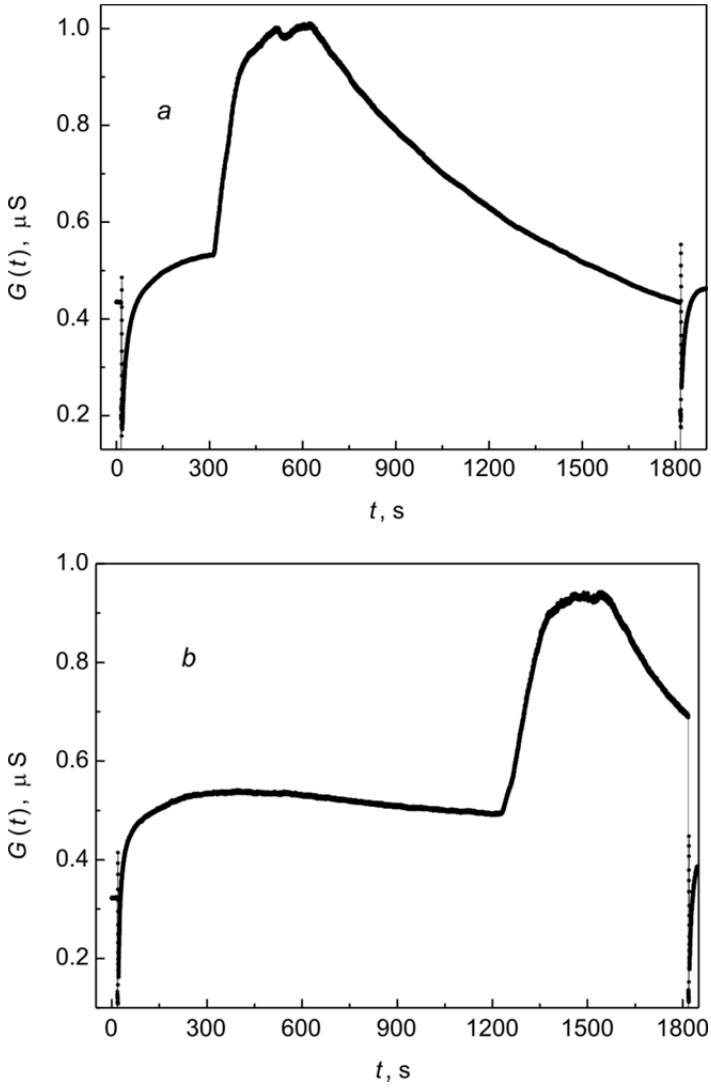

Fig. 4. Time dependences of the conductivity of the sensors from series (ii) during the fire tests. Cellulose smoldering was performed after 5 min (*a*) and 20 min (*b*) after the start of the cooling cycle lasting 30 min.

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